
**E-BEAM LITHOGRAPHY AND DRY PROCESSING FOR
SUBMICRON FABRICATION**

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ADDENDA

Less familiar abbreviations

IC	Integrated Circuits
LSI	Large Scale Integration
VLSI	Very Large Scale Integration
ULSI	Ultra Large Scale Integration
RIE	Reactive Ion Etching
SAW	Surface Acoustic Wave
CI	Cambridge Instruments
NPL	National Physics Laboratory
CRT	Cathode Ray Tube

Added comments

Section 1.2.2 p22	Spot position: The manual adjustment of this dial on the T220 and T100 SEM's controls the current and the diameter of the electron beam.
p83 (1st para)	Approximately 100 generated pairs (holes and electrons) are produced for an incident electron of 2keV energy.
p84 (3rd para)	The last sentence should read: Biasing the substrate, which effectively reduced the escape of low energy secondary electrons, had no obvious effect on the decomposition rate.

p112

(Fig. 5.2)

Addition of O_2 increases the fluorine concentration available for etching by forming CO and CO_2 . This leads to an increase in the F/C ratio causing a reduction in the polymerisation as shown in the figure. Adding H_2 has the opposite effect, ie. fluorine is depleted by forming HF leading to a greater polymerisation effect.

The loading effect is a measure of the quantity of reactive species available for etching. With a low F/C ratio this effect is seen to increase due to the reduction in F species.

An increase in the DC bias leads to an increase in the reactive species (possibly by an ion-assisted process, see section 4.3.3) and thus retarding the onset of polymerisation as shown by the dotted boundary.

ABSTRACT

Inorganic materials useful as resists in microcircuit fabrication have been investigated by various workers because of their potential for high resolution and high etch resistance in plasma etching. This work is especially concerned with thin film studies of inorganic halide resists for pattern replication in silicon and silicon dioxide using e-beam lithography and dry processing.

Cadmium chloride resists have been examined as an e-beam, plasma-compatible, volatile resist by previous workers in these laboratories. Knowledge of the etching characteristics of this resist has been extended using a Plasmalab 80 reactive ion etcher. A way of improving the contrast associated with this resist by employing a two level scheme of $\text{CdCl}_2/\text{CdI}_2$ is described. The method used CdCl_2 as a cap on CdI_2 with the former being decomposed by the beam and the more volatile CdI_2 removed by raising the sample to a suitable temperature. Thin films of CdCl_2 and CdI_2 ($\sim 300 \text{ \AA}$) have also been examined under e-beam irradiation at elevated temperatures with CdI_2 proving to be more efficient in decomposing than CdCl_2 . This has been discussed with the references to several theories of electron beam scattering in solids namely Bethe, Everhart and Kanaya and using Monte Carlo simulations.

A lift-off scheme using CdF_2 and PMMA has been developed, which couples the high etch selectivity of the inorganic resist and the high resolution of the PMMA resist to produce deep submicron structures in Si, SiO_2 and Cr.

Finally, CsCl films have been used to produce random arrays of hemispheres, which after dry etching results in a coverage of pillars on the substrate. Arrays of mean diameters ranges of $800 \text{ \AA}$, $3000 \text{ \AA}$ and $6500 \text{ \AA}$ have been made in silicon. The technique may be used for fabricating useful semiconductor opto-electronic devices, such as quantum dot arrays.

*To my
Mother and Father*

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" It seems good for philosophers to move to fresh ways and systems; good for them to allow neither the voice of the detractor nor the weight of ancient culture, nor the fullness of authority, to deter those who would declare their own views. In that way each age produces its own crop of new authors and new arts.."

FERNEL, 16th Century.

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INTRODUCTION

Fabrication technology is a mixture of science and art. The 'science' part is essential to the fundamental understanding of the processing phenomena involved and the 'art' part is the selective application of this acquired knowledge to tailor the processing needs to meet individual requirements. The semiconductor industry have followed such a trend where one constantly hears of IC manufacturers pushing the limits of their present equipment to increase yield and throughput.

E-beam systems are employed in a wide variety of applications particularly where submicron geometries are required but cannot be met by other photolithography techniques. Fabrication of photomasks, SAW devices, metal gate structures are only a few examples but recent improvements in the e-beam column as well as dry etching systems have paved the way for submicron structures and opened the door to quantum device physics. This has been possible due to the small beam diameter ($\sim 100 \text{ \AA}$) with high brightness achieved with e-beam columns of today and coupled with highly selective and anisotropic etching provided by the RIE systems: structures below 100 nm may be fabricated. The highly sophisticated e-beam systems of today can now write complex patterns performing automatic proximity and registration corrections from wafer to wafer with minimum interference by the user. The ability to provide a complete system under computer control have been one of the important points for its almost universal acceptance for mask making in the semiconductor industry.

The features which make dry etching attractive over wet etching are high selectivity and anisotropy with almost no undercutting thus allowing precise dimensions to be etched in a wide range of substrates. It is an environmentally clean system to operate involving only gases and is also highly suited to automation.

While rapid improvements have been made in the specifications of e-beam and dry processing equipment, resist processing have somewhat lagged. Scientists have yet to find the ideal resist which will fulfill all processing requirements, namely high sensitivity for high throughput and high etch resistance for good selectivity. The image reversal technique for device fabrication described in chapter 6 is an effective method of overcoming some of the problems associated with resist processing. Inorganic resists although capable of offering high etch selectivity are marked down by very poor sensitivity figures. There are various ways of improving the sensitivity such as a two layer 'cap' scheme (chapter 3) but this is conditional upon finding two materials having a vapour pressure response curve quite wide apart and the top layer being e-beam decomposable. The image reversal technique takes advantage of the sensitivity of the organic resist and the high etch selectivity of the inorganic resist.

Although, beam diameters are of the order of a few nm, the inherent resolution in the resists is limited by the degree of electron scattering in the resist. Such imposed limitation sets the minimum dimensional structures that can be produced on the substrate. In order to overcome e-beam restrictions another path has been taken. 'Natural' lithography has been proposed by several groups of workers involving packed spheres etc. We have set out to use resists of inorganic nucleated island (chapter 7) to make 'dot' structures of dimensions of tens of nanometres. This may open the way to interesting and useful semiconductor devices for opto-electronics applications.

E-BEAM SYSTEMS

Electron-Beam systems for the fabrication of submicron devices have evolved from the early scanning electron microscope based instruments to highly automated computer controlled systems. Research at Cambridge University into scanning electron microscope was the cornerstone for the first electron beam fabrication experiments. The late 1960's and early 1970's led several major companies notably Bell Laboratories, Hughes Research, IBM, Thompson CSF and Texas Instruments to pave the way for fully developed systems for the generation of VLSI chips [1-5].

Most of the commercial electron-beam systems in use today are for mask fabrication for optical projection printers and 5-10x reticles for step and repeat printers. Direct device writing is employed for metallisation of submicron gates where accurate registration between source and drain is of prime importance in limiting adverse high frequency effects [6]. There are several options available to the system designer for his selection in configuring a particular system. Some of these options are for example 1) a round Gaussian probe versus a shaped beam 2) a step and repeat table versus a continuously moving table 3) electron source: a tungsten filament, or LaB₆ emitter, field emission tip, a single source versus multiple sources (and images): 4) beam energy or voltage, 5-100keV: 5) vector scan or raster scan systems.

Vector scan systems are usually faster than raster scan systems. In this mode of operation the beam is deflected to the start of the exposure pattern to be written and exposes the region to be patterned only. By breaking the pattern down into a series of simple shapes such as squares or triangles it is possible to pattern a complicated image (ie windows for the implantation of impurities in a CMOS process). Raster scanning employs a continuously

scanned beam similar to a TV scan and the beam is blanked on and off depending on the digitised pattern data on the frame.

A major departure from the round Gaussian probe is the IBM manufacturer system (EL3) [7]. Variable shaped beams have been developed to increase the throughput. This is an advantage since large shapes such as a wiring pad can be written at one time. A major disadvantage of this system is that strong electron-electron interactions resulting through the column from the large probe current can degrade the performance. Variable aperture e-beam systems are therefore not suited for submicron fabrication and Gaussian beam vector scan systems are widely employed where proximity corrections can be easily made.

1.1. EBMF6-5 (Cambridge Instruments)

1.1.1. System Configuration

A description of the Cambridge Instruments (CI) EBMF6-5 in this study used for the fabrication of the chromium mask plates using the lift-off technique will be presented here. The machine (Fig. 1.1) in its basic form is a Gaussian vector scan system with LaB₆ thermal emitter and beam currents and voltages variable from 0 to 1 nA and 1 to 30 keV respectively. It is a general purpose instrument used for mask and reticle fabrication and direct wafer writing.

Silicon wafers and mask plates are loaded through a load-lock which can accept up to 10 chucks. The machine is capable of writing on a wide variety of different substrate from 2" wafers up to 5" mask plates. Astigmatism corrections are automatically performed using quadrapole lenslets located above the final lens. When the beam is deflected off-centre compensation for the field curvature is achieved by applying an additional focussing field through a subsidiary coil associated with the final lens. This and other factors

such as nonlinearity due to maximum drive current, drive speed and heat dissipation limit the size of the deflection field to just a few mm [8].

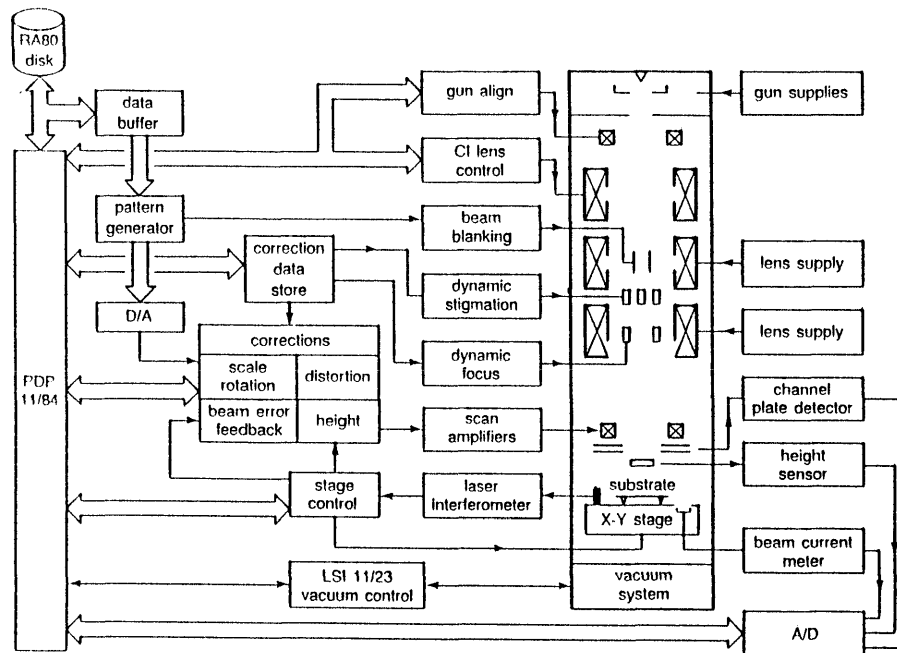


Fig. 1.1. EBMF6-5 system block diagram.

To expose larger patterns than the deflection field it is necessary to move the stage very accurately so that adjacent fields are stitched together. This is accomplished using an X-Y stage with a laser interferometer mounted orthogonally on the stage. The position of the stage is measured and tracked continuously to an accuracy of 13 nm in both X and Y axis.

Stitching errors can occur due to height variations in the substrate and this is compensated for by a height sensor utilising a local area capacitance measurement. Registration marks are essential to provide a reference for a multilayered mask patterns or a multilevel writing scheme. This is provided by a gold fiducial marks on the wafer and the computer repeatedly scans the area and measures the backscattered signal until it locates a marker whose signal is comparable to the one stored in the computer.

1.1.2. Gaussian Beam Formation and Column Aberrations

An electron beam microfabrication system consists of an electron optical column. The quality of construction of this column and proper choice of materials determines the minimum beam diameter and the maximum current density that can be obtained with the system which is of prime importance in submicron fabrication. These two quantities place restriction on the resolution limit and the throughput of the machine. Choice of proper materials will prevent charging of inner insulating materials. Column elements, lenses must be designed with great precision to reduce the number of extra alignment devices such as coils added to compensate for the poor design or manufacture. A schematic cross section of the column is shown in Fig. 1.2. The electron gun which forms an emission cross-over having a Gaussian intensity distribution which is imaged by three demagnifying or condenser lenses.

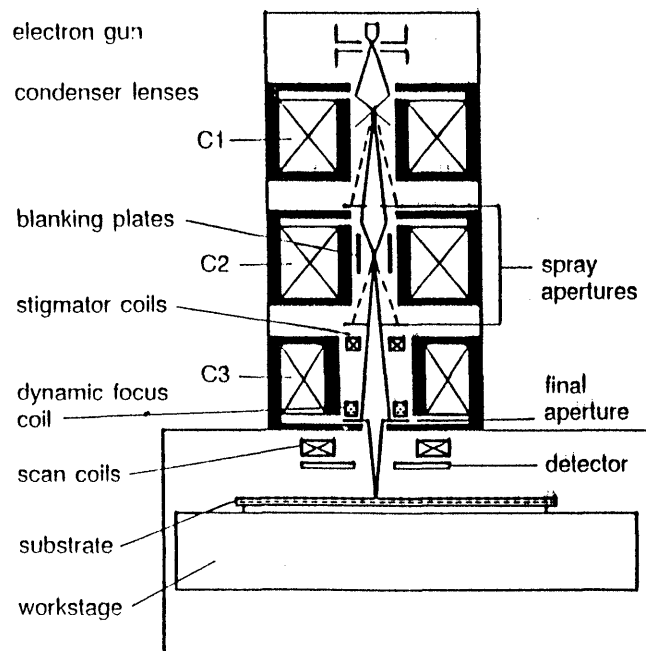


Fig. 1.2. Schematic cross section of electron beam forming column.

The brightness of the source, β , is defined as the current density/unit solid angle, so that:

$$\beta = J/\pi\alpha^2 \quad (1.1)$$

where α is the solid angle into which the electrons are emitted.

The beam current density profile of the final probe can be described by a Gaussian intensity distribution:

$$J = J_0 \exp(-r^2/2\sigma^2) \quad (1.2)$$

where J_0 is the peak current density at the centre of the distribution radius r , and standard deviation σ .

The total beam current is obtained by integration, viz.

$$I_0 = 2\pi\sigma^2 J_0 \quad (1.3)$$

The beam diameter d is defined as the point at which the current density falls to one half of its maximum value, ie $J_0/2$, which is the diameter which encloses 50% of the total beam current.

Thus from (1.2), $d = 2.35\sigma$

Assuming brightness is conserved through the length of the column, the beam current can be expressed as a function of beam diameter, brightness and the convergence angle.

$$I_0 = 3.57\beta\alpha^2 d^2 \quad (1.4)$$

Column Aberrations

Ideally the electron beam should be of Gaussian form and any deviation from this is termed the total aberration of the beam. The major aberrations of the electron column are dominated by the characteristics of the final lens, and it is necessary only to consider this lens. Aberrations will account for the 'disk of confusion' which can be combined to determine the overall diameter for the electron probe [9].

Spherical aberration

This is caused by the deviations of the intersection from the Gaussian image points. It is a function of the geometry of the refracting field ie. the shape of the equipotential surfaces. Spherical aberration of the beam can be represented by a diameter d_s varying as a function of spherical aberration constant and the convergence angle.

$$0.5 C_s \alpha^3$$

The reduced diameter for the previously defined Gaussian is 59% of this value [11], so that:

$$d_s = 0.3 C_s \alpha^3$$

Chromatic aberration

This arises from the differences in the initial velocities of the electrons. An analogy of this is the variation of refractive power of optical lenses for different wavelengths of light. The deflecting power of electrons are affected by their initial velocities. A chromatic aberration disk of diameter d_c is given by:

$$d_c = (\Delta E C_c \alpha) / E_0$$

where C_c is the chromatic aberration coefficient and E_0 and E are the beam voltage and FWHM energy spread respectively.

Diffraction effects produced by the final aperture also contribute to a confusion disk, with diameter d_d given by:

$$d_d = (1.22 / \alpha) \sqrt{150 / E_0}$$

These aberrations limit the minimum on-axis beam diameter that can be achieved at the focus and it has been shown [10] that they can be combined geometrically to yield the total beam diameter d_0

$$d_0^2 = d^2 + d_s^2 + d_c^2 + d_d^2$$

i.e.

$$d_0 = \left[\frac{I_0}{3.57\beta\alpha^2} + 0.09C_s^2\alpha^6 + \left(\frac{\Delta E}{E_0} \right)^2 C_c^2\alpha^2 + \left(\frac{1.22}{\alpha} \right)^2 \cdot \frac{150}{E_0} \right]^{\frac{1}{2}} \quad (1.5)$$

Only the first term varies with current so that the minimum diameter is determined by the three aberration terms. The equation and its individual terms are plotted from the aberration coefficients for the CI EBMF column [11]. From this it can be seen that the chromatic term dominates at small apertures, whereas the spherical aberration is greatest at larger apertures. The diffraction term is not significant for this system (Fig. 1.3).

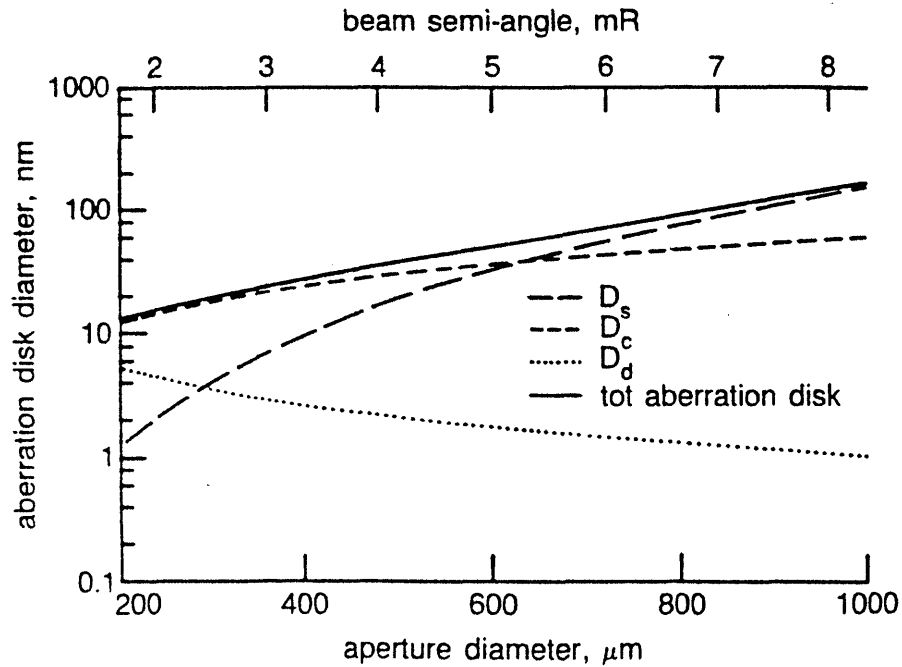


Fig. 1.3. Aberration limits at 30 keV for CI EBMF-10 column as a function of the final aperture diameter. (After Jones and Dix, Ref 12)

An optimum aperture can be determined for a specified diameter or current, defined as the condition for maximum current density in the focussed spot. Fig. 1.4 shows the optimum aperture beam diameter as a function of current for 30 keV energy, a source brightness of $1.2 \times 10^6 \text{ Acm}^{-2}\text{sr}^{-1}$ and an energy spread of 3 eV. In practice choice is restricted to several fixed size apertures which, during normal operation, can be interchanged under vacuum.

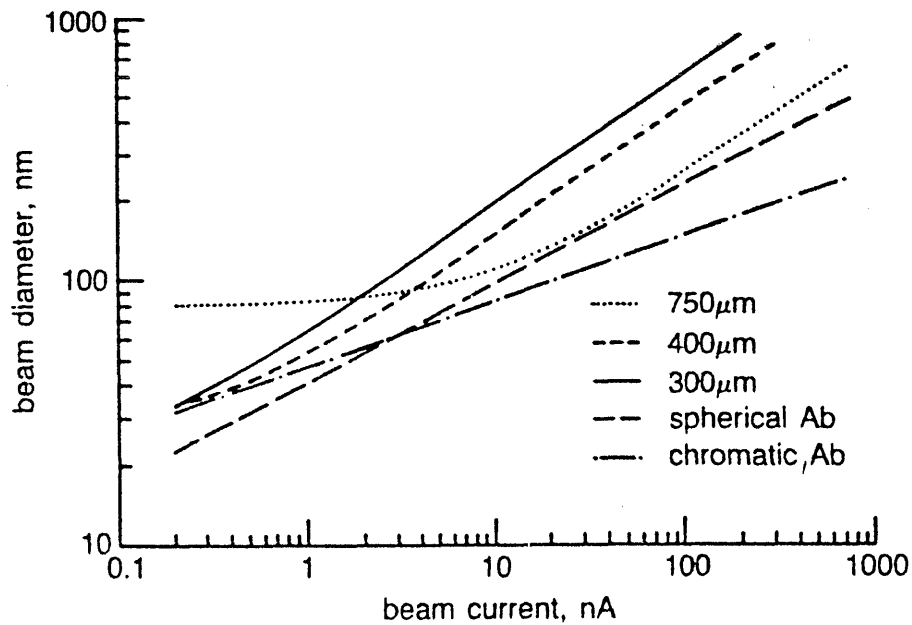


Fig. 1.4. Theoretical relationship between beam diameter and current with final apertures of 300, 400 and 750 μm diameter: 'optimum' aperture curves assuming spherical or chromatic aberration are also shown. (After Jones and Dix, Ref [12])

1.1.3. Electron Source

As discussed previously, the electron source is a critical factor in determining the performance of the electron column. Its stability and lifetime are important for lithographic purposes and the ultimate resolution is dominated by the electron energy spread.

Many SEM based systems like our JEOL T100 and T220 have employed a tungsten wire filament heated to about 2700 K as a thermionic source. It has a low emission current ($1-8 \text{ Acm}^{-2}$) and a short life time of approximately 20-40 hours, therefore it is unsuitable for commercially based lithographic applications. Other 'cold' cathodes such as field emission cathode have considerably longer lifetimes and produce very high current densities of $>10^6 \text{ Acm}^{-2}$. The disadvantage is that they require a ultra high vacuum and can be rather unstable. LaB_6 thermionic emission cathode is the most common type of source used in the current generation of machines.

Recent developments of directly heated single crystal LaB_6 cathodes have led to increased reliability and improved lifetime.

The EBMF6-5 lithography system has a triode electron gun assembly of a 'Wehnelt' grid and an anode (Fig. 1.5). Electron emission from the cathode is controlled by the retarding bias field (500-1000V) of the Wehnelt aperture and an accelerating potential (10-40 keV) of the anode. Electrons are emitted near the top and converge to a crossover having a Gaussian distribution about the axis.

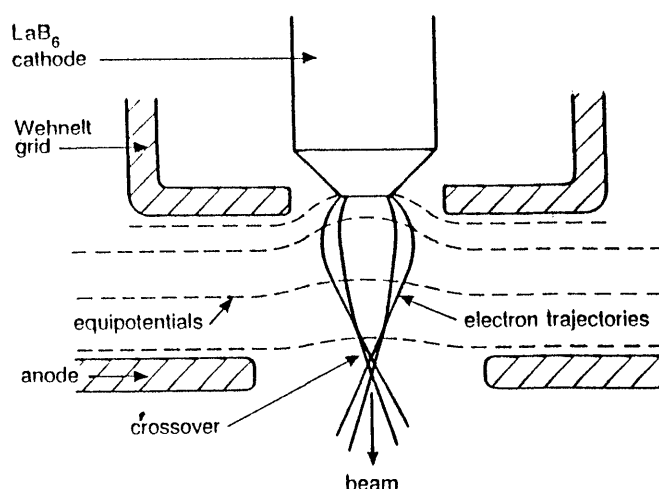


Fig. 1.5. Cross-section of the electron gun.

The brightness of the beam is dependent upon J_c (Eqn.1) and this is related to the Richardson equation for thermionic emission expressing J_c in terms of the cathode material work function ϕ , temp. T_c and the Richardson constant A .

$$J_c = AT_c^2 \exp(-e\phi/kT_c) \quad (1.6)$$

and

$$\beta = (AT_c eE_0/k)(\exp(-e\phi/kT_c))$$

For LaB_6 , the work function varies according to the orientation of the emitting crystal face, and it has been found [13] that the highest current density is obtained for the {100} plane. The emitting area of the cathode tip must be small to obtain a high current densities and brightness. Typical values of $J_c = 20 \text{ Acm}^{-2}$ and emission current $I_e = 60 \text{ }\mu\text{m}$, gives an area of $300\mu\text{m}^2$.

In the operation of an electron gun for microfabrication, the time stability of current and beam operation are important considerations. The heater and high voltage power supplies must exhibit a high degree of stability. Pressure is maintained at 10^{-7} to 10^{-8} torr to avoid contamination of the tip which results in instabilities in current and uniformity of emission. Cathode lifetime is ultimately dependent upon the evaporation rate of the LaB_6 and they typically last for 1000 hours.

The lateral and axial position of the emitter tip with respect to the Wehnelt electrode can affect the transverse position of the spot at the target and the current trajectories, respectively.

1.2. JEOL T220 E-Beam Writing Machine

1.2.1. System Configuration

The T220 is a conventional scanning electron microscope for observing small specimens and also 3" wafers up to a magnification of 200k. Briefly, the system (Fig. 1.5) configured, by us, as an e-beam writing machine consists of an IBM AT to produce the digitised pattern which is then converted to the analogue form by the 14 bit D-A convertor which drives the external x-y deflection plates. The D-A convertor constructed by M. Applebaum and the software written in Pascal by C. J. Aidinis were both done in this department. The machine operates in the vector scan mode.

The total area of the scanned beam is determined by the magnification setting. For example, at a magnification of 1k and 15k the maximum area covered by the beam is $135\text{ }\mu\text{m} \times 90\text{ }\mu\text{m}$ and $9\text{ }\mu\text{m} \times 6\text{ }\mu\text{m}$ respectively. Since the horizontal scan consists of 16,384 (2^{14}) address pixels, overlap of the beam will not occur below a particular magnification setting as this is determined by the beam diameter.

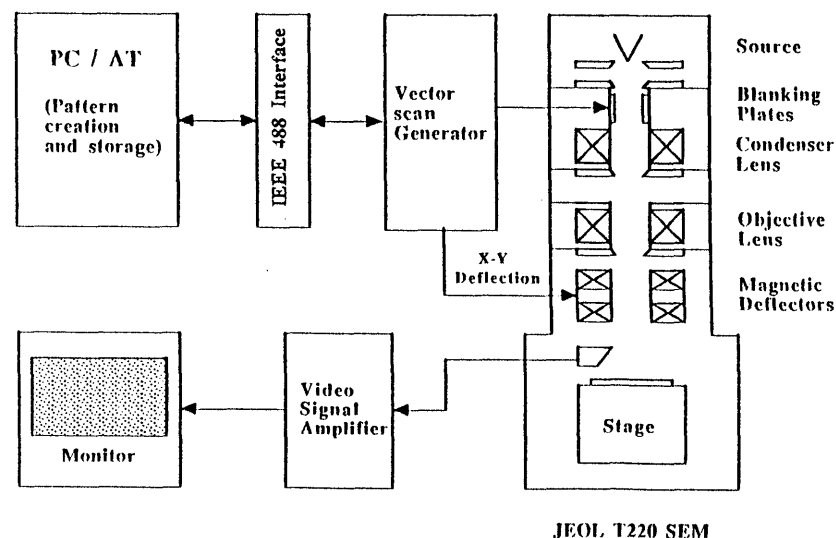


Fig. 1.5. System configuration of the e-beam writing machine.

1.2.2. Beam Diameter Measurements

It is important to look at the beam diameter as this determines the resolution capabilities of the system. The beam diameter is a function of several system variables and the most important ones being the beam current, working distance of the substrate from the objective lens and the beam energy.

Beam diameter measurements employing the 'knife-edge' technique have been reported in several papers [1, 2,]. One of the difficulties of making such a measurement for high resolution work is to fabricate an edge which is opaque to electrons. Cleaver and Smith [3] have made spot measurement of about 20 to 30 nanometers using etched copper foils but it is difficult to achieve simultaneously a sharp edge and sufficient thickness of film to provide adequate opacity. Rishton et al [1] have used etched silicon wafers to produce the knife-edge and by mounting the etched plane vertical to the electron beam they were able to make consistent beam diameter measurements down to 10 nm. They also argue that by mounting the etched Si wafer horizontally the tapered Si edge was too thin and hence transparent to electrons close to the edge and could not be used for high resolution measurements. A recent publication by Chisolm [2] has shown that by using a Si edge mounted horizontally, accurate measurements of the beam diameter greater than 25 nm could be obtained. High beam energies will lead to a greater transmission of the the electrons near the edge, and this is also dependent on the angle of the cleaved Si edge. Scattering of the electrons at the edges will also occur but this is small and can be ignored. A cleaved Si knife-edge have been chosen for measuring the beam diameter on the T220 SEM to characterise this variable in terms of working distance, beam energy and spot position of the dial.

Assuming that the beam is Gaussian in nature, the current measured in

the Faraday cup is the error function ($\text{erf}(x)$). The mathematical derivation of the error function from the Gaussian distribution is given in Appendix I. From the conventional definition of the beam diameter σ , this corresponds to the points at 26% and 84% in the graph of the error function.

1.2.2.1. Results and Discussion.

Fig. 1.6 shows the experimental layout for the measurement of the electron beam current. The beam is driven by a high quality waveform generator using a sawtooth waveform. As it passes over the Si edge the current is detected in the Faraday cup and amplified by the current amplifier to the digital oscilloscope. Since the currents measured are in the region of a few nA, coaxial cables were employed from the cup to the current amplifier to improve matching and avoid pick-up.

The knife edge was obtained by pressing a diamond tipped pen at one end of a Si {100} wafer and cleaving it across the plane. After mounting the edge on the Faraday cup, it was examined in the SEM at a high magnification for any signs of contamination or defects. Defective edges were rejected and only those which displayed a sharp edge were used for the measurements. The surface of the Si was grounded using fine stranded (Litz) wire bonded by silver dag (Fig. 1.7). Insulating tape was wrapped around the Faraday cup to isolate it from the grounded stage.

At a magnification of 500x the field width scanned by the electron beam is 270 μm and the edge of the Si was located at the centre of the stage where distortions of the beam is less likely. To measure beam diameters of 0.1 μm the beam must be scanned at a reasonable rate at low magnifications so as to be within the time response of the amplifier. The oscilloscope has a maximum sampling rate of 20 MHz and so in this case the limiting factor is the response rate of the amplifier. The Keithley 616 Digital Electrometer did

not give a fast response rate for measuring beams at low magnifications and low currents although it was useful for measuring the current. The current amplifier used was built around a very fast low noise, high gain OPA1Z8KM (Burr-Brown) op. amp. The output voltage was $\pm 15\text{V}$ which was required to drive the beam over the entire fieldwidth. Sweep speed was variable from approximately 30s to 300s.

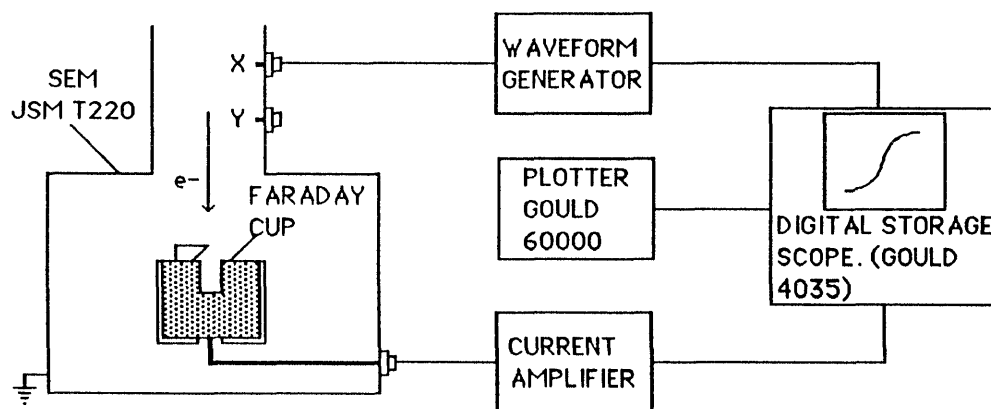


Fig. 1.6. Experimental layout of the equipment employed for the beam diameter measurements.

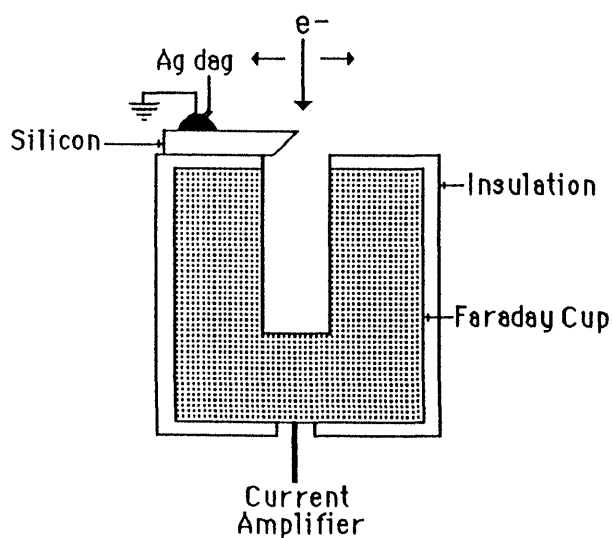


Fig. 1.7. Faraday cup used for the beam current measurement.

Coaxial cables were used to minimise noise and avoid pickup. The cables from the SEM to the amplifier were made as short as possible to avoid losses and noise interference.

Fig. 1.8(a) shows a typical output current taken for the indicated settings of the scanning electron microscope. The corresponding Gaussian distribution is shown in Fig. 1.8(b) with the calculated function also shown. Spot position is a variable knob on the console which serves to increase or reduce the electron beam current depending on its position on the dial. Working distance is the distance between the mounting stage and the objective lens of the microscope.

Fig. 1.9 shows the variation of beam diameter with the working distance. Variations in repeated measurements occurred up to a maximum of $\pm 20\%$ for identical settings of working distance, spot pos. and beam energy. At the shortest working distance, the beam diameter is at its minimum, which explains the high image quality obtained at this position. The beam diameter as function of the working distance for different energies is shown in Fig. 1.10. At 20 keV the beam diameter at the 10 mm working distance is $0.2\ \mu\text{m}$ which is satisfactory for e-beam lithography work for device fabrication. Contrary to what one expects for the e-beam column (see section 1.1), the highest beam energy (20 keV) gives a larger value of the diameter than at lowest setting (10 keV). This could be explained by the higher penetration of the beam at the vicinity of the knife-edge at 20 keV. From Monte Carlo simulations in chapter 2 the range at 20 keV in Si can be up to several microns, so the effect of this near the edge is to broaden the current measurement and hence leading to a greater value in the measured diameter.

For the PMMA exposures carried out for the lift-off scheme described in chapter 6, a spot position around 11 and a beam energy of 20 keV gives linewidths of about $0.1\ \mu\text{m}$ for a single scan of the beam. A typical area of 0.2

$\mu\text{m} \times 10$ on PMMA and with doses of $1000 \mu\text{C}/\text{cm}^2$ requires an exposure time of 0.15 seconds using Eqn. 3.3 .

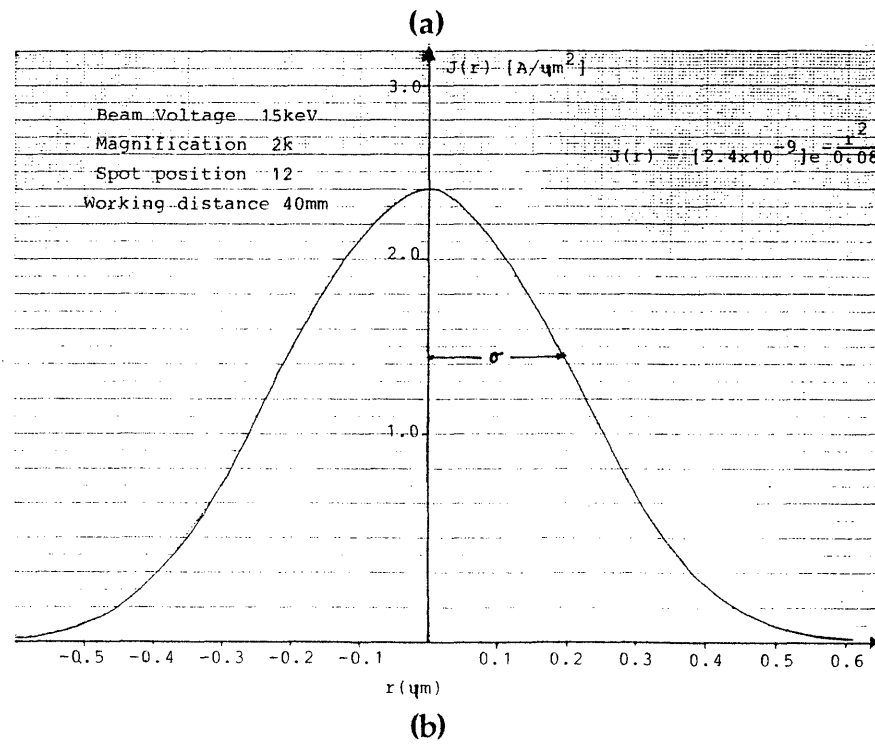
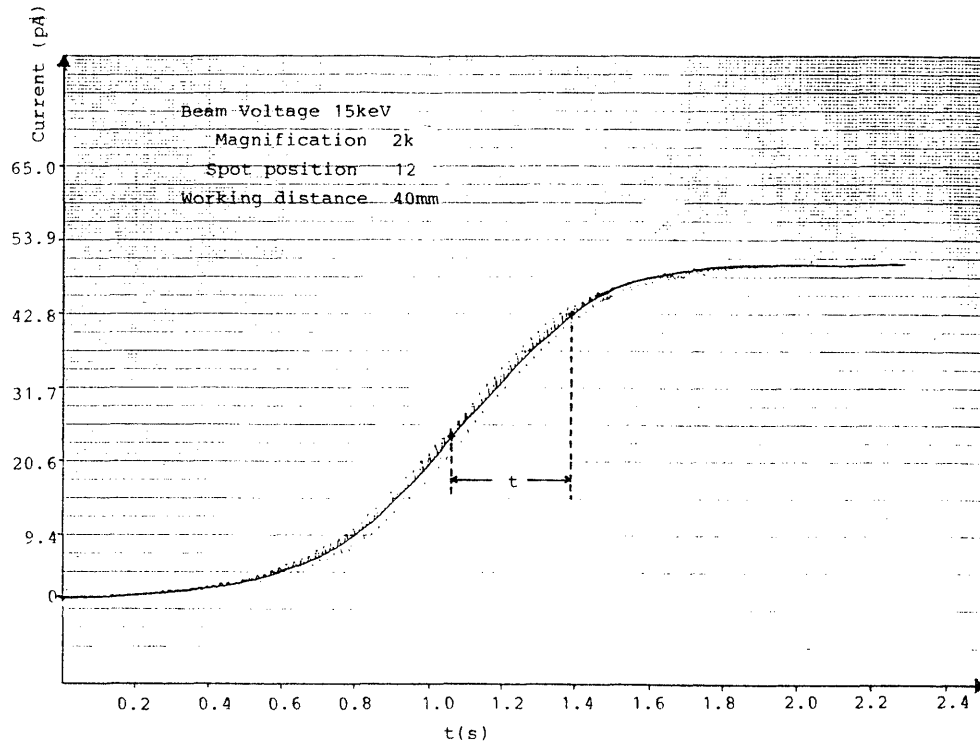


Fig. 1.8. (a) Typical output current measured for the deflected beam and the corresponding calculated current distribution (b).

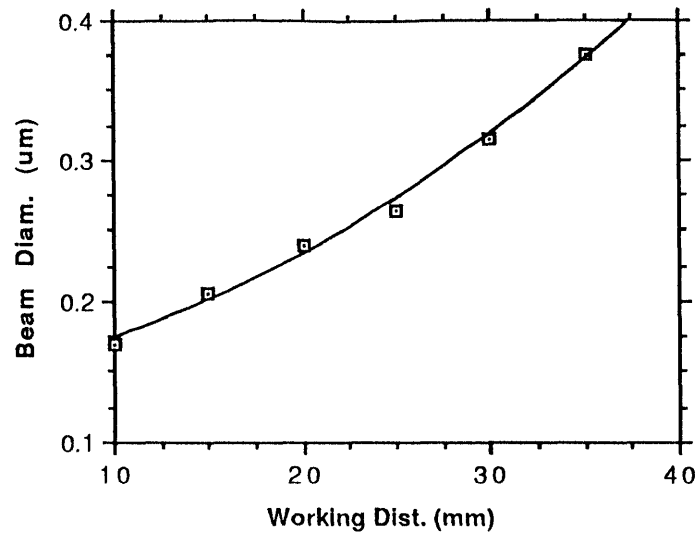


Fig. 1.9. Beam diameter versus working distance at 15 keV, mag. 2k and spot pos. 12. obtained using Si knife edge.

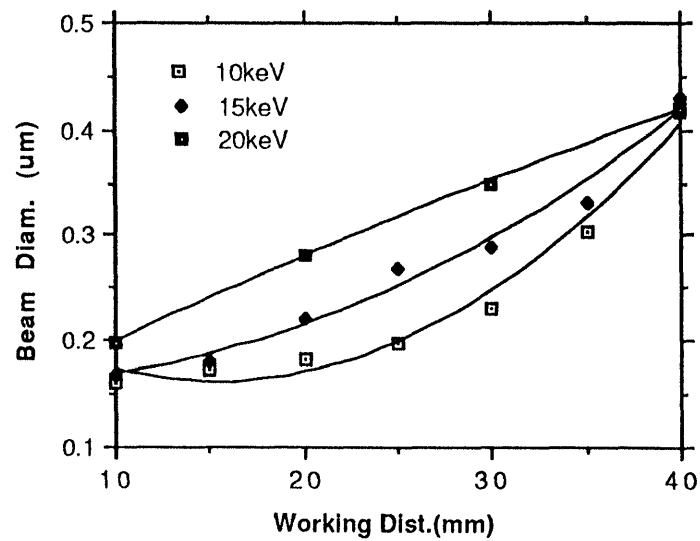


Fig. 1.10. Beam diameter versus working distance for 10, 15 and 20 keV energies at spot pos. 12.

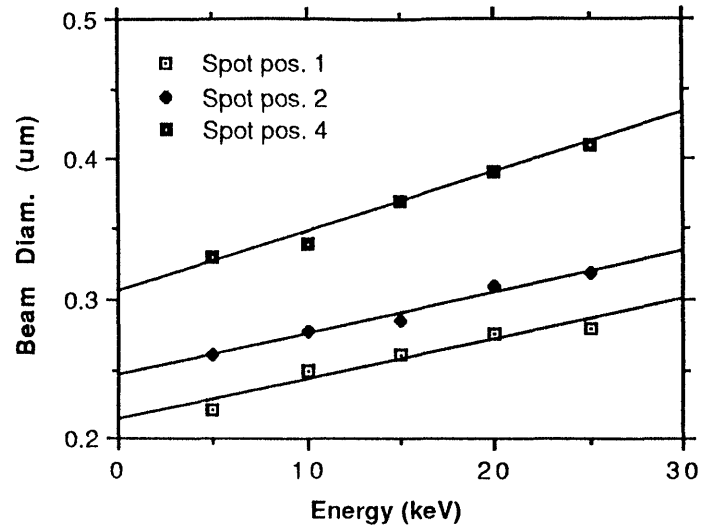


Fig. 1.11. Beam diameter versus energy for several spot positions at 10 mm working distance.

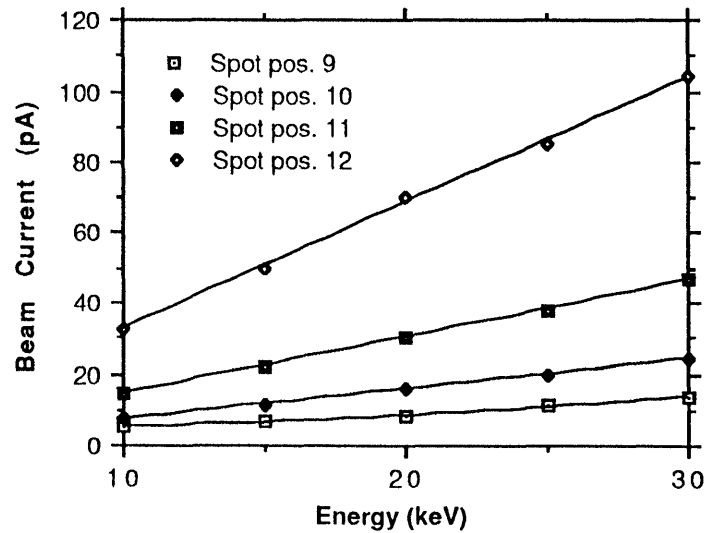


Fig. 1.12. Beam current as a function of the beam energy for several spot positions used for PMMA exposures at a working distance of 10 mm.

1.2.3. Conclusions

The knife-edge technique for beam diameter measurements is effective providing the energy is not too great which leads to penetration of the beam and hence leads to errors in the beam diameter measurement. The linewidths obtained in PMMA for a single scan is about $0.1\text{ }\mu\text{m}$ at a 10 mm working distance, beam energy 20 keV and spot pos. of 11 which is smaller than the measured value and is possibly explained by the above 'transparency' effect.

For satisfactory exposure on PMMA a compromise between spot position and beam current must be made with regards to resolution. A low a spot position setting though providing the smallest diameter could lead to unnecessarily long exposure times owing to the decreased beam current (Fig. 1.12). From experimental techniques a suitable setting for the linewidths of interest is a spot position of 11.30 at 20 keV. A magnification area of 1k gives a maximum area of $135\text{ }\mu\text{m} \times 95\text{ }\mu\text{m}$ available for a single exposure. This has found to be adequate for the lithography work undertaken in the section and also ensures overlap of the beam.

1.3. Calibration of Line Measurement on the JEOL T100

Linewidth measurements discussed below can vary from one instrument to another so it is important to calibrate the instrument to obtain an accurate measurement. The purpose of this section is to describe the calibration of the JEOL T100 scanning electron microscope for effective linewidth measurements at low and high magnifications and comparing it to the values obtained with the Cambridge Stereoscan 2000 which is assumed to give the more accurate results.

Most of the inspection equipment used for linewidth measurement are optical microscopes with their advantages of fast and non- destructive testing.

The use of this instruments to measure linewidths to submicron accuracy is effectively a problem of choosing a suitable setting criterion on the image intensity profiles obtained from the edges of the line. It is possible with a correctly aligned microscope and knowing both the instrument parameters and the characteristic of the specimen to calculate theoretically an edge setting criterion from which an accurate linewidth value can be realised. A paper by D. M. Rickey [1] accounts for variation in edge profile and film thickness on the signal threshold value of the optical microscope. By comparing this measurement with the measurements obtained from an SEM he was able to determine an offset weighting to calibrate the microscope. In this way a high degree of measurement reproducibility was obtained.

The Division of Mechanical and Optical Metrology at the National Physical Laboratory has standard facilities and services for dimensional measurement for the microelectronics industry. Results of an intensive survey in the industry indicated that the main dimensional problems were those of sizes and positions of features on photomasks and wafer film thickness and flatness. A prototype mask linewidth standard was built and issued to interested parties with results of the survey compiled in their report "NPL Linewidth Measurement Audit." [2]. Three types of measuring system were encountered during the audit, these were 1) a manual technique using the Vickers image shearing microscope , 2) ITP microscope which generates an intensity profile photoelectrically, using the scanning information from a television camera, 3) the Nanoline microscope which uses a scanning slit and photomultiplier detector. Results of the measurements revealed linewidths variation of up to $0.4\mu\text{m}$ from the standard NPL measurement.

Swyt [3] made several comparisons of optical measuring tools and found there was a notable difference ($\sim 0.2\mu\text{m}$) of chromium lines on glass measured in the transmission and reflection illumination of the image shear microscope. A study of the semiconductor device manufacturers [4] concluded

that the most urgent problem was the serious difficulty in making linewidth measurements on the smallest pattern elements. With geometries approaching submicron dimension it is clear that low voltage SEMs are at an advantage providing a high degree of measurement reproducibility.

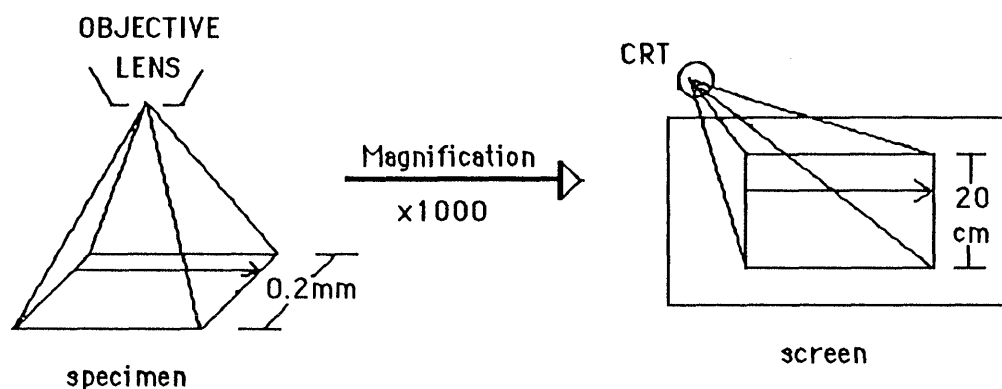


Fig. 1.13. Dependence of specimen area and screen area on magnification.

Magnification of an image in scanning microscopy is the direct relationship between the area scanned on the specimen and the size of the CRT (Fig. 1.13). The magnification control adjusts the size of the area of specimen scanned. Variation in the working distance (Fig. 1.14) must be considered either by a "working distance factor," or a "compensated magnification display." In most systems today, change in the focussing of the scanned area from b to a is usually compensated for automatically.

The JEOL T100 does not incorporate such a feature and specimens have to lie at a fixed working distance specified by the manufacturers. The following theory along with experimental results is an attempt to calculate the exact working distance and hence the magnification factor. This could be prove to be useful for awkward specimens which cannot be directly mounted at the specified working distance ie. optical fibres.

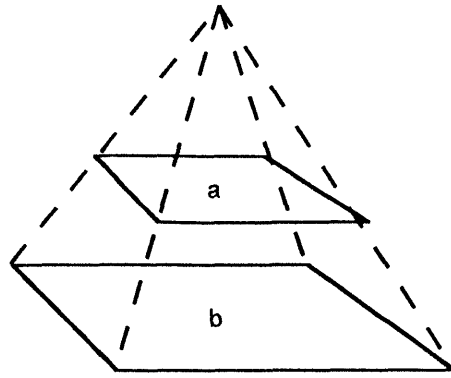


Fig. 1.14. Effect of working distance on magnification.

1.3.1. Theory

The T100 SEM is a general purpose instrument for observation of samples placed on a brass or aluminium stub of 1cm height and diameter. Samples should ideally be gold coated to prevent charging by the electron beam although it would be possible to observe samples without gold coating and at low beam voltages but at the expense of a poorer image at high magnifications. The stub is mounted on a stage inside the chamber and has external micrometer screws for rotation and movement in the x-y plane. The whole stage can be tilted manually through an angle of 90° , the angle of tilt being read off by markers placed around the external cylindrical head. Most of the standard controls for image observation are manual namely beam current, beam voltage (5, 15, 25 keV), focus and astigmatism correction. The mark and space distances for line measurements at a particular magnification is imprinted automatically on the film when it is exposed. This measurement is set for a working distance of 20mm so the stub must lie flush with the top rim of the sample holder for an accurate measurement.

When a stub holding the sample is mounted onto the holder the sample will not be imaged at the exact 20mm working distance particularly if the sample is not flat. This variation in working distance leads to errors in the magnification scale which can be quite significant at high magnifications. The

T100 was calibrated based on the following theory in order to estimate a magnification weighting for an accurate feature size measurement.

A good reference point to base all calculations of the working distances is the rotation point O (Fig. 1.15) assuming this point remains stationary during rotation of the stage. This is the ideal case since a very tight tolerance in the machining of the cylindrical head is required for this to be true. In any case preliminary measurements indicate that the degree of movement is small compared to the change in working distances. Assuming the image is located at a particular distance in space C from O then an image shift will occur as indicated. Suppose the image point lies at C', then rotating the specimen stage about O in an anticlockwise direction will result in an image shift in the -x direction an image at C'' will be seen to move in the opposite direction ie. +x. This is exactly what is observed in the T100 and is an indication of the position of the image point C whether it is above or below the rotational axis O.

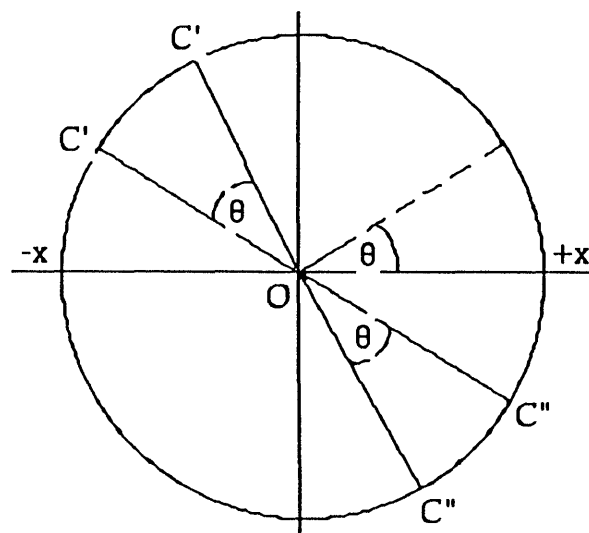


Fig. 1.15. Movement of image placed above and below the rotation point.

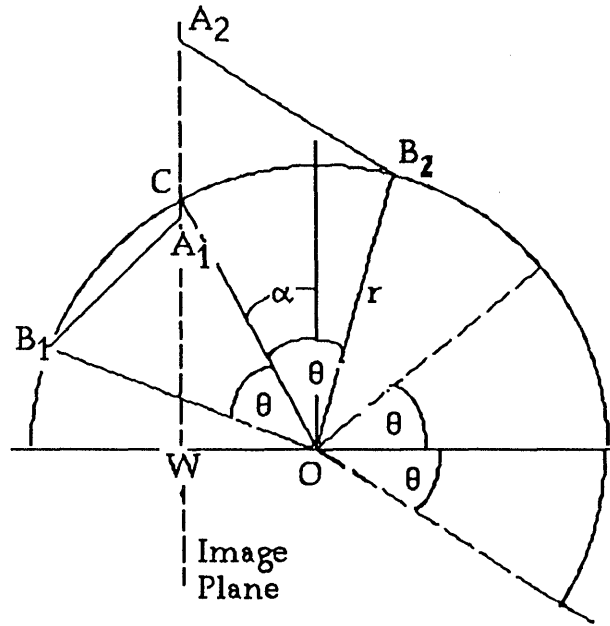


Fig. 1.16. Image displacement with tilt and the distances required to bring it back to the image plane.

The stage is tilted in the clockwise and anticlockwise direction by an angle θ (Fig. 1.16) and the distances A_1B_1 and A_2B_2 travelled to bring it back to the image plane is noted for both cases. WA_1 and WA_2 are now the working distances of the image points from the reference point when tilted through angles $+\theta$ and $-\theta$ respectively. Analytical expressions can be derived from this figure to give the following solutions of α , r , WA_1 and WA_2 .

$$\alpha = \tan^{-1} \left[\frac{1}{\tan(\theta/2)} \left(\frac{A_2B_2 - A_1B_1}{A_2B_2 + A_1B_1} \right) \right] \quad (1.7)$$

$$r = \frac{A_1B_1 \cos \theta}{2 \sin(\theta/2) \cos(\theta/2 + \alpha)} \quad (1.8)$$

$$WA_1 = r \cos(\theta + \alpha) + A_1B_1 \sin \theta \quad (1.9)$$

$$WA_2 = r \cos(\theta - \alpha) + A_2B_2 \sin \theta \quad (1.10)$$

If the image plane is coincident with the rotational point than the distances travelled in both cases should be equal. An offset will result in one or the other being greater with the degree of offset being indicated by their difference.

Fig. 1.16 shows the conditions for this simple case of an image C of distance r from O rotated through an angle θ in an anticlockwise direction. Solving the equations for triangles A_1B_1W and B_1WO gives the following relationships:

$$r = \frac{A_1B_1}{\tan \theta} \quad (1.11)$$

$$OA_1 = r \cos \theta + A_1B_1 \sin \theta \quad (1.12)$$

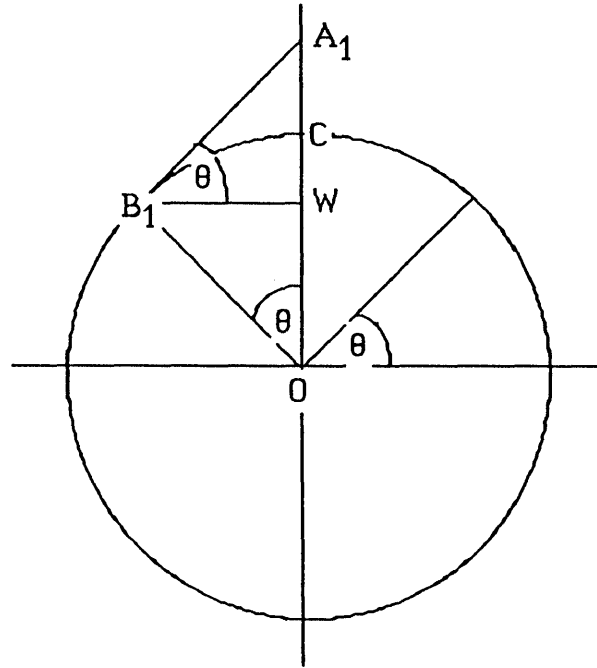


Fig. 1.17. Image plane coincident with the rotational axis O .

Table 1.1.

Values of the radius described by the image point and their corresponding working distances for various tilt angles.

$\theta(\text{deg.})$	A_1B_1	A_2B_2	$r(A_1B_1)$	$r(A_2B_2)$	OA_1	OA_2
10	0.07	0.07	0.40	0.40	0.40	0.40
20	0.15	0.15	0.41	0.41	0.44	0.44
30	0.24	0.22	0.42	0.38	0.48	0.44
40	0.35	0.33	0.42	0.39	0.55	0.51
50	0.47	0.48	0.39	0.40	0.61	0.63

length in mm

Values of r and the working distances obtained from Eqns. 1.11 & 1.12 are shown in Table 1.1 for a random image focussed at 3k magnification. The small differences in the values of A_1B_1 and A_2B_2 indicate that the image lies almost coincident with the rotational axis. Since the stage is rotated manually and aligned with external markers, the discrepancy could be due to a slight mismatch. The radius of the image point from O is about 0.4 mm with a small variation with tilt. As expected, the working distance increases with tilt. α in table 2 points to an image offset of not more than 10 which could have been due to a slight displacement of the rotational axis O in the x plane.

Table 1.2.

Values of radius described by the image point using Eqns. 1, 2, 3, 4

$\theta(\text{deg.})$	A_1B_1	A_2B_2	α (deg)	r	WA_1	WA_2
10	0.07	0.07	0.0	0.40	0.40	0.40
20	0.15	0.15	0.0	0.41	0.44	0.44
30	0.24	0.22	-9.2	0.40	0.50	0.50
40	0.35	0.33	-4.6	0.41	0.56	0.51
50	0.47	0.48	1.3	0.40	0.61	0.63

length in mm

Since r remains constant we can assume that this error will not lead to significant errors in the working distance and it can be ignored. The working distance in both tables are very similar so we can use the simplified equations of $\frac{1.1}{r}$ and $\frac{1.12}{r}$ for all subsequent calculations.

1.3.2. Results

Group 6f chromium lines* fabricated in Chapter 6 were used for this calibration. SEM pictures were taken of this whole group of 10 lines and the first line (Figs. 1.18, 19, 20) mainly at 5k and 15k magnifications. Images were placed centrally on the screen so that horizontal line measurements could be carried on the same cross sections of the chromium lines. Line measurements were compared with the measurement obtained from the Cambridge Stereoscan 2000 (GEC Hirst) which were assumed to be the true values, 17.6 μm for 10 lines and 1.23 μm for a single line. Group linewidth measurements at 0° do not vary by more than 0.3 μm at magnifications 2k, 3k, and 5k. Results of the measurements of the taken from the negatives together with the calculated working distances are shown in table 3. Linewidth increases by as much as 0.25 μm for a change in working distance of only 1.6 mm and substantially more at lower magnifications (2.3 μm). The percent change relative to the field size at low and high magnifications are similar.

Table 1.3.

Line measurements of chromium lines taken from the negatives.

WD (mm)	Width (μm)	
	10 lines	1 line
1.9	20.0	1.50
0.9	19.5	1.36
0.6	18.0	1.30
0.3	17.7	1.25

* Refer to Fig. 6.13

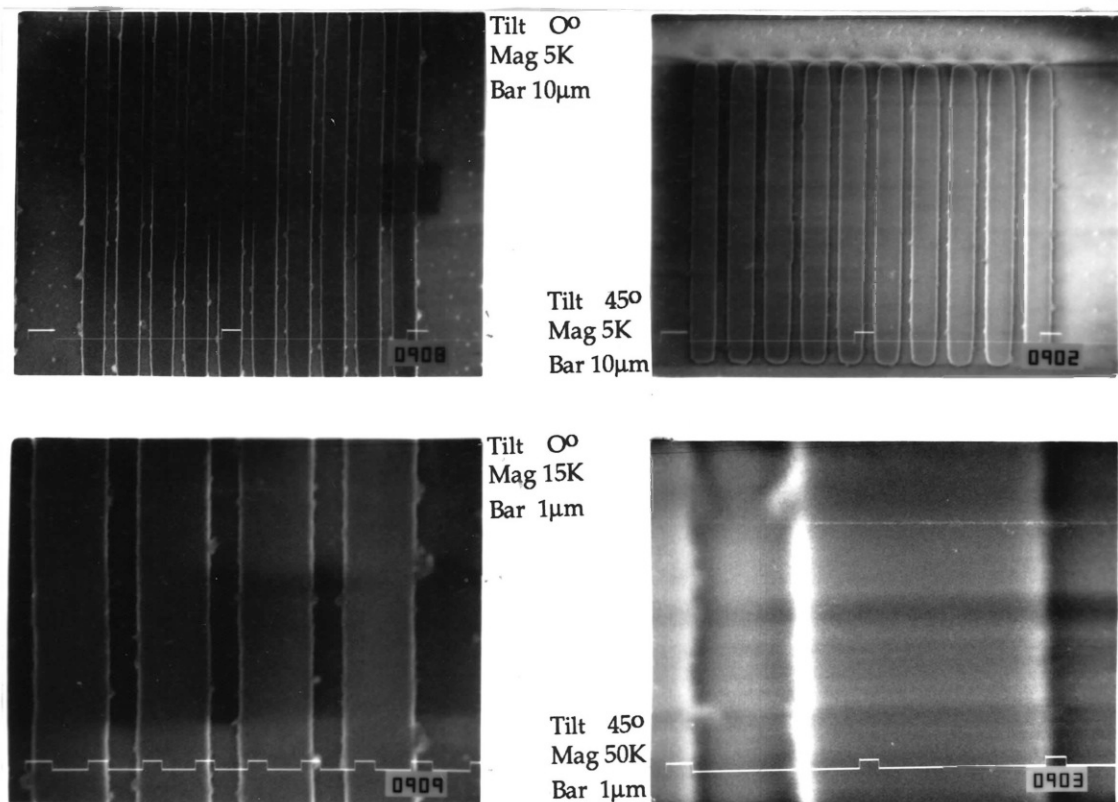


Fig. 1.18. SEM images of chromium lines taken at (a) 0° and (b) 45°.

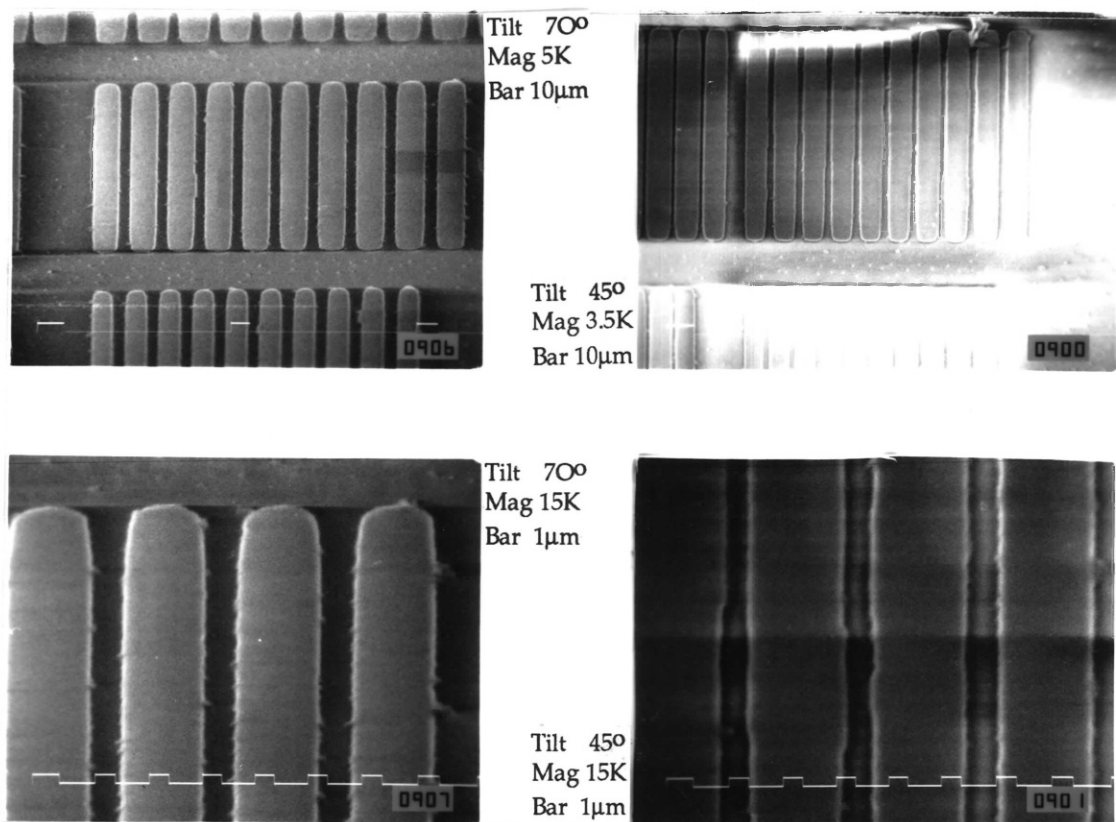


Fig. 1.19. (a) Image at 70° tilt and 5k mag., (b) Image of group 7f at 5k and 20k

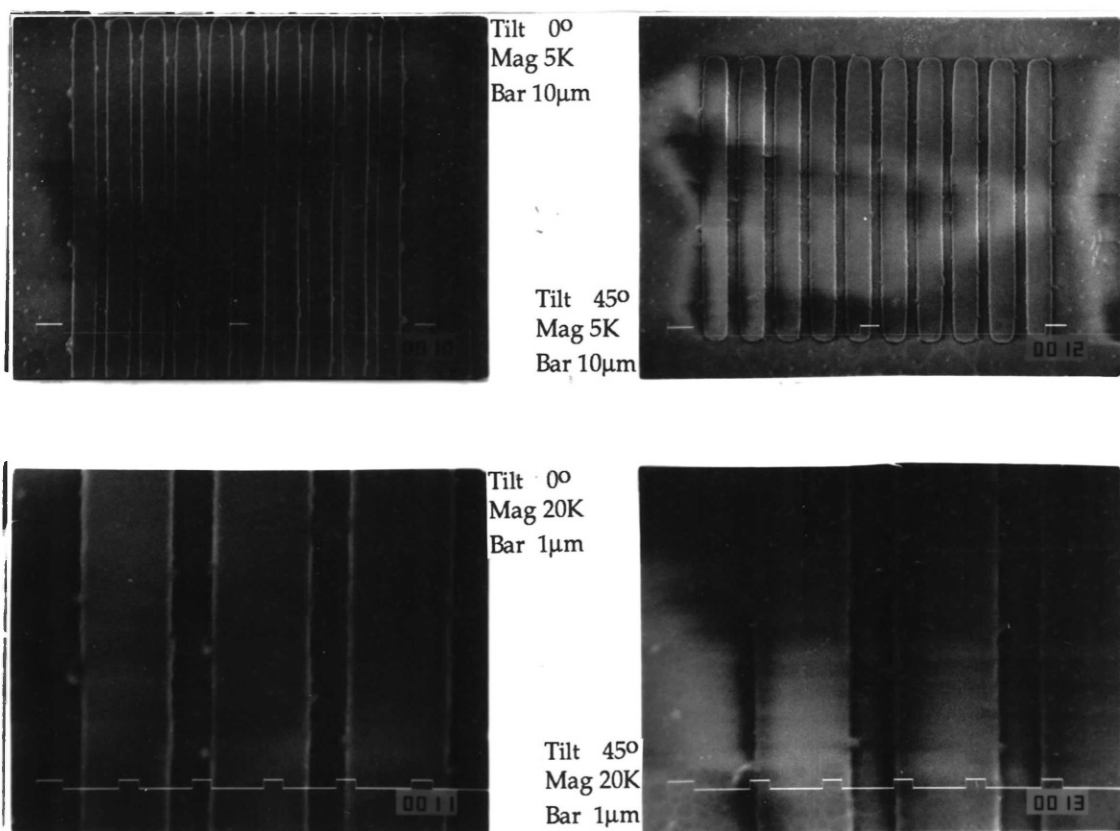


Fig. 1.20. (a) Images at 0°, (b) 45°, with specimen remounted.

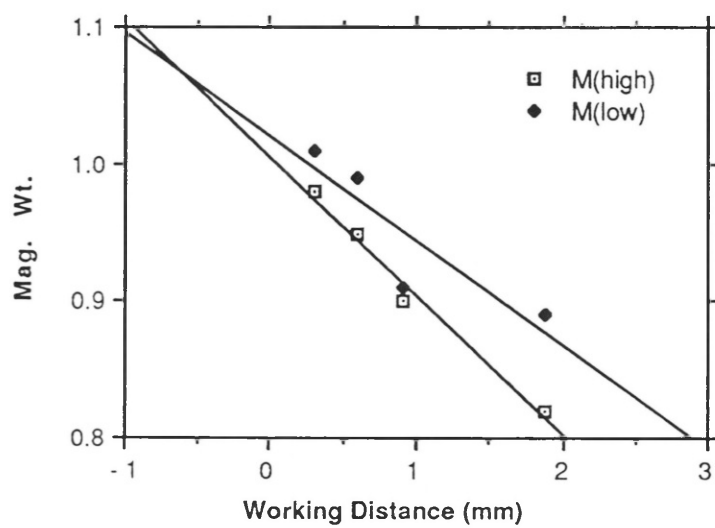


Fig. 1.21. Magnification weighting versus working distance calculated from the SEM negatives at high and low magnifications.

Magnification weightings were calculated from these results and plotted in Fig. 1.21. The manufacturers data of the weighting factor of 1.0 at the 20mm working distance appears to be accurate since the magnification weighting of 1.0 lies very close to the rotational point O. Polynomials curves of reasonable fit were selected for the two sets of data [M(low), M(high)] and are also shown on the figure:

$$M = 1.0055 - 0.10108W \quad (1.13)$$

$$M = 1.0197 - 7.5809 \times 10^{-2}W \quad (1.14)$$

M is the weighting factor, and W is the working distance calculated from Eqns. 1.11 & 1.12. These equations can be applied to an image lying a few mm to the rotational axis and hence a magnification factor can be found to correct for the scale.

1.3.3. Conclusions

The correction factor required for the magnification weighting when the sample is tilted is not very significant provided the specimen for observation is placed in the middle of the stub. This ensures that the working distance when the stage is tilted does not shift a significant amount thus enabling measurements to be made accurately without the need for a correction factor. When specimens were placed at a shorter working distance than 20 mm to obtain a better image a magnification weighting was taken into account from Eqns. 1.13 & 1.14. For specimens such as optical fibres where the working distance of the observed specimen may change considerably, the magnification correction factor may be used to obtain an accurate measurement.

ELECTRON BEAM PROCESSES

By using finely focussed electron beams, very complex device patterns with high resolution (submicron) can be created on polymer resist layer. Resolution is in general superior to presently available optical lithography, because the electron probe size may be made smaller than the corresponding diffraction limited image in optical lithography (see chapter 1).

It is important to understand how the resist image is produced by the electron beam. Resolution is limited by the electron scattering in the resist. The effects of beam energy, type of resist, resist thickness, substrate type and several other variables are critical in producing an optimal pattern in the resist. Exposure and development characteristics exert dominant influence on the quality of the written pattern. In order to characterise these effects in organic or inorganic resists, the phenomena of e-beam scattering in solids must be understood.

Electron penetration into solid material have been studied for over 70 years. Most of the theoretical relationships are only applicable at high energies [1, 2, 3, 4]. Important contribution by Wentzel [5, 6], Moliere [7, 8], Lenz [9], Marton et al [10] and Smith and Burge [11] were concerned with plural scattering events. Based on experimental data, the results have been presented in a collected and generalised form by Cosslett and Thomas [12, 13, 14]. Experimental results from different collision models have been reported by Goudsmit and Saunderson [15], Spencer [16], Lenz [17], Meister [18], Archard [19], Everhart [20], Makhov [21, 22, 23], Shimizu and Shinoda [14] and Dashen [25].

The theory of Bethe "continuous slowing down approximation" (csdsa) of incident electrons in solids leading to the derivation of range and electron energy dissipation will be considered. Monte Carlo simulations which traces

the path of many of these electrons based on this theory will be presented particularly with reference to the materials, CdCl₂, CdI₂ and PMMA used in some of my experiments. The theory proposed by Kanaya [34] which has excellent agreement with experimental results will also be given as this enables analytical solutions to be obtained for the computation of range, lateral scattering, backscattering coefficient, energy dissipation and secondary emission. Finally, discussion of how these parameter variables affect organic resist profiles will be given in context to the results of the above theories. In chapter 3, it will be shown that the application of range, backscattering, energy dissipation derived from these basic theories can be extended to the case of inorganic resists namely CdCl₂ and CdI₂ for predicting the limits of resolution.

2.1. Bethe Approximation

When a stream of electrons penetrates into a solid target, electrons may be scattered either elastically or inelastically. Inelastic collisions result in a loss of energy and occurs between the incident electrons and the atomic electrons. The atomic electrons are either excited or ejected in which case secondary electrons are produced. In such collisions, the momentum transfer is small but the energy loss is very large. Elastic collisions occurs between the incident electrons and the atomic nuclei, with transfer of both energy and momentum. The electrons travel straight into the target, suffering energy loss due to the electronic collisions, and also to be deflected by the nuclear collisions. Backscattering electrons experience large angle scattering (> 90°) due to nuclear scattering.

For non relativistic energies, the Bethe rate of energy loss differential equation [26] adequately describes the mean rate of energy loss along the electron path. The Bethe equation can be written as,

$$-\frac{dE}{ds} = \frac{1}{8\pi\epsilon_0^2} N_A e^4 \left(\frac{Z\rho}{A} \right) \left[\frac{1}{E} \ln \left(\frac{aE(s)}{I} \right) \right] \quad (2.1)$$

where E is the electron energy, Z and A the atomic number and gram atomic weight of the solid respectively. N_A is the Avogadro's number, e the electron charge, I is the mean excitation energy for energy loss in the solid and the constant a has the value 1.1658 [26]. An empirical formula attributed to Sternheimer, relating to experimentally determined values such as [27]

$$I = (9.76 + 58.8Z^{-1.19})Z \quad (2.2)$$

which is valid for $Z \geq 13$. For compounds, the average atomic number and atomic weight may be used in Eqns. 2.1 and 2.2. For a compound of the form XY_n , Z_{av} and A_{av} can be calculated from the following equations,

$$Z_{av} = Z_x \frac{A_x}{MW} + nZ_y \frac{A_y}{MW} \quad (2.3)$$

$$A_{av} = \frac{(A_x)^2}{MW} + n \frac{(A_y)^2}{MW} \quad (2.4)$$

Where MW is the molecular weight of the compound XY_n , Z_{av} is the calculated average atomic number, A_{av} is the average atomic weight. Eqn 2.1 is usually termed the "continuous slowing down approximation". The Bethe Range (R_B) is the total path travelled by the average electron in the solid before it loses all of its energy. Bethe range is plotted in Fig. 2.1 as a function of energy for several common materials used in e-beam lithography. The curves below 10 keV are shown dotted, since Eqn. 2.1 is valid only at high energies. For energies above 10 keV, approximate expression of the form $R_B \propto E^n$ with $1.5 \leq n \leq 1.8$ are often used. For the most common energy range (20 keV-30 keV) used in lithography today, R_B varies from 2.1 μm to 14.5 μm in PMMA and 1.5 μm to 10 μm in SiO_2 .

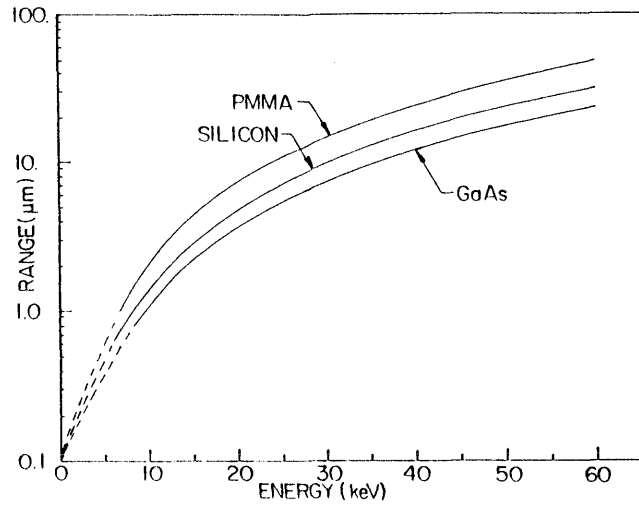


Fig. 2.1. The Bethe range (R_B) as a function of incident beam energy for PMMA, Si and GaAs materials. (After Greinweich, Ref. [28])

Grun has measured the energy dissipation versus penetration distance in air [29]. He showed that the shape of the depth-dose curve is practically invariant if penetration distance is normalised to R_G as shown in Fig. 2.2 and energy is normalised to E_B . The extrapolation of the linear portion of the curve defines the Grun range (R_G) and E_B is the incident beam energy. The work reported by Everhart and Hoff [30] showed that these general conclusions can be extended to solids using the Bethe equation (Eqn 2.1). In a similar way, if the energy as a function of path length is normalised to the incident energy and the path length is normalised to the range in the solid, the relationship between E/E_0 and s/R_B is only weakly dependent on material properties. Fig. 2.3 shows the relation for typical parametric values of $\xi_0 = aE_0/I$; for example at 20 keV, ξ_0 is 135 and 355 for Si and PMMA respectively.

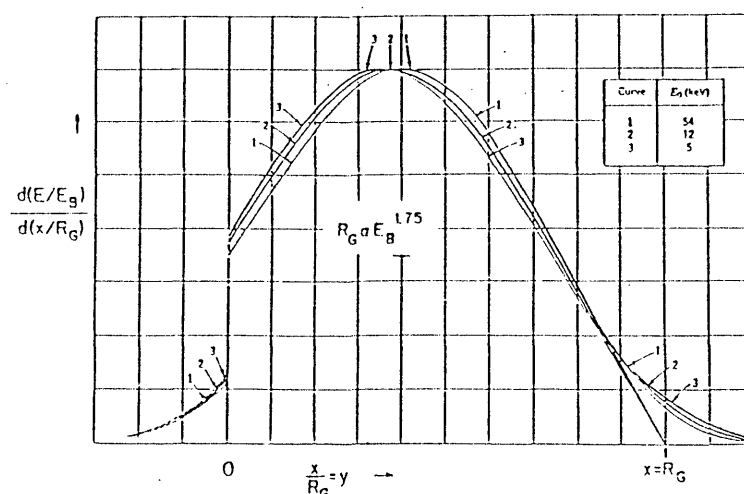


Fig. 2.2. Normalised depth-dose curve for an incident energy E_g and Grun range R_g showing the invariant property at various energies at 54, 12 and 5 keV. (After Grun, Ref. [29])

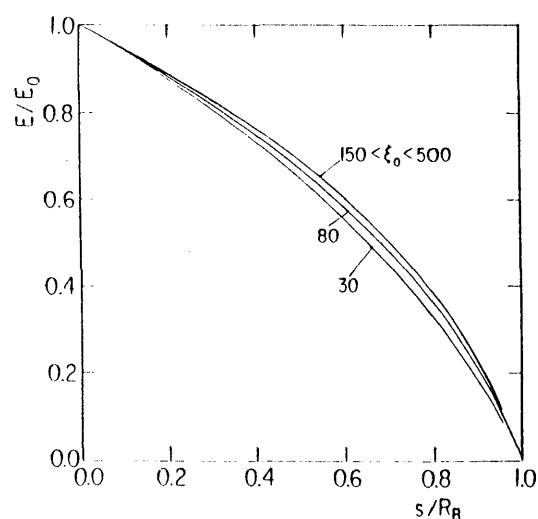


Fig. 2.3. Normalised energy path length function for various values of the parameter $\xi_0 = aE_0/I$. (After Greeneich and Van Duzer, Ref [31])

The probability of scattering through an angle ϕ during a distance of travel Δx in a material characterised by Z , ρ , and A is

$$p(\phi, E) = \frac{N_A e^4}{(4\pi\epsilon_0)^2} \left(\frac{Z\rho}{A} \right) \left(\frac{Z}{E^2} \right) \frac{\Delta x}{\sin^4(\phi/2)} \quad (2.5)$$

The probability that this same electron will suffer a fractional energy loss $\Delta E/E$ is obtained from Eqn. 2.1,

$$\frac{\Delta E}{E} = \frac{1}{8\pi\epsilon_0^2} (N_A e^4) \left(\frac{Z\rho}{A} \right) \left(\frac{1}{E^2} \ln \left(\frac{aE}{I} \right) \right) \Delta x \quad (2.6)$$

This expression is derived by treating the atoms in the resist as individual scattering spheres, which is valid since the electron wavelength is itself short (0.1 Å). Probability of angular scattering to fractional energy loss:

$$\frac{p(\phi, E)}{(\Delta E/E)} = \frac{1}{32\pi} Z \frac{1}{\ln(aE/I) \sin^4(\phi/2)} \quad (2.7)$$

Therefore, for a given scattering angle ϕ and energy e , the large angle scattering per unit fractional energy loss increases rapidly with Z . Hence, a more zig-zagged path is obtained for high Z materials and the peak of the energy dissipation will move towards the surface as Z increases. Backscattering of electrons will also be expected to increase with Z and a decrease in beam energy. This has found to be the case in practice as Fig. 2.4 shows. Backscattered electrons can spread over distances equal to the electron range, so device pattern features separated by a distance less than this range can experience exposures dependent on the neighbouring patterns.

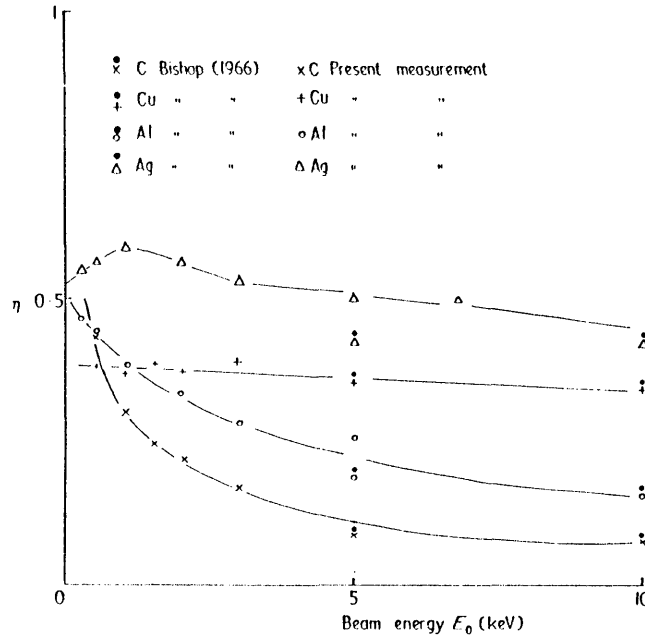


Fig. 2.4. Backscattering coefficient η at normal incidence as a function of beam energy for several targets. (After Darlington and Cosslett, Ref [32])

2.2. Monte Carlo Simulation

In this simulation, the electron is assumed to travel in a succession of short straight paths between elastic events as shown in Fig. 2.5. To model elastic scattering, the screened Rutherford formula is used for the differential cross-section,

$$\frac{d\sigma}{d\Omega} = \frac{Z^2 e^4}{(4\pi\epsilon_0)^2} \left[\sin^4 \frac{\theta}{2} + \frac{\theta_o^2}{4} \right]^{-1} \quad (2.8)$$

where $d\sigma/d\Omega$ is the differential cross section per unit angle and θ_o is the screening parameter given by,

$$\theta_o = 3.7Z^{1/3}E^{-1/2}$$

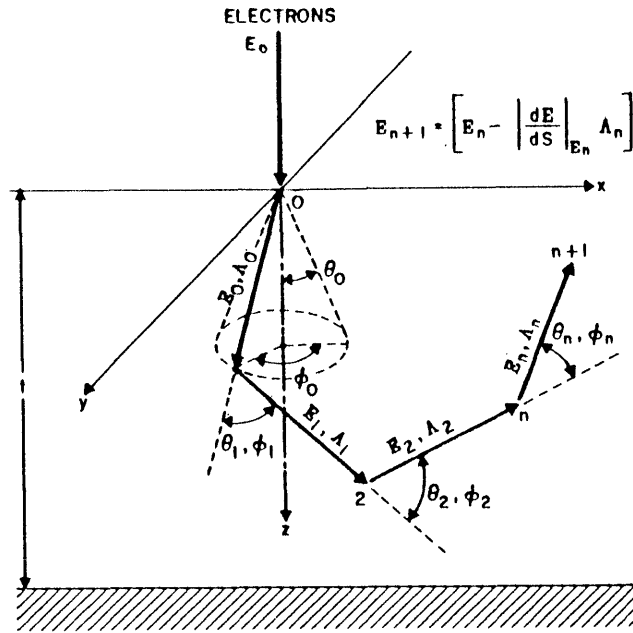


Fig. 2.5. Path of an electron in a solid target showing the calculated and predicted angles of scattering and path lengths between collisions. (After Kyser and Murata, Ref. [33])

At each scattering point, the resulting azimuthal angle θ is determined by selecting a random number weighted with differential cross-section (Eqn. 2.8). The path length λ_i between scattering events is selected by weighting the mean free-path between collisions by another random number in the zero to one range. The energy of the electron is reduced at each step by multiplying the path length by the Bethe energy loss rate (Eqn. 2.1). The process is repeated until the electron comes to rest.

Fig. 2.6 shows the simulation of electron trajectories in $0.35 \mu\text{m}/1 \mu\text{m}$ (PMMA/SiO₂) on Si substrate. The programme was developed by the Dr. E. Napchan of the Materials Science Group, Imperial College. Simulated paths of 1000 electrons are shown with an initial beam energy of 20 keV. The beam is incident along the z axis and trajectories have been projected onto the xz plane. This figure qualitatively shows the degree of lateral forward scattering

within the resist as well as the degree and position of backscattering. Also shown, is the energy dissipation (dE/dz) as a function of z . Most of the energy deposited is in the SiO_2 and this is why a low beam energy is more efficient in writing since the energy loss per unit length is greater and the maximum deposited energy shifts towards the surface. This also accounts for the increase in the decomposition rate observed for CdCl_2 and CdI_2 at low beam energies due to the high concentration of Cl^- and Cd^{2+} produced and thus available for reaction (chapter 3).

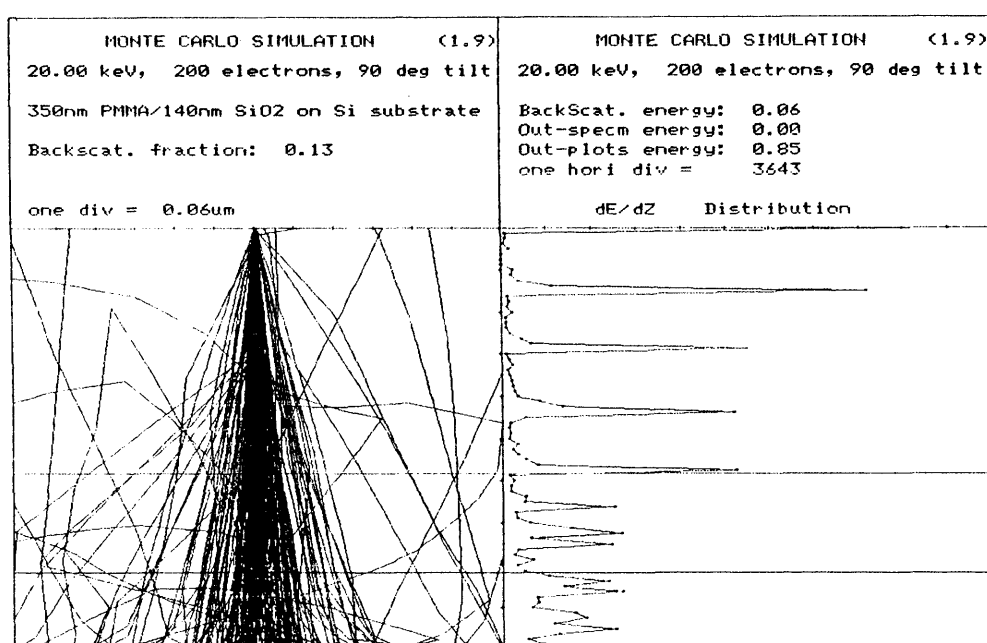


Fig. 2.6. Monte-Carlo simulation of 200 electron trajectories on 0.35 μm PMMA /0.14 μm SiO_2 on Si substrate. (software by Dr. E.Napchan)

The range in a target is a useful indicator of the scattering processes in the solid ie. a high Z will lead to greater lateral scattering and therefore a reduced depth of range compared to low Z materials. Thin films can be characterised by the average number of elastic events P_e which an energetic electron suffers in passing through the film. When energy loss is neglected, P_e is obtained by multiplying the single atom elastic scattering cross section, which is the

integral of Eqn. 2.8, thus

$$P_e = \pi Z^2 e^4 t_0 N_A / A E_0^2 \theta_0^2 \quad (2.9)$$

where t_0 is the film depth at which the flux is being determined. For typical electron resists Eqn. 2.17 becomes

$$P_e = 400 t_0 (\mu\text{m}) / E_0 (\text{keV})$$

Hence at 20 keV and $t_0 = 0.5 \mu\text{m}$, $P_e = 10$ events. The number of events is very important since the amount of scattering increases exponentially with P_e and minimising P_e is very desirable.

2.3. Kanaya's Unified Theory

A diffusion model of electron beams penetrating in a target has been proposed by Kanaya and Okayama [34] based on the atomic power potential between electrons and atoms. The centre is located at the most probable energy dissipation depth (Fig. 2.7), with r_B as the backscattering range, x_D the diffusion depth and R the maximum range. In this section, analytical solutions of the above variables derived from the power potential will be obtained for CdCl_2 and CdI_2 . Readers are asked to refer to the paper by Kanaya and Ono [35] for full details of the derivations of these functions.

Following Lindhard's theory, the potential $V(r)$ between the electron and the target atom is assumed to be

$$V(r) = Z e^2 a^{s-1} / r^s \quad (2.10)$$

with $a = 0.8853 a_H Z^{(-1/6)} (\text{\AA})$

where Z is the atomic number of the target, e the electronic charge and a the

effective screened radius of the atom, a_H is the Bohr radius of the hydrogen atom. s is a numerical parameter, with $s = 1$ corresponding to Rutherford scattering.

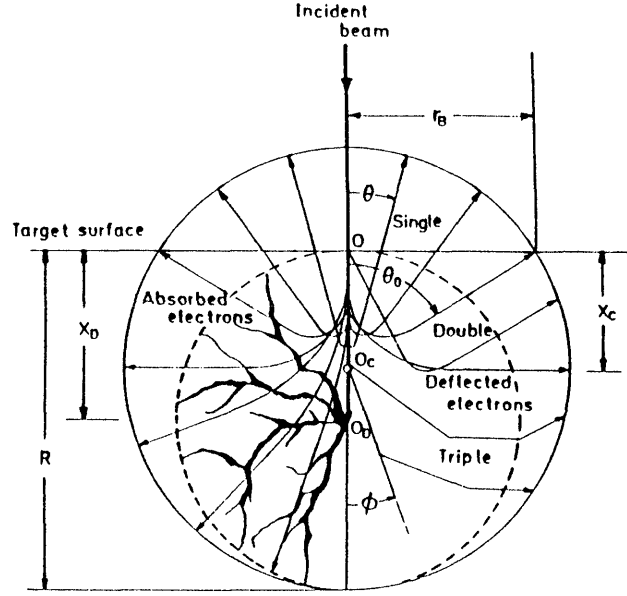


Fig. 2.7. The diffused model of electron-beam penetration in a target: R is the maximum range; x_D the diffusion depth; x_C the maximum energy dissipation depth; r_B the backscattering range.

The total differential scattering cross-section due to nuclear scattering is,

$$\sigma_n = \lambda_s \frac{2.97 \pi a^{1/\beta} e^{10/\beta} Z^{5/\beta}}{E^{5/3}} \quad (2.11)$$

where E is the incident energy of electrons [eV] and λ_s is a constant determined empirically.

The differential energy loss due to inelastic collisions with electrons is,

$$\lambda_s = \frac{3 \times 2^{5/3} \pi a^{1/\beta} e^{10/\beta} N Z}{E^{2/\beta}} \quad (2.12)$$

where N is the number of atoms per unit volume in the target: $N = N_a \rho / A$; N_a is the Avogadro number, 6.023×10^{23} . Equations 2.10 and 2.11 are the fundamental equations of elastic and inelastic scattering theory.

2.3.1. Range-Energy Relationship

The maximum range can be derived from the energy loss equation (Eqn. 2.11),

$$R = \int_0^{E_0} \frac{dE}{dE/dx}$$

$$\rho R = 5.025 \times 10^{-12} A E_0^{5/3} \lambda_s Z^{8/9} \quad (2.13)$$

where E_0 (eV) is the incident electron energy. The above equation can be rewritten under the relativistic corrections of energy $E_0(1 + 0.978 \times 10^{-6} E_0) / (1 + 1.957 \times 10^{-6} E_0)$ and $a = 0.8853 a_H Z^{-1/3} (1 + 1.957 \times 10^{-6} E_0)^{-1}$,

$$\rho R = \frac{2.76 \times 10^{-11} A E_0^{5/3}}{Z^{8/9}} \frac{(1 + 0.978 \times 10^{-6} E_0)^{5/3}}{(1 + 1.957 \times 10^{-6} E_0)^{4/3}} \quad (2.14)$$

Range obtained from this equation for various targets (Al, Cu, Au, Ag, U, C) agree very well with experimental results in the 10-1000 keV range obtained by Cosslett and Thomas (1964b) and Berger and Seltzer (1964). Fig. 2.8 shows the range for $CdCl_2$ and CdI_2 compared to the Bethe range for beam energies in the region 0-5 keV.

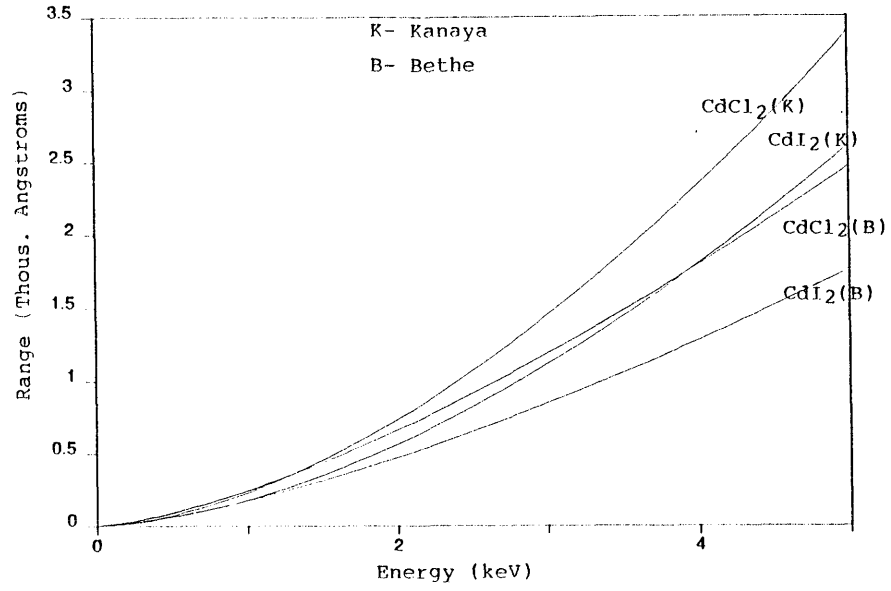


Fig. 2.8. Range of electrons in CdCl₂ and CdI₂ using Eqn. 2.14.

From Eqns 2.13 and 2.14 the energy E of electrons at depth x is simply expressed in terms of the reduced depth $y = x/R$

$$E/E_0 = (1-y)^{3/5} \quad (2.15)$$

This is the energy retardation relationship from which the fractions of transmission, backscattering, and absorption of electrons can be obtained.

2.3.2. Backscattering

The fraction of the primary electrons transmitted into the forward hemisphere is assumed to obey an exponential relation similar to the Lenard law and is given by,

$$\eta_T = \exp\left(-\frac{\gamma y}{1-y}\right) \quad (2.16)$$

The parameter γ takes into account diffusion loss due to multiple collisions for returning electrons and energy retardation due to electronic collisions. It is related to the atomic number as follows;

$$\gamma = \frac{2.97}{5 \times 2^{5/3}} Z^{2/3} = 0.187 Z^{2/3} \quad (2.17)$$

The general form of the backscattered electrons is assumed to have the same exponential relationship as the transmitted electrons but the absorption factor γ_B must be greater than γ because of diffusion loss due to multiple collisions. The backscattered fraction η_B may be obtained from the expression.

$$\eta_B = \frac{6}{5} \int_0^y \frac{\gamma_B}{(1-y)^{7/6}} \exp\left(-\frac{\gamma_B y}{1-y}\right) dy - \frac{6}{5 \times 2^{5/6}} \left\{ 1 - \exp\left(-\frac{\gamma_B y}{1-y}\right) \right\} \quad (2.18)$$

This has been solved numerically using the Simpson rule for CdCl_2 and CdI_2 targets and plotted in Fig. 2.9.

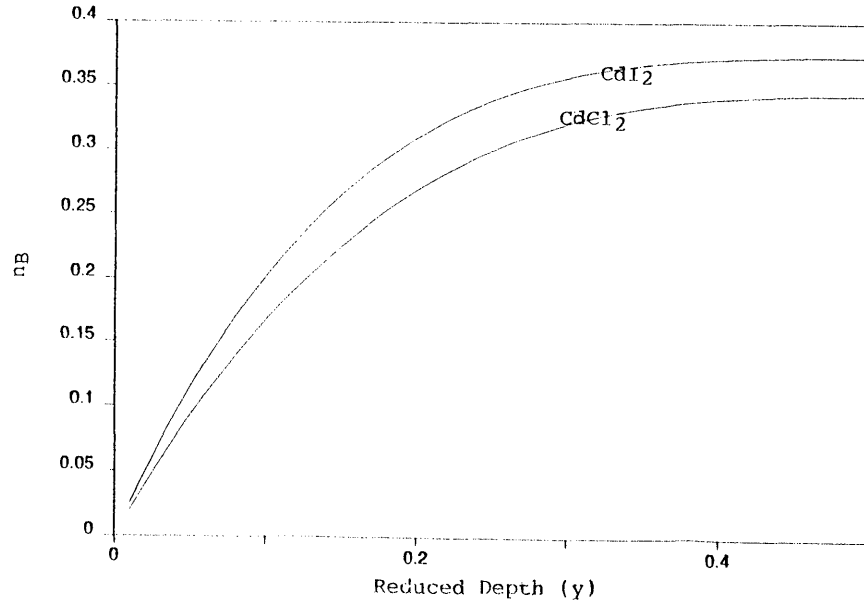


Fig. 2.9. Fractional electron backscattering η_B for CdCl_2 and CdI_2 targets.

2.3.3. Diffusion Model

The distributions of electrons penetrating a target can be represented by a sphere whose centre is located at a depth x_E of energy dissipation (Fig. 2.7). From the definition of diffusion depth x_D where the transmitted fraction is $1/e$, it follows that

$$x_D = \frac{R}{1 + \gamma} = \frac{R}{1 + 0.187Z^{2/3}} \quad (2.19)$$

The backscattering range r_B is given by

$$r_B = \frac{CR\gamma}{1 + \gamma} \quad (2.20)$$

where the best fitting is obtained by taking $C = 1.1$

The maximum energy dissipation depth x_E can be obtained by a simple geometrical relation:

$$x_E = \frac{R}{2} \left(1 - \frac{C^2 \gamma^2}{(1 + \gamma)^2} \right) = \frac{R(1 + 2\gamma - 0.21\gamma^2)}{2(1 + \gamma)^2} \quad (2.21)$$

The values of x_E/R for CdCl_2 and CdI_2 are 0.23 and 0.19 respectively.

The backscattering coefficient r can be obtained from the following equation:

$$r = \frac{1}{4\pi} \int_0^{\theta_0} 2\pi \sin \theta d\theta = \frac{1}{2} (1 - \cos \theta_0) \quad (2.22)$$

with

$$\tan \theta_0 = \frac{r_B}{x_E} = \frac{2.2\gamma(1 + \gamma)}{1 + 2\gamma - 0.21\gamma^2}$$

For CdCl_2 , $r=0.35$ and CdI_2 , $r=0.39$.

2.4. Resist Images

In section 2.3, modelling of electron scattering in solids was shown with analytical (Bethe and Kanaya) and statistical (Monte Carlo) solutions to energy dissipation, backscattering and substrate range. This section will discuss the importance of these parameters on key issues in lithography such as resist profiles, resolution and proximity effects with emphasis on organic resists. Much of the discussion as will be shown in chapter 3 also applies to inorganic resists.

2.4.1. Energy Density Profiles

One of the most illustrative way of representing electron scattering in solids is to view a cross section of the resist profiles and plot contours of constant energy absorption. Fig. 2.10 shows the results of a single line scan for three different beam energies. The solid lines represent contours of constant energy density for two different doses neglecting any developer effects. The outer contours in each case represents 3.3 times the dose of the inner contours. Also shown in dotted lines are the experimental data of Wolf et al. [48]. The modelling of the resist image is very good except near the top of the resist which is due to developer effects.

2.4.2. Resolution and Linewidth Control

The smallest linewidth obtainable is highly dependent on the exposure conditions and resist properties. Typically four passes of the beam spaced at the Gaussian half-width of the beam are used to generate the minimum feature size in the circuit designer's pattern. Such a writing strategy improves linewidth control. Effects of backscattering of electrons from the resist and the substrate on the linewidth can be seen by varying the total dose. In Fig. 2.11 the experimental data are compared with theoretical predictions for a single pass of a 200 Å, 20 keV beam

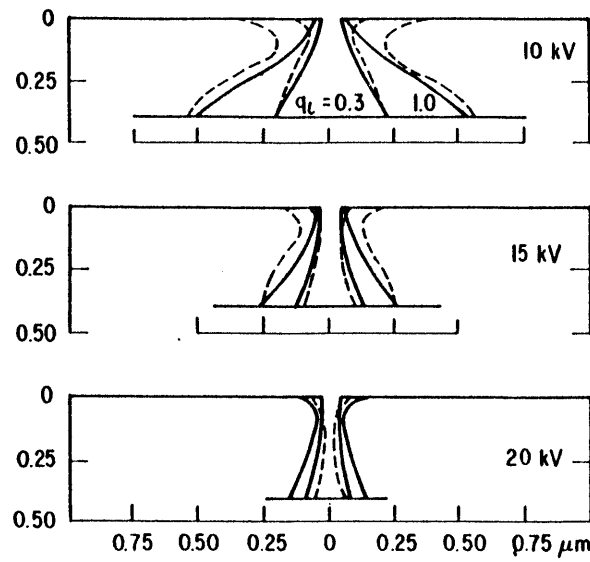


Fig. 2.10. Resist profiles obtained in 0.4 μm PMMA on Si substrate, with incident doses q_1 in units of $10^{-8}\text{C}/\text{cm}$. Dashed lines are the experimentally developed profiles and the theoretical profiles are given in solid lines. (After Greeneich and Van Duzer, Ref. [47])

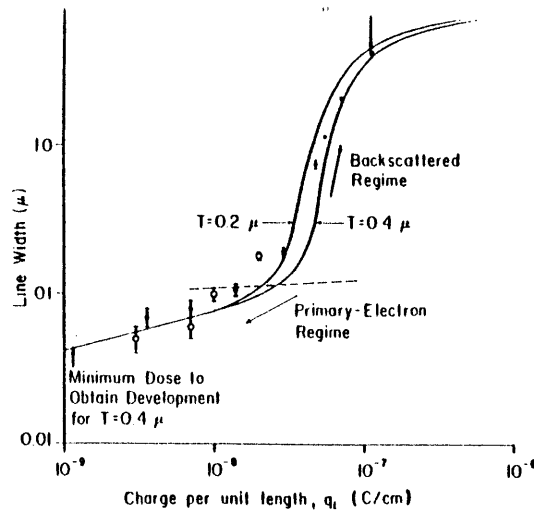


Fig. 2.11. The linewidth as a function of incident charge per unit length for PMMA resist. The data is from Wolf et al. [48]; open circles (SiO_2 - Si, $T = 0.4 \mu\text{m}$) and Greeneich and Van Duzer [49], solid circles (glass, $T = 0.3 \mu\text{m}$). $E_0 = 20 \text{ keV}$; PMMA on Al; $\epsilon_C = 6.8 \times 10^{21} \text{ eV}/\text{cm}^3$. (After Greeneich and Van Duzer, Ref. [49])

on 0.2 and 0.4 μm of PMMA coated on Al substrate. A developer model where development occurs to a critical energy level is assumed for the theoretical predictions. The critical energy level for development was taken as 6.8×10^{21} eV/cm³. Substrate and backscattering range of the electrons in an Al target is 4.08 μm and 2.28 μm from Eqns. 2.14 and 2.19 respectively.

The dotted line represents the linewidth at which half the energy density is contributed by primary electrons and half by backscattered electrons. At low doses the linewidth is dominated by primary electrons and the change in width is marginal. At higher doses the backscattered electrons dominate giving a larger slope and the response flattens off as the linewidth approaches twice the range in the substrate. Fig. 2.12 illustrates the expected linewidth variation for focussed beams at 10, 15, 20 keV beam energies. Linewidth is smaller at low incident doses for the higher beam energies due to less scattering at high energies.

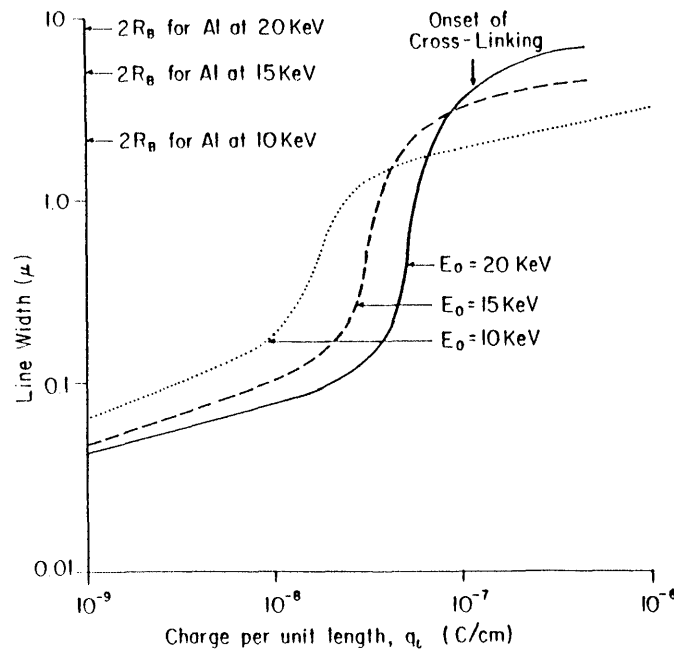


Fig. 2.12. The linewidth as a function of dose for 10, 15, 20 keV beam energies (PMMA, $T = 0.4 \mu\text{m}$, Al substrate). After Greeneich and Van Duzer, Ref. [49])

For minimum linewidth, it is desirable to expose in the region of primary (forward) scattered electrons. Therefore, a smaller number of elastic events should be utilised as Eqn. 2.16 shows, implying high beam energies and thin resist films. Increasing the beam voltage dictates increasing the resists exposure to reach a required critical energy density. Since the backscattered range is a function of the substrate range (Eqn. 2.19) proximity effects are also increased over a larger area.

Most e-beam lithography systems employ operating voltages between 20 keV to 30 keV but it can be shown that an optimum beam voltage can be utilised for a particular film thickness. Heidenrich et al. [50] used Monte Carlo methods to calculate the effects of film thickness on e-beam energy on the contour widths (effectively the linewidths) after complete development up to a critical energy density. The results are summarised in Fig. 2.13. The data indicates two clear trends. For a given resist thickness the linewidth remains a minimum constant value beyond some incident electron energy. A decrease in linewidth occurs over a broad range of beam energies for thick films. For film thicknesses less than $0.5\ \mu\text{m}$ it should be possible to operate at a beam voltage of 10 keV without any significant loss in linewidth.

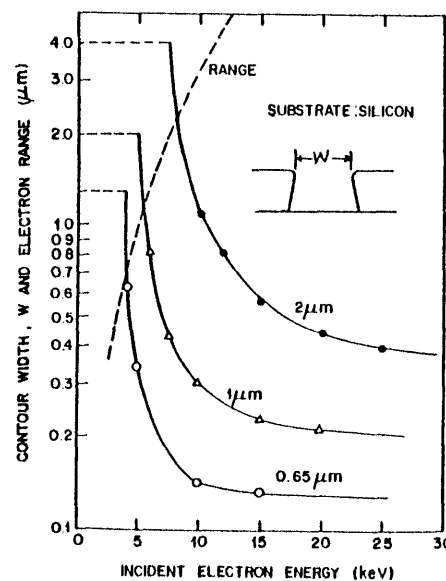


Fig. 2.13. Linewidth as a variation of film thickness. (After Heidenrich et al. Ref. [50])

Sujita and Tamamura [51] have shown that by utilising low beam energies (2-5 keV), sensitivity and intra-proximity effects are considerably improved. Fig. 2.14 shows the normalised dose required for development by beam energies of 1-20 keV. The sensitivities at 2 and 5 keV were improved by factors of 16 and 6 times respectively, as compared with that at 20 keV. Linewidth as small as 40 nm on SNR/Carbon were obtained with 2-5 keV exposures. Resist profiles for 5-10 keV exposure are shown in Fig. 2.15. All patterns were overexposed by a factor of 100% compared with the dose providing the saturated developed depth. The resist patterns show an undercut for the energies than 8 keV. This because the range in the backscattering of relatively low energy from the substrate surface is limited and the maximum position of the electron energy dissipation increases with increasing energy.

We can see that the advantages of using thin films and low beam energies can be put into good effect for the lift-off scheme described in chapter 6. It will also be shown that an undercut profile is not required for complete lift-off to be successful.

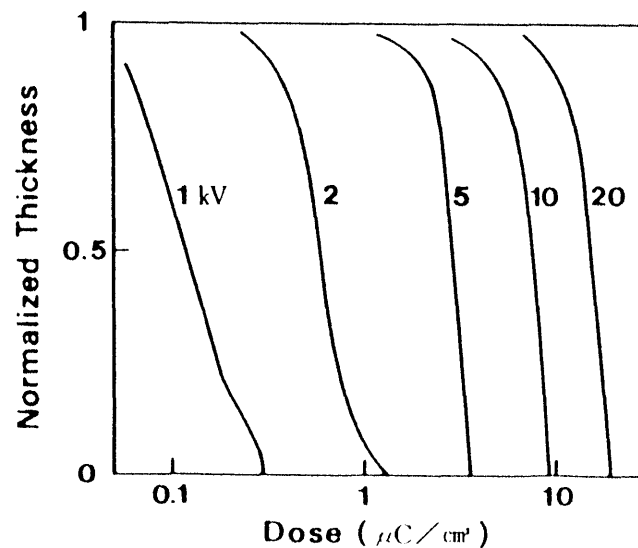


Fig. 2.14. Resist sensitivity curves of 1 μm thick ϕ -MAC at various electron energies. (After Sujita and Tamamura, Ref. [51])

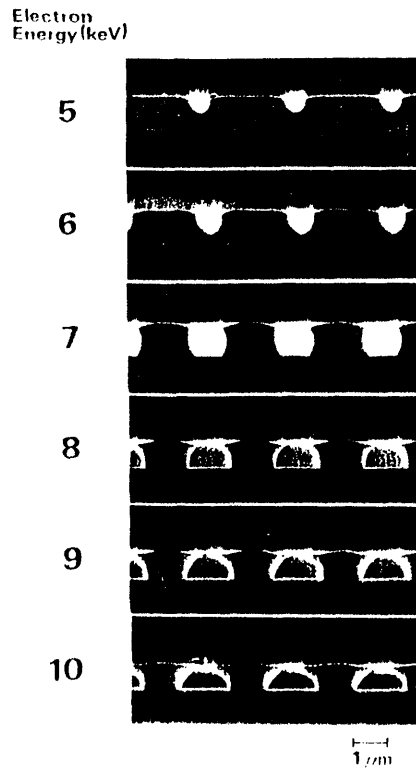


Fig. 2.15. Cross-sectional view of resist profiles for 5-10 keV exposure at 100% over exposure dose. (After Sujita and Tamamura, Ref. [51])

2.4.3. Proximity Effects

Electron scattering over large distances contribute to the total energy deposited at any given point. This means that the energy deposited at any given point in the resist depends on the dosage received by adjacent exposures. In Fig. 2.16, point B will receive half the dose of point A and C receives a quarter the dose of point C. The shaded area represents the developed image which clearly shows this variation in energy density. Intra-proximity effects results from the deviation of pattern fidelity within the exposed area. Backscattered electrons lead to the inter-proximity effect which is evident with features placed close together.

Proximity effects can be corrected by altering the dose locally [52], by either varying the dwell time of the beam or changing the current, but this requires huge computer resources. A more systematic approach was implemented by Parikh for large area, high density patterns. In this technique, the desired

pattern is divided into primitive shapes, such as trapezoids and rectangles. The incident dose is varied in each primitive shape such that the average dose in each shape is equal.

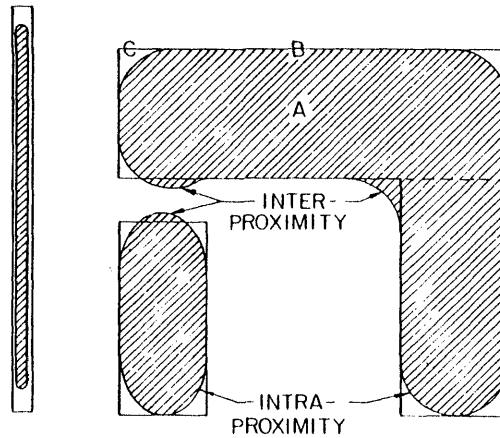


Fig. 2.16. Exposed pattern on resist (shaded area) showing inter and intra-proximity effects. (*After Greeneich, Ref [28]*)

DECOMPOSITION OF THIN FILMS OF CADMIUM CHLORIDE AND CADMIUM IODIDE

Much of the interest in inorganic resists as an alternative to organic polymer resists has been due to the high selectivity and high resolution of pattern transfer.

Yoshikawa et al [1] used direct e-beam writing of GeSe glass film doped with Ag by dipping into AgNO₃ solution. After exposure, the unexposed region is easily removed in an acidic solution of HNO₃-HCl-H₂O leaving the negative image on the substrate. Linewidth of less than 0.3 μm was achieved. The GeSe glass film also behaves as a photoresist and Tait et al [2] were able to print 0.5 μm lines using a commercial optical stepper. The sensitivity of the resist was found to be $4 \times 10^{-5} \text{ C/cm}^2$ when using 5 keV electrons but no mention of the selectivity in dry etching between resist and substrate was made. Employing a thin membrane of Si₃N₄ as a substrate reduced electron backscattering [3]. This was put into good effect by Singh et al [4] in producing ~40 nm linewidth in silver sensitized GeSe film. The disadvantage of using this resist is that stripping is difficult.

Fe₂O₃ films deposited on Si₃N₄ as a negative type e-beam resist was developed by Kammlott and Sinclair [5]. Apart from the poor sensitivity, linewidths of only 0.8 μm were achieved. More recent work by Murray et al [6] used AlF₃ films in order to write aluminium patterns. Selectivity to Si₃N₄ by reactive ion etching was very high but sensitivity was about 10 C cm^{-2} by 100 keV. In-situ monitoring by electron energy loss spectroscopy of the e-beam exposure of the film revealed that the fluorine ions were first removed followed by displacement of the metal ions. Trenches of less than 20 nm were achieved by similar work [7] using NaCl as the resist. Further work on fluorides namely CaF₂ has been used for sub nanometer line definition [8, 9,

10]. A developing step was required in which the end product CaO of radiolysis was removed in deionised water.

It would appear from the results obtained so far that the combination of high selectivity and sensitivity, high pattern definition, easy deposition are still a goal to be achieved with inorganic resists.

In this work, thin films of CdCl_2 and CdI_2 are examined as an e-beam resist. Previous studies on CdCl_2 [11, 12, 13,] have shown a relatively poor sensitivity so a technique for improving the sensitivity of the inorganic resist by employing a two layer film will be described. Results of decomposition of thin films of CdCl_2 and CdI_2 ($\sim 300 \text{ \AA}$) is given in section 3.2 as their use as a highly selective resist has been verified (see chapter 5). Finally $\text{CdCl}_2/\text{CdI}_2$ as a pattern for aluminium lift-off will be presented in section 3.3.

3.1. Two Layer Cap Scheme

The bi-layer scheme (Fig. 3.1) first proposed by Green and Albrecht [14] is a two layer resist scheme to enhance the sensitivity. This is achieved by e-beam decomposing only the first layer (MA) which has a lower vapour pressure than the underlying layer. By operating at a temperature at which MB is removed by evaporation considerably faster than MA we can obtain a pattern on the two resist layer in one single step. If MA is of the order of several hundred angstroms thick then an improvement in the writing time may be achieved. The choice of materials for MA and MB depend on a number of factors and these are listed as follows;

- 1) MA must be sufficiently e-beam decomposable otherwise it does not satisfy the whole objective of obtaining sensitivity enhancement.
- 2) MB should have a higher vapour pressure than MA. A wet processing step could also be employed where MB may be dissolved in a suitable solvent after removing MA by the electron beam.
- 3) Finally, as we are concerned with pattern transfer to the substrate MB

therefore should be etch resistant in a wet or dry etching processing step.

All metal halides are compatible with dry etching schemes employing halo-carbons gases so discussion will be restricted to these group of compounds.

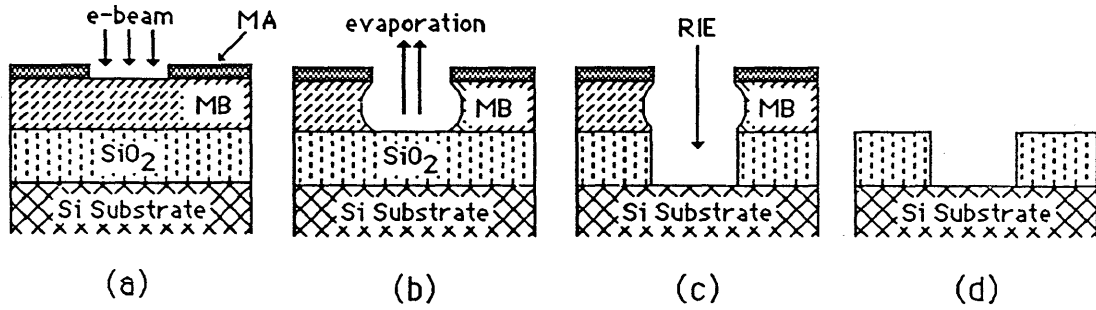


Fig. 3.1. Bi-layer scheme, (a) e-beam decomposition of 1st layer MA, (b) removal of the more volatile MB, (c) etching of SiO₂ and (d) stripping of resists for final pattern replication.

3.1.1. Vapour Pressure Curves

The log vapour pressures versus temperature relation for various metal halides are shown in Fig. 3.2: these curves have been plotted using the relation,

$$\log p = A.T^{-1} + B \log T + C.T + D \quad (3.1)$$

where p is the pressure in mmHg, T is the temperature in degrees Kelvin and A, B, C, D are constants obtained from the tables of vapour pressures [15]. The equation is only valid over a specified temperature range and is plotted for each material accordingly. The number of molecules with molecular weight m leaving a source at temp. T per unit area can be determined using elementary kinetic theory and is given as,

$$\Gamma = \frac{p}{\sqrt{(2\pi mkT)}} \quad (3.2)$$

where here p is the vapour pressure in pascals.

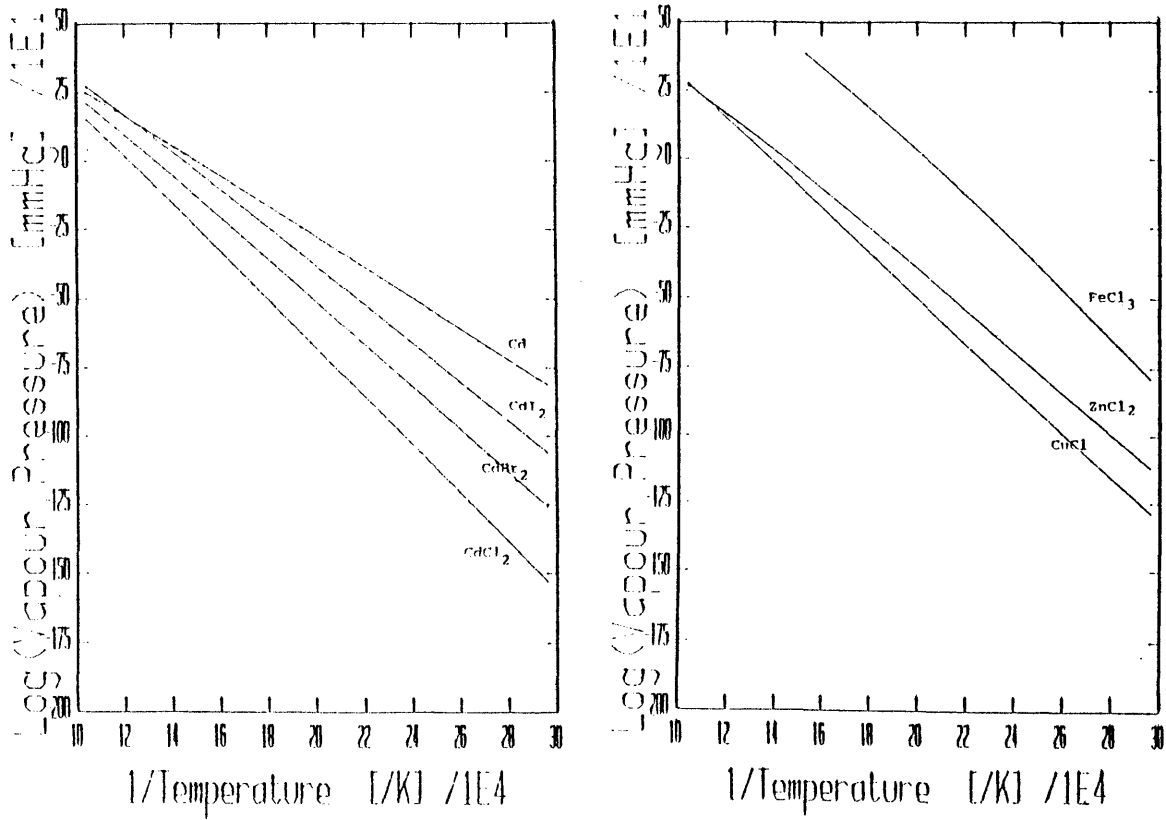


Fig. 3.2. Vapour pressures of various metal halides for the bi-layer scheme.

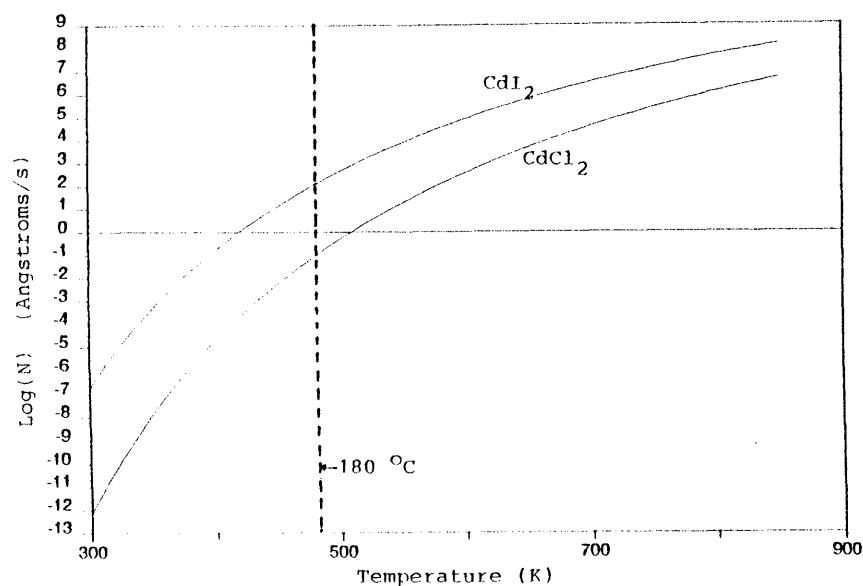


Fig. 3.3. Rate of evaporation of CdCl_2 and CdI_2 versus temperature.

An obvious choice for the MA layer is CdCl_2 since we are already familiar with the decomposition kinetics of this material [13]. Although ZnCl_2 and FeCl_3 have lower vapour pressures than CdCl_2 , they are highly deliquescent and so unsuitable for the MB layer.

The following describes the resist combination of $\text{CdCl}_2/\text{CdI}_2$. The rate of material removal as a function of temperature is shown in Fig. 3.3 using Eqn. 3.2. At a temperature 180°C the rate of evaporation of CdCl_2 and CdI_2 are 0.01 Å/s and 20 Å/s respectively. So a safe operating point would be around this temperature.

The main objective of this part of this work was to examine the minimum thickness of CdCl_2 that could be achieved which provided complete integrity of the two resist film through the heating stage. The e-beam step has been omitted and instead, the CdCl_2 layer has been evaporated through a stainless steel mask as shown in Fig. 3.4.

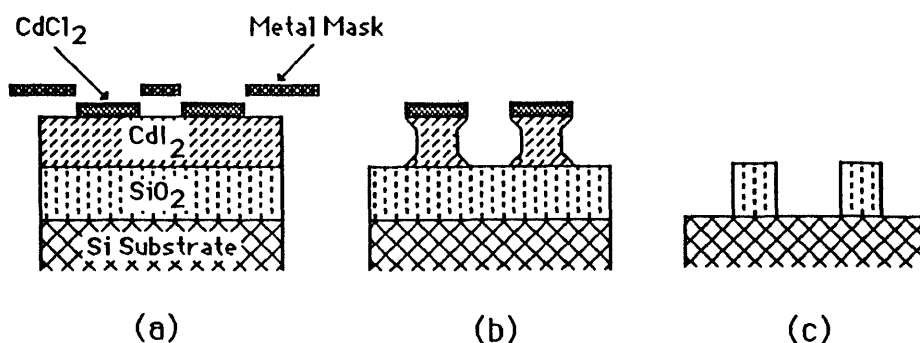


Fig. 3.4. Formation of the two-layer resist for examining the minimum allowable thickness of CdCl₂

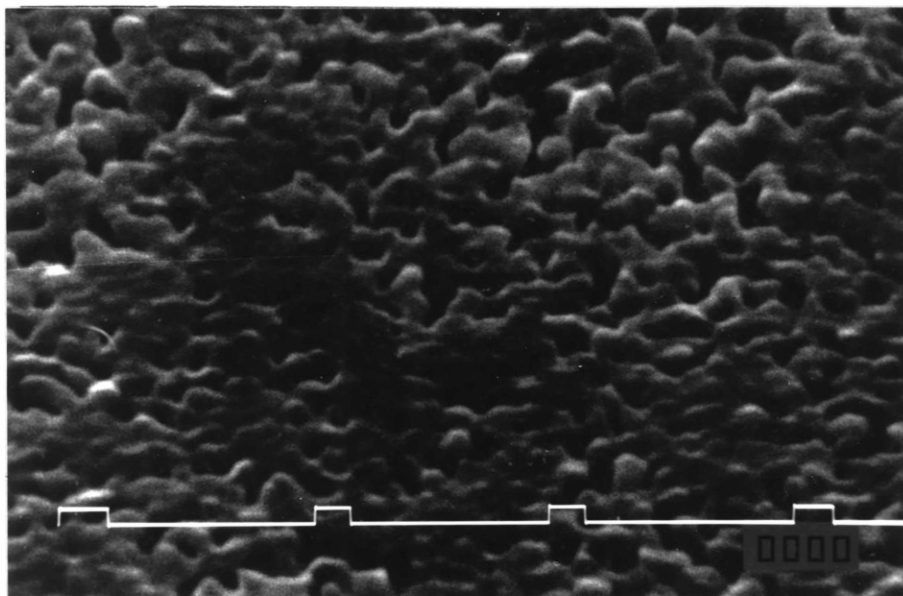
3.1.2. Experimental Results

Thin films of CdCl₂ and CdI₂ were deposited from a heated molybdenum boat in an Edwards evaporation unit at a base pressure of 10^{-6} torr. As before film deposition rate was monitored by a crystal 'pick-up' placed near to the target and was kept constant at approximately 30 Å/s for the CdI₂ film and 10 Å/s for the CdCl₂ film. All thickness measurements were carried out by the ellipsometer (Rudolph) and the Talystep (Rank Taylor).

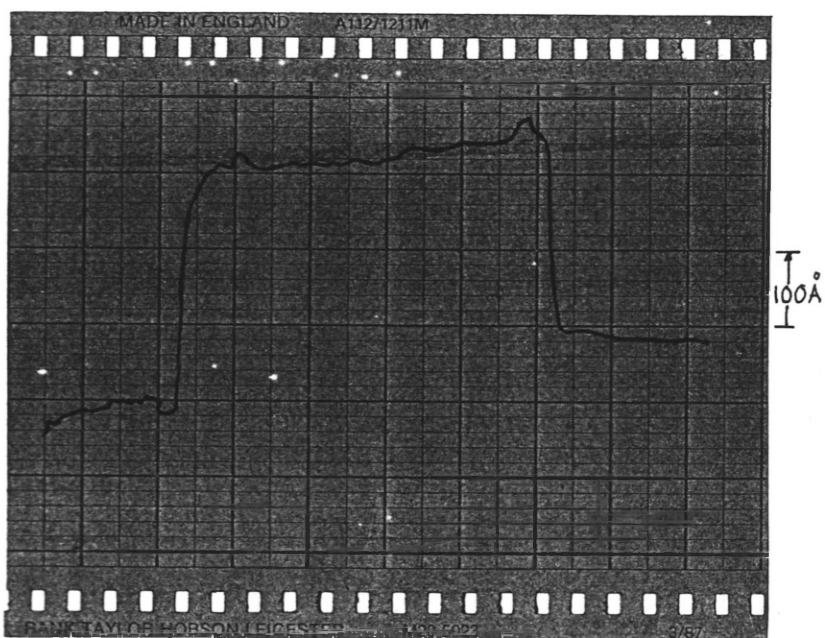
Test samples were gradually heated to a temperature at which all the CdI₂ came off. Visible changes to the colour of the CdI₂ film were observed through the glass port of the evaporation unit during the heating stage. The heater was switched off immediately after the bare SiO₂ was observed leaving the capped pattern of the CdCl₂/CdI₂ layers on the substrate. This occurred around a maximum temperature of 170 °C.

Profile measurements of the above sample were made after removal of the CdI₂ by heating. Rate of growth of thin films can vary with the type of substrate used [16] but in the case of CdCl₂ films the thickness was found to be approximately the same for CdI₂/SiO₂/Si substrate and SiO₂/Si substrate from measurements before and after heating. A series of experiments were

performed with various thickness of CdCl_2 ranging from 100 Å - 1000 Å and it was found that a minimum thickness of 300 Å was required for complete retention of the underlying film. Also at this thickness, the maximum temperature could not be maintained for more than 15 minutes as this resulted in excessive loss of the CdCl_2 film. Fig. 3.5 shows the SEM micrographs of the sample after heating and the corresponding talystep profile measurement of the 'capped' pattern. Heating at this temperature appears to have created 'fast evaporation points' at the weak regions of the grain boundaries thus opening up this region further and leading to CdI_2 evaporation. Although, the grain structure hence the relative roughness of the CdI_2 film is a measure of the effective screening by the CdCl_2 film, the minimum thickness is largely dominated by the rate of material loss through the heating stage. Fig. 3.4 reveals that at the operating temperature used for the CdI_2 removal, CdCl_2 evaporation rate is approximately 1 Å/min, so for a film of a few hundred monolayers the loss can be significant leading to exposure of the underlying film which is subsequently evaporated off.



(a)



(b)

Fig. 3.5. (a) SEM micrograph of the capped pattern of $\text{CdCl}_2/\text{CdI}_2$ (330 Å/1000 Å) after heating to 170 °C, (b) Talystep profile measurement of the film.

3.1.3. Conclusions

CdCl_2 and CdI_2 was used as the 'cap' for the two layer resist combination for sensitivity enhancement. A minimum thickness of 300 Å was required to provide complete resist integrity through the most critical process which is heating to remove the underlying CdI_2 film. The maximum temperature could not be maintained for more than 15 minutes as this resulted in the loss of the capping CdCl_2 layer. These problems will have its drawbacks when patterning for long exposure times. Resist sensitivity was found to be 10 mC/cm² which was similar to the dose required to remove 300 Å of the bulk CdCl_2 [13]. All these factors rule out the possibility of using this scheme as an alternative e-beam resist scheme for submicron fabrication. Owing to the high selectivity of CdCl_2 (see chapter 5), a much better technique is to deposit a thin film of CdCl_2 (~300 Å) and use this as the resist for direct e-beam writing and plasma etching.

3.2. E-Beam Decomposition of Thin films of CdCl_2 and CdI_2

It will be shown in chapter 5, that the selectivity of CdCl_2 to SiO_2 in reactive ion etching is very high, therefore, it is of interest to look at the dose required for the complete removal of thin films of CdCl_2 .

In this work, samples of thin films of CdCl_2 and CdI_2 (~300 Å) deposited on 1400 Å SiO_2 on Si substrate were decomposed under the irradiation of an electron beam at substrate temperatures of 120 °C. The experimental rig (Fig. 3.6) used for the study of the decomposition kinetics of CdCl_2 [17] and $\text{CdCl}_2/\text{PbCl}_2$ [18] was used for these experiments. Electron beam energies (1-5keV) were employed for these experiments and it was found that CdI_2 decomposed at a faster rate than CdCl_2 consistent with the theories of range, energy dissipation and backscattering for different Z materials discussed in the previous chapter. Rate of decomposition is found to be mainly influenced by the energy dissipation in the film and this is a consequence of the

electron-hole pairs created which takes part in the surface decomposition. The generation rate of e-h pairs is higher at low beam energies. Films of thicknesses less than the Grun range were also found to decompose at a faster rate than films greater than this range. This effect could be partly attributed to the higher backscattering of electrons from the substrate which contributes to the overall decomposition kinetics.

3.2.1. Experimental Results

Brief details of the UHV system used for this study will be given. A more complete description of the system can be found in the PhD thesis by C. J. Aidinis [17] and O. A. Fakalujo [18]. Basically, the system (Fig. 3.6) is configured around a combination of four vacuum pumps. The rotary pump and the diffusion pump are operated first to obtain a base pressure of 10^{-6} torr. These pumps are valved off and switched to a titanium pump running in parallel with an ion-pump to give an ultimate pressure of 10^{-8} torr. All e-beam decomposition were carried out at this base pressure, but heating the sample increased the pressure to 10^{-7} torr.

The sample holder was used to position the specimen for electron beam irradiation, and also had provisions for heating the sample, measuring the sample temperature and the beam current by utilising a Faraday cup.

Thin films of CdCl_2 and CdI_2 ($320 \pm 10 \text{ \AA}$) were evaporated (rate $\sim 10 \text{ \AA/s}$) on a silicon substrate with about $1400 \text{ \AA}$ SiO_2 . For these set of experiments, beam currents and a substrate temperature were kept constant at $23.0 \pm 2 \text{ \mu A}$ and $120 \pm 4 \text{ }^\circ\text{C}$. Fig. 3.7 shows the remaining film thickness after exposing areas of 3.0 mm^2 at specified time intervals at these conditions with change in beam energies. Dosage D ($\mu\text{C/cm}^2$) was calculated from the equation,

$$D = It/A \quad (3.3)$$

where I (μA) is the beam current, t (s) is the time of exposure and $A(\text{cm}^2)$ is the area of exposure.

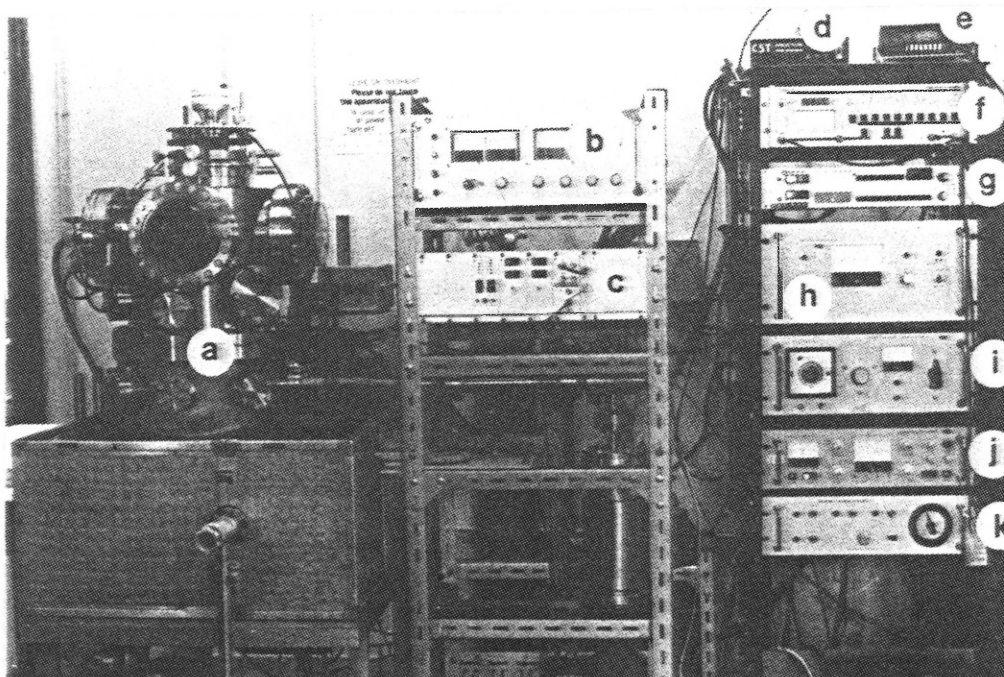


Figure 3.3.1:

Electron beam decomposition apparatus.

- (a) Vacuum chamber (schematically drawn in Figure 3.3.2)
- (b) Electron gun power supply
- (c) Scanner and Temperature controller unit
- (d) IEEE 488 Inter-Face
- (e) Keithley 480 pico-ammeter, for beam current measurement
- (f) EG-G 5205 Lock-in amplifier
- (g) SX 300 QMS Controller
- (h) Ion-pump power supply
- (i) Titanium sublimation pump power supply
- (j) Pirani/Ion gauge control unit
- (k) Bake-out heater control.

Fig. 3.6. Experimental rig used for the decomposition of CdCl_2 and CdI_2 thin films.

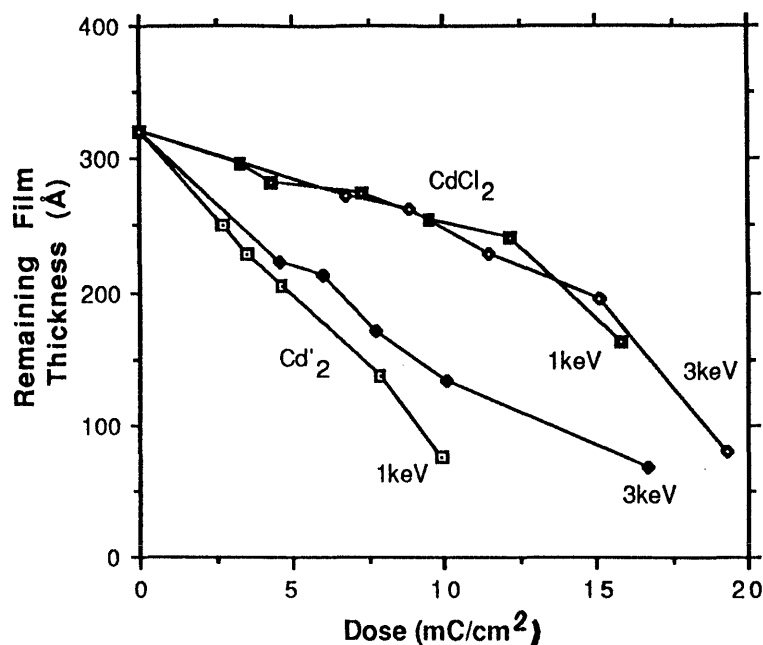


Fig. 3.7. Remaining film thickness of CdCl₂ and CdI₂ on 1400 Å SiO₂ on Si substrate versus dose at 120 °C and 22.6 μA with 1 and 3 keV beam energies.

Clearly, CdI₂ which is of higher Z, shows a notably faster rate of decomposition than CdCl₂. The rate of decomposition is faster at low beam energies. Fig. 3.8 shows the initial rate of decomposition for 320 Å CdCl₂ with beam energies in the range 1-5 keV. Following exposure, the thickness of the decomposed regions were measured with the ellipsometer. Film thickness values obtained with the ellipsometer varied by not more than ± 40 Å with repeated measurements. A programme on the Auto EL3 was selected which iteratively computes film thickness and refractive index simultaneously.

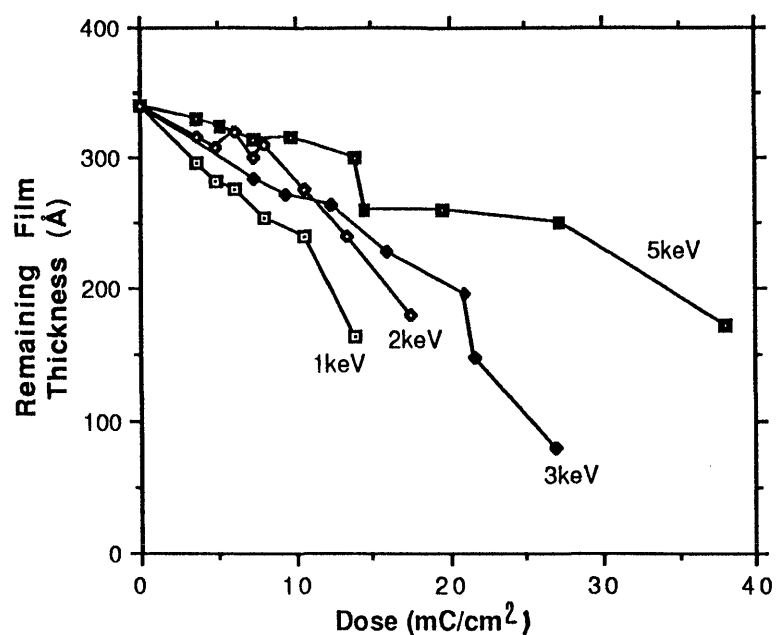


Fig. 3.8. Energy dependence on the decomposition rate of CdCl_2 at 120°C , $23\mu\text{A}$.

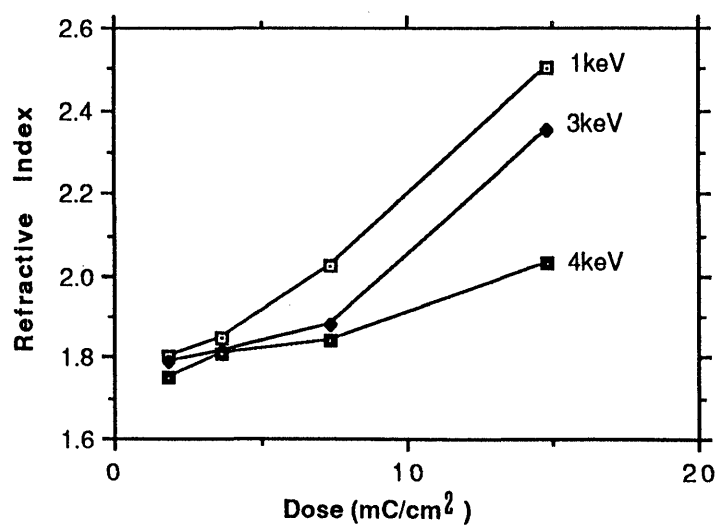


Fig. 3.9. Increase in the refractive indices of the CdCl_2 film as it thins down to the bare substrate.

Refractive indices of the film (Fig. 3.9) increases with an increase in dose (ie. decrease in film thickness). This has been attributed to the break-up in the film structure as the film thins down to the substrate and occurs possibly beyond a film thickness of around 100 Å or so. As the decomposition rate of 1 keV beam is the highest, the corresponding refractive index change is also high. Ellipsometric measurements made beyond the point of the fragmented film can be assumed to be reasonably accurate. By extrapolating part of the curves at the lower dosage a reasonable fit to the measurements is obtained for high dosages.

Contrast of the CdCl₂ samples exposed at various beam energies are shown in Figs. 3.10-3.12. This has been calculated from the conventional definition of contrast for organic polymer resists namely,

$$\gamma = [\log_{10}(D_c/D_o)]^{-1} \quad (3.4)$$

A polynomial of the first order was chosen for the curve fit for all the points. The values obtained should not be taken as to be indicative of the true contrast since an 'overexposure' is required to remove the residual film below 100 Å. A more useful basis for these results is in the comparison of the efficiencies at different beam energies. The figures give a relative measure of the efficiencies with the lowest beam energy (2 keV) showing the highest efficiency.

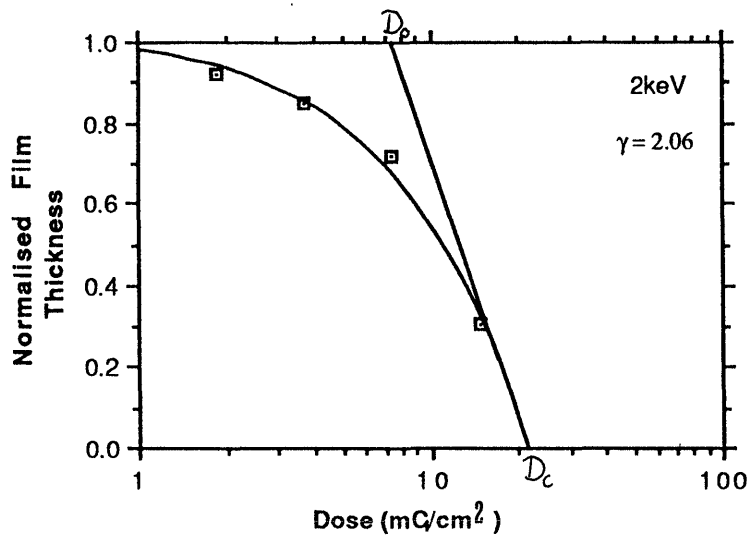


Fig. 3.10. Contrast of CdCl₂ film at 2 keV beam energy.

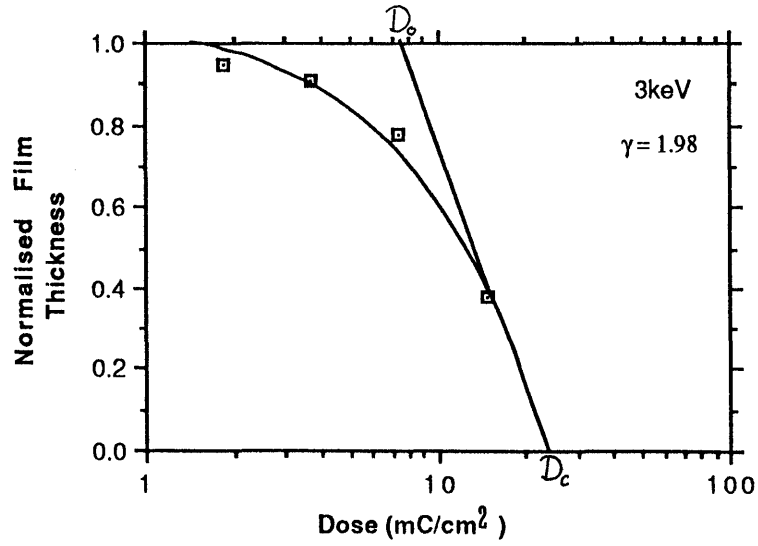


Fig. 3.11. Contrast of CdCl₂ film at 3 keV beam energy.

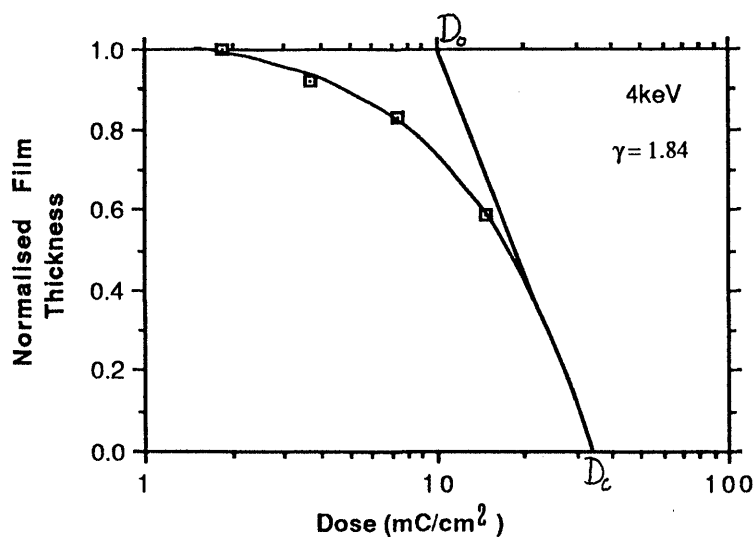


Fig. 3.12. Contrast of CdCl₂ film at 4 keV beam energy.

In the previous work on CdCl₂ [13], thicker films of CdCl₂ (~2000 Å) were found to give a slower rate of decomposition than films of thicknesses less than the Gr $\ddot{U}$ n range. Fig. 3.13. shows the remaining film thickness versus the dose for an initial CdCl₂ thickness of about 1000 Å. Comparing the results of the previous thin film measurements, the initial rate of decomposition is significantly lower than the thin film of 320 Å. Biasing the substrate at 30V had no obvious effect on the decomposition rate as Fig. 3.14 shows.

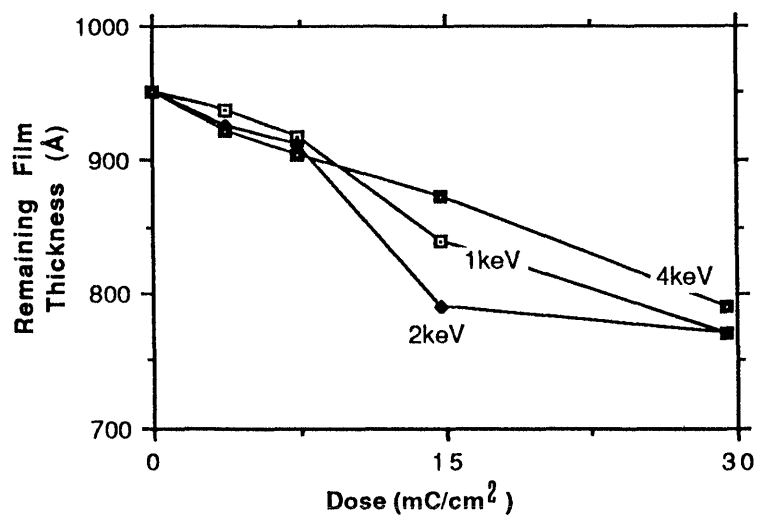


Fig. 3.13. Film thickness of CdCl_2 as a function of dosage for initial thickness of $960\text{\AA}$

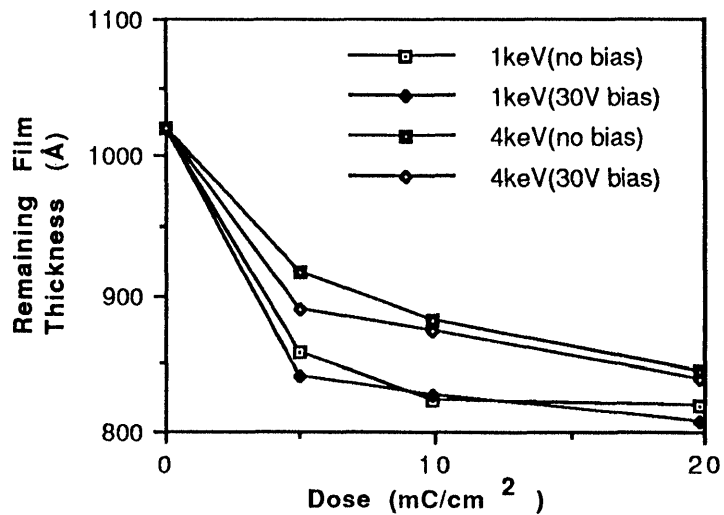
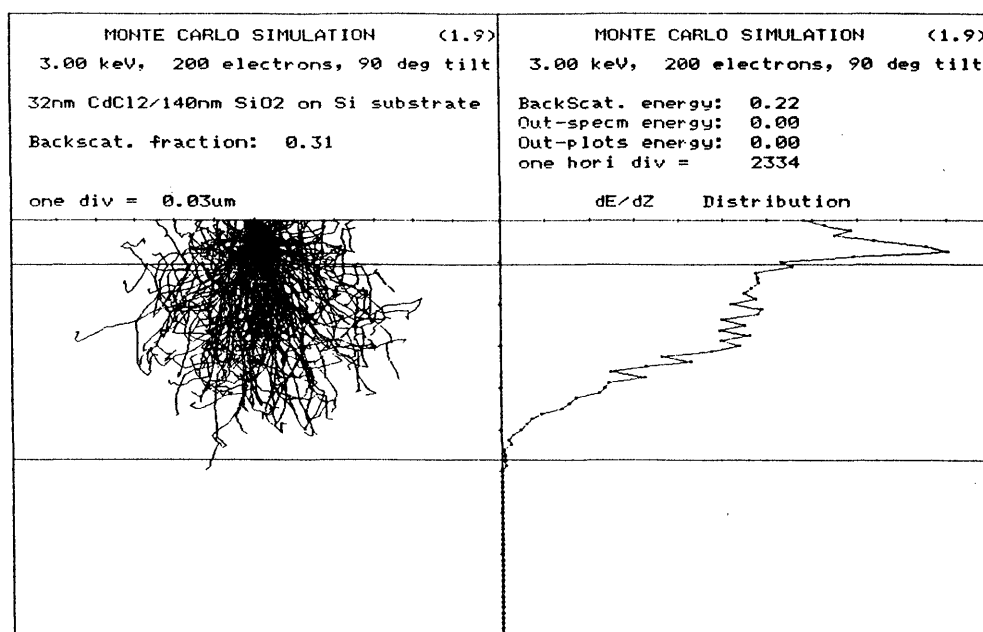


Fig. 3.14. Film thickness as a function of dose for initial thickness of $1020\text{\AA}$ with no bias and 30 V bias.

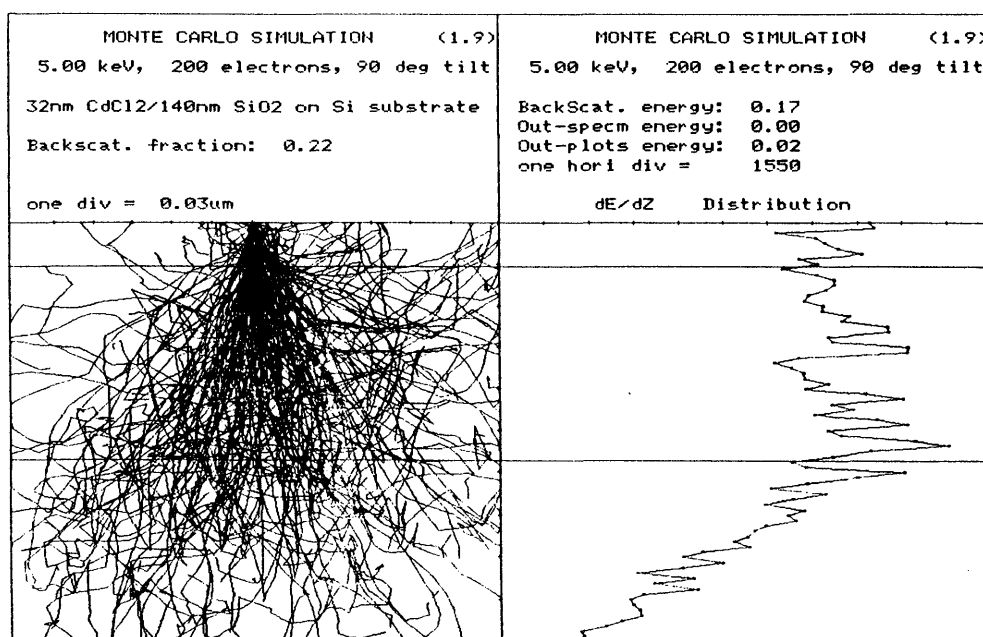
3.2.2. Discussion

Since the Bethe energy loss relationship (Eqn. 2.1) is only valid for higher energies, the precision of the Monte Carlo simulation below 10 keV is reduced. However, as a basis for comparison the simulation can be used to obtain the energy dissipation in CdCl_2 films at 3 and 5 keV. Fig. 3.15. (a) and (b) show the simulation for beam energies of 3 and 5 keV respectively for the CdCl_2 film (320 Å) and SiO_2/Si substrate used in these experiments. Simulation for the CdI_2 film is shown in Fig. 3.16. The Bethe range (Fig. 2.8) for these energies for CdCl_2 are 1200 Å and 2400 Å respectively and the corresponding range for CdI_2 are 750 Å and 1700 Å. A rough estimate of the mean range obtained from the MC simulation indicates a slightly lower value than the Bethe range. The MC simulation is assumed to give a more accurate description of the electron trajectories as it accounts for the SiO_2 layer and the Si substrate in its calculation.

For a beam energy of 3 keV, the backscattering fraction for the CdI_2 film is 0.38 and for CdCl_2 it is 0.31 (Figs. 3.15a & 3.16). The energy dissipation (dE/dz) within the CdI_2 film is about 1.4 times that in CdCl_2 . The increase in the decomposition rate observed for CdI_2 is due to this greater energy dissipation and the lower activation energy required for the desorption of iodine to the gaseous phase at the surface. The variation in the decomposition rate for 3keV and 5keV beam energies appears to be dependent on the energy dissipation in the film which is proportional to the number of electron-hole (e-h) pairs created (cf. Figs. 3.15. (a) & (b)). It would appear from the experimental results obtained, that the backscattering of electrons may also have an effect on the decomposition kinetics which could explain the reduced rate at an initial film thickness of 960 Å. This is not immediately apparent in the Monte Carlo simulations for the 320 Å and 960 Å film at 3keV beam energy as shown in Figs. 3.15(a) and 3.17.



(a)



(b)

Fig. 3.15. Monte-Carlo simulation of 200 electrons in CdCl₂ film with initial film thickness of 320 Å at beam energies of (a) 3 keV and (b) 5keV. (software by Dr. E. Napchan)

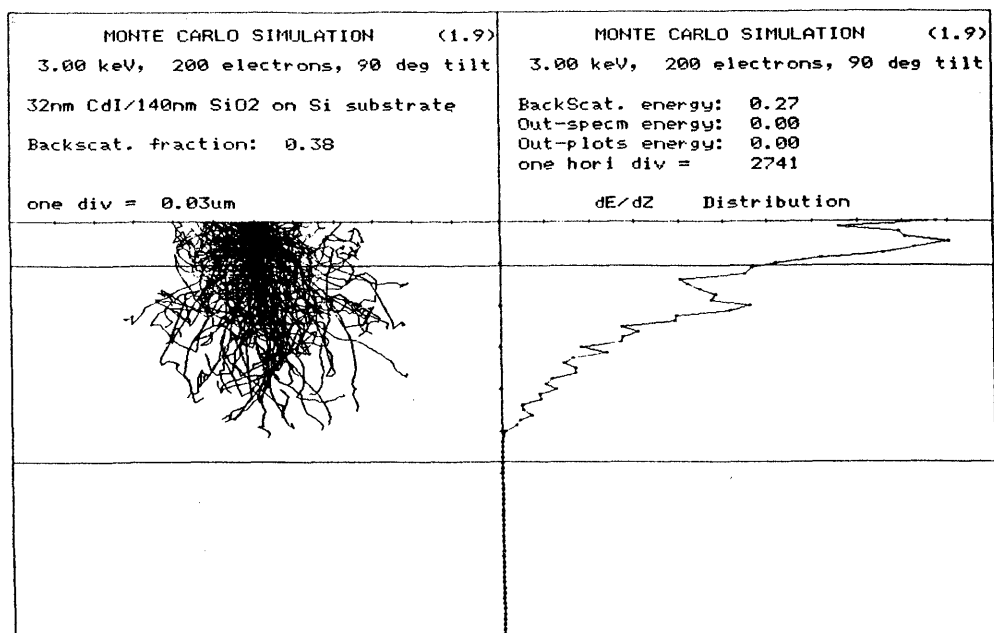


Fig. 3.16. MC simulation of 200 electrons for a 320 Å CdI₂ film at 3 keV.
(software by Dr. E. Napchan)

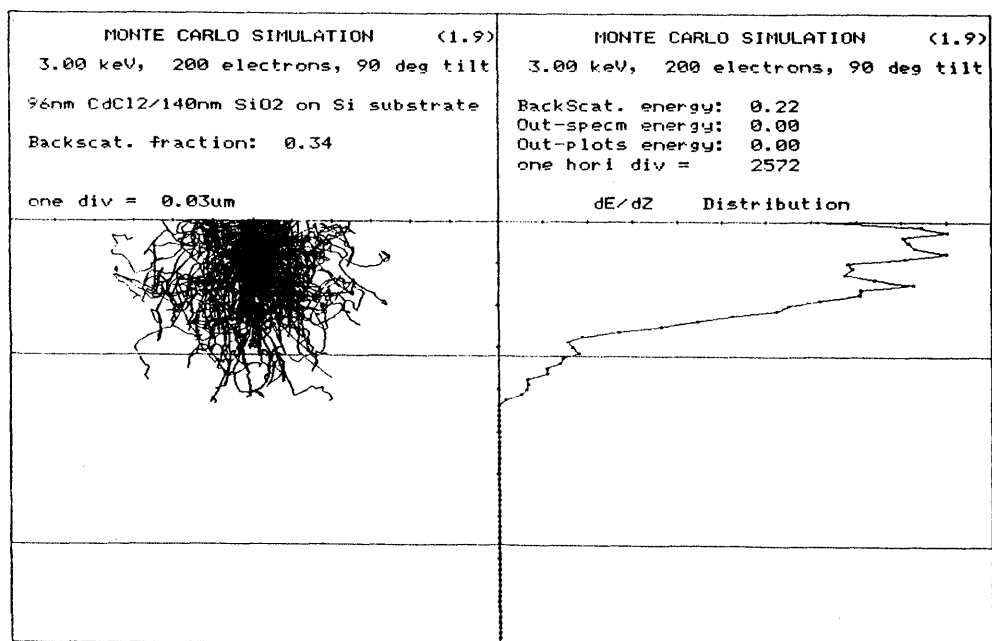


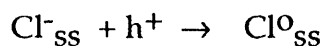
Fig. 3.17. MC simulation of 200 electrons in 960 Å CdCl₂ film at 3 keV.
(software by Dr. E. Napchan)

3.2.2.1. Decomposition Sequence

For the decomposition kinetics at the surface, the following mechanism is proposed after Aidinis and Green [13] with the additional factor of the backscattered electrons which will determine linewidth and resolution,

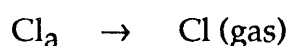
1) Electron-hole pairs are created by inelastic collisions with primary and backscattered electrons. Assuming an average energy of $3E_g \sim 18\text{eV}$ per electron-hole pair for CdCl_2 [19] then about 100 generated pairs are produced. The majority are recombining or released as secondary emission (with substrate not biased) and only about 3% are employed in the chemical decomposition reaction. For CdI_2 , E_g is smaller than this and the number of e-h pairs produced is correspondingly greater.

A quasiequilibrium state is assumed to exist where holes are trapped and emitted according to the following reactions.



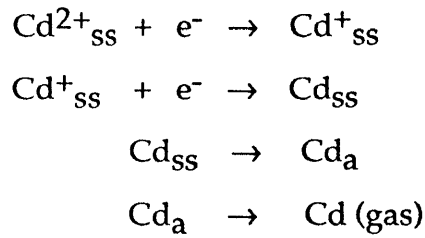
where Cl_{ss}^0 represents a special site with a trapped hole.

Evolution of chlorine species occur via the reaction sequence



where Cl_{a} represents adsorbed species. The thermal activation energy $\Delta E^+ \sim 0.2\text{ eV}$ measured for the decomposition reaction is associated with this step. This value would be smaller for the desorption of adsorbed iodine species. It is thus postulated that the rate of chemical decomposition is limited by the chlorine-ion discharge reaction. Following this reaction sequence, an isolated cadmium ion having lost neighbouring chloride ion would be in a much

better position, energetically, to trap electrons and desorb, vis.,



3.2.4. Conclusions

CdI₂ decomposes at a faster rate than CdCl₂ for similar conditions of beam energy, current density and temperature. This is due to the combination of , 1) the reduced energy required to create e-h pairs compared to CdCl₂, 2) increased energy dissipation in the CdI₂ film (see Monte Carlo simulations), 3) and the lower activation of desorption. For a 1keV beam energy, the dose required for complete removal of 320 Å CdCl₂ and CdI₂ are 13 mC/cm² and 28 mC/cm² respectively at 23 µA current density and a substrate temperature of 120 °C (Fig. 3.7).

For films of ~1000 Å thick the initial rate of decomposition for CdCl₂ is less than for a thin film of 320 Å. This could be ascribed to the greater backscattering of electrons for the thin film which would effectively increase the generation of e-h pairs participating in the surface chemistry. Biasing the substrate which effectively reduced the low energy secondary emission had no obvious effect on the decomposition rate.

These findings indicate, that decomposition is dominated by the energy loss process in the film and the electron-hole pairs thus produced participates in the chemical reaction. The increase in the initail rate of decomposition with thinner films can be explained by the backscattering of electrons from the SiO₂ interface. At 2 keV the range of the electrons in CdCl₂ is about 800 Å, so for films thinner than this the backscattering of electrons from the resist-SiO₂ interface will predominate.

As described in chapter 2 backscattering of electrons will affect linewidths since these electrons have high energies and a greater range (Fig. 3.15) than the primary electrons and consequently contribute to the overall decomposition kinetics. We have already seen that for organic resists, linewidths become a function of the backscattering at high doses (Figs. 2.11 and 2.12). For the doses required for the CdCl_2 film, this effect should be even greater, leading to substantial line broadening. Resolution will now be determined by the degree of backscattering and is inevitably poor at low beam energies. This was noticeable when examining exposed regions of the resist at 1 keV and 4 keV beam energies. Although, the beam diameters was of the order of 300 μm , the higher contrasting image obtained with a 4 keV beam energy was clearly evident.

From Fig. 2.7 the backscattered range r_B is represented by the fraction of the backscattered electrons deflected inside the limiting angle θ_0 . By solving Eqn. 2.20, r_B is found to be 0.7 times the maximum range at a particular beam energy for the CdCl_2 film. This means that backscattered electrons effectively spreads to adjacent grains in the film and thus partakes in the chemical decomposition.

For high beam energies, the backscattered range is greater but the fraction generating e-h pairs in adjacent grains in the film is much higher for a low beam energy. Since the decomposition kinetics is surface controlled, the smaller range and high backscattered fraction at low beam energies enhances this line broadening effect.

3.3. Two Layer 'Cap' for Al Lift-Off

3.3.1. Results and Discussion

Part of this work came about through the need to make 'T' bar gates for microwave integrated circuits. In order to fabricate this gate a three layer resist of $\text{CdCl}_2/\text{CdI}_2/\text{CdCl}_2$ is deposited. The top two layers is now e-beam decomposed in a similar way to the cap scheme described earlier leaving the third bottom layer which after a second pass of the beam forms the base of the 'T' bar. Gold is evaporated on top followed by a lift-off in deionised water leaving the 'T' structure on the substrate. The complete sequence of steps could not be carried out at this department at the submicron regime since no apparatus was available instead the experimental rig described earlier was used to do a preliminary run on a two layer resist with a copper mask.

For this scheme a two layer resist was used consisting of 1000 Å CdCl_2 and 7500 Å CdI_2 . A copper mask (Fig. 3.18) supplied by EMI Electronics Ltd. was placed in contact with the resist and the whole exposed by the e-beam. The exposure was carried out at 2 keV, $34.8 \mu\text{A}/\text{cm}^2$ and 200 °C. A dosage of approximately $5 \text{ mC}/\text{cm}^2$ was used to decompose the CdCl_2 layer and a high substrate temperature selected to remove the more volatile CdI_2 . Following exposure, $\sim 2000 \text{ Å}$ of Al was evaporated from a heated boat in vacuum at a rate of about $20 \text{ Å}/\text{s}$ with the copper mask removed. A subsequent rinse in de-ionised water gave the resulting pattern in Al as shown in Fig. 3.19.

There appears to be a degradation of the reproduction of the Al pattern from the mask image. This is due to a combination of two factors; 1) the edges of the mask is not well defined and more importantly 2) the mask which is in direct contact with the sample will cause local evaporation of the CdCl_2 resist. These effects leads to a somewhat poor definition of the resist image which after lift-off causes the metal film to break around the edges as shown in Fig. 3.18.

For submicron fabrication, a number of problems are associated with this

technique and this stems mainly from the decomposition rate of the CdCl_2 and the time lapse for the removal of the CdI_2 film. As mentioned in section 3.1., the minimum thickness of the CdCl_2 film required to retain the CdI_2 film is approximately 300 Å. But the temperature ($\sim 180^\circ\text{C}$) at which CdI_2 is removed at a reasonable rate could not be maintained for more than 15 mins. as this resulted in loss of the CdCl_2 film. So, depending on the thickness of the CdI_2 film, the CdCl_2 film thickness has to be adjusted to compensate for the longer time required to remove CdI_2 . The thick film of CdCl_2 will now require a longer exposure time, hence, broadening of the exposed regions mentioned previously will occur due to the backscattered electrons making it unsuitable for submicron fabrication.

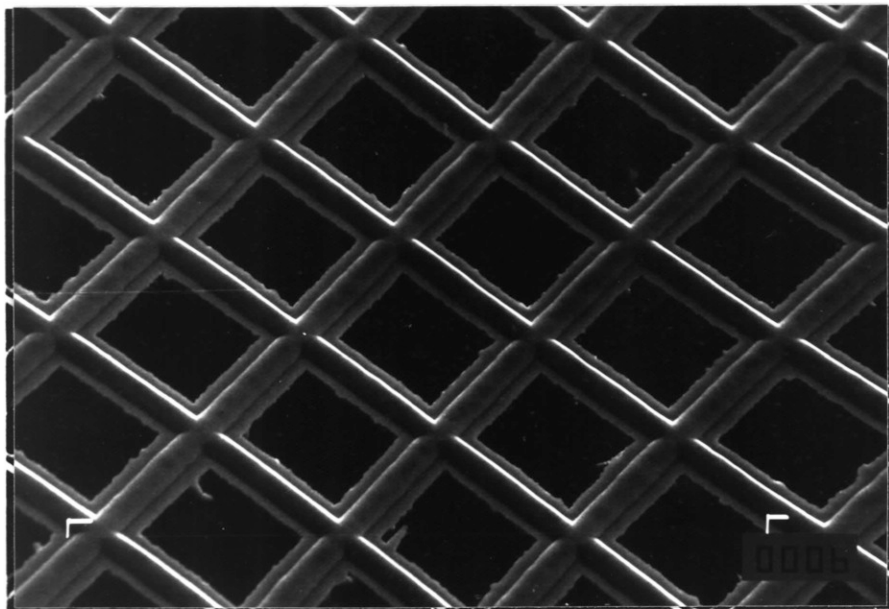


Fig. 3.18. Copper mask pattern used for the decomposition of the two layer resist scheme.

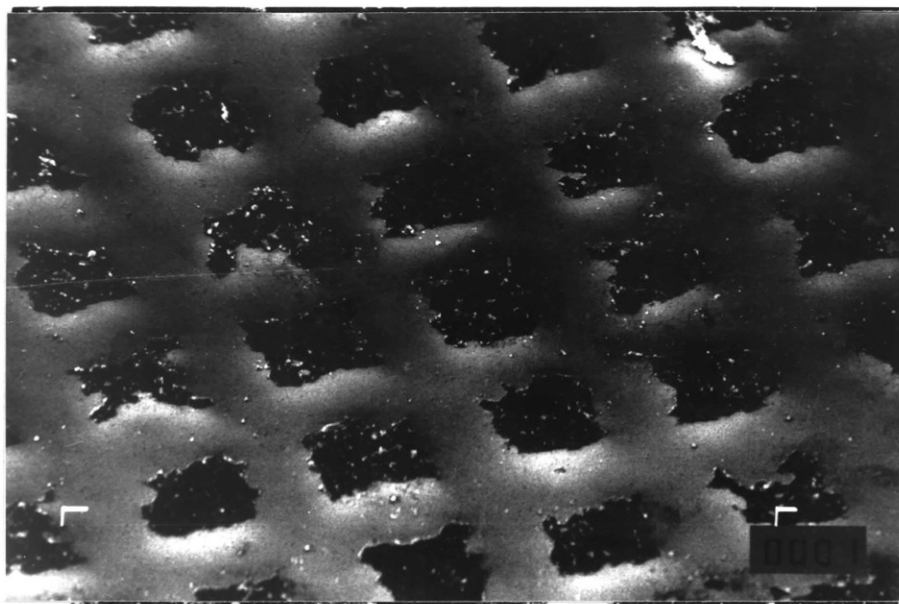


Fig. 3.19. Al lift-off pattern obtained on SiO_2/Si substrate.

3.4. Conclusions

The two layer resist scheme of $\text{CdCl}_2/\text{CdI}_2$ did not give the expected results mainly due to the temperature for the fast removal of CdI_2 being close to the range at which CdCl_2 is also evaporated. One way of circumventing this problem is to choose a material for the bottom layer which is more volatile than CdI_2 . An aluminium lift-off pattern was obtained using the two-level scheme but resolution was affected by the quality of the mask edge and the evaporation of the top CdCl_2 film around its edges.

An improvement in the sensitivity of thin films ($\sim 300 \text{ \AA}$) of CdCl_2 was obtained compared to a thicker film of $1000 \text{ \AA}$ possibly due to the greater backscattering of electron from the SiO_2/Si substrate. For complete development a slight overexposure would be required to remove the 'residue' as the film thins down to the substrate. Due to the high dosage (20

mC/cm²) required for complete removal, significant backscattering will lead to a greater increase in linewidth and hence loss in resolution. These drawbacks have accounted for the much interest in recent literature to use a high power beam current so that the resist is literally evaporated off at the exposed regions.

Although e-beam inorganic resists are a source of stimulating research, its application in nanolithography is rather limited. The lift-off technique described in chapter 6 which couples the high sensitivity of an organic resist and the high etch resistance of the inorganic resist have potential use in high resolution photomask fabrication and submicron lithography.

DRY PROCESSING

With the advent of ULSI, dry processing such as reactive ion etching is the only technique available today for achieving submicron dimensions. This chapter discusses the trends in dry processing and the important system parameters governing etch rates, selectivity and uniformity which is necessary to the work reported further on. Due to the complex behaviour of ions, electrons and reactive species in the plasma and the difficulty in measuring their concentration, a complete understanding of the physics of plasmas related to etching has not yet been achieved. All the above factors depend much on the geometry of the system and the material used for their construction. Provided that the system variables are accurately known it is possible to characterise the etch rate, selectivity, etc. and improve on them. A way of optimising an output from a set of runs will be shown which not only minimises the number of runs, but also provides an understanding of the effects of the interactions of input variables.

4.1. Pattern Transfer

'Pattern transfer' refers to the transfer of a pattern, defined by a masking layer, into a film substrate by chemical or physical methods that produce surface relief. The subtractive and additive methods of pattern transfer (Fig. 4.1) are widely used techniques employed today for pattern replication at the VLSI level. There is a growing interest in research [1, 2] at overcoming the lithography step so that direct etching or deposition of the film can be made by using finely focussed ion beams or laser beams. Although, this technology is at an early stage, their use in circuit and photomask [3] repair is already being exploited.

A measure of the resolution of an etching process is the bias (Fig. 4.2). This is the difference in the lateral dimensions between the etched feature and mask image. An extreme of anisotropic etching has zero bias with perfect vertical edge profile having no lateral etch. Isotropic etching has a bias equal to twice the film thickness and is usually obtained with liquid etchants. The bias obtained in the etching process places a restriction on the minimum spacing obtainable between two adjacent features.

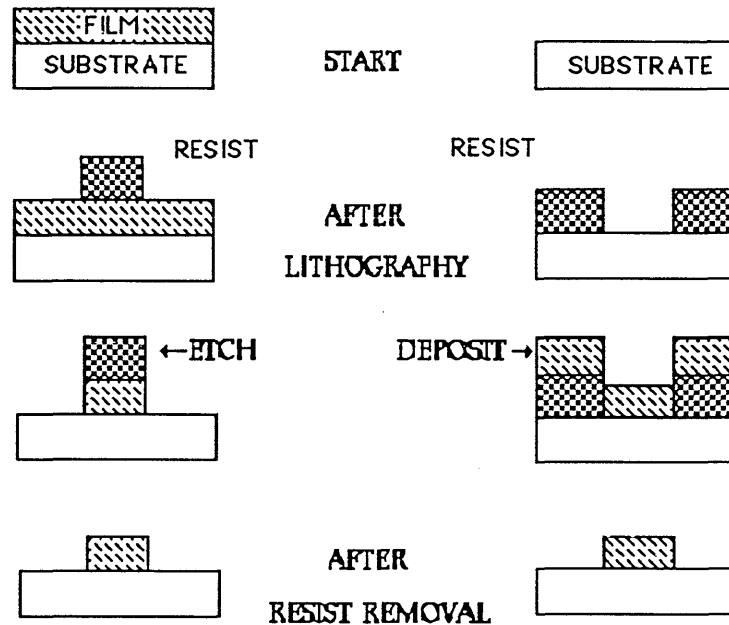


Fig. 4.1. The additive and subtractive methods of pattern transfer.

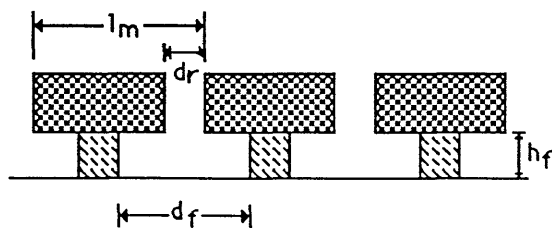


Fig. 4.2. Limitation imposed on the minimum feature spacing due to lateral etching.

Consider the lithography step having openings in the resist of width d_r and spaced at intervals l_m on a film of thickness h_f (Fig. 4.2).

Now the bias B is given by;

$$B = d_f - d_r \quad (4.1)$$

For the worst case, when etching is completely isotropic then;

$$B = 2h_f$$

To be able to resolve the lines, l_m must be greater than or equal to d_f , so substituting in Eqn. 4.1 we have the condition for minimum linewidth spacings;

$$l_m = 2h_f + d_r$$

So in the case of an isotropic etch, smaller linewidths can be achieved with thin films. Thick planarising layers always employ dry etching techniques to produce the anisotropic profiles in order to minimise the bias. Linewidth can also be controlled by compensating for the bias at the initial lithography step and is a common practice in LSI technology. It will be shown in Chapter 6, that the minimum linewidth spacing in Cr is limited by the e-beam scattering in the lithography step and bias is almost negligible.

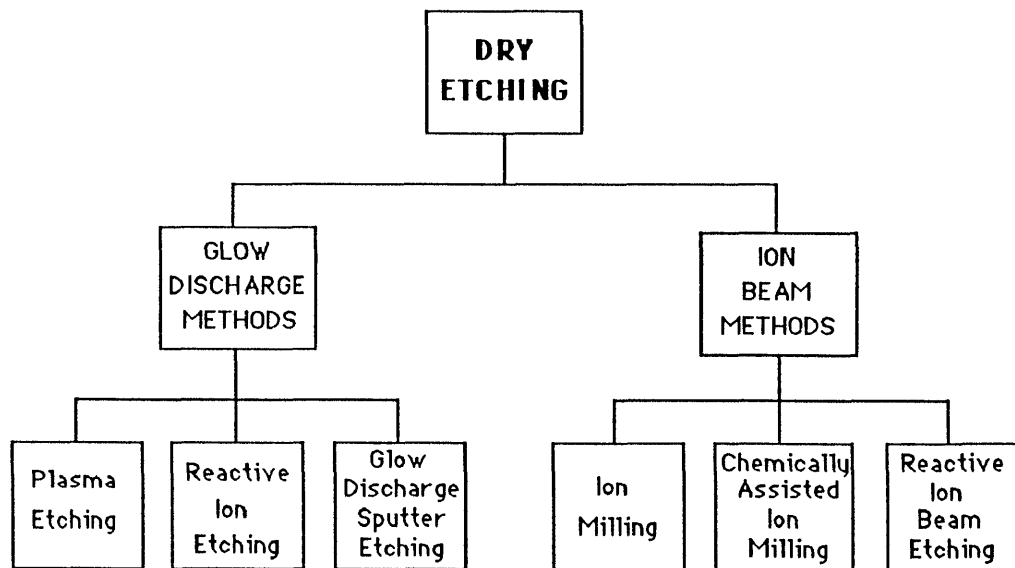


Fig. 4.3. Dry etching methods using rf glow discharges and widearea ion beams.

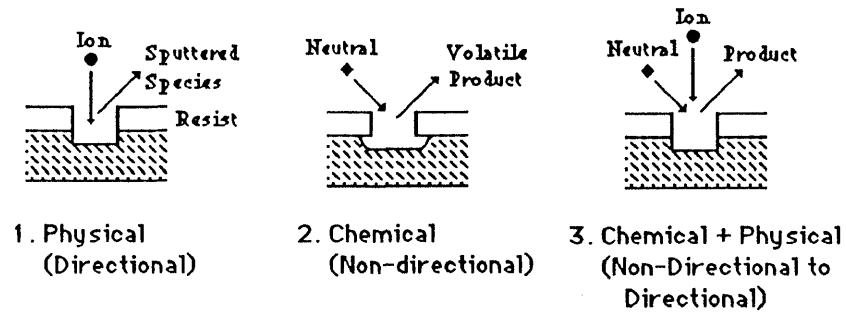


Fig. 4.4. Mechanisms involved in dry etching.

Glow Discharge Sputter Etching Ion Milling	Reactive Ion Beam Etching	Chemically Assisted Ion Milling	Reactive Ion Etching			Plasma Etching
			Intensified Discharges	Low Pressure	High Pressure	
No Undercut	'Controllable' Undercut					Isotropic Etching
Poor	Selectivity					Excellent
300	Etch Rate (Å/min)					1000
Submonolayer			Mono- layer		Multilayer	
Low	Reactive Neutral Flux Ion 'Flux-Energy' Product					High

Fig. 4.5. Qualitative representation of various dry etching methods in terms of the reactive neutral flux-to-ion 'flux energy' product and the resulting halogen coverage.

4.2. Dry Etching Methods

Dry etching methods are the only real solution for producing high yield microstructures having minimum features less than $1\text{ }\mu\text{m}$. Reactive Ion Etching (RIE) forms one class of a large category of dry etching systems employed for VLSI fabrication (Fig. 4.3).

In industry today the principle requirements of the systems for on-line

processing are a fast etch rate to produce a high throughput, control over feature size and profiles, selectivity, uniformity and defect or impurity introduction. Barrel type plasma etching has already been introduced in the production line of LSI processing and can produce etch rates of up to 1000 Å/min [4]. Although selectivity for these systems can be very high, the profiles produced is often isotropic in character thus limiting its use for submicron lithography.

Planar-type plasma etching such as used in the RIE mode, makes possible more precise etching. RIE systems with wafers located on the driven electrode are now in widespread use owing to its flexibility in controlling the etched profiles and the ability to etch features of submicron dimensions.

Although, ion-beam etching has some problems not yet solved, the possibility of the application to VLSI processing is under investigation because of its simple etching mechanism and its good controllability. The sputter etching, however, is now almost disregarded because it has no special advantages except for the relatively simple structure of the equipment.

4.3. Factors Influencing Etch Rates and Edge Profiles

Etching of the film can be grouped into three main types of mechanism shown in Fig. 4.4. The mechanism of physico-chemical can be further subdivided by having electrons [5] or photons [6] instead of ions inducing the chemical reactions. The degree of anisotropy can be related to the reactive gas flux/ion flux ratio and is illustrated in Fig. 4.5 in a very qualitative way. Sputter etching and ion milling techniques employ high energy ions and consequently there is greater erosion of the resist leading to lower selectivity. Typical values of the etch rates are also shown. In the RIE configuration there is a flexibility in controlling the undercut and the etch rates by adjusting the pressure and power (this will be discussed in more detail later). The steady

state halogen coverage of the etched surface expected is also shown and can be quite high for plasma processing [7]. All three mechanisms will be discussed briefly with particular emphasis on ion-assisted chemistry which is the most important mechanism for RIE.

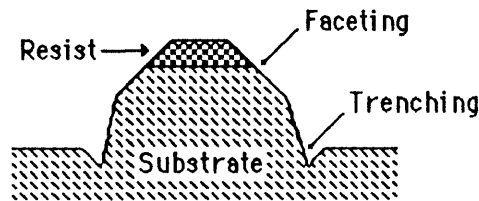


Fig. 4.6. Schematic illustration of faceting and trenching.

4.3.1. Physical Etching

This mechanism uses the impact of incoming ions created in a plasma to sputter material of the surface to be etched [8, 9]. It is highly anisotropic but not very selective, since everything can be physically sputtered. Sputter etching is usually limited to materials which do not readily form volatile compounds in reactive gas environments. Examples of such materials are compounds or alloys containing such elements as Fe, Co, Cu, Mg, Be, Na, Li etc. The halides and oxides of these materials are not volatile at temperatures compatible with resists and microfabrication processes in general. One of the major problems encountered in pattern transfer with physical sputtering is redeposition [10] and backscattering [11] in which the products are deposited on the sidewalls or scattered to other parts of the wafer.

Another problem which degrades the fidelity of pattern transfer is faceting [12] caused by the physical sputtering of the original resist feature (Fig. 4.6). Trenching which is also depicted in Fig. 4.6 results mainly from an enhanced ion flux at the base of a step due to ion reflection off the side of the step. These effects also occur to a smaller degree in the RIE mode, particularly at high bias

voltage condition when ion energies are also high (see Chapter on CsCl etching).

4.3.2. Chemical Etching

This type of etching occurs when a chemical reaction takes place on the surface to be etched and the resulting volatile product is pumped off. The mechanism is non-directional and due to the nature of the chemical reactions it is highly selective. Etching is entirely dominated by reactions with radicals and excited neutrals in the plasma usually giving an isotropic profile to the feature edge. As mentioned before, the barrel-type plasmas are of this type and is more suited to LSI processing.

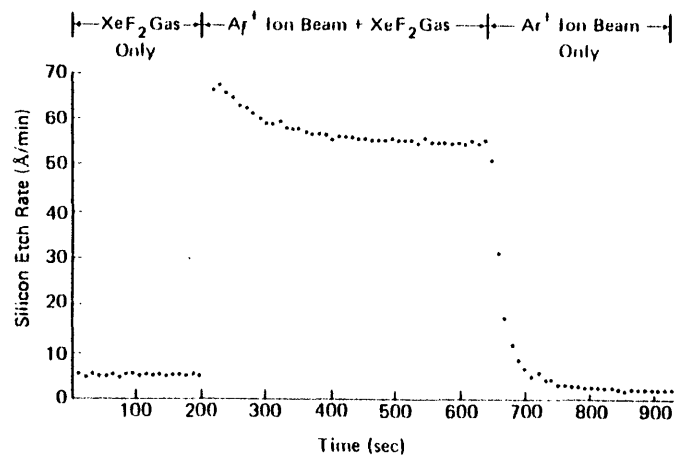


Fig. 4.7. Enhanced etch rate of Si due to ion bombardment of Ar⁺ ions. (After Coburn Ref. [5])

4.3.3. Chemical and Physical Etching

Mechanism 3 (Fig. 4.4) shows the combined physical and chemical effects of 1 and 2. The selectivity and anisotropy for this chemical-physical mechanism can be very good due to the surface chemical reactions with the reactive species in the plasma and the line of sight effect of energetic ions. The concept of ion-assisted chemical etching can be best understood when we consider an example. Fig. 4.7 shows the etch rate of obtained with the reactive gas (XeF_2) flux and the ion beam (450 eV Ar^+) incident on the Si surface simultaneously and of the etch rates obtained with XeF_2 and Ar^+ ions separately. The etch rate with the combined gases is much greater than the sum of the etch rates of the two gases obtained separately. Ion-assisted etching gives an anisotropic profile owing to the directional flux of the positive ions (Ar^+). This phenomena of ion enhanced etching is used in the etching of most materials in the RIE configuration to produce anisotropic profiles. It is also found that Cl atoms are much less effective in etching Si without ion bombardment and a faster etch rate with more directional etching of Si is observed when irradiated with a 450 eV Ar^+ beam [13].

The increase in etch rates observed in ion-enhanced etching can be explained by the following three mechanisms:

- 1) Chemically enhanced physical sputtering [14, 15] in which loosely held reaction products held on the substrate surface are physically removed by the interaction of free radicals and ions mainly. This could also involve removing involatile residues that could otherwise retard etching.
- 2) Ions are thought to create damaged surface sites by ion bombardment which are particularly suitable for reaction [5, 16].
- 3) In the third mechanism ion bombardment provides the energy required for certain exothermic reactions to occur resulting in desorption of products into the gas phase [17].

Directional etching can also be accomplished by taking advantage of certain gas phase species which deposit on the sidewalls. This could be polymeric species [17] in gas discharges containing carbon source gases or involatile products such as in sputter etching. Ion bombardment will remove the deposit formed on the horizontal surfaces and continue etching in the vertical direction but the deposits on the sidewalls are not easily removed and acts as a protection for any lateral etch. In this way highly anisotropic profiles with very little lateral etch can be obtained.

4.4. Reactive Ion Etching (RIE)

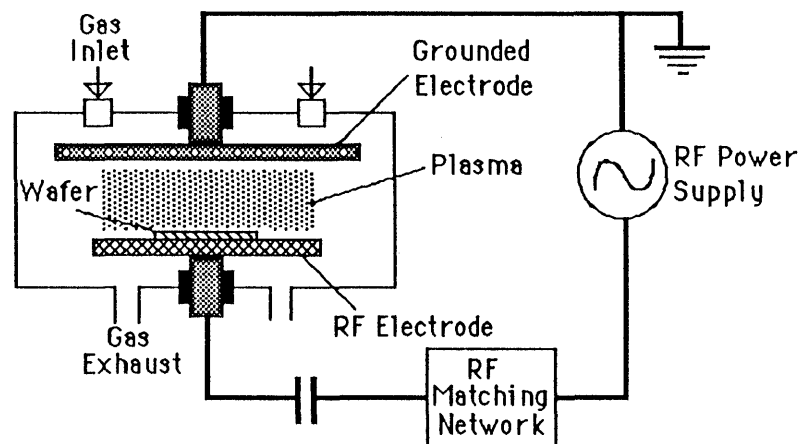


Fig. 4.8. Basic configuration of the Plasma Technology RIE (Series 80).

4.4.1. System Configuration

As mentioned before, the characteristic ability of RIE is its use of controlled energetic ion bombardment to assist in chemically reactive etch processes. The basic configuration of the RIE (Plasmalab Microprocessor, Series 80) used in my experiments is shown in Fig. 4.8. The cathode work-table can be interchanged between a graphite and aluminium tops. The choice of electrode materials depends on whether they are chemically or physically inert to the

plasma environments. Quartz and aluminium are examples of electrode materials that do not substantially deplete the discharge of fluorine [19]. Carbon, "Teflon", or other organic electrode coatings present surfaces that deplete fluorine atoms in the etching of SiO_2 . Metal electrodes through chemical or sputtering reactions can result in heavy metal and other contamination of etched surfaces [20].

For the RIE shown, the wafer etched on the rf driven electrode can take on an electrical potential with respect to the plasma substantially higher than that for a plasma mode configuration (ie. wafers located on the grounded electrode). Consequently, the energetic ion bombardment (>100 eV) then plays a stronger role in driving the etch process (Fig. 4.4). The primary design feature of which allows such energetic ion bombardment is that etching occurs on the rf driven electrode which is capacitively coupled to the rf power supply. When the rf power at 13.56 MHz is applied to the rf driven electrode through the 'blocking capacitor' the dc current must be zero. An average number of positively charged ions and negative electrons must arrive at the electrode. The cathode will take on a negative dc bias since the electrons are of much higher mobility than the ions. The average effect is that the high electron current over a short period of the rf cycle is balanced by a low ion current over the bulk of the cycle. Therefore, the ion current arriving at the cathode has an average energy proportional to the negative dc self-bias.

The rf coupling across the ion sheaths is capacitive and can be approximated to a capacitance which is determined from the area and thickness of the capacitance. Hence, the ratio R of the area of the rf-powered electrodes to the area of all the grounded surfaces in contact with the plasma determines how the applied voltage is distributed among the ion sheaths [21, 22]. As R decreases the potential $V_p - V_{dc}$ increases with the following resultant advantages.

- 1) Very low energy ions strike the grounded electrode, therefore no sputtering or contamination occurs.
- 2) The small area of the cathode reduces the sputtering that can occur.
- 3) Since the plasma potential is fixed near the ground, the self-bias voltage of the rf driven electrode is than an accurate measure of the resulting ion bombardment energy to the cathode (a very important parameter in controlling the etch characteristics).

As mentioned previously, the ions in a plasma play a significant role in the etch characteristics. Therefore, the potentials that develop at various points in the rf discharge are important and this is shown in Fig. 4.9. The electrical discharge can be divided into three regions, the plasma and the dark spaces of the anode and the cathode vis.

- 1) The plasma region encompasses most of the volume between the electrodes. The applied rf field causes the electrons to oscillate which through collisions ionises and fragment the gas molecules to create the etched species (ions and chemically reactive free radicals).
- 2) The cathode sheath thickness is approximately equal to the Debye Length which for a concentration of N ions per cc is,

$$L_D = \left(\frac{\epsilon \epsilon_0 kT}{q^2 N} \right)^{\frac{1}{2}} \approx 120 (N)^{-\frac{1}{2}}, \quad \text{cm} \quad (4.2)$$

while the mean free path λ_D is,

$$\lambda_D = \sqrt{2} / \pi \sigma^2 n$$

where n is the number of molecular species and σ the collision diameter. Say $\sigma = 3 \times 10^{-8}$ on average then,

$$\lambda_D \sim 0.25 \times 10^{-15} n \text{ cm}$$

so for $N = 10^9$ per cc and $a = 3 \times 10^{15}$ per cc we have $L_D = 4 \times 10^{-3}$ cm and $\lambda_D = 0.1$ cm. Ions from the plasma undergo few collisions and arrive almost normal to the wafer surface.

3) The anode sheath is the boundary layers along the anode and keeps the plasma at a small +ve potential with respect to ground with the effect that low energy ions are drawn from the plasma and balance the electron current to the anode.

Etching occurs, as shown in Fig. 4.10 with the plasma ions being accelerated through the cathode sheath to bombard the wafer. Material is also being etched with the reactive species created from the discharge. As a consequence of this, physical-chemical mechanism, the etch proceeds without undercut leading to high anisotropy.

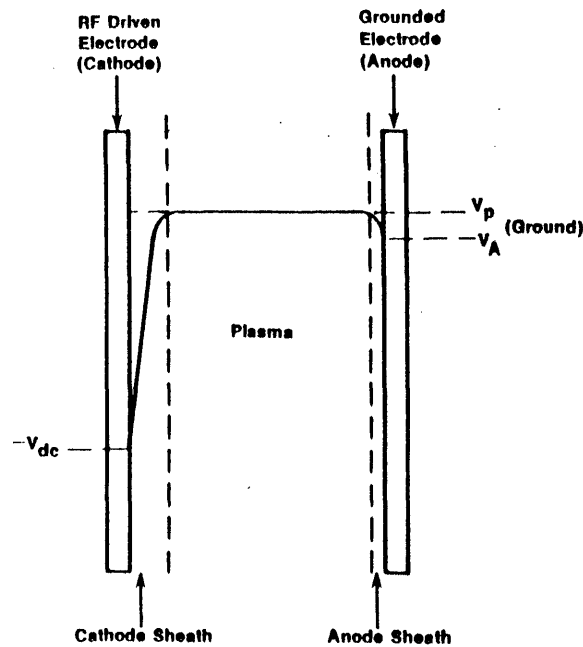


Fig. 4.9. Electrical potential across the discharge region, V_{dc} is the average self-bias voltage, V_p is the plasma potential and V_A is the grounded anode potential. (After Ref. [14])

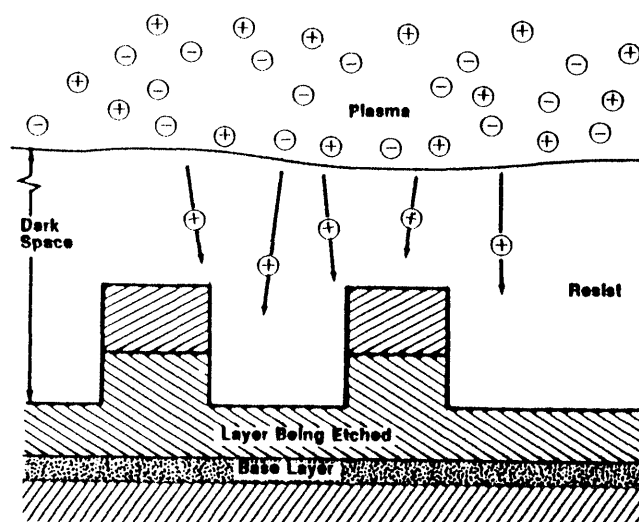


Fig. 4.10. Schematic of ion bombardment in an RIE process. (After D.Bollinger et al. Ref. [14])

4.4.2. Process Parameters

In the RIE (Series 80) machine, three important parameters can be controlled to obtain the desired etch characteristics. These are as follows:

Power (30- 500 Watts)

Pressure (30- 500 mT)

Gas Flow (10- 50 sccm)

Also indicated, are the operating ranges of power, pressure and gas flow settings commonly used for etching of most materials. The dc-bias was measured on an analogue meter with an accuracy of ± 10 V. For the experimental work, specimens were mounted either on a six inch Si wafer on an Al cathode or on a graphite top covering the cathode. Since these materials

are conducting, the dc bias reading can be assumed to be a measure of the ion energies at the specimen surface.

The system has been adapted to accommodate carbon and aluminium cover plates for chlorine and fluorine plasmas respectively. Other factors which are not variable are the electrode geometry and the gap spacings which are fixed at 240mm diameter anode, 170mm diameter cathode and gap spacing of 50mm. A 3-line gas inlet allows control of three types of gases into the chamber.

RIE operation is rather insensitive to electrode separation [23] but the main requirement is that the separation be large enough to ensure that the oscillating electrons in the discharge have sufficient path length for electron-neutral excitation collisions. At a pressure of 50mT mean free paths for electron-neutral ionisation collisions are of the order of 1 cm. So a minimum electrode separation is dependent on the operating pressure (ie. lower pressure increases mean free path between collisions).

Because of the flexibility in choosing a range of values for the process parameters a technique of process optimisation is needed and will be presented in section 4.5. This involves reducing the number of runs for arriving at the optimised value of a given output such as selectivity, etch rate, uniformity etc.

Gas Pressure and Power

These two effects are inter-related and both affects the discharge conditions ie. the formation of free radicals and ions, and self-bias voltage. High pressure increases etch rate because of increased free radical formation leading to isotropic etch mechanism. As a result, the self-bias voltage is reduced which is critical to the ion-assisted mechanism. Consequently, there is an operating pressure range above which undercutting will be significant. The anisotropy

which may be lost at high pressures can be compensated by increasing the rf power (ie. increase in self bias voltage). Self bias-voltage V_{dc} , is related to pressure (P) and power (W) by the following expression [24]:

$$V_{dc} = Ce^{\frac{\alpha P}{W}} \quad (4.3)$$

where C is a constant, α is a constant.

Gas Flow and Distribution

The removal of volatile products and the replenishing of reactive species is characteristic of this process parameter. Excessive gas flow rate will lead to reduced residence time of the gas (ie. the reactive species) observed and hence a decrease in etch rate [38]. Similarly, a low flow rate will lower the generation of active species. For a large etch area the loading effect is evident [25] and the distribution of gas flow over a wafer will have a significant effect on etch uniformity.

Gas Composition

Due to the nature of a plasma an 'additive' gas can have a profound effect on the density of free radicals and the corresponding etch rate. For fluorocarbon gases, polymer formation can be prevented by adding oxygen to the chamber thus allowing operation at higher pressures. This is discussed in length in Chapter 6 with particular emphasis to Si and SiO₂ etching. For anisotropic etching, the addition of heavy inert gases such as Ar will produce the bombarding ions (Ar⁺) required for ion-assisted etching.

End Point Detection

A number of techniques are available for end-point detection namely, optical spectrometry, mass spectrometry, laser reflectance, plasma impedance and pressure monitoring. Optical spectrometer offer a low cost solution for

production facilities. The method involves measuring the intensity of specific wavelengths of light emitted by electronically excited species in the discharge. The intensity of an emission line characteristic of an active or molecular species is representative of the relative amount present in the plasma. None of these techniques were used for our research machine but knowing the etch rate for an initial test run of a sample enabled the end point to be calculated with respect to time.

4.5. Process Optimisation

The ability to minimise the number of experimental runs to optimise the output(s) can be an extremely time saving process. This is particularly useful in a set of runs involving a large number of inputs. In the one dimensional approach all input parameters except one are fixed and the level settings for this parameter are varied and the output(s) optimised. This procedure is repeated for the second parameter and so on. A complete 'map' of the effect of the interactions of the input parameters on the output(s) can be obtained this way, but the procedure is very long and tedious.

Consider the case of 4 input parameters with 3 level settings (Table 4.1). We can see that 81 runs (Table 4.2) are required in the multidimensional space. Whereas optimisation based on the orthogonal design tables requires only 9 runs (Table 4.3).

Table 4.1.

Process with 4 input parameters with 3 level settings each.

INPUTS			
x_1	x_2	x_3	x_4
s_{11}	s_{21}	s_{31}	s_{41}
s_{12}	s_{22}	s_{32}	s_{42}
s_{13}	s_{23}	s_{33}	s_{43}

x_n = nth input variable

s_{nr} = input setting for the nth variable
and the rth row

Table 4.2.

Multidimensional approach to a process optimisation.

Number of Runs	INPUTS				OUTPUTS		
	x_1	x_2	x_3	x_4	1_y	2_y	n_y
1	s_{11}	s_{21}	s_{31}	s_{41}	1_{y1}	2_{y1}	n_{y1}
2	s_{12}	s_{21}	s_{31}	s_{41}	1_{y2}	2_{y2}	n_{y2}
3	s_{13}	.	.	.	.	.	.
.	.	.	.	.	.	.	.
81	s_{13}	s_{23}	s_{33}	s_{43}	1_{y81}	2_{y81}	n_{y81}

Table 4.3.

Orthogonal table for process optimisation.

Number of Runs	INPUTS				OUTPUTS		
	x_1	x_2	x_3	x_4	1_y	2_y	n_y
1	s_{11}	s_{21}	s_{31}	s_{41}	1_{y1}	2_{y1}	n_{y1}
2	s_{11}	s_{22}	s_{32}	s_{42}	1_{y2}	2_{y2}	n_{y2}
3	s_{11}	s_{23}	s_{33}	s_{43}	1_{y3}	2_{y3}	n_{y3}
4	s_{12}	s_{21}	s_{32}	s_{43}	1_{y4}	2_{y4}	n_{y4}
5	s_{12}	s_{22}	s_{33}	s_{41}	1_{y5}	2_{y5}	n_{y5}
6	s_{12}	s_{23}	s_{31}	s_{42}	1_{y6}	2_{y6}	n_{y6}
7	s_{13}	s_{21}	s_{33}	s_{42}	1_{y7}	2_{y7}	n_{y7}
8	s_{13}	s_{22}	s_{31}	s_{43}	1_{y8}	2_{y8}	n_{y8}
9	s_{13}	s_{23}	s_{32}	s_{41}	1_{y9}	2_{y9}	n_{y9}

Orthogonal tables (or matrix) satisfy the following relationships:-

- 1) The number of occurrences of each level setting must be equal within each column.
- 2) All rows having identical level settings in a given column must have equal number of occurrences of all other level settings in the other columns.
- 3) The matrix for a given number of columns must be the one with the minimum number of rows that satisfy the above conditions.

We can see that the orthogonal table (Table 4.3) satisfies all the above conditions. This orthogonal table is designated $L_9 3^4$ where 3, 4, 9 corresponds to the number of level settings which is 3, the four input parameters and, 9, the number of runs required. The outputs are represented by $r y_n$ where n is the n th output function and r , the output value for the r th run.

It is the above properties of orthogonality which describes its usefulness in optimising an output. Suppose we wanted to look at the effects of changing an input parameter x_1 (Table 4.3) on an output y_1 . We can see that the first order effects of the other input parameters (x_2, x_3, x_4) cancel out because the level settings for these input parameters occur with equal frequencies. We can thus obtain an average value of the output function dependent on the values S_{11}, S_{12}, S_{13} . Similarly the average output function for the other input parameters can be derived and thus obtain a statistical analysis of the effects of the various level settings on the output(s).

The choice of level settings is extremely important. A well designed experiment will include level settings which are not too coarse otherwise an output maximum or minimum could be bracketed. The maximum and minimum are clearly missed by choosing level settings 0 and 1 as shown in Fig. 4.11. By choosing input settings which lie between 0 and 1, this problem will not occur. Previous experience with the process from one dimensional searches will assist the engineer in selecting the correct level settings for the

smallest orthogonal matrix.

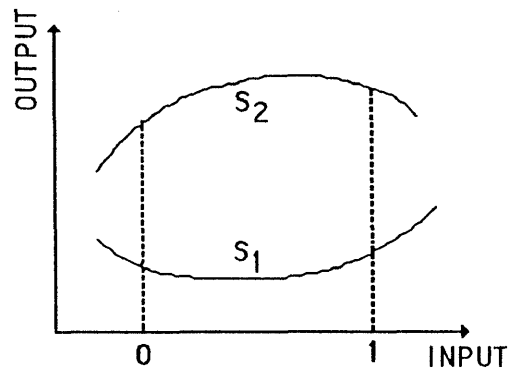


Fig. 4.11. Illustration of the importance of choosing level settings which are not too coarse.

Readers are encouraged to read the paper by Yin and Jillie [26], which gives an excellent example of the use of an $L_9 3^4$ orthogonal table for optimising the selectivity and etch rate of Silicon Nitride.

Optimisation based on the orthogonal tables can be efficiently used with our present RIE equipment and this is used whenever possible (see for examples, Chapter 5 (selectivity), Chapter 7 (anisotropy). Appendix. II contains a list of useful orthogonal tables that could be used for optimising etch rates, selectivity, uniformity and anisotropy. As we are primarily concerned with the etch rate and selectivity, I have selected these two as the output functions. It is easily possible to quantify other output functions (ie. anisotropy or uniformity) but the calculations remain the same. A first time user with no knowledge of the etch rate and selectivity or someone running a completely new process can utilise the $L_4 2^3$ orthogonal table. This table requires only 4 runs to be made and will provide a preliminary test into the effects of power, pressure, and gas flow on the etch rate and selectivity. A $L_{16} 4^5$ table can take into account the effects of 3 different gases and this table only requires 16 runs. A listing for the $L_9 3^4$ matrix is also given.

SELECTIVITY STUDIES OF CADMIUM CHLORIDE RESIST ON SILICON DIOXIDE AND SILICON

Previous studies on the selectivity of $\text{CdCl}_2/\text{SiO}_2$ have been carried out using CF_4/O_2 etch gases on an "in-house" modified plasma etcher which operated as a reactive-ion-etcher [1]. In this work SiO_2 was etched with thin films of CdCl_2 resist (approx. $1000\text{\AA}$ CdCl_2 , $1500\text{\AA}$ SiO_2) using CHF_3/O_2 etch gases in order to determine the selectivity. Details of the RIE system used for these experiments have already been described in chapter 4. Process parameters such as power, pressure, O_2 concentration were varied to see the effects on the etch rates and the selectivity. Optimisation of selectivity using the L_42^3 orthogonal table was carried out. Edge profiles obtained in $1\text{ }\mu\text{m}$ SiO_2 using the image reversal technique (chapter 6) was examined in the electron microscope. Before moving onto the results of the experiments obtained in this study, the significant literature on Si/SiO_2 etching using CF_4/O_2 and CHF_3/O_2 will be presented.

5.1. Etching of Si and SiO_2

SiO_2 etching processes are required to fabricate many structures including contact cuts, implant masks and metal-oxide semiconductor (MOS) gates [2]. Polycrystalline Si is typically used as an MOS gate material and important etch parameters for this gate etch are: selectivity to SiO_2 and anisotropy and line profile control. A list of commonly used chlorinated and fluorinated gases for etching these two materials are given in Table 5.1.

Si and SiO_2 etch rates in a CF_4 plasma is low, but the addition of O_2 to the gas feed affects the etch rates of these materials considerably (Fig. 5.1). The percent concentration of oxygen is the molar concentration in sccm. The etch

rate of SiO₂ increases to a peak at about 23% O₂ while the peak of the Si etch rate occurs at a lower O₂ concentration. This behaviour has been attributed to the concentration of F species in the plasma which mainly contributes to the etching and forms the volatile product SiF₄. The reactive species are F and CHF₃ in CF₄ [3] and these are formed by electron impact dissociation of CF₄. F atoms are consumed by combination with CF_x radicals (≤ 3) and the rates of these processes determine the steady state concentration of F atoms, which is low with no O₂ additive. Added oxygen depletes the CF_x radicals by the formation of COF₂, CO and CO₂ hence the concentration of F atoms increases resulting in an increased etch rate. The F atom concentration increase to about 20% and decreases thereafter because of dilution. The peak obtained for Si occurs at lower O₂ concentration and is due to the O radicals being chemisorbed on the surface and partially blocking the direct access by F atoms. This effect will increase with more O₂ added and the maximum etch rate will occur at an oxygen concentration much less than 23%.

Table 5.1

A list of commonly used gases and gas mixtures for reactive ion etching of Si and SiO₂.

Si	CF ₄ , CF ₄ + O ₂ , SF ₆ , SF ₆ + O ₂ , NF ₃ , Cl ₂ , Cl ₂ + Ar, CCl ₄ , CCl ₃ F, CCl ₂ F ₂ , CClF ₃
SiO ₂	CF ₄ , CF ₄ + H ₂ , C ₂ F ₆ , C ₃ H ₈ , CHF ₃

Quite different effects are noted when H₂ is added to a CF₄ plasma [4, 5]. The etch rate of SiO₂ is nearly constant for H₂ additions up to about 40% (mole) while the etch rate of Si decreases monotonically to a value near zero at $\geq 40\%$ H₂. Unwanted polymer formation on Si can occur when H₂

concentration exceeds 40% (this will be explained in more detail later). A reasonable explanation for these results is as follows: F atoms are depleted by forming stable HF radicals which are potential Si etchants. CF_x ($x \leq 3$) radicals etch SiO_2 by chemisorption which ultimately results in formation of SiF_4 . The C derived from these radicals are removed by combining with oxygen from the SiO_2 to form volatile CO, CO_2 and possibly COF_2 gases.

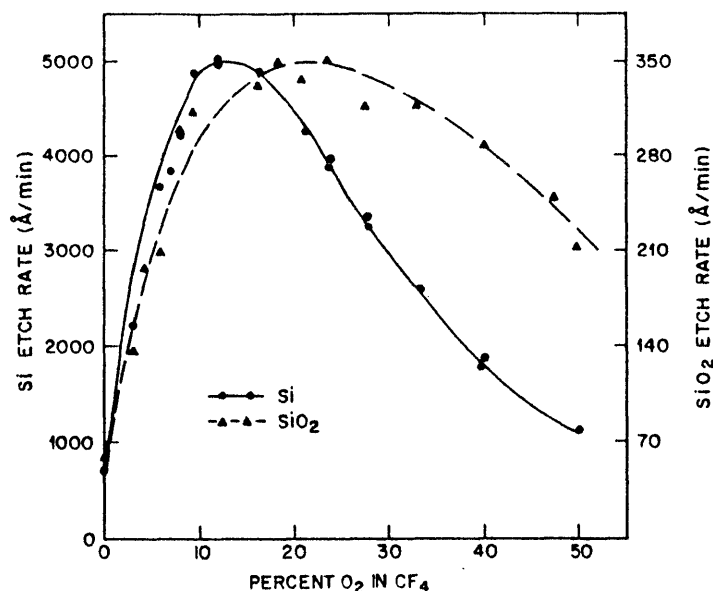


Fig. 5.1. Etch rates of Si and SiO_2 in a CF_4 plasma with controlled addition of oxygen into the feed chamber. (After Mogab et al Ref [3])

Polymer Formation

The concept of fluorine-to-carbon (F/C) ratio is a useful indicator of the extent of polymerisation in a fluorocarbon glow discharge [6] and is illustrated in Fig. 5.2. CF_4 with no additive gas has an F/C ratio of 4. If oxygen is added to the system the carbon will be oxidised to form CO or CO_2 with a corresponding increase in the F/C ratio. Hydrogen will reduce the F/C ratio by depleting the concentration of active fluorine species to form stable HF. An increase in applied voltage to the surface retards the onset of polymerisation

possibly by ion-assisting the fluorine atom reaction with the carbon or even by physical sputtering. The shape and location of the boundary between polymerisation and etching will depend on many system parameters. It will also depend on the nature of the substrate material (ie. polymerisation will occur more readily on Si than on SiO_2).

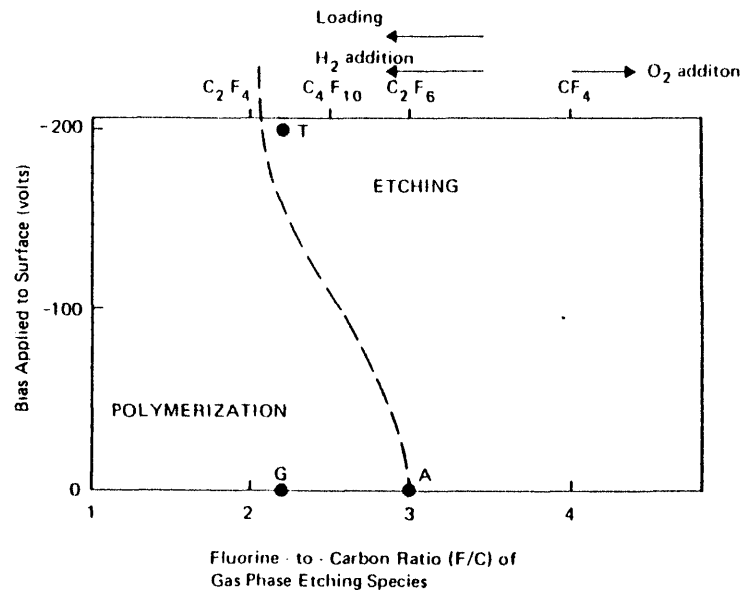


Fig. 5.2. The F/C ratio and how it affects polymer formation. (After Coburn and Winters Ref [6])

Selective etching can be utilised when a high degree of selectivity and anisotropy is required when etching silicon dioxide over polysilicon and single crystal silicon. If the film thickness and the etch rate were perfectly uniform, selectivity with respect to substrate would not be a concern. This ideal is rarely encountered in VLSI and overetching is always required in stepped topography. Fig. 5.3 shows the overetching needed to remove the residue at the steps for proper linewidth control, hence the high degree of selectivity required between film and substrate.

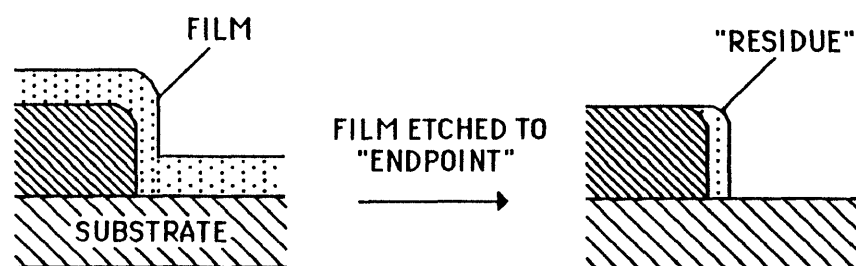


Fig. 5.3. If etching is anisotropic, overetching is required to remove the residual material at the steps (the risers).

Organic photo resists [7] have selectivities of about 6 which requires comparatively thick resists layers to avoid complete resist erosion. In e-beam and photo resists, thin films are favoured for high resolution and minimum linewidth [8, 9] so there is an increasing need for thin highly selective resists.

It is not always desirable to have vertical sidewalls, for example in the case of metal step coverage [10]. In this case a tapered wall etch is needed for contact holes through a SiO_2 layer due to the non-conformal coverage of the metal.

5.2. Etching using CHF_3/O_2

The mechanism involved in etching Si and SiO_2 with CHF_3/O_2 is very similar to CF_4/O_2 plasma etching [11]. Pan and Steckl [12] have recently made a study of Si/ SiO_2 etching in the RIE mode using CHF_3/O_2 plasmas. The results of their investigations are given in Figs. 5.4, 5.5, 5.6, 5.7. The maximum of the fluorine conc. peak (20% O_2 conc.) coincides with the maximum SiO_2 etch rate. This is the expected result as obtained by Mogab and his co-workers [3]. The F atom conc. increase to about 20% and decreases thereafter because of dilution.

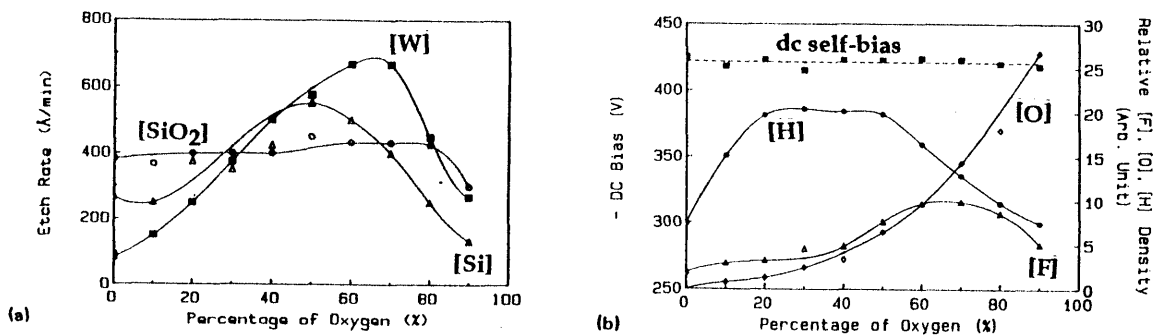


Fig. 5.4. Etch rates of Si, SiO₂, W vs percentage of O₂ in CHF₃ and O₂ plasma at 200 W (0.42 W/cm²), 20 sccm, 20 mT, (b) dc self-bias and relative [F], [O] and [H] atomic density vs percentage of oxygen. (After Pan and Steckl, Ref [12])

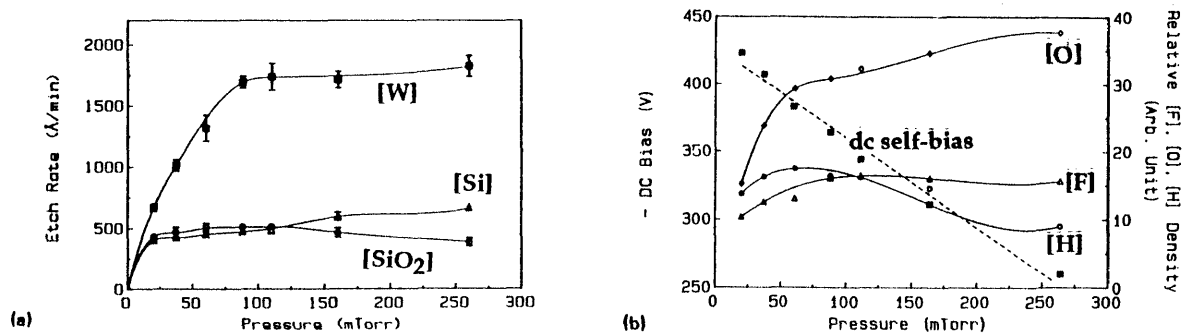


Fig. 5.5. Etch rates of Si, SiO₂, W vs pressure in 30%CHF₃/70% O₂ plasma at 200 W, 20 sccm, (b) dc self-bias and relative [F], [O] and [H] atomic density vs pressure. (After Pan and Steckl, Ref [12])

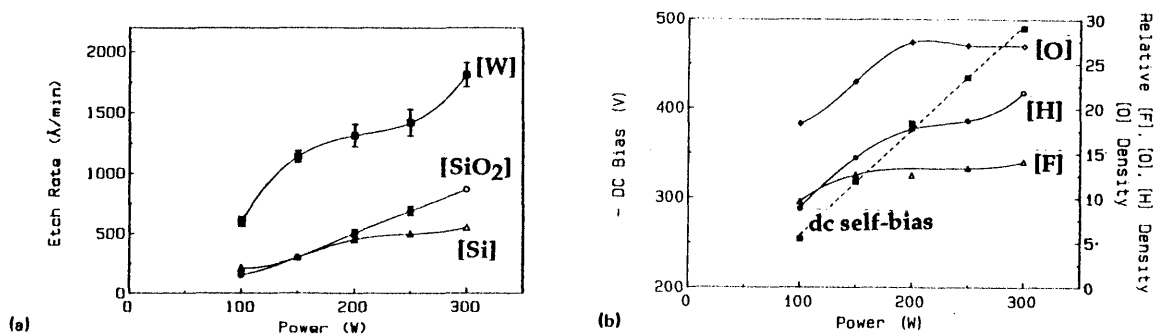


Fig. 5.6. Etch rates of Si, SiO₂, W vs power in CHF₃ and 70% O₂ plasma, at 20 sccm, 60 mT, (b) dc self-bias and relative [F], [O] and [H] atomic density vs power. (After Pan and Steckl, Ref [12])

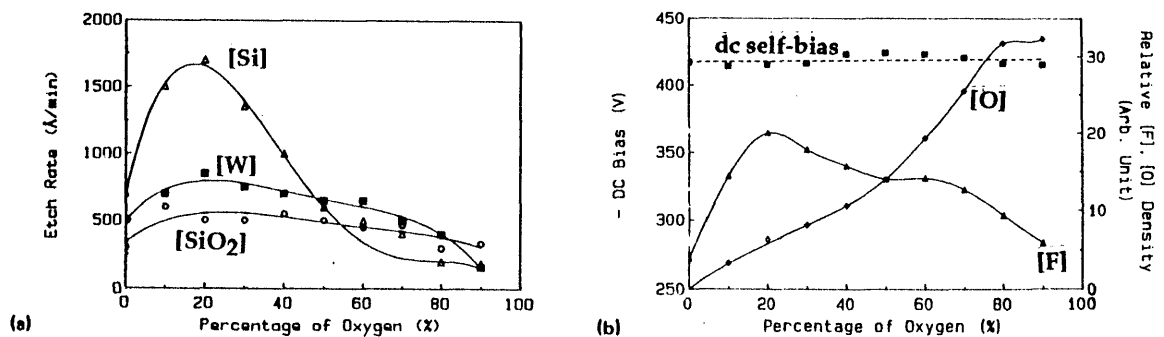


Fig. 5.7. Etch rates of Si, SiO₂, W vs percentage of O₂ in CF₄ and O₂ plasma at 200 W, 20 sccm, 60 mT, (b) dc self-bias and relative [F], [O] and [H] atomic density vs percentage of oxygen. (After Pan and Steckl, Ref [12])

CHF_3/O_2 plasmas have a low F:C ratio and consequently the etch rate of Si is reduced with little change to the SiO_2 etch rate (Figs. 5.4, 5.5). The SiO_2 etch rate is roughly constant (approx. $400\text{\AA}/\text{min}$) with the addition of O_2 into the system (Fig. 5.4), but this could alleviate the problem of polymer formation when operating at higher pressures. The etch rate of SiO_2 falls slightly with an increase in pressure (Fig. 5.5). As expected the etch rate of SiO_2 increases linearly with power (Fig. 5.6). The advantage of using CHF_3 or other higher fluorocarbons is that it offers good selectivity when etching silicon dioxide over polysilicon. The high selectivity of SiO_2/Si will ensure that overetching of the polysilicon does not occur.

5.3. Results and Discussion

In this work SiO_2 was etched with thin films of CdCl_2 as the resist (approx. $1000\text{\AA}$ CdCl_2 , $1480\text{\AA}$ thermally grown SiO_2 on a Si substrate). CdCl_2 films were evaporated from a heated molybdenum boat in vacuum (10^{-6} T) containing the powdered sample supplied by BDH Chemicals Ltd (95% pure). A shuttered evaporation unit with a liquid nitrogen trap together with a digital crystal monitor (Intellemetrics) enabled film thicknesses of $\pm 50\text{\AA}$ to be deposited on a 3" wafer. CdCl_2 films were deposited at a rate of about $30\text{\AA}/\text{s}$. The mean grain size is of the order of the film thickness [1]. The wafer was half deposited with the CdCl_2 film so that small samples (Fig. 5.8) typically $1\text{cm} \times 2\text{cm}$ could be used for etching. CdCl_2 deposited in vacuum collects water when exposed to air and it has been experimentally confirmed [13] that hydrated $x\text{H}_2\text{O} \cdot \text{CdCl}_2$ grows to about 20% of the thickness of the anhydrous CdCl_2 . The process is reversed when the sample is put in vacuum. Film thicknesses before and after etch were measured using the stylus depth measuring instrument (Talystep, Rank Taylor Hobs. Ltd. UK) and the ellipsometer (Rudolph Research Auto El3).

Results of the etch rates of SiO_2 and CdCl_2 with the corresponding selectivities with variation in pressure, power and oxygen concentration are shown in Figs. 5.9 to 5.11. The dc-bias could not be measured accurately since a 6" silicon wafer was placed over the Al cathode to contain the small samples. In any case the measurements indicated can be assumed to give a reasonable idea of the ion energies to the substrate. The cathode diameter is 170 mm giving a power density of 0.88 W/cm^2 at 200 W which is half (0.42 W/cm^2) that of the RIE used by Pan and Steckl [12]. Etch rates obtained in these experiments are therefore twice the values of their results for the same power settings.

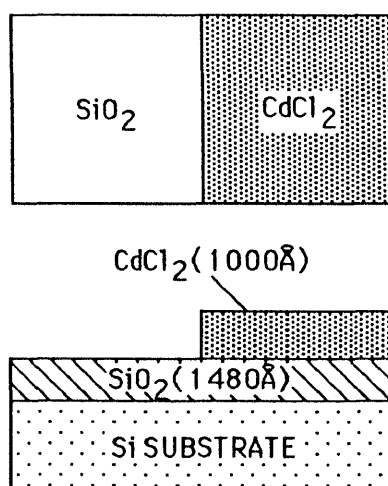


Fig. 5.8. Sample used for the etching of SiO_2 and CdCl_2

5.3.1. Characterisation of SiO_2 etching

Dependence on Pressure

A sharp drop in selectivity is observed below 100 mT for etching at a constant 83 W rf power (Fig. 5.9) and 200 mT for etching at a constant 107 W rf power (Fig. 5.10). Selectivity is the highest at 83 watts, implying high ionic bombardment at rf powers greater than this value (average dc bias : 83 W-200

V, 107 W-230 V) with a corresponding increase in the etch rates. The etch rates of SiO_2 in both cases exhibit a maximum around 100 mT.

At low pressures (approx 50 mT) the loss in selectivity can be explained by the sputtering of the CdCl_2 film owing to the high energy of the reactive ion species and its greater mean free path. At higher pressure the etch rates fall gradually due to the decreased ion energy range (E/p relationship). These results point to the fact that the dominant etching mechanism is ion-enhanced in agreement with Steinbruchel's [11] results. Selectivity is found to increase with pressure with no polymer formation below 260 mT.

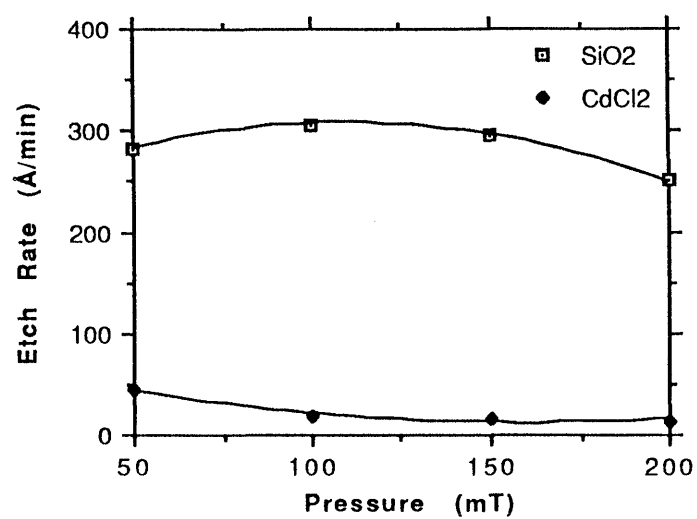
Dependence on O_2 concentration.

A slight increase in the etch rate of SiO_2 (Fig. 5.11) is observed as the oxygen concentration is increased which is similar to the results obtained by Pan (Fig. 5.4). This is attributed to the increase in the F concentration which participates in the overall etching of SiO_2 . The etch rate of CdCl_2 is observed to decrease slowly with the oxygen concentration possibly as a result of Cl and F exchange which inhibits further etching (see section 5.3.2.1.). Selectivity increases slowly with a peak at 60% O_2 which could be attributed to the peak in the F radical concentration (Fig. 5.4(b)) thus giving a high etch rate of SiO_2 . Increasing the oxygen concentration above 60% at low powers (<107 W) and high pressure (>240 mT) affects the grain structures of the film (this will be shown later).

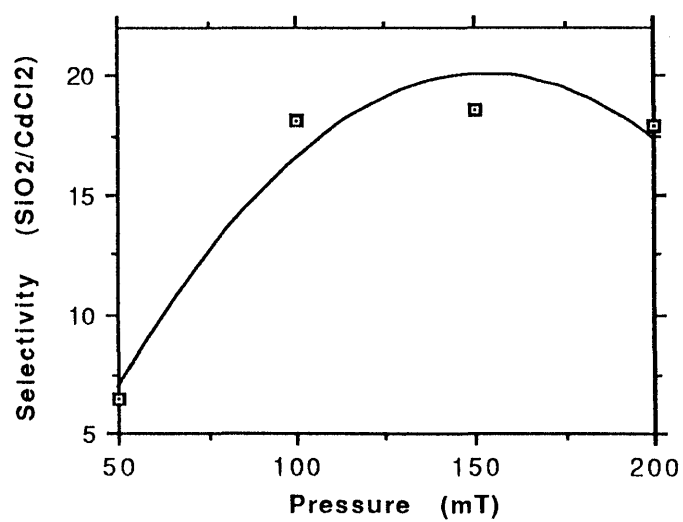
Dependence on Power

As expected the etch rate of SiO_2 increases linearly with power (Fig. 5.12) and the selectivities are 18 and 15 at 57 W and 107 W respectively. Working at pressures higher than 100 mT would increase the selectivity substantially but at a reduced etch rate. Higher rf power results in generation of more ions and

free radicals and hence increased etch rate. Selectivity can be improved further by maintaining the 107 Watts rf power for an efficient etch rate and operating at a higher pressure. The trade-off between power and pressure (effectively the dc-bias) will ensure optimum etch rate of SiO₂ and high selectivity of SiO₂/CdCl₂.

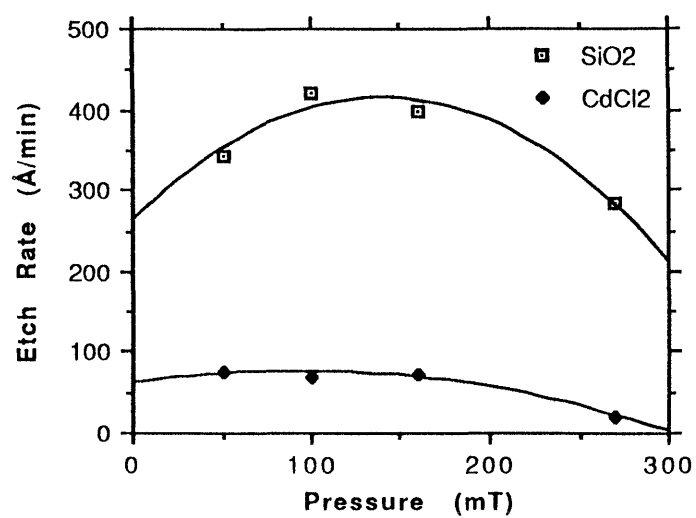


(a)

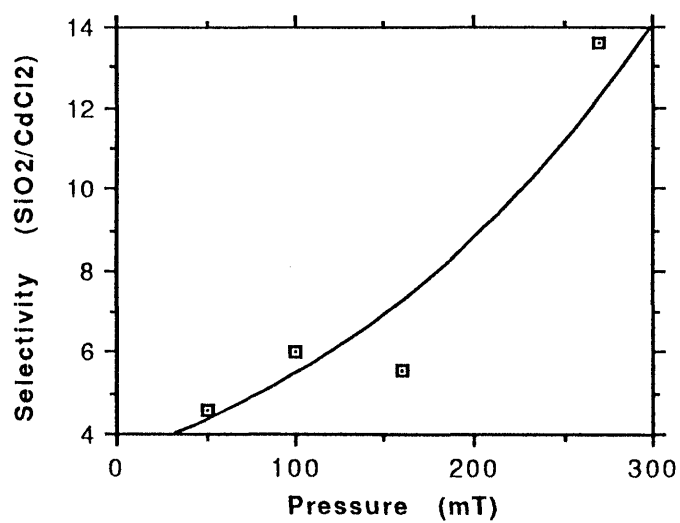


(b)

Fig. 5.9. (a) Etch rate of SiO₂, CdCl₂ vs pressure (mT) at 83 W, 30 sccm CHF₃, 10% oxygen concentration, temp. 17 °C, (b) the corresponding selectivity.

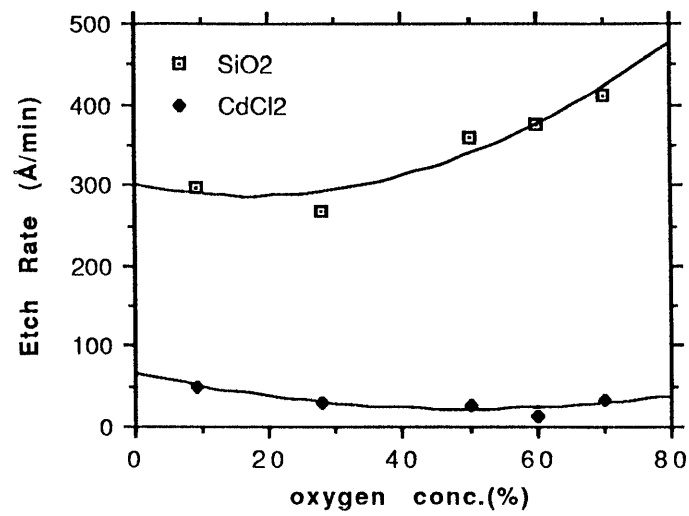


(a)

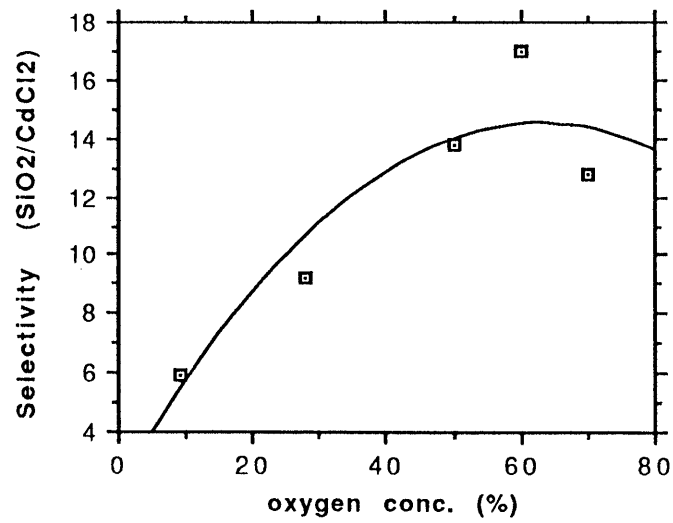


(b)

Fig. 5.10. (a) Etch rates of SiO₂/CdCl₂ and the dc bias (V) versus pressure (mT) at 107 W, 30 sccm CHF₃, 17% oxygen conc., (b) the corresponding selectivity.

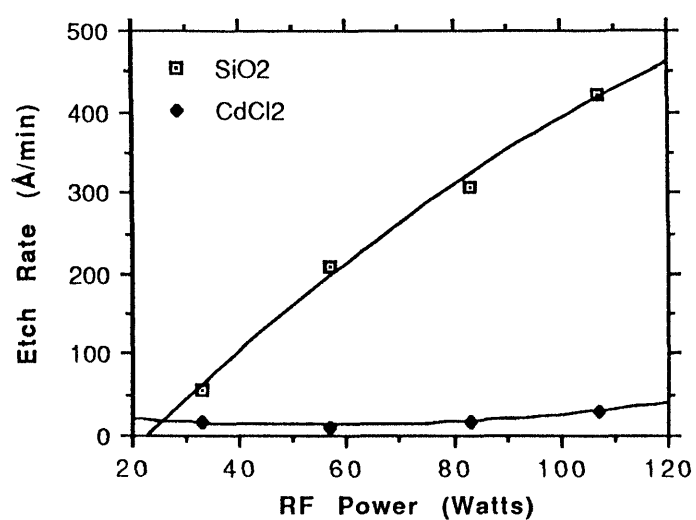


(a)

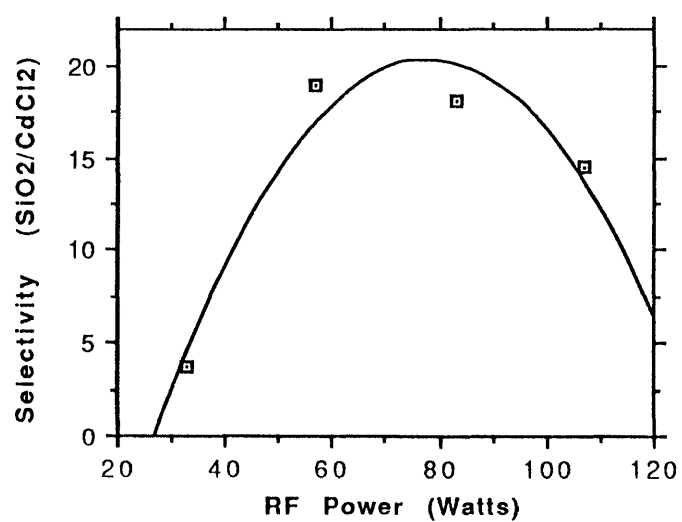


(b)

Fig. 5.11 (a) Etch rates of SiO₂, CdCl₂ vs percent oxygen conc. at 107 W, 30 sccm CHF₃, 240 mT, (b) the corresponding selectivity.



(a)



(b)

Fig. 5.12 (a) Etch rates of SiO₂/CdCl₂ vs rf power at 100 mT, 300 sccm CHF₃, 17% O₂, (b) the corresponding selectivity.

5.3.2 Optimisation of Selectivity

Having understood the effects of the process parameters influencing etch rate and selectivity, it is fairly easy to optimise these output functions further by selecting an L_42^3 orthogonal table. The completed table for the input parameters chosen is shown in Table. 5.2.

Table 5.2

Level settings for the L_42^3 orthogonal table to optimise selectivity.

LEVEL SETTING	POWER (W)	PRESSURE (mT)	O ₂ (%conc.)
1	90	320	67
2	107	270	14

The power settings have been restricted to 90 and 107 W as these provide a reasonable etch rate of SiO₂ (Fig. 5.9). It is not quite clear yet how oxygen affects the selectivity apart from an increase in the SiO₂ etch rate (Fig. 5.11). Two extreme values have been chosen ie. at 14% and 67% to predict the effects at low and high concentration respectively. Selectivity is substantially improved by operating at high pressures (Fig. 5.8). Values of 270 and 320 mT were chosen to give the highest pressure conditions before the onset of polymerisation.

Test samples of SiO₂ (1 μ m thermal SiO₂ grown on Si substrate) and the bare Si substrate with deposited CdCl₂ were prepared as before to determine the etch rates of Si, SiO₂, CdCl₂. The etch rates were determined using the Talystep at the edge of the film (Fig. 5.7). Initial and final thicknesses of CdCl₂ were measured accurately with the ellipsometer with an error margin of not more than $\pm 30\text{\AA}$.

Table 5.3*Etch rates of SiO₂, Si and CdCl₂ for the four run conditions.*

RUN	POWER (W)	PRESSURE (mT)	O ₂ CONC. (%)	ETCH RATE (Å/MIN)			SiO ₂ /CdCl ₂ (SELEC.)
				SiO ₂	Si	CdCl ₂	
1	90	320	67	250	217	0.00	∞
2	90	270	14	300	129	3.12	96
3	107	320	14	300	135	5.17	58
4	107	270	67	350	329	9.95	35

SEM micrographs of the four etched samples including an unetched one are shown in Figs. 5.13 to 5.18. Micrographs of runs 1 (Fig. 5.17) and 4 (Fig. 5.16) show areas of 'opening' in the CdCl₂ film along preferential grain boundaries. The oxygen concentration for these two runs is at a maximum (67%) and this produces the maximum fluorine concentration (Fig. 5.4 after Pang). Fig. 5.18 shows the structure of the underlying SiO₂/Si after stripping CdCl₂. It is proposed that these data can be explained as follows:- weak regions in the grain boundary (Fig. 5.19) of the film are attacked by these radicals (or other species) creating an opening through the resist. Etching of the SiO₂ and in particular the Si substrate which etches spontaneously with F species in the plasma then occurs. This can be clearly seen in Fig. 5.18 where CdCl₂ has been stripped by dissolving in deionised water and agitated in an ultrasonic bath for 1 minute. The large crevices formed beneath the CdCl₂ film stretch beyond the SiO₂ layer and into the Si substrate. This effectively produces an overhang film of the CdCl₂ as shown in Fig. 5.19 which after stripping reveals the undercut features of the SiO₂/Si substrate. Runs 2 and 3 have a lower concentration of F radicals due the lower oxygen feed and the underlying SiO₂/Si was well protected.

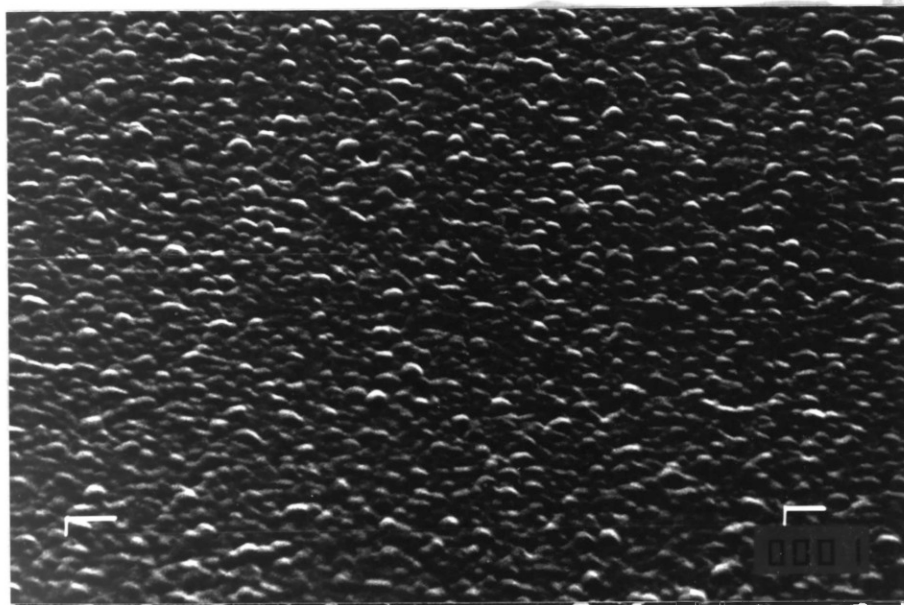


Fig. 5.13. CdCl_2 as deposited, film thickness 1010 Å, deposition rate 30 Å/s, mark spacing 10 μm, tilt 45°.

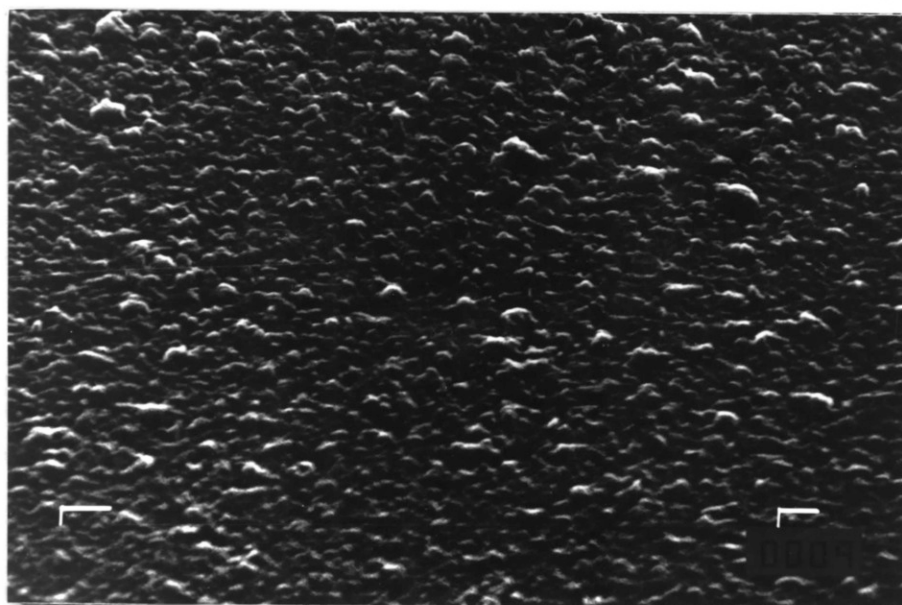


Fig. 5.14. Etched sample of run 2 in CHF_3/O_2 plasma at 90 W, 270 mT, 14% O_2 . (mark spacing 10 μm, tilt 45°)

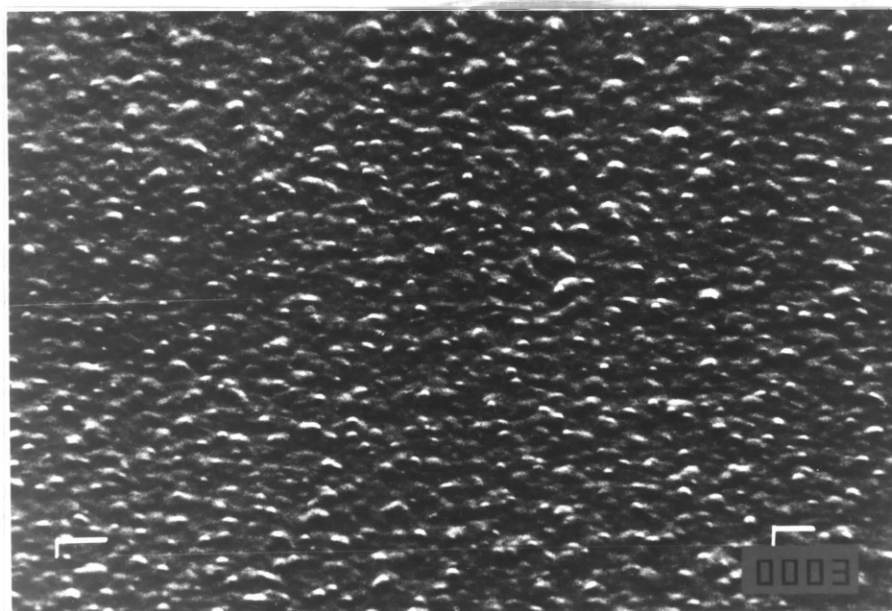


Fig. 5.15. Etched sample of run 3 in CHF_3/O_2 plasma at 107 W, 320 mT, 14% O_2 . (mark spacing 10 μm , tilt 45°)

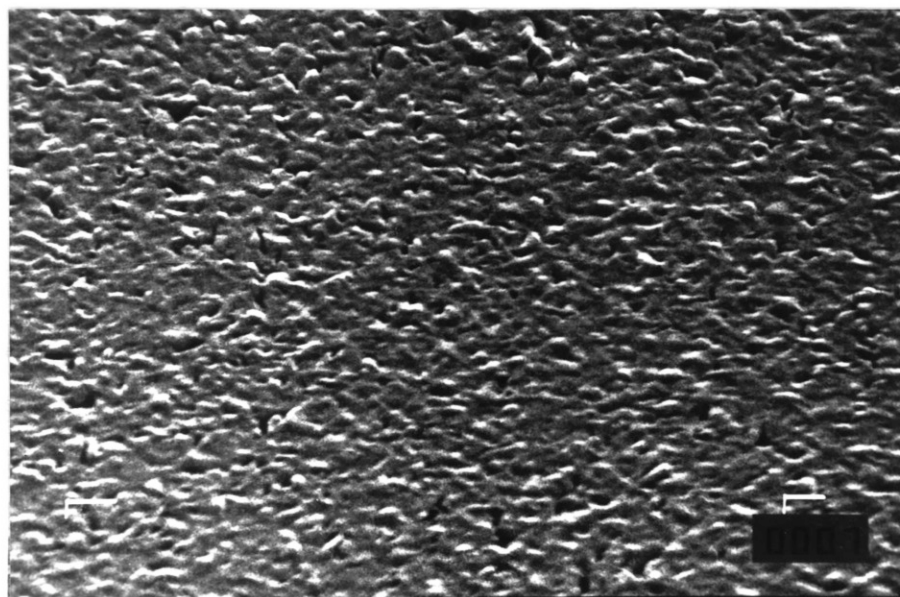


Fig. 5.16. Etched sample of run 4 in CHF_3/O_2 plasma at 107 W, 270 mT, 67% O_2 . (mark spacing 10 μm , tilt 45°)

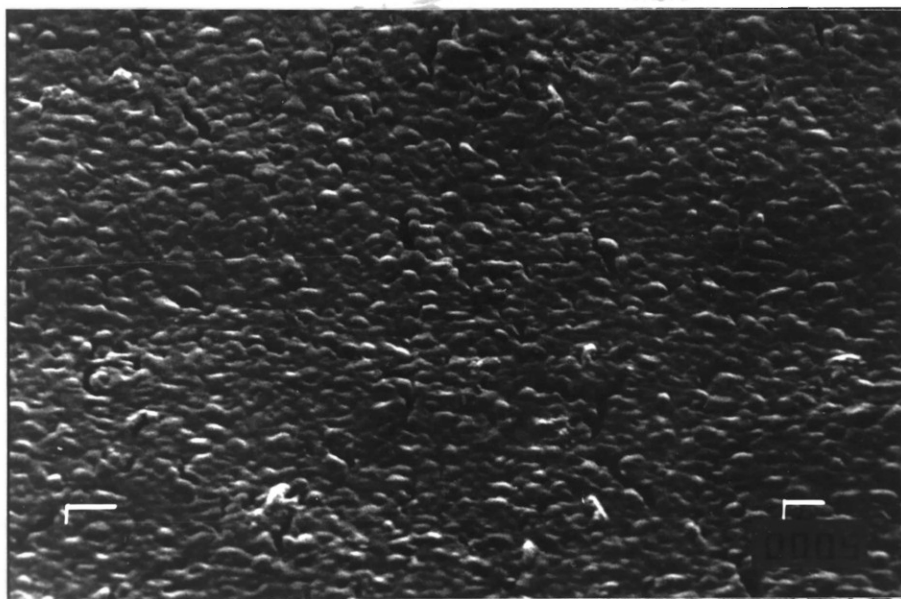


Fig. 5.17. Etched sample of run 1 in CHF_3/O_2 plasma at 90 W, 270 mT, 67% O_2 . (mark spacing 10 μm , tilt 45°)

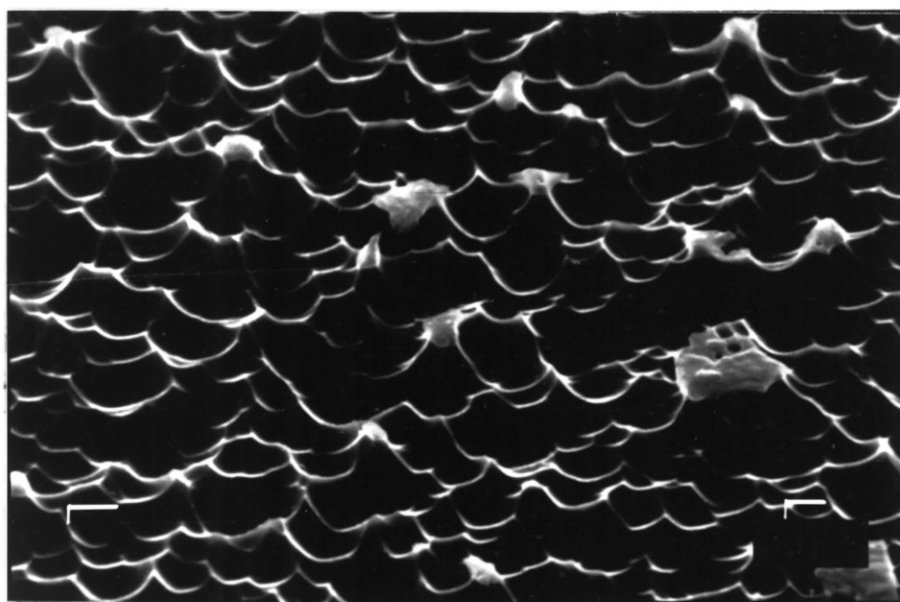


Fig. 5.18. CdCl_2 stripped to show the undercutting of SiO_2/Si through the thin regions of the grain boundaries. (mark spacing 10 μm , tilt 45°)

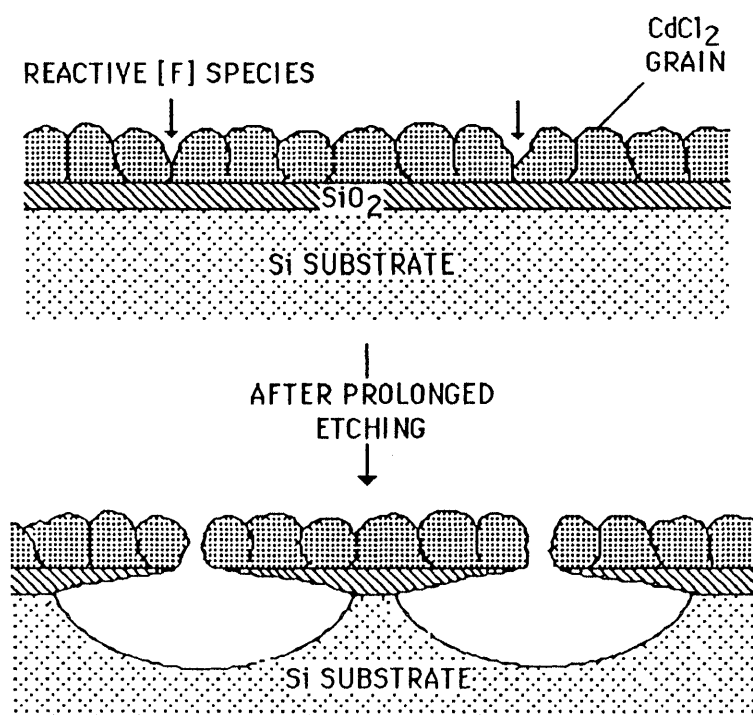


Fig. 5.19. Attack of weak regions in the grain boundaries of the CdCl_2 film leading to undercutting of SiO_2/Si substrate shown in Fig. 5.18.

5.3.2.1. EPMA Results

Electron-Probe-Micro-Analysis (EPMA) was carried out to determine qualitatively the relative concentrations of cadmium and chlorine in the pure, unetched resist thin film and the resist thin film after an etch. Results of the analysis are shown in Figs. 5.20 to 5.25. The most noticeable difference for all four thin resist films after etching is the reduction in relative chlorine concentration compared to the unetched sample. For runs 1 and 4 the chlorine signal levels are much lower than for runs 2 and 3. This correlates well with the maximum (67%) and minimum (14%) oxygen gas feed to the RIE. Olas [1] work to determine the extent of substitutional process between the fluorine and the chlorine atoms showed this to occur for only a few monolayers. Runs 2 and 3 appear to be 'fluorinated' this way, but the results

of runs 1 and 4 show the film to have been affected beyond a few monolayers possibly some type of atomic mixing. SIMs analysis was carried out next on sample from run1 to determine how the composition of the film has changed through the etching.

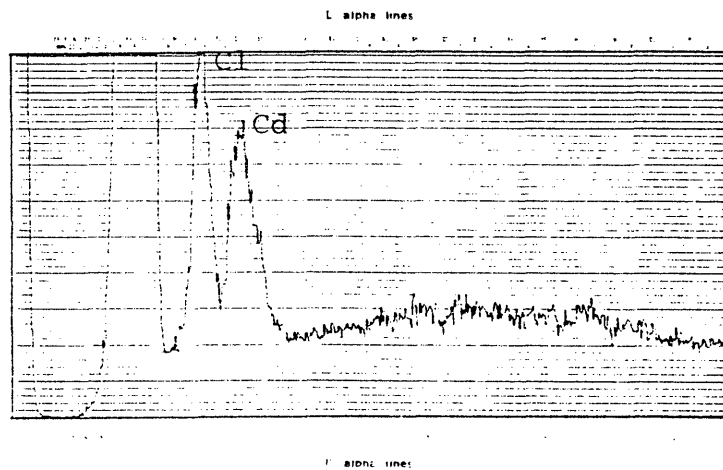


Fig. 5.20. EPMA of the unetched CdCl_2 film.

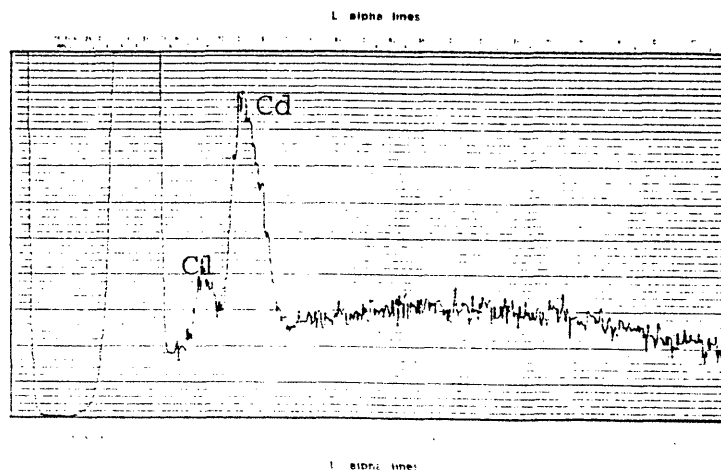


Fig. 5.21. EPMA of the etched sample of run 1.

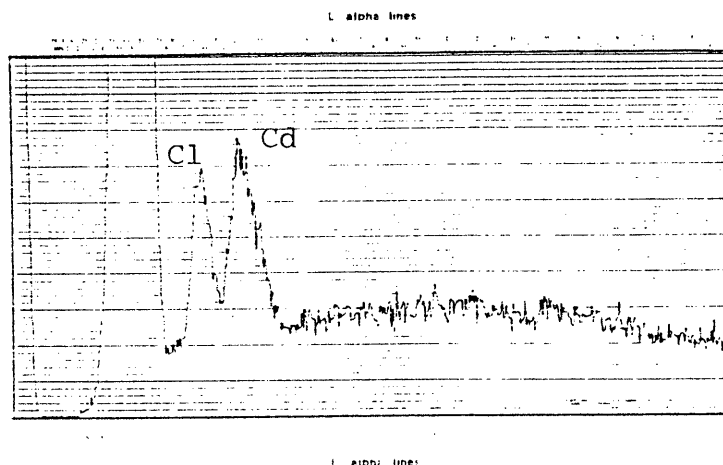


Fig. 5.22. EPMA of the etched sample of run 2.

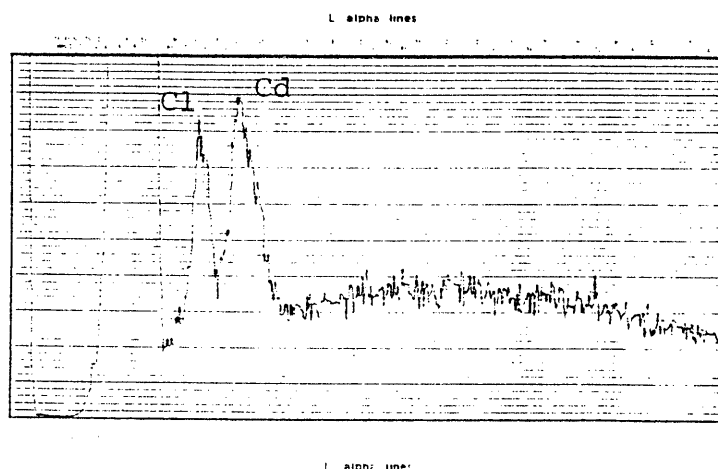


Fig. 5.23. EPMA of the etched sample of run 3.

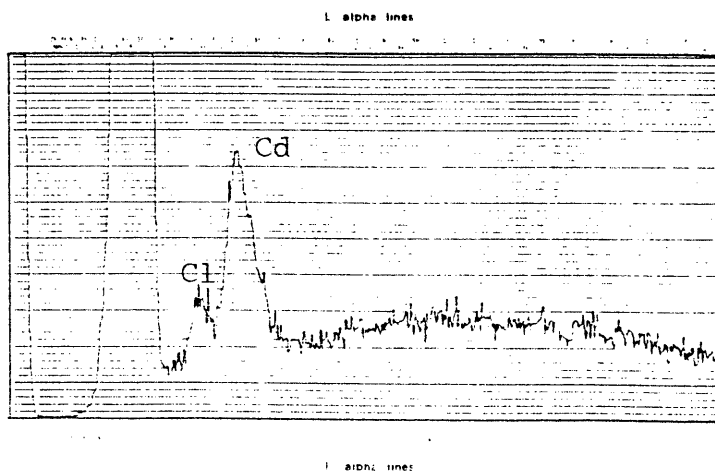


Fig. 5.24. EPMA of the etched sample of run 4.

5.3.2.2. SIMS Analysis

SIMS in-depth profile analysis of the sample from run 1 and an unetched sample was carried out (Figs. 5.25 and 5.26). An Atomika-a-DIDA R-2010 quadrupole SIMS instrument was used with a primary ion beam of xenon (Xe^+) of energy 3 keV and current of $0.03 \mu\text{A}$. A frame area of 1 mm^2 was scanned with a rate of 16 sec/frame. To prevent charging, 500 eV electrons were co-bombarded at oblique incidence. The sputtering rate of CdCl_2 is much higher than SiO_2 or Si and consequently the depth at which the sputtering occurs at a given time is different for the two materials. Provided the interfaces between the regions is known accurately, the sputtering ratio for both films can be calculated. The logarithmic intensity of the signal levels of species $^{16}\text{O}^-$, $^{19}\text{F}^-$, $^{28}\text{Si}^-$, $^{35}\text{Cl}^-$ and $^{12}\text{C}^-$ are recorded on the vertical axis. The horizontal axis of Figs. 5.25 and 5.26 have been divided into three regions namely CdCl_2 , SiO_2 and Si. From this we can obtain the relative concentrations of the respective sputtered atoms in the CdCl_2 and SiO_2 layers. At the $\text{CdCl}_2/\text{SiO}_2$ interface of the unetched (Fig. 5.25) sample, the ^{35}Cl falls off exponentially due to the primary ion beam having a depth of resolution $\sim 70 \text{ \AA}$ which causes continuous atomic mixing of the profiles and thus broadening of the penetration profile.

The most remarkable result is the relatively high level of fluorine in the sample. This probably indicates that a high degree of 'fluorination' has taken place with the possibility of atomic mixing. Previous work [1] on the etching of SiO_2 with a CF_4 gas at 50 mT have revealed the degree of 'fluorination' to occur for only a few monolayers. The combination of high oxygen concentration (67%) and high pressure (320 mT) have enhanced the chlorine and fluorine exchange to several hundred angstroms. The data points to approximately 75% conversion of the CdCl_2 to CdF_2 during the course of this RIE run. When attempting to strip this layer in deionised water, the film was

not readily soluble which further indicates the presence of CdF_2 which is not readily soluble in water like CdCl_2 .

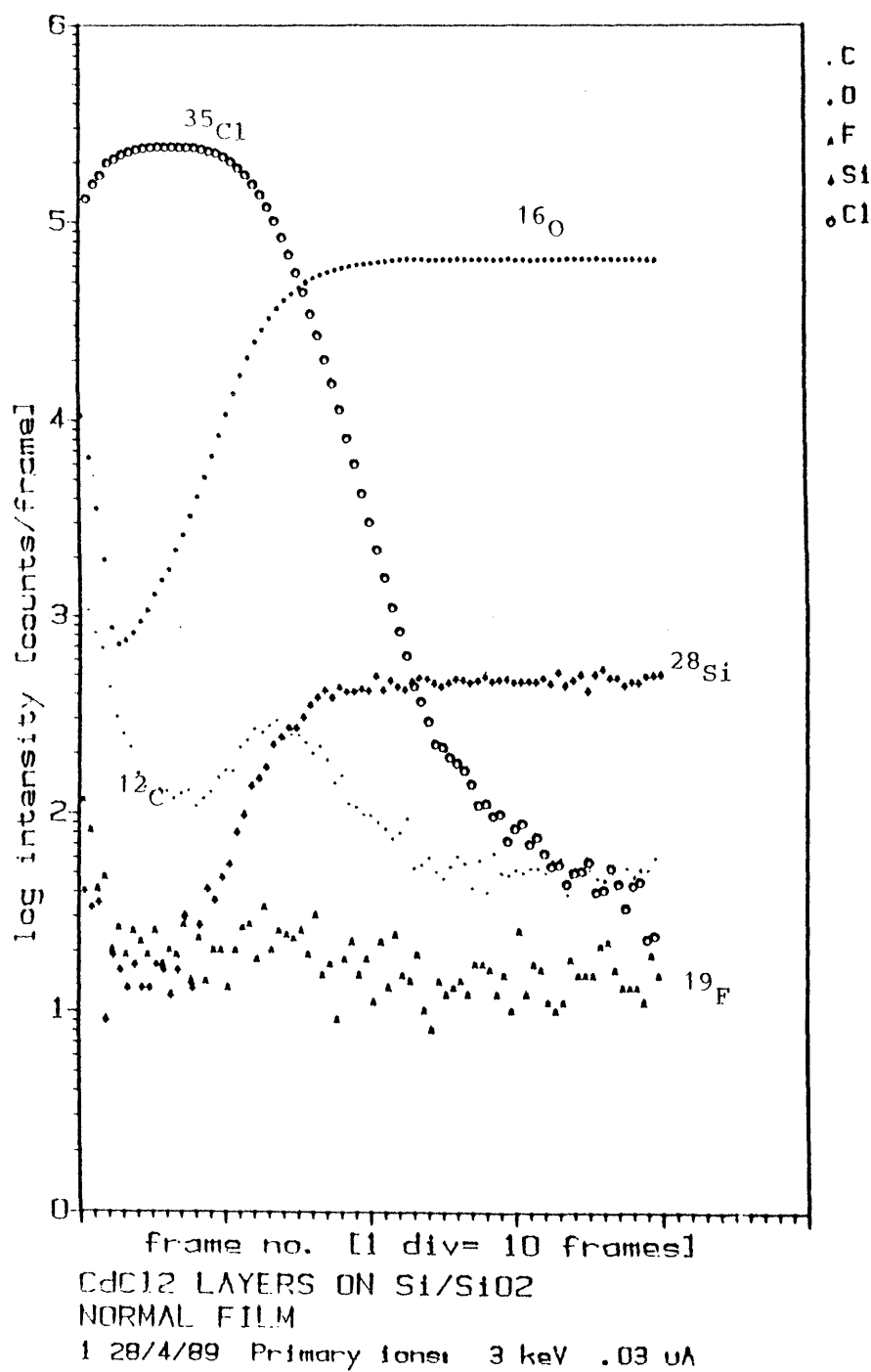


Fig. 5.25. SIMS in depth analysis of the unetched CdCl_2 film.

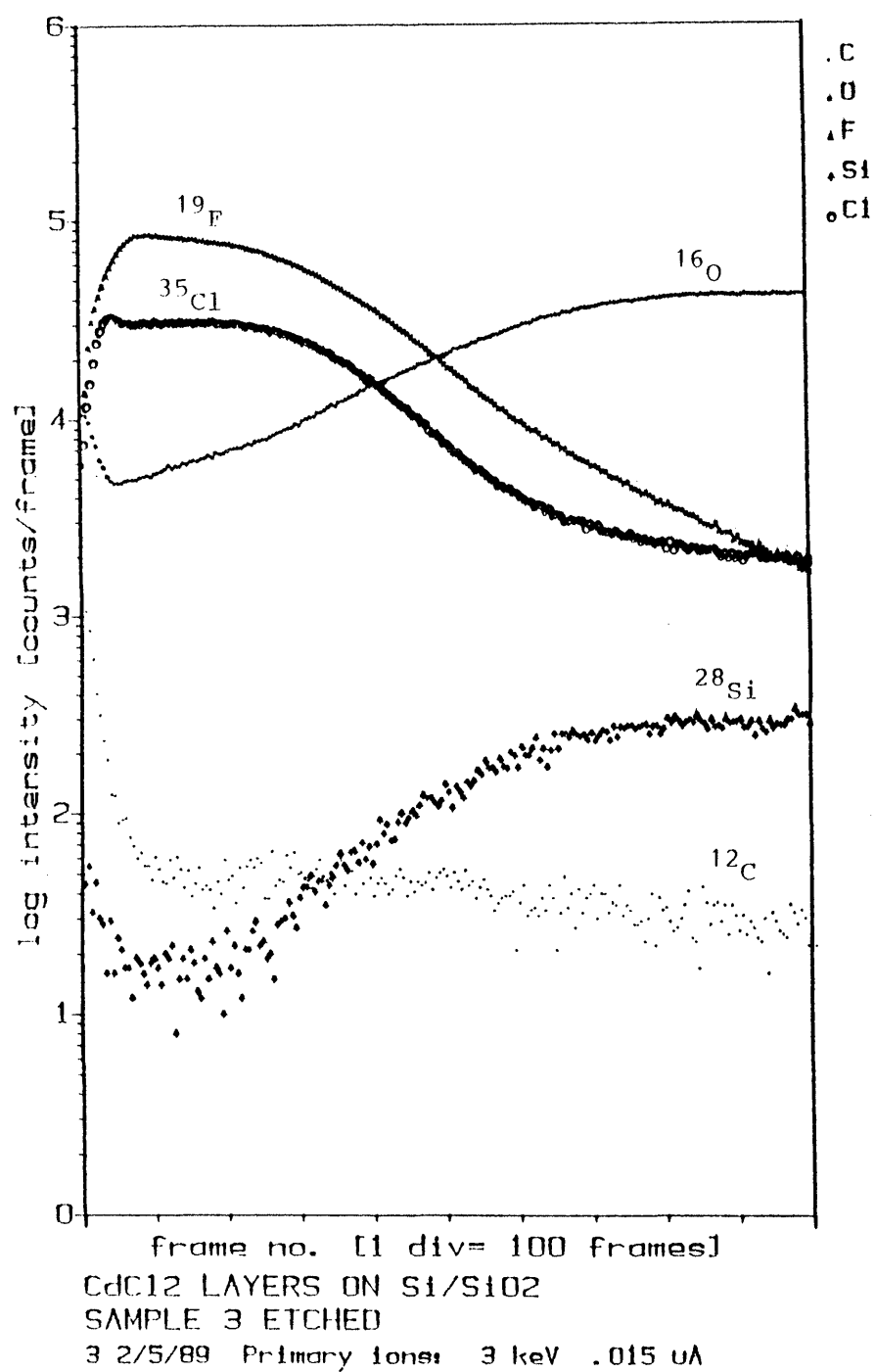


Fig. 5.26. SIMS in depth analysis of the etched film of run 1.

5.3.3. Effect of Dc-Bias on Selectivity

In the results obtained there is a good correlation between selectivity and the dc self-bias. With the previous assumption that etching is predominantly ion enhanced it is not surprising that selectivity is influenced by the dc-self bias. Using Eqn. 4.1, it is possible to obtain simulated results of the dependency of dc bias on the selectivity which can be compared to the measured values. Fig. 5.27 shows the measured V_{dc} values and the calculated values using this equation for the process conditions of Fig. 5.10. The first two values of 50 mT and 100 mT with 107 W rf power were used to calculate the constants α and C . There is good agreement between the measured and calculated values, therefore selectivity can be improved further by operating at a high enough pressure to give a dc self bias below 160 V. Alternatively, by reducing the power (but possibly at the expense of a reduced etch rate of SiO_2) and using a reduced pressure setting to give a dc bias below 160 V.

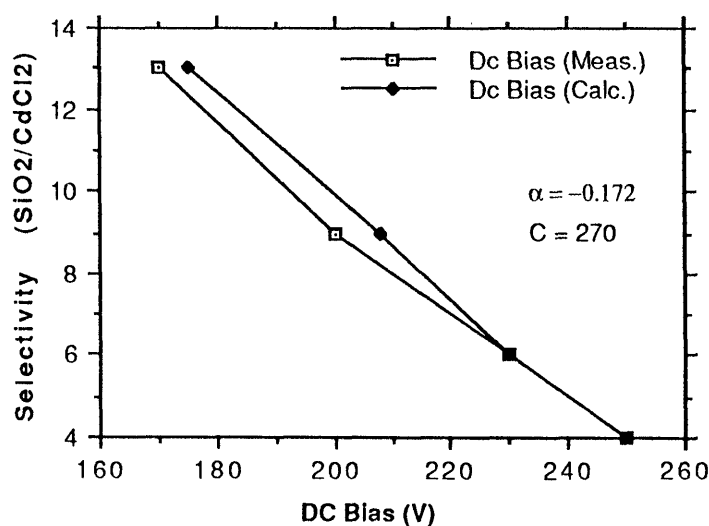


Fig. 5.27. The effect of dc- bias on the selectivity for RIE conditions: 107 W, 17% O_2 .

5.3.4. Edge Profiles

The image reversal technique for producing submicron structures in SiO_2 is an effective method for looking at edge profiles. This is mainly due to the high edge resolution obtained in the lift-off pattern of CdF_2 (discussed in more detail in chapter 6).

Fig. 5.28 shows the edge profile obtained in $1\ \mu\text{m}$ SiO_2 etched in a CHF_3 and O_2 plasma at 93 W, 270 mT, 30 sccm CHF_3 , 14% O_2 , dc bias 145 V and etch time of 60 minutes. These conditions are similar to run 2 (Table 5.3).

Fig. 5.29 shows the etched profiles on $1\ \mu\text{m}$ SiO_2 at 150 W, 50 mT, 25 sccm CHF_3 , 25 sccm Ar, 385 V dc bias for an etch time of 15 mins.

Edge profiles obtained for the first etch conditions (cf Fig. 5.28) is anisotropic with a slight degree of isotropic etching. At these conditions of high pressure ion energies are low (dc bias 145 V) and the corresponding selectivity is high (low sputtering of the CdF_2 resist) giving an etch rate of $\sim 300\ \text{\AA}/\text{min}$. A much sharper edge profile (wall angle 75°) is obtained with the second etch conditions (cf Fig. 5.29) and the etch proceeds at a slightly faster rate ($\sim 450\ \text{\AA}/\text{min}$). Ion energies are much higher than the previous case (dc bias 385 V). The profiles for these two extreme etch conditions indicate that the mechanism involved is ion driven.

If the main constituent reaction involves SiO_2 reacting with the [F] species in the plasma to produce the volatile product SiF_4 then the profile in Fig. 5.28 would be more isotropic. A second and possibly the only mechanism involved in SiO_2 etching has been described by Steinbruchel [11] in which he states that the ions themselves do most of the etching. He terms this 'direct reactive etching' and this conclusion is based on his finding that etch yields per ion are largely independent

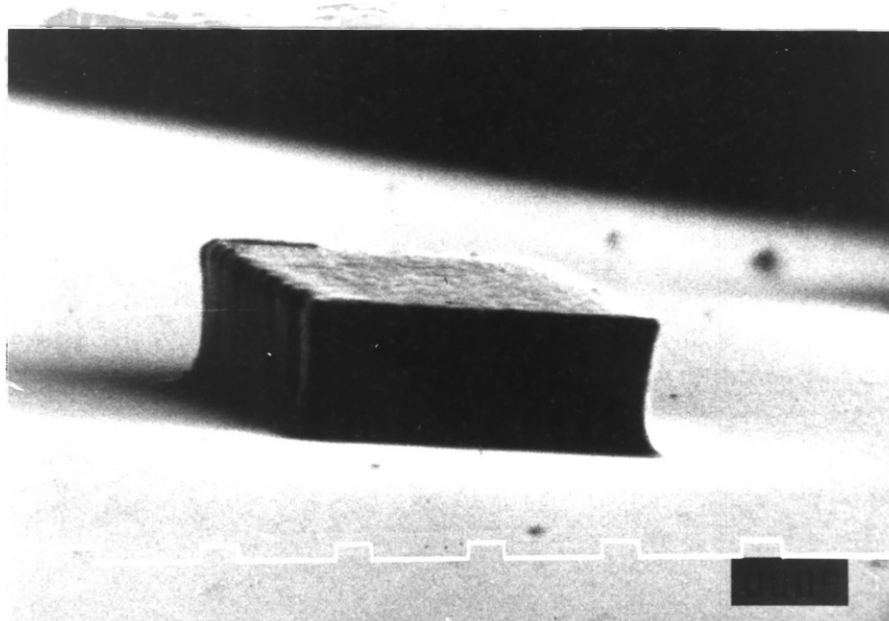


Fig. 5.28. SiO₂ profile obtained with RIE conditions: 90 W, 270 mT, 35 sccm CHF₃, 14% O₂, 145 V dc self bias, etch time 60 mins. (specimen tilt 80°, mark spacing 1 μm)

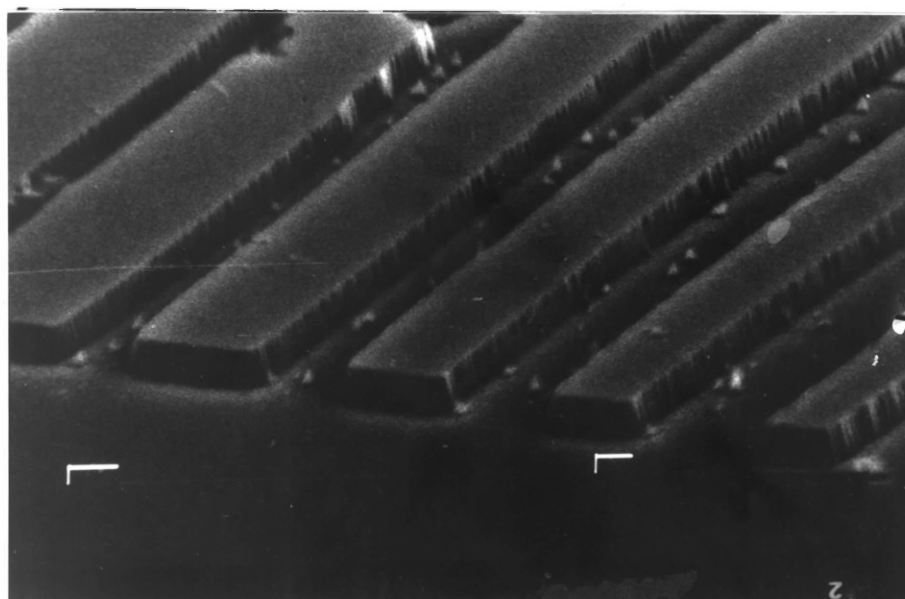


Fig. 5.29. SiO₂ profile obtained with RIE conditions: 25 sccm CHF₃, 25 sccm Ar, 150 W, 50 mT, 385 V dc self bias, etch time 15 mins. (specimen tilt 85°, mark spacing 1 μm)

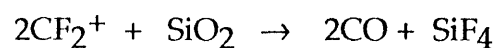
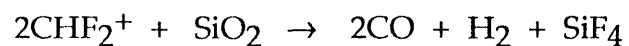
of the flux of radicals to the substrate. From this we can expect that for the pressure and power settings in the first etch, the ions will on average be directed towards the substrate but will be more localised leading to the smooth anisotropic edge profiles shown. In the second case, even though the ion energies are very large the number of reactive ion species are small (50 mT), hence the increase in the etch rate is not significantly greater than the previous case. The combination of slight resist thinning at the edges and the highly directional bombardment of the reactive ion species leads to the tapered wall as shown.

5.4. Conclusions

CdCl_2 has proved to offer high selectivity over SiO_2 in reactive ion etching with no polymer formation. The ideal conditions for etching is an rf power of 107 W to maintain a high etch rate for SiO_2 and a pressure of 240 mT and a low oxygen concentration. At high oxygen concentration fluorine radicals attack preferential grain boundaries in the film leading to undercut etching of SiO_2 and Si. The above conditions offer a low damage to the underlying Si layer due the low energy ions in this regime. No polymer formation occurs at these settings and the etch rates for SiO_2 and CdCl_2 are 300 Å/min and 5.2 Å/min correspondingly giving a selectivity of 1 : 58. The dc bias is approximately 140V which gives a near anisotropic edge profile. CdCl_2 etching occurs entirely through the sputtering process as can be seen from the SEM micrographs, and from the EPMA results.

Apart from the three mechanisms mentioned in chapter 4 (pp 97) Steinbruchel [11] contends that the dominant mechanism in SiO_2 etching involves the ions which do most of the etching and he terms this 'direct reactive ion etching.' His explanation, is probably a good one , particularly with reference to the etch rate and selectivity in terms of the dc self-bias.

SiF₄ is the main Si bearing product in the etching of SiO₂ by a CHF₃ plasma. Two other products are COF₂ and SiF₂. In CHF₃/O₂ mixtures the production of CO, CO₂ and COF₂ is greatly enhanced, probably because of the efficient oxidation of polymeric species as well as CHF₃. The following reactions can be visualised:



CADMIUM FLUORIDE AS A LIFT-OFF MASK FOR SUBMICRON FABRICATION

This chapter discusses, with experimental results, the advantages of an image reversal technique for fabricating submicron structures in silicon dioxide and chromium. Using a similar technique, Scherer and Craighead [4] have fabricated quantum well structures with a barium/strontium fluoride alloy. Owing to the high plasma etch resistance of CdF_2 and compatibility with most halo-carbon gases, the possibility of using other substrates such as InSb, GaAs, Si etc. exists. Fig. 6.1 shows the general procedure for producing a lift-off image in SiO_2 . Chloroform is used to remove the PMMA at the lift-off stage and the stripping of CdF_2 is achieved by agitating the sample in a dilute solution of phosphoric acid.

The attractiveness of this technique is the ability to use very thin film of PMMA ($< 2000 \text{ \AA}$) for high resolution work since the etch selectivity of CdF_2 to the substrate can be extremely high depending on the plasma conditions. Unlike metal lift-off where an undercut profile is required, the CdF_2 works independent of the wall angle allowing the use of a variety of organic resists. For lift-off to be successful the CdF_2 thickness should be less than one third of the thickness of the PMMA film. Resolution of the final pattern obtained in SiO_2 and Cr is mainly dependent on the resolution obtained on the PMMA which is limited only by the scattering of the electrons in the resist and noise on the e-beam. Through preferential etching of the CdF_2 film in a dilute solution of H_3PO_4 the grain size was determined to be about half the mean film thickness (see section 6.1.4).

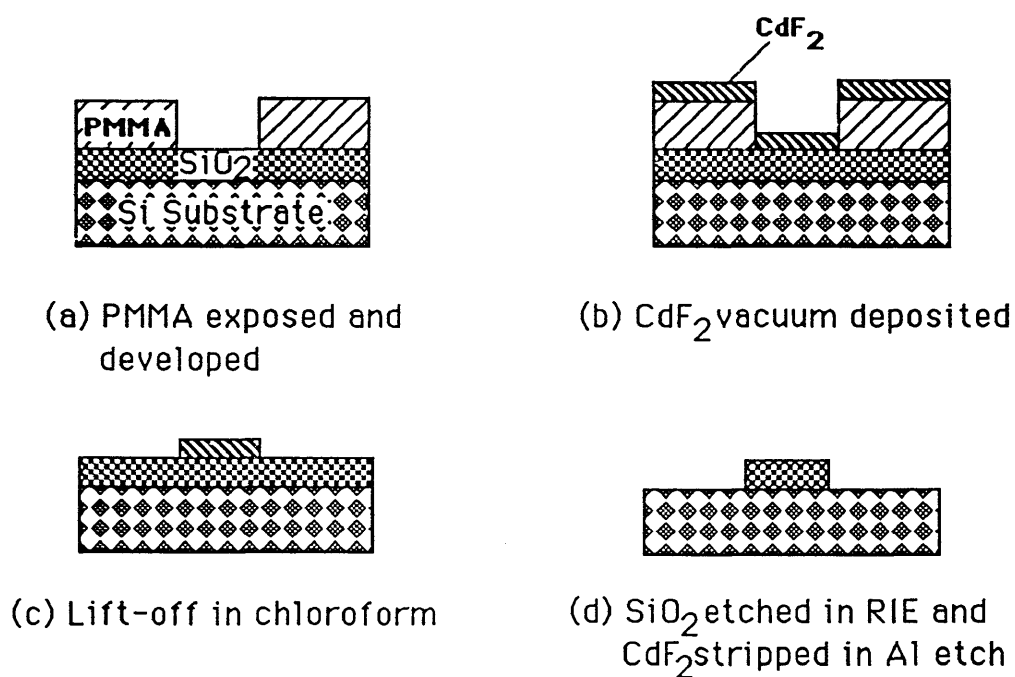


Fig. 6.1. Image reversal technique for producing submicron lines in SiO₂.

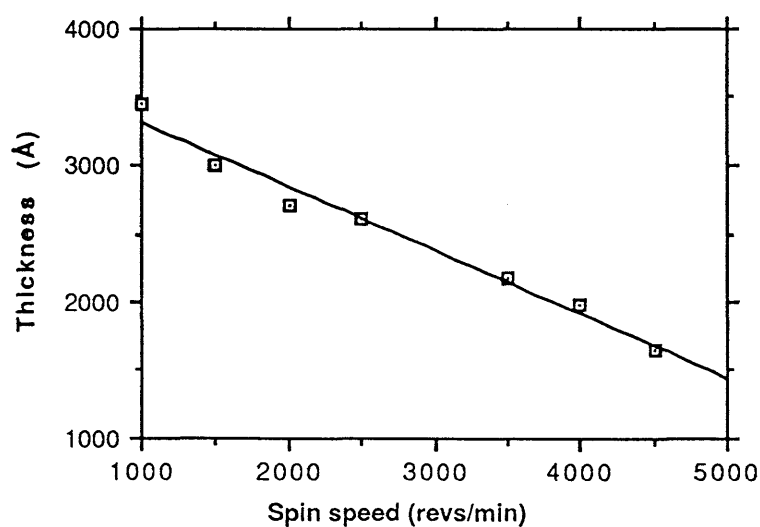


Fig. 6.2. Variation of film thickness of the PMMA versus spin speed.

6.1. Submicron Structures in SiO₂

The PMMA (Mol. Weight 300-500k) supplied by British Telecom consisted of 5% by weight of the pure powder form in a xylene solvent. Graph of the spin speed versus film thickness on SiO₂/Si wafers are shown in Fig. 6.2. Film thickness towards the bevelled edges were 100 Å less than at the centre due to some solvent being removed by the centrifugal force. The conventional approach to PMMA processing requires a post baking after exposure so that an improvement in the etch resistance may be achieved in the wet or dry processing step. However, in examining the image reversal technique, this step may be omitted which is a great advantage particularly when resist flow distorts the linewidth during baking.

CdCl₂ was initially tried out for this technique but conglomeration of the film (Fig. 6.3) occurred during lift-off. This has been attributed to the CdCl₂ film dissolving in the xylene solvent of the PMMA. Pre-baking the sample in an oven for half an hour at 120 °C did not improve matters due to the incomplete removal of the solvent.

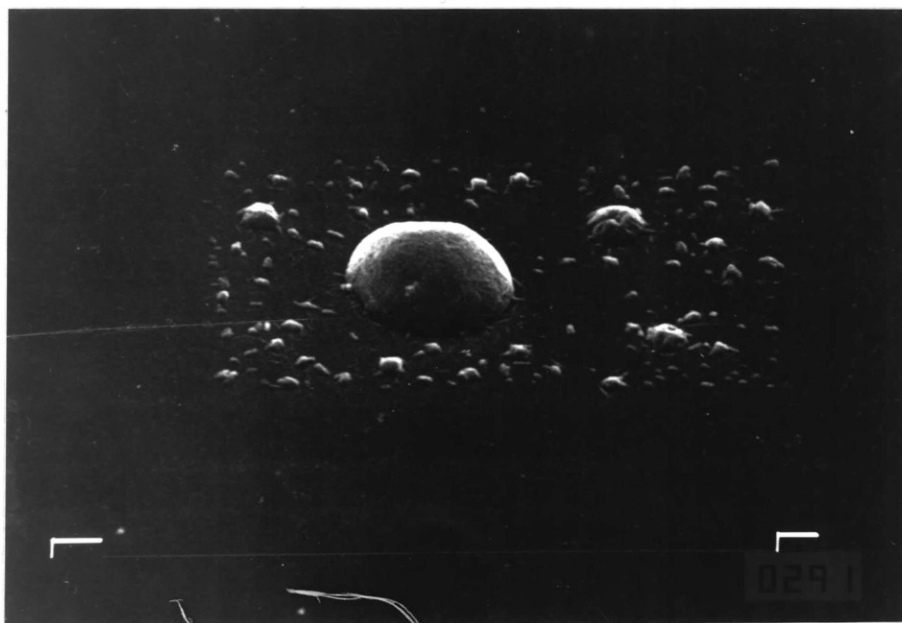


Fig. 6.3. Conglomeration of the CdCl₂ due to the film dissolving in the xylene solvent.

6.1.2. Selectivity

CdF_2 (Alfa Products, ultrapure grade) was used for all the following lift-off experiments. Fig. 6.5 (cf Fig. 5.28) shows the etched features on $1\text{ }\mu\text{m}$ SiO_2 on Si substrate using a high pressure conditions (250 mT) in the RIE mode. E-beam exposure was carried out in the T100 SEM in the photo mode at 10 K magnification giving an exposure area of $13\text{ }\mu\text{m} \times 10\text{ }\mu\text{m}$. The CdF_2 which is of initial thickness of $540\text{ }\text{\AA}$ shows the extremely high etch selectivity that may be achieved with this resist. After a prolonged etch time of 1 hour, the film is seen to be breaking up at the surface and some of this film is redeposited on the rest of the substrate. Selectivity to SiO_2 etching obtained with these etch conditions is found to be 1:20 which is better than the results of the CdCl_2 etching (see chapter 6). This is expected, since CdF_2 has a higher melting point than CdCl_2 owing to its greater ionic bonding. Fig. 6.6 shows a close up of the corner of the etched feature. It is apparent that the edge definition around the perimeter of the rectangular feature is very high indicating that the CdF_2 film thickness is greater at the steps of the PMMA. An obvious explanation of this is that film growth is faster at the edges (Fig. 6.4) resulting in a film thickness which is greater than the average film thickness over the whole surface.

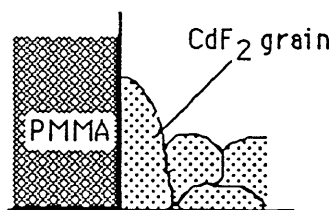


Fig. 6.4. CdF_2 film growth at the PMMA edge.

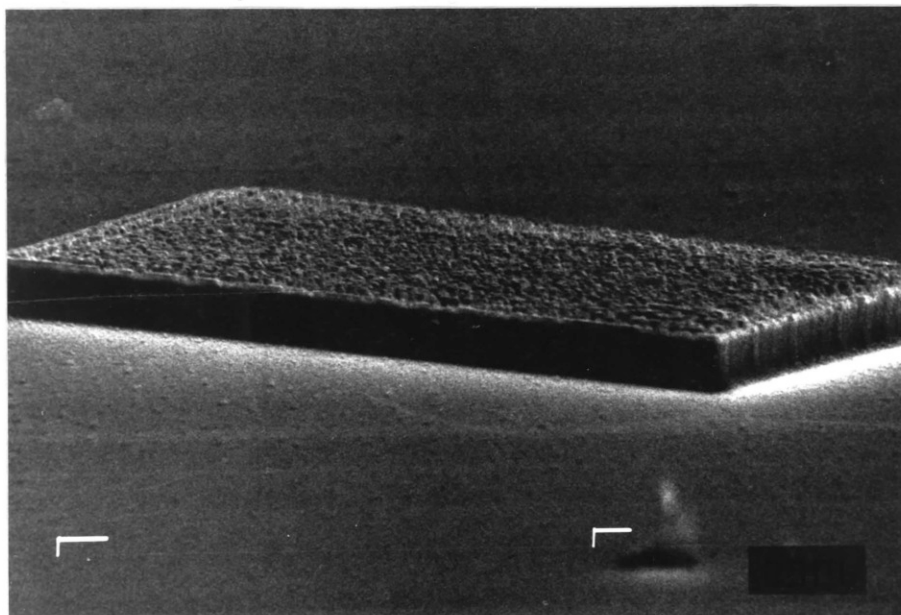


Fig. 6.5. Rectangular etched feature obtained in SiO₂ using RIE conditions: rf power 93 watts, pressure 270 mT, 35 sccm CHF₃, 14% O₂, dc self-bias 145 V, etch time 60 mins. The rough surface is due to the thin film breaking during prolonged etching. (e-beam exposure in JEOL T100, specimen tilt 80°, mark spacing 10 μm)

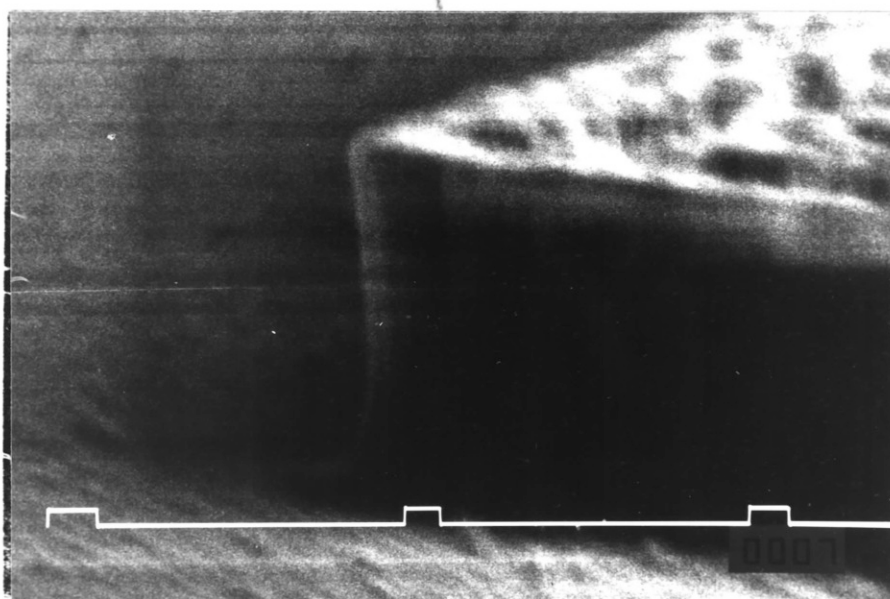


Fig. 6.6. Corner of the etched feature obtained above showing enhanced CdF₂ film growth. (specimen tilt 80°, spacing distance between marks 1 μm)

6.1.3. High and Low Pressure Conditions

The images shown in Figs. 6.7 and 6.8 were exposed using the T220 SEM modified for e-beam writing. Rectangular and square patterns were generated on the IBM AT and exposed at a magnification of 1000. The parameters selected for the RIE process were: rf power of 200 watts, pressure of 50mT and gas flows of 25 sccm CHF₃ and 25 sccm Ar were employed for this process. Initial PMMA film thickness of 4000 Å and a CdF₂ film 1800 Å thickness were deposited to produce the reverse pattern. Slight tapering of the etched feature is evident for this set of conditions. This is due to the slight lateral CdF₂ resist erosion around its perimeter. For these conditions, the selectivity of SiO₂ to CdF₂ is ~10. Considerable ion bombardment of Ar⁺ occurs at this power and pressure (DC Bias 210V) leading to very sharp edges at the base of the structure and a relatively high etch rate of SiO₂ (450 Å/min).

The etch rate of Si was determined for the same conditions mentioned immediately above. Fig. 6.8 shows the small degree of etching of Si (CdF₂ stripped). Clearly, the etch rate selectivity of SiO₂/Si is very high as noted by Coburn and Winters [2] for etching in CHF₃ where SiO₂/Si selectivity is very dependent on the C:F ratio. It should be possible to tailor the edge profiles by changing the power and pressure settings.

Fig. 6.9 shows rectangular and square etched features produced in SiO₂ obtained using a two stage etch process. This involved a 10 mins. oxygen etch (20 sccm) at 30 mT and 100 watts followed by a CHF₃/O₂ (25 sccm/6 sccm) for 40 mins. at 250 mT and 100 watts. It is interesting to note that oxygen has effectively etched the SiO₂ due to the high ionic bombardment (noticeable due to the chipping around the edges of the features). The 'soft' etch conditions (ie. high pressure) of the second stage has resulted in a slight tapering of the edges and gives a more rounded feature at the base of the structures. The minimum linewidth obtained is about 0.3 µm.

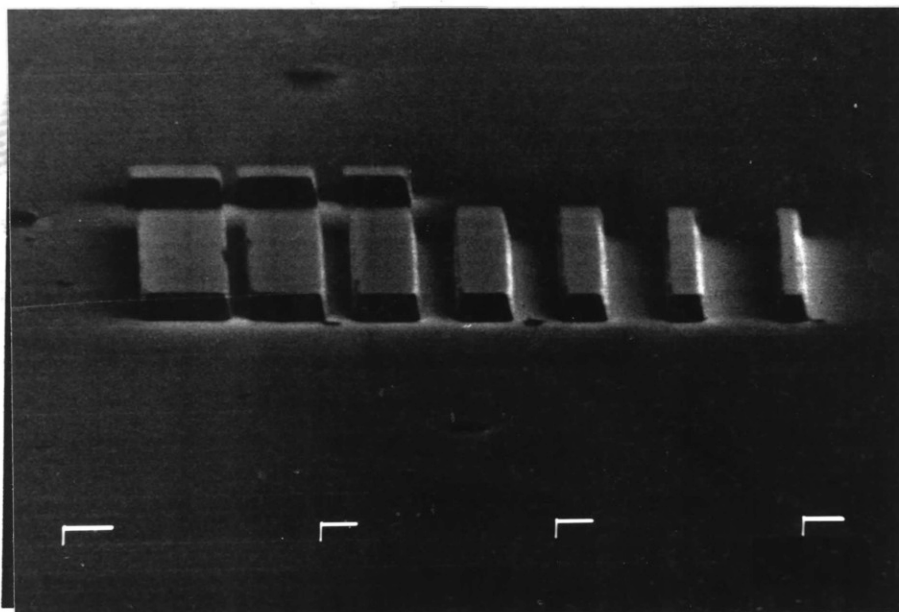


Fig. 6.7. Line and square features in SiO_2 , minimum linewidth $0.4\mu\text{m}$. Etching conditions: rf power 200 watts, 50mT pressure, 25sccm CHF_3 , 25sccm Ar, dc bias 210V, etch time 20 mins (e-beam exposure in JEOL T220, specimen tilt 70° , mark spacing $10\mu\text{m}$).

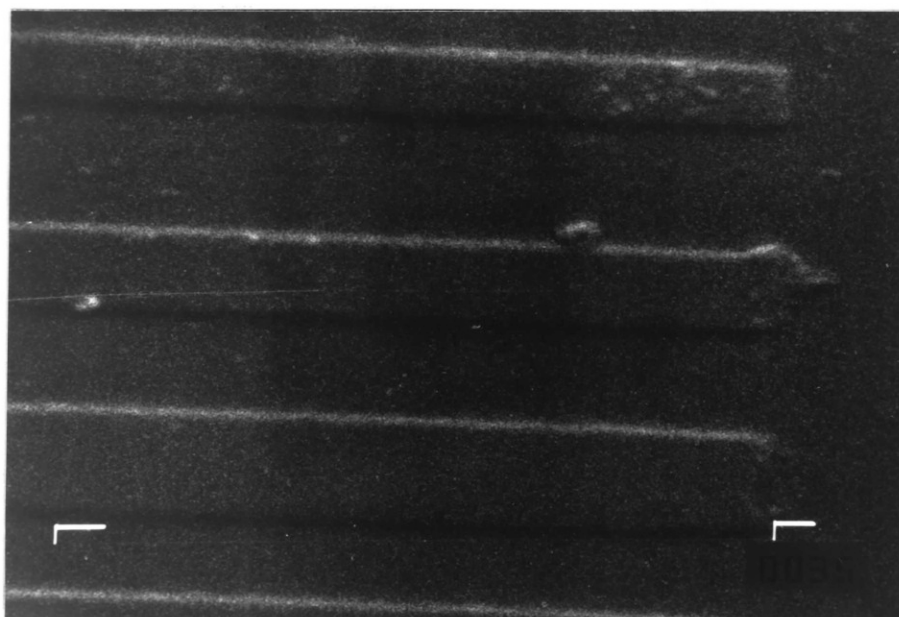


Fig. 6.8. Si substrate etched with the same conditions as in Fig. 6.9 to show the high selectivity obtained with the combination of CHF_3 and Ar (specimen tilt 45° , mark spacing $10\mu\text{m}$).

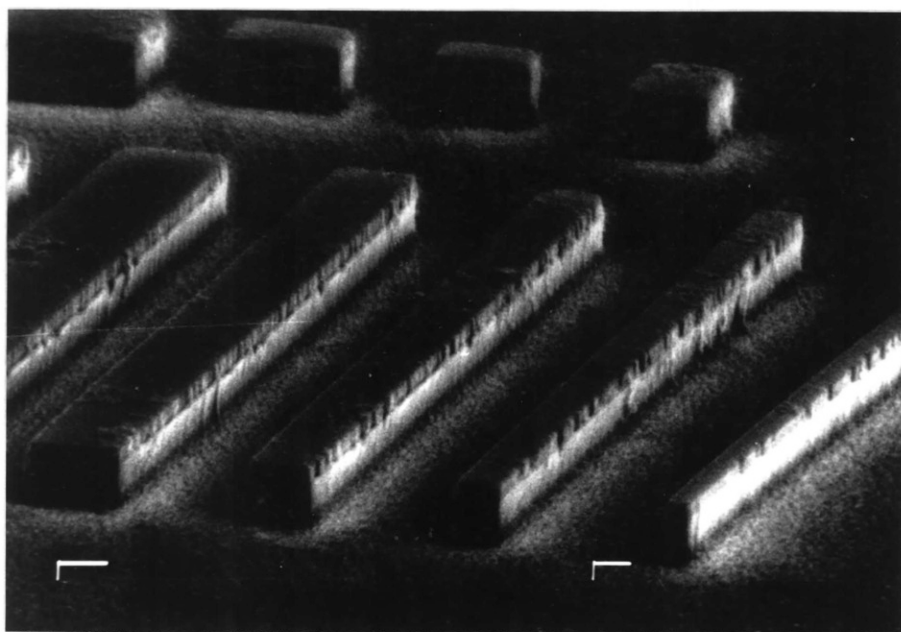


Fig. 6.9. SiO₂ features etched on Si substrate in a two stage process.

6.1.4. Grain Size

Several techniques are available for measuring the grain size of inorganic films 1) use of an X-ray diffractometer for measuring the line broadening in the peaks and 2) use of a suitable solvent which etches preferentially along a grain boundary so that the grain structure can be seen in an SEM and measured. Both techniques were used for carrying out this measurement. A thin film of sample of CdF₂ (~2000 Å) was assessed using a 15° glancing-angle X-ray, with nickel filtered Cu K α radiation. The sample was also examined using a Phillips PWN50 powder diffractometer. The resulting diffraction pattern revealed the presence of a weak phase of the film with no evidence of any preferred orientation. Fig. 6.10. shows the small diffraction peak obtained for this film revealing the weak crystallite structure of the film. This suggests the grain size is equal to or possibly much less than the film thickness.

Grain size was determined for the CdF₂ film by etching the film in a dilute solution of H₃PO₄ (pH=0.9) for 15s followed by rinsing in deionised water (Fig. 6.11). The grain size was determined by drawing a line across the

micrograph and dividing this length by the number of grain boundaries intersecting this line. The grain size was found to be approximately equal to half the film thickness.

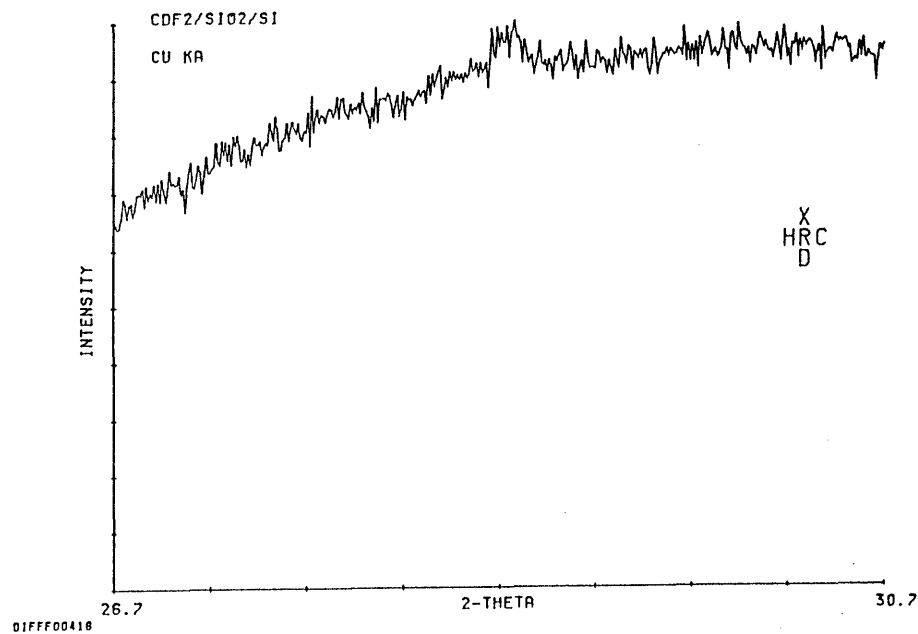


Fig. 6.10. X-ray data of the CdF_2 film showing weak signal at $28.8^\circ(2\theta)$.

In direct e-beam writing of inorganic resists [2], the resolution is determined by the grain size of the resist and the film thickness. The attractiveness of this lift-off technique is that resolution is not determined by grain size but more by the resolution of the inorganic resist such as the PMMA used here. Resolution of the PMMA resist is mainly due to the range of primary electron scattering (see MC simulation) in the resist, beam diameter and to a smaller extent, noise on the beam introduced by the electron beam forming column.

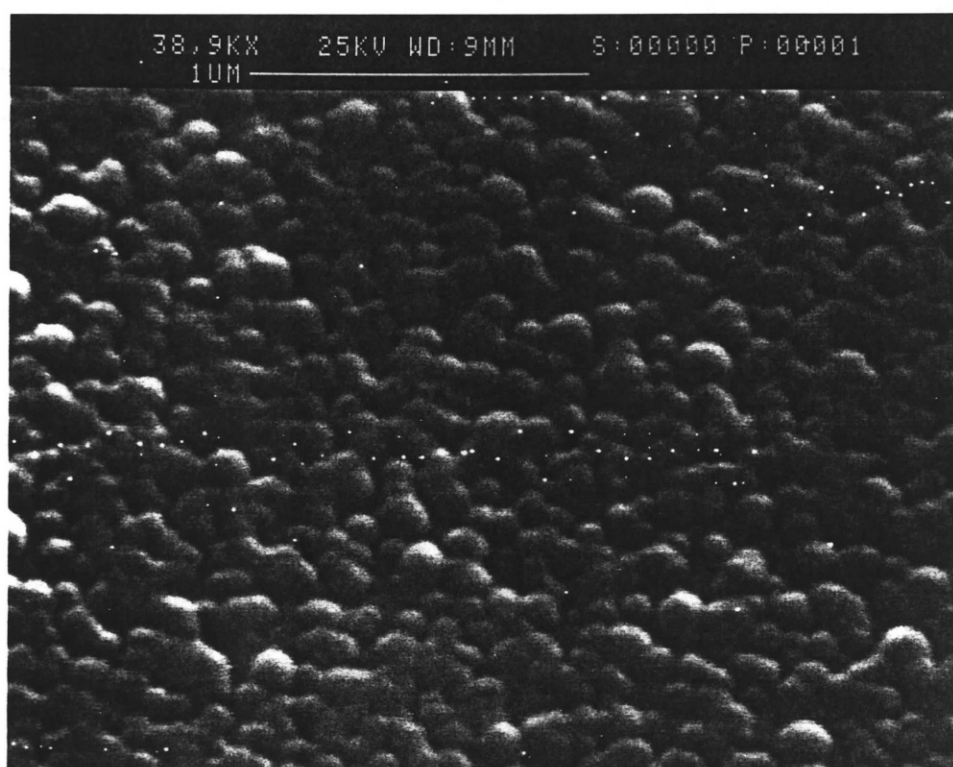


Fig. 6.11. Grain size of $940 \text{ \AA}$ for a film thickness of $1800 \text{ \AA}$ CdF_2 .

6.2. Chromium-on-glass photomask fabrication

Part of this work was undertaken in the E-beam Lithography Section at GEC Hirst Research Centre. The Cambridge EBMF6-5 described in section 1.1 is used for chromium-on-glass photomask fabrication and for direct e-beam writing onto wafers. The e-beam resists commonly used are EBR-9 (positive) and CMS (negative) of thicknesses $5500 \text{ \AA}$ which require electron doses of 2 to $9 \mu\text{C}/\text{cm}^2$. After exposure and development, the chrome ($1000 \text{ \AA}$) areas not protected by the resist image are removed in a bath of "can etch" consisting of cerium ammonium nitrate, de-ionised water and perchloric acid. With careful control, linewidths down to $0.5 \mu\text{m}$ are obtainable with this process. The substrate is made of very low expansion borosilicate glass to minimise problems of thermal expansion and to provide an extremely flat surface both for proper registration of stitched fields of the beam and for subsequent use in

optical projection or step-and repeat cameras.

One of the difficulties of using organic resists for dry processing is that they have poor etch resistance in a plasma. A considerable amount of research work has gone into looking at novolac resists [1] which offer high etch resistance to plasma without sacrificing resolution. A general problem with this type of resist, apart from their relatively poor sensitivities, is that redeposition of polymers can be formed over the surface to be etched which sometimes inhibits further etching.

Electron beam inorganic resists have very high etch resistance to plasma etching but their popularity has been restricted due to their poor sensitivities [2]. Previous work on etching of SiO_2 [3] using CdF_2 as a lift-off mask has shown the high selectivity that can be obtained with CHF_3 reactive ion etching (RIE). The high etch resistance obtained with this resist should also make it amenable to Cl_2 RIE and redeposition is not a problem as with organic resists. This section describes the technique of lift-off mask fabrication of chromium glass plates with the aim of looking at the resolution limits and the minimum linewidth possible.

6.2.1. Pattern Generation

Complex patterns are normally created on a CAD workstation (eg. Mentor or Applicon) which can output patterns in formats suitable for optical pattern generators. For use on the EBMF6-5 these formats are converted on a VAX 11/750 to Cambridge Source Pattern Data (SPD) format and thence to machine-readable Cambridge Binary Pattern Data (BPD) format.

Simple patterns can be readily digitised by hand in SPD format. SPD files from whatever source are then checked using an in-house graphics package and a Tektronix 4114A graphics terminal before submitting the files to a batch queue for conversion to BPD. The in-house graphics package is capable of viewing an entire 5 inch mask plate with facilities for zooming down to a

window of 1 pixel ($0.1\mu\text{m}$) $\times$ 1 pixel.

The EBMF-6 can write a maximum field size of $5\times 5\text{mm}$ without moving the stage, but writing area is usually restricted to an area of 1.09 or 3.2768 mm^2 to minimise beam distortions at the field edges.

A complex data pattern as in the case of a mask plate for an IC is broken down into a series of rectangles, triangles and polygons, hence a large pattern will consist of these simple shapes which the EBMF6-5 can write sequentially.

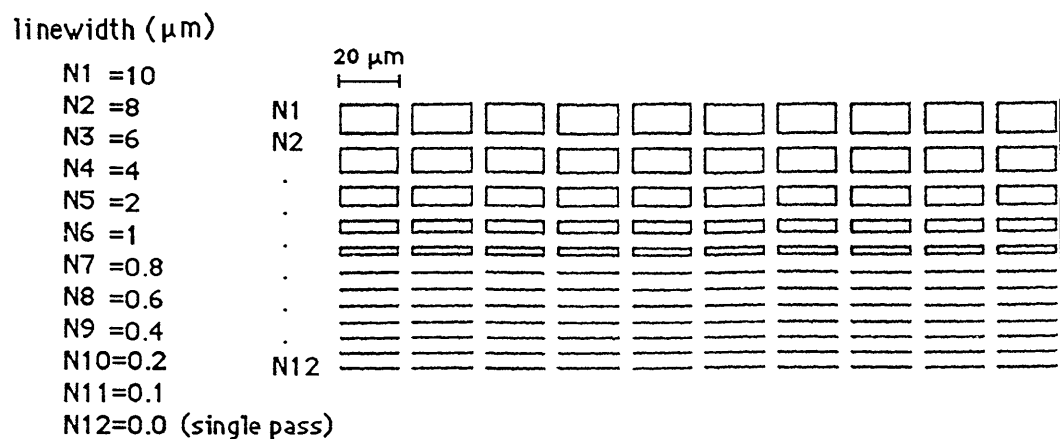


Fig. 6.12. Regular array of lines patterned for lift-off.

For this work, two types of pattern were created (see Figs. 6.12 & 6.13) to test resolution limits. Figs. 6.12 and 6.13 show a printed output of the pattern data created on the Tektronix in the SPD format. Lines between $0.1\mu\text{m}$ and $1\mu\text{m}$ were produced to test the resolution limits of the technique. To examine the proximity effects lines were spaced at increasing distances from each other down each column. In Fig. 6.13 each column represents lines of equal widths and each row having equal spacings. As an example, group 6f consists of lines $0.8\mu\text{m}$ and spaced $1\mu\text{m}$ apart.

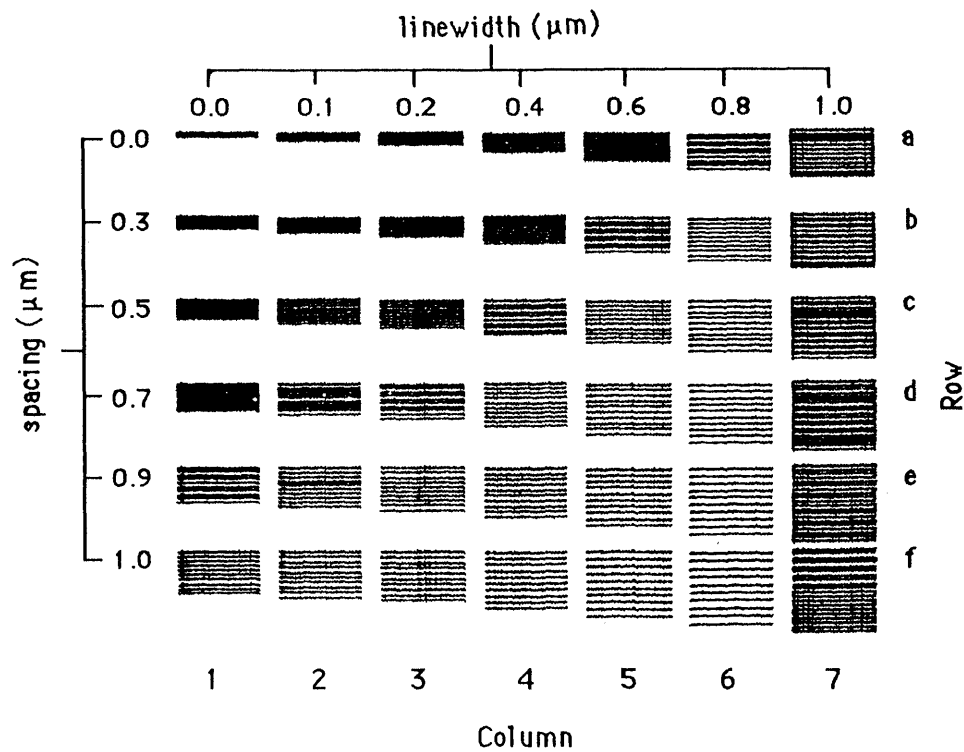


Fig. 6.13. Closely spaced lines to examine the resolution limits of the system and to check for proximity effects.

6.2.2. Linewidth Measurement

When using optical microscopy technique, an accurate measurement of the type of structure shown in Fig. 6.14 is very dependent on the image intensity profile at its edges. Therefore, a proper line measurement involves choosing a suitable edge criterion from which an accurate linewidth value can be realised. Defocussing affects the contrast of the image and a natural tendency of an observer is to choose best focus which gives a high contrast leading to an appreciable error from the image edge shifting from the geometrical position at this focus setting [5]. The microscope should be properly aligned and calibrated using a standard photomask plate such as the one supplied by NPL. A survey conducted by the NPL Audit programme showed that linewidths were accurate up to $0.5\ \mu\text{m}$ for the Vickers image shearing microscope.

Measurements of lines below $0.5\ \mu\text{m}$ can lead to appreciable errors. Fig. 6.15 shows the calculated intensity profiles of two ideal lines, one $4\ \mu\text{m}$ wide and one $0.5\ \mu\text{m}$ wide imaged by an ideal microscope. If the 'width', of each image is measured at the 50% levels on the image intensity profiles, errors in the measured width of $4\ \mu\text{m}$ and $0.5\ \mu\text{m}$ lines are 5% and 30% respectively. Any deviation away from the ideal step shown such as in the real case of a rough edge and tapered walls will lead to further uncertainty in the result. Broadening of the intensity profile will occur with a tapered wall [6] and large error may result due to misalignment with rough edges.

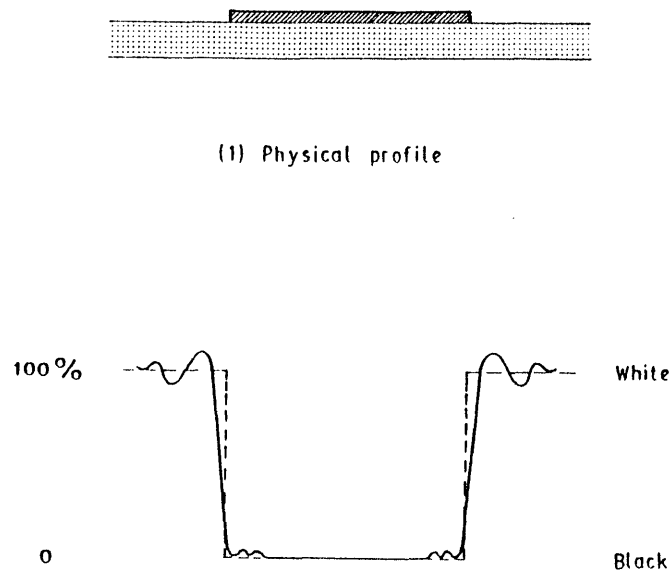


Fig. 6.14. Edge intensity image of an ideal profile.

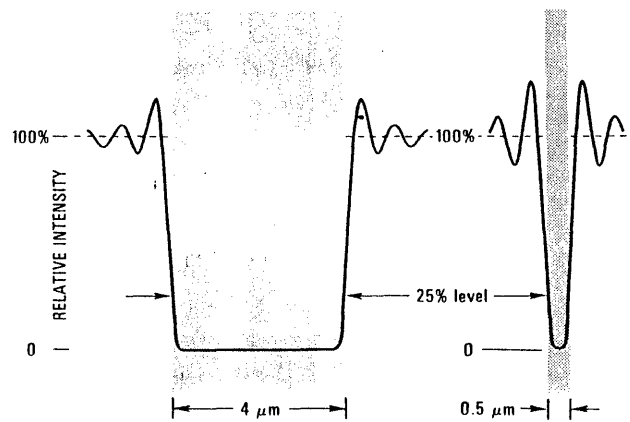


Fig. 6.15. Errors in line measurements resulting from the resolution limits of the optical microscope. (*After Swyt, Ref. [5]*)

Line measurements and general observation were carried out on a Vickers Optical Shear Microscope, a Cambridge Stereoscan 200 SEM, and on a JEOL T100 SEM. The Vickers instrument displayed a slight offset compared to the measurements taken on the SEM's. Comparison of the SEM results agreed very well with variations of not more than 1%, provided the working distance of the JEOL was kept at 20 mm (see section 1.3). Chromium lines were measured in the incident and the transmitted mode of the Vickers microscope. In the transmitted mode measured linewidths were found to be larger than in the reflected mode which is in agreement with Swyt's results [7]. Exposed lines on PMMA did not give a high contrasting image on this microscope but measuring the lines as shown in Fig. 6.16 gave a value close to that of the SEMs'. The values obtained with the Cambridge Stereoscan 200 SEM were assumed to be the more accurate ones and the Vickers Image Shear microscope was used only for comparison of line measurements.

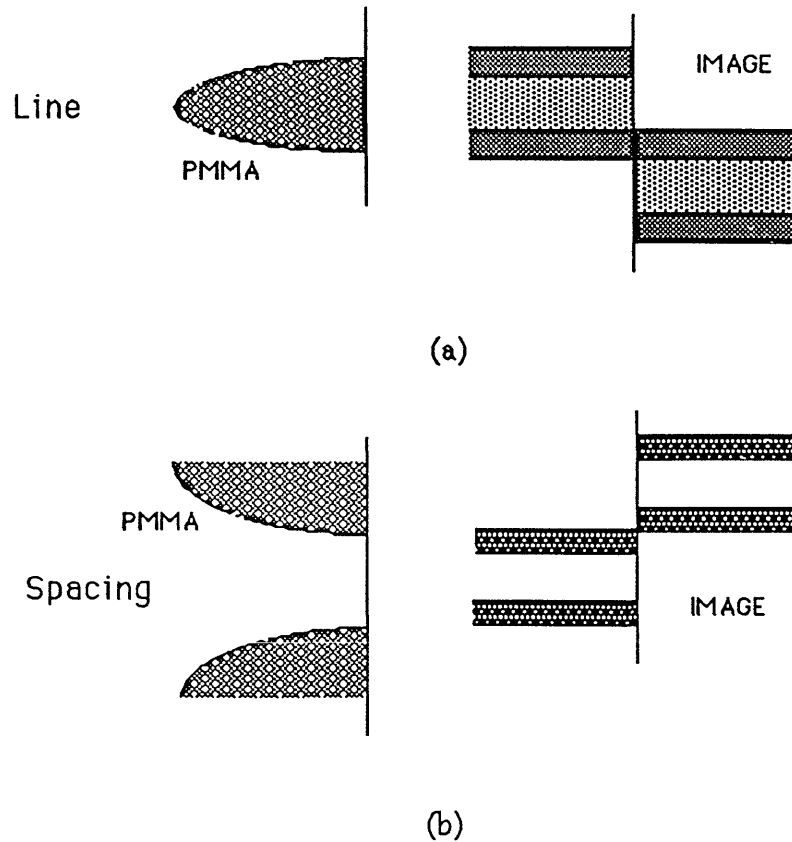


Fig. 6.16. Accurate linewidth measurement of images in PMMA resist using the image shear microscope for a) PMMA line and b) spacing.

6.2.3. Experimental Results

6.2.3.1. Exposure and Development

The data pattern was exposed on a 2.5 inch square plate with approximately 1000 Å chromium and 6000 Å PMMA. The operating voltage utilised was 20 keV, with a beam current of 0.3 nA and an aperture of 200 μm. Four such patterns were exposed and spaced a few mm apart so that the plate could be broken into four sections for individual testing. The exposed lines were developed in a solution of 1 part MIBK and 3 parts meths by volume for 30s at a temperature of 21 °C. The stop bath used was 100% meths. Figs. 6.17 and 6.18 show the developed lines on the plate as seen under the Vickers optical microscope.

Preliminary exposures revealed proximity effects which are clearly evident for the broader lines of Fig. 6.12 which are all overexposed implying a substantial contribution of dose from neighbouring lines. Table 6.1 shows the extent of proximity effect for exposed lines of equal widths and doses for the two sets (Figs. 6.12 & 6.13). In order to achieve the design linewidths, the dose for the groups of lines in Fig. 2 needs to be reduced while the dose for the similar set of lines in Fig. 6.13 needs to be higher and will be more dependent on dose. Group 7f was undeveloped when the dose was reduced to 50 $\mu\text{C}/\text{cm}^2$ and the linewidth measured for N6 was 0.4 μm .

The set of lines in rows a and b (Fig. 6.13) could not be resolved. Attempts to correct for the dose caused the lines to be either overexposed or undeveloped. This sets a limit of 0.1 μm minimum spacing obtainable with this system configuration.

Table 6.1

Proximity effect on the linewidths of the two data patterns (Figs. 6.12 and 6.13).

Line (μm)	Dose ($\mu\text{C}/\text{cm}^2$)	Group (fig.2)	L.width (μm)	Group (fig.3)	L.width (μm)
1.0	100	N6	4.90	7f	1.03
0.8	100	N7	4.44	6f	0.65
0.6	100	N8	4.05	5f	0.30
0.4	110	N9	3.43	4f	0.27

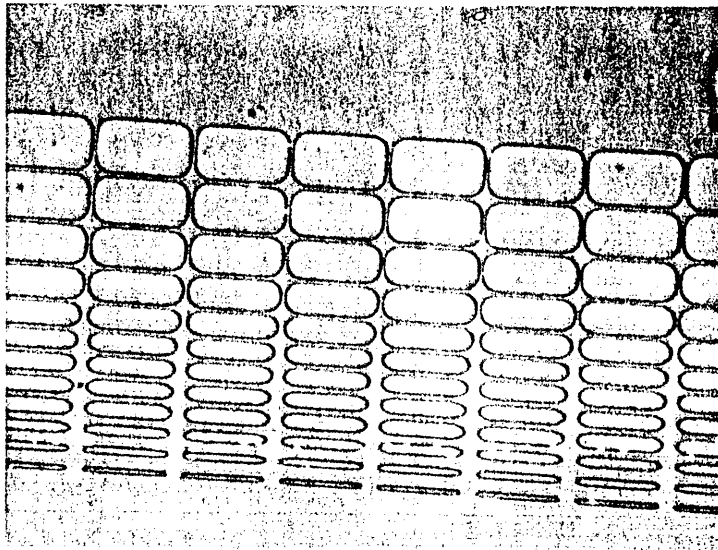


Fig. 6.17. Exposed lines of the set of lines shown in Fig. 6.12.

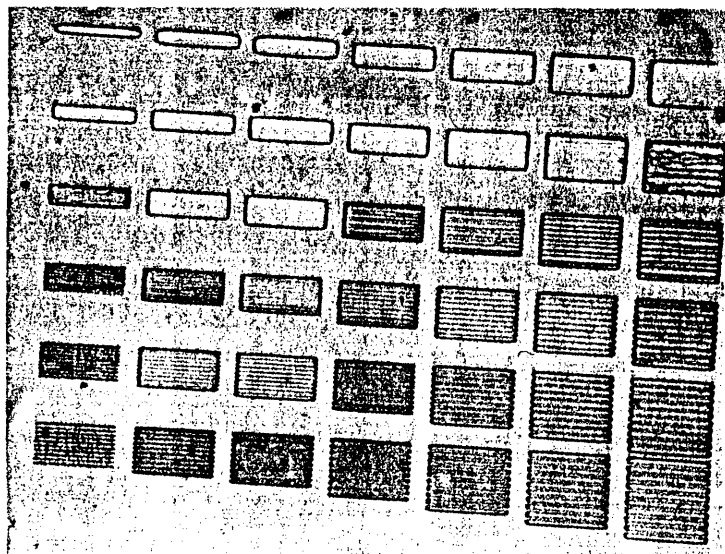


Fig. 6.18. Exposed lines of the pattern data shown in Fig. 6.13.

6.2.3.2. Dose Correction

Similar linewidths in Figs. 6.17 and 6.18 require totally different doses for proper exposure depending on the line/space ratio. The dose for similar sets of lines in Fig. 6.17 needs to be reduced considerably to achieve the same linewidth as in Fig. 6.18. The proximity effect can be related to a proximity function $f(r)$. This is a function of two Gaussian distributions [8] with standard deviations β_f and β_b and relative areas η_E , where β_f represents the characteristic width of the primary electrons and β_b represents the characteristic width of the backscattered electrons and K is a constant,

$$f(r) = K \left[\exp \left[\frac{-r^2}{\beta_f^2} \right] + \frac{\eta_E \beta_f^2}{\beta_b^2} \exp \left[\frac{r^2}{\beta_b^2} \right] \right] \quad (1)$$

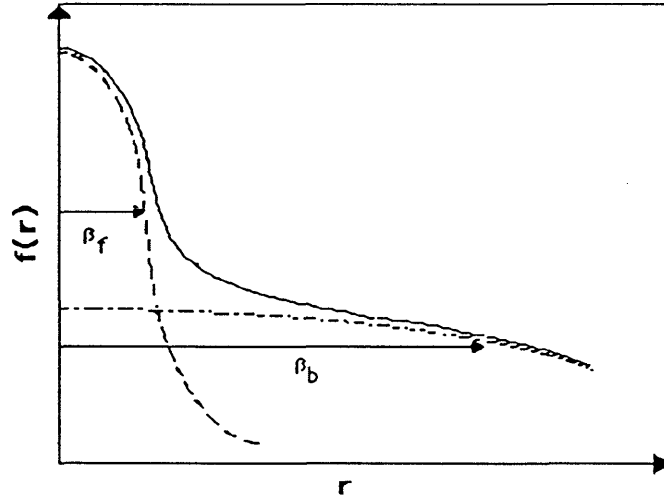


Fig. 6.19. Proximity function $f(r)$ for an arbitrary resist, substrate, and for incident electron energy with characteristic widths β_f (forward -scattered electron distribution) and β_b (backscattered electron distribution). (After Parikh, Ref.[12])

Monte Carlo calculations and experimental techniques are used to obtain the parameters in Eqn. 6.1 for each particular resist-substrate situation and energy E . The energy absorbed by the backscattered electrons is lower than the primary low angle scattered electrons but the characteristic width is bigger (Fig. 6.19). Greenwich [9] has shown that the contribution of backscattered electrons is quite significant at high doses. Fig. 2.7 shows the effect of primary and backscattered electrons on the linewidth based on theoretical predictions on a developer model that assumed complete development up to a critical energy level. At low doses, linewidth is dominated by the primary electrons and at higher doses the backscattered electrons dominate.

This effect is clearly seen when we compare the linewidths of Figs. 6.17 and 6.18. In Fig. 6.17 the larger linewidths ($>1\mu\text{m}$) receive more electrons (higher doses) and generates a high number of backscattered electrons which affect neighbouring lines. In these regions, a much lower dose is required than expected to achieve the desired linewidth. The total dose received by the group of lines in Fig. 6.18 is small and the contribution of the backscattered electrons is low and linewidths are dependent mainly on the secondaries produced by the primary electrons.

Balladore and coworkers [10] made a comparison of the proximity effects at 20keV and 100keV. Their results point to characteristic widths of $4.3\mu\text{m}$ in Si at 20keV and $70\mu\text{m}$ at 100keV. For Cr ($Z=24$) we can expect a characteristic width of about $5\text{--}10\mu\text{m}$ at 20keV. A 20keV incident beam deposits an energy a thousand times greater than at 100keV by the backscattered electrons. This implies that proximity effects are quite significant at 20keV and can be reduced substantially by operating at high beam voltages. On the other hand it was shown that proximity effects and increased sensitivity can be obtained by utilising a fine beam of energy less than 10 keV (see section).

Since the total writing time for the pattern in Fig. 6.12 is higher than in the groups in Fig. 3, the average absorbed energy in this area from the

backscattered electron distribution is high. This leads to thinning of the resist around the gaps between the lines which leaves the CdF_2 intact within this region (characteristic width β_f and β_b increases). This was found to be the case with the pattern of Fig. 6.12 where a significantly lower dose was required on average to expose the region properly.

To summarise, the two exposed groups in Figs. 6.12 & 6.13 are typical of the two dominating factors governing exposure latitude. Lines in Fig. 6.17 are dominated by the backscattered electron contribution and a lower dose is required for proper exposure. Lines in Fig. 6.18 are dominated by the primary electrons and the secondaries produced and thus a higher dose is required on average for proper exposure. As the lines in Fig. 6.18 are more closely spaced, linewidth will be mainly determined by the spread of the primary and secondary electrons.

6.2.3.3. Resist Profiles

To look at the resist profiles on PMMA, groups of lines of 50mm in length were exposed on the plate. A small section of the plate was cleaved perpendicular to the lines and the ends examined in the SEM. Figs. 20 and 6.21 show the edge profiles of two different sets of lines. The lines in Fig. 6.20 have been overexposed and do not show any undercut profile due to exposures by secondary electrons near the top of the resist. It would be correct to say that, for any given exposure and developing conditions, an undercut profile would not be possible for lines spaced below $1\mu\text{m}$. An undercut profile would be possible for the conditions where the line spacing is larger than the diffusion length of the secondary electrons.

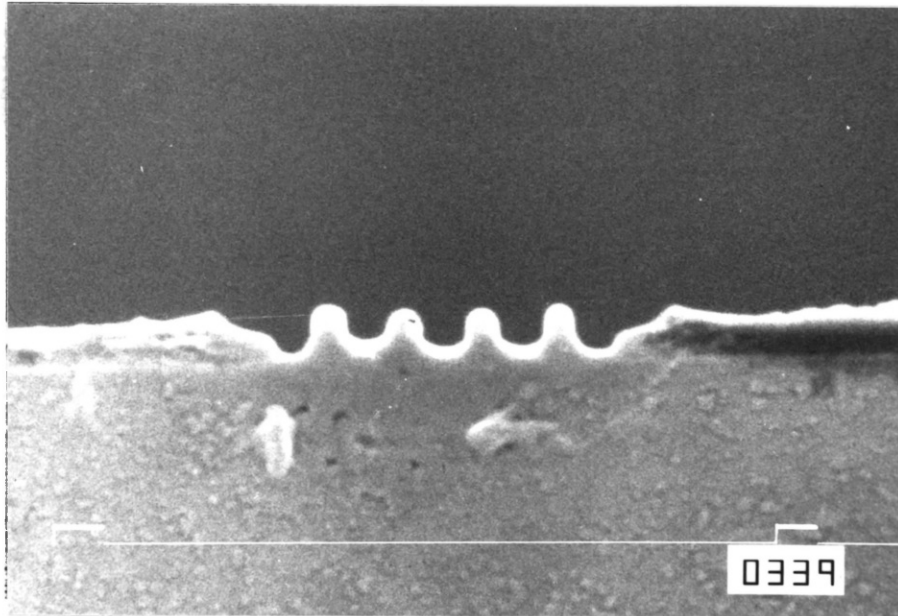


Fig. 6.20. Set of five lines exposed at $300 \mu\text{C}/\text{cm}^2$ for line spacings of $1\mu\text{m}$ (single pass of the beam)

For lift-off to be successful, the minimum allowable resist thickness of the CdF_2 film is limited by the height of the sidewall structure of the PMMA and this is a minimum at both ends of the exposure. Considering the features obtained it is obvious that an undercut profile is not required for lift-off to be successful

Complete lift-off occurs for the two edge profiles shown in Figs. 6.20 and 6.21. From several repeated experiments, it was found that the maximum allowable thickness of the CdF_2 for satisfactory lift-off is about $1/3$ of the PMMA thickness.

When considering resist profiles, the energy deposited in the resist as well as developer effects must be taken into account. The resist profiles of the lines in Figs. 6.20 and 6.21 show rounded features which is mainly due to the developer effects (section 2.4.1). However, the height variation of the lines can be attributed to the e-beam scattering in the resist. The energy density is at a maximum at the centre of the image and the heights of the two inner lines are therefore slightly smaller than the two outer lines.

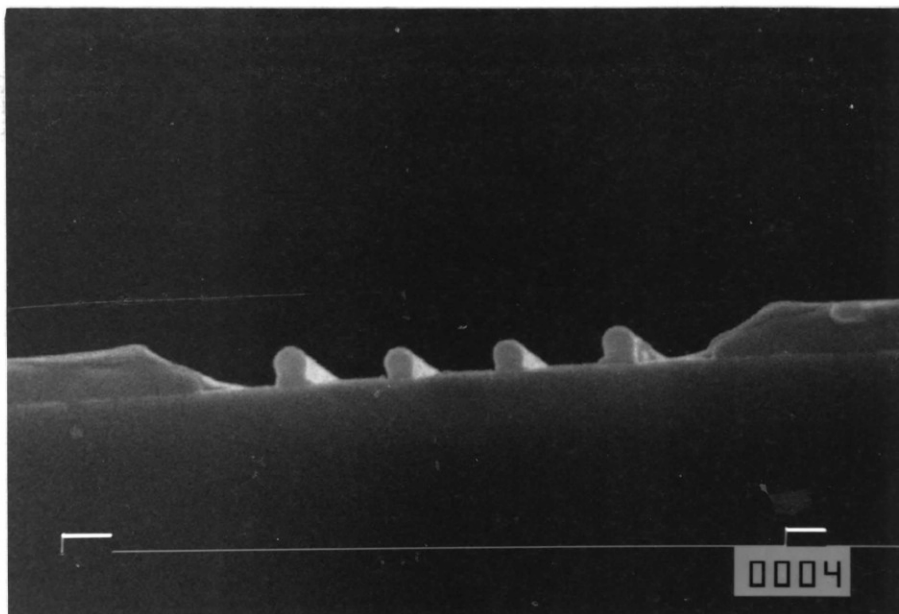


Fig. 6.21. Lines exposed at $110 \mu\text{C}/\text{cm}^2$ for predicted linewidths of $0.4 \mu\text{m}$ and $1 \mu\text{m}$ spacing.

6.2.3.4. Monte Carlo Simulation

Monte-Carlo simulation was performed for the PMMA and Cr combination using the software package described earlier in section 2.2.

Fig. 6.22 shows the simulation of 1000 electron trajectories in $5500 \text{ \AA}$ PMMA/ $1000 \text{ \AA}$ Cr on silica. The left hand side of the figure shows the electron trajectories calculated from weightings given to the Bethe energy loss equation and the Rutherford nuclear cross-section. An estimate of the energy distribution in the targets is shown on the right hand side. Forward scattering of the primary electrons are only limited to very small range at the surface of the PMMA resist but increases to $0.2 \mu\text{m}$ at the PMMA/Cr interface. For isolated lines, this results in an undercut profile which is commonly used for metal gate lift-off. Lines exposed in close proximity will be affected by this scattering process and hence restricts the minimum spacing possible.

Backscattered electrons have a far greater range (Fig. 6.23) and depending on the total dose, neighbouring areas close to the exposed region will be affected.

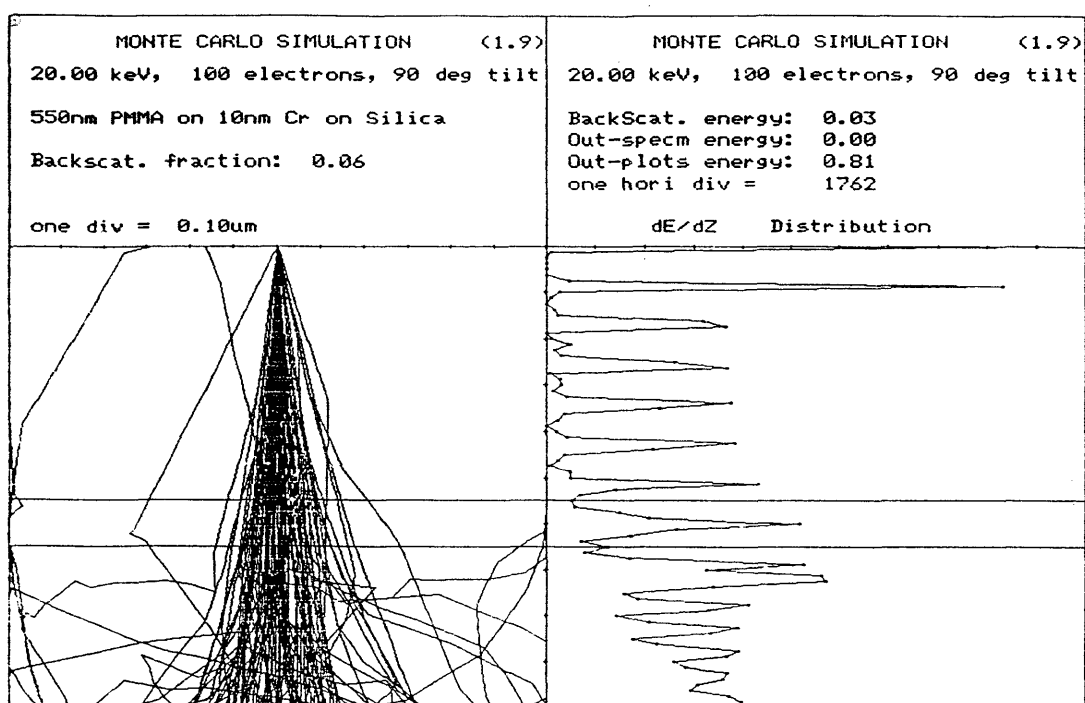


Fig. 6.22. MC simulation of 1000 electrons on 5500 Å PMMA/1000 Å Cr on silica substrate.*

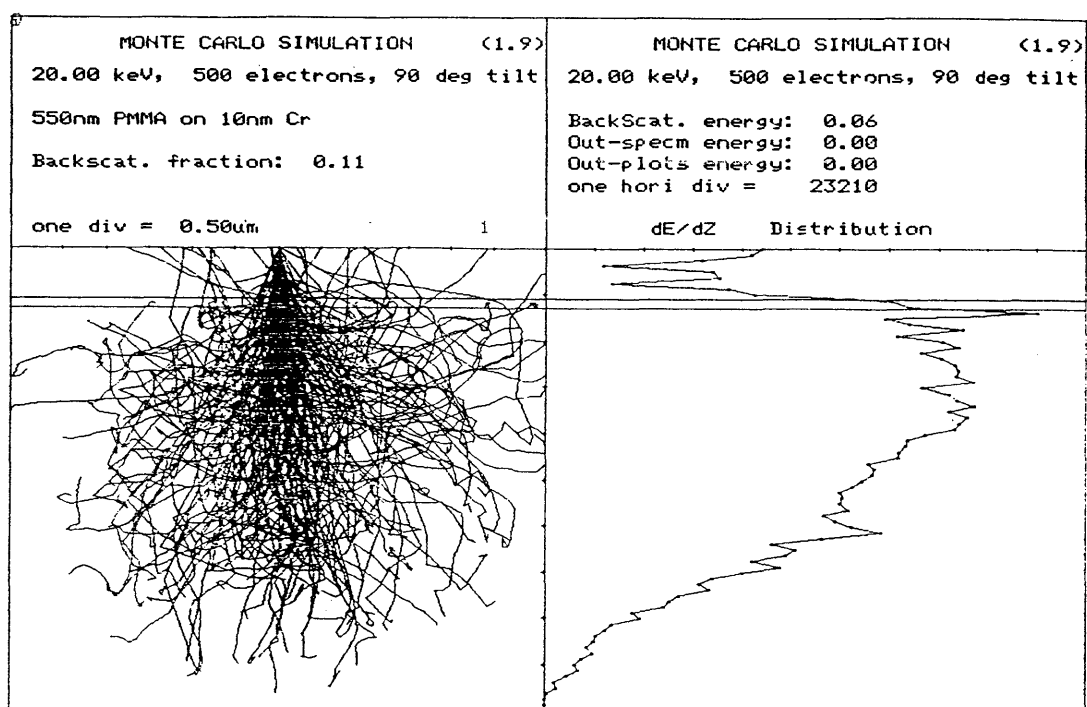


Fig. 6.23. MC simulation for 500 electrons showing the range of forward and backscattered electrons.*

* Software written by Dr.E.Napchan,
Materials Dept., Imperial College.

6.2.3.5. Chromium Etching

To etch chromium in a plasma the end product needs to be volatile. A mixture of chlorine and oxygen with the proper discharge conditions will lead to the volatile product CrO_2Cl_2 . Nakata and coworkers [13] have studied Cr and CrO_x plasma etching in the following mixed gas conditions:-

- (1) $\text{CCl}_4 + \text{air}$
- (2) $\text{CCl}_4 + \text{O}_2$
- (3) $\text{CCl}_4 + \text{Ar} + \text{O}_2$
- (4) $\text{CCl}_4 + \text{N}_2 + \text{O}_2$
- (5) $\text{Cl}_2 + \text{Ar} + \text{O}_2$
- (6) $\text{Cl}_2 + \text{He} + \text{O}_2$

Oxygen was found to play an important role in all the etching reactions of Cr. Cr etching increases rapidly with O_2 concentration in the mixture and saturates at an O_2 concentration of 50%. Owing to the similar etch rates for (3) and (4), Ar and N_2 do not strongly influence the etch rate characteristics. With plasma conditions for (5) of 300mT pressure, 160 Watts RF power, and concs. of 3:11:11 (CCl_4 : Ar: O_2) an etch rate of 100 Å/min was obtained.

On the basis of Nakata's results chromium was etched in a Plasmalab RIE (Microprocessor Series 80) with a 170mm diameter graphite cathode and 240mm Al anode and electrode spacings of 50mm. The following conditions were used:

- pressure = 30mT
- RF power = 100 Watts
- O_2 (conc) = 10 sccm
- Ar (conc) = 10 sccm
- Cl_2 (conc) = 20 sccm

The etch rate of Cr for these conditions was found to be 440 Å/min with Cr/ CdF_2 selectivity greater than 6. Results of the etching from the previous deposition of CdF_2 are shown in Fig. 6.24.

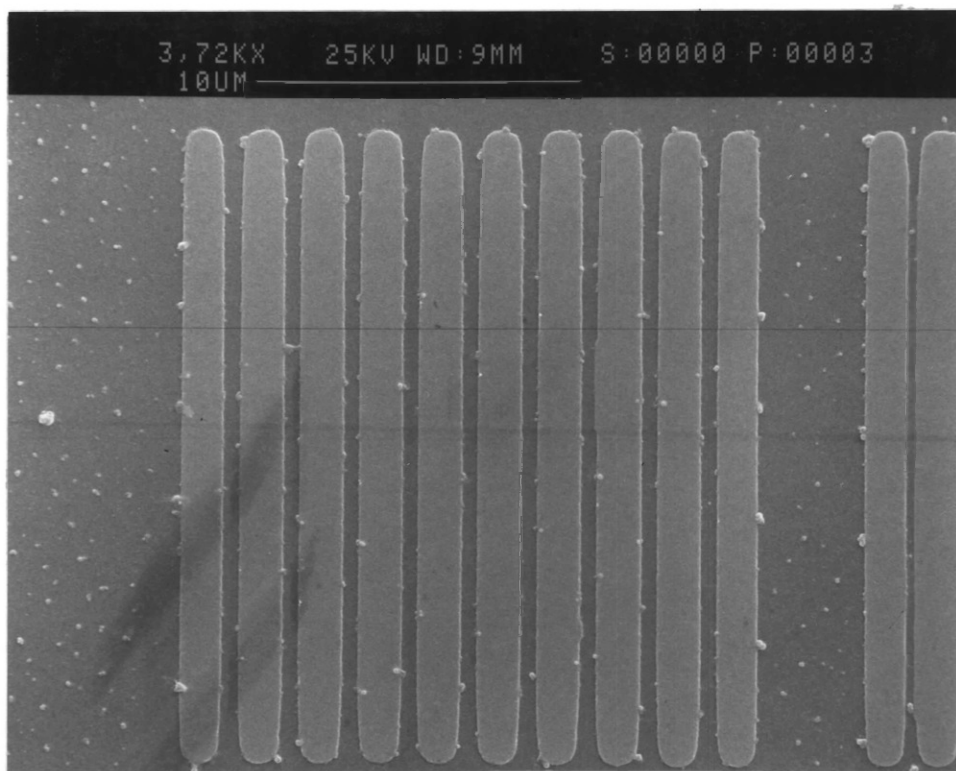


Fig. 6.24. Etched chromium lines of group 6f at 30mT, 100W, Etch Time 3.5mins, 10sccm O₂, 10sccm Ar, 20sccm Cl₂. (dust particles have collected on the substrate outside the clean room)

6.2.3.6. Linewidth and Edge Resolution

The edge resolution obtained in Cr is largely dominated by the resolution of the PMMA resist, because the CdF₂ film grows along the wall of the PMMA boundary and therefore assumes the shape of the PMMA structure. As mentioned earlier grain growth is faster at the edges (Fig. 6.4) consequently the edge definition is very high. Fig. 6.25 shows the features obtained after depositing approximately 4000 Å of CdF₂ followed by lift-off. The hole produced in the CdF₂ is the dissolved PMMA line and as the film is relatively thick it grows over PMMA line. It is clear that CdF₂ grows well against the PMMA wall and also grows faster at the steps. The features thus formed are very useful in withstanding edge erosion during plasma etching and hence preventing lateral erosion (Fig. 6.26).

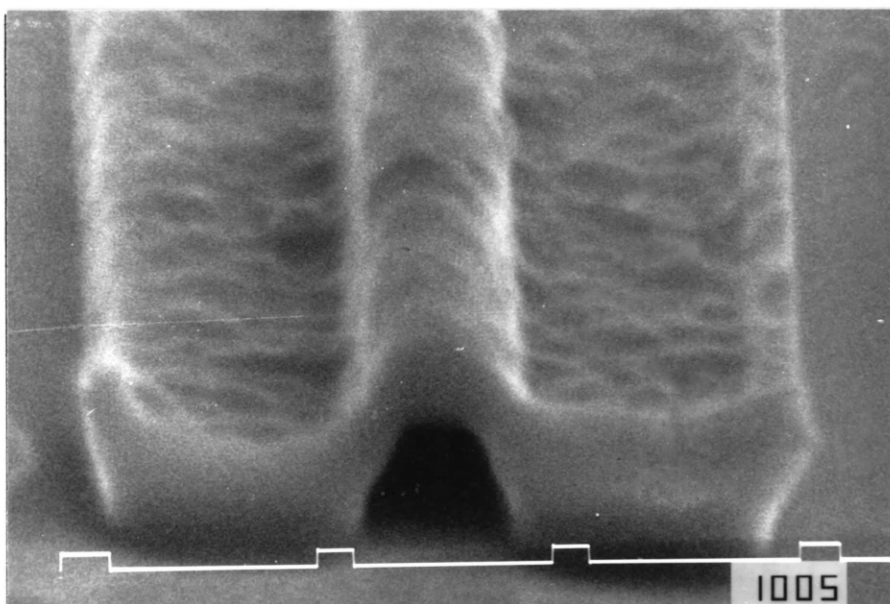


Fig. 6.25. Growth of CdF₂ film at the boundary of the PMMA resist.

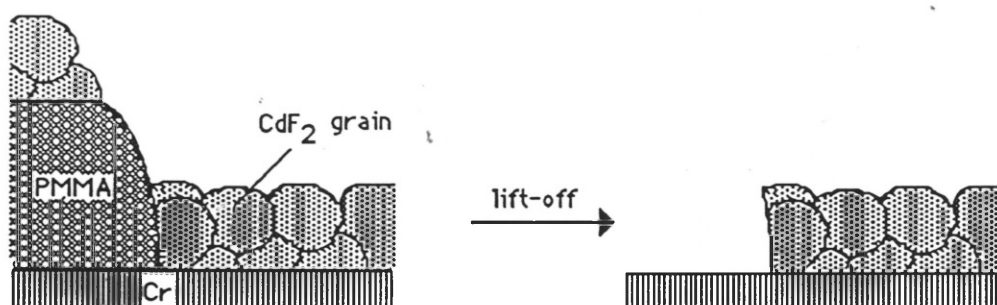


Fig. 6.26. Edge resolution as determined by the PMMA wall structure.

The edge resolution of the chromium lines is better than 300 Å (Fig. 6.27) which is superior to any resolution obtained by wet etching. The minimum linewidth obtained is shown in Fig. 6.28, giving a linewidth of 0.38 μm for group 1f (Fig. 6.13). Stripping of the CdF₂ was carried out in an ultrasonic bath containing phosphoric acid (H₃PO₄) although an Al etch was also found to give the same results.

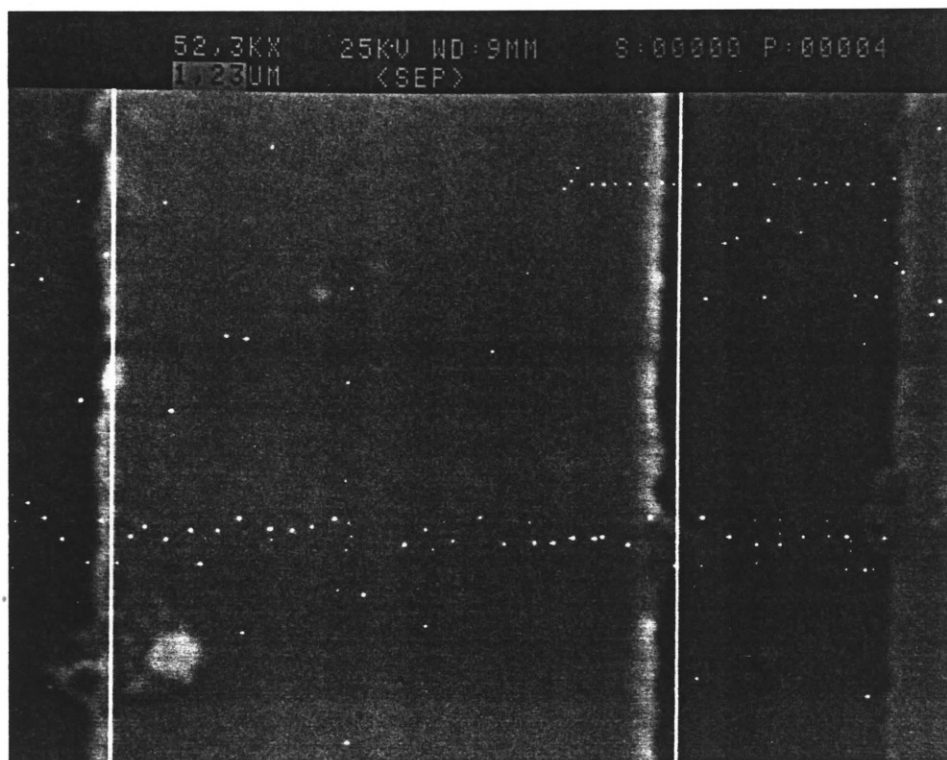


Fig. 6.27. Edge resolution of Cr lines.



Fig. 6.28. Linewidth of $0.38\ \mu\text{m}$ obtained with the group 1f lines.

6.2.4. Conclusions

A minimum linewidth of $0.38\ \mu\text{m}$ and an edge resolution better than $0.02\ \mu\text{m}$ was obtained with this technique of lift-off mask fabrication. This was achieved with groups of lines spaced $1\ \mu\text{m}$ apart but for isolated lines the linewidth would be much less than this, limited only by the resolution of the PMMA resist, the beam diameter and the degree of electron scattering.

Proximity effects due to backscattered electrons were found to be quite significant for the exposure in Fig. 6.17 possibly due to the large backscattering coefficient of Cr/Silica substrate. The prolonged exposure of the total area leads to an increase in the average absorbed energy from backscattered electrons which reduces the effective incident dose required for these lines. As a result of this, resist thinning of the PMMA occurs between the exposed regions leading to incomplete lift-off.

The lines in Fig. 6.13 have a much more critical dependence on dose due to the primary electrons and the secondary electrons produced. Linewidth control of these groups of lines can be controlled by making an on-dose correction for each line [14]. The minimum spacing possible is limited by the spread of the primary and secondary electrons and the height possible on the PMMA for proper lift-off.

An undercut profile was not required for this lift-off process since it was shown that lift-off was possible even for a tapered wall structure of the PMMA. This should enable the use of a more sensitive^{resist} such as EBR-9 where the edge resolution is not as good as PMMA.

To summarise, the combination of a fast sensitive organic resist and an inorganic resist appears to be a very viable technique for fabricating Cr mask plates. The fast organic resist would provide the high sensitivity required for e-beam writing and the inorganic resist would provide the high etch resistance required for anisotropic dry processing. The possibility of other metal halides instead of CdF_2 may be worth investigation.

THIN FILM PROPERTIES OF CESIUM CHLORIDE FOR QUANTUM DOT FABRICATION

Quantum confinement in semiconductors has led to improved two dimensional (2D) devices, such as high mobility field effect transistors and low threshold lasers. The field of multi-layer quantum-well structures is now well established [1]. This chapter is concerned to report on a new type of lithography aimed at quantum dot (0D) structures which will allow the fabrication of new and useful semiconductor devices.

Various workers have attempted to use special structures in order to make very small (cu 100-300 Å) quantum dot structures. Thus Deckman and Dunsmuir [2] have used colloidal particles and Fang et al. [3] used latex spheres as masks. These technologies have been called 'natural lithography' [2], they have not yet yielded sufficiently useful pattern to be termed successful. E-beam [4], ion beam [5] and x-ray [6] lithography are capable of very small structures, but always give a low size to dot coverage, ie. 1 to 10% of the surface is dots.

We have worked on a natural lithographic scheme which has its origins in the idea of using the grain structure of thin films of metal halides to achieve nanostructures. Thus we know that a thin film of metal halides is usually polycrystalline and one grain thick. We also know that these thin films can be etched preferentially along grain boundaries to give isolated island structures. It was such a set of isolated structures that we thought to use as resists in an 'island lithography' scheme as depicted in Fig. 7.1.

We chose CsCl as a resist material and found that exposure to the (moist) atmosphere was sufficient to create an island structure (Fig. 7.2). In this case it is simply that CsCl is deliquescent and totally dissolves in moist laboratory air forming hemispherical droplets of saturated CsCl solution. The size and

distribution of these droplets appears to depend upon three variables, given a fixed CsCl deposition rate and a particular substrate: the variables are, film thickness, ripening time in the laboratory, and relative humidity of the laboratory air.

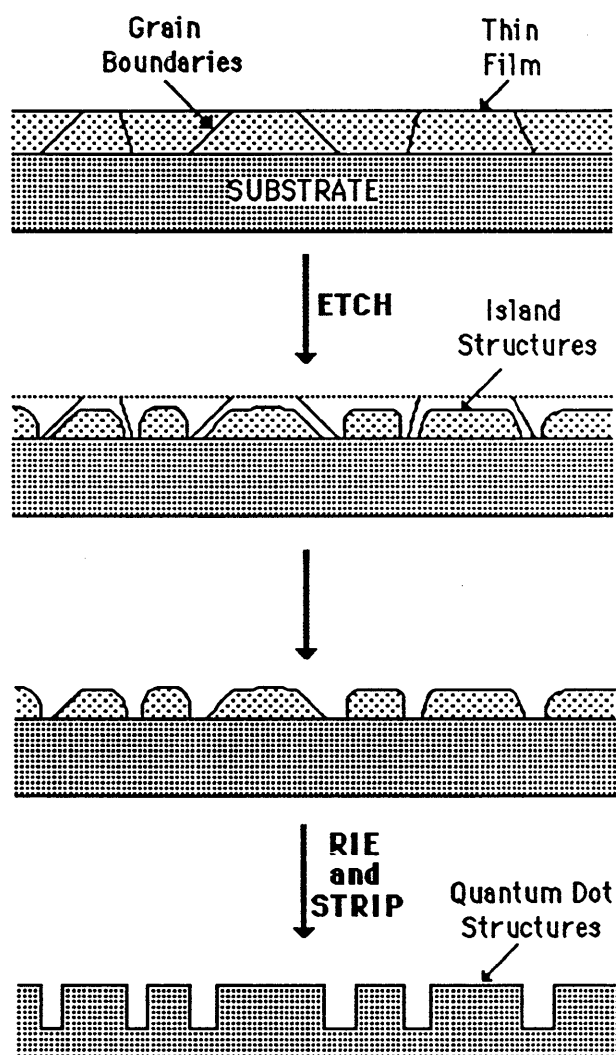


Fig. 7.1. Preferential etching of thin films through grain boundaries to produce island structures which after subsequent RIE produces the quantum 'dot' structures in the substrate.

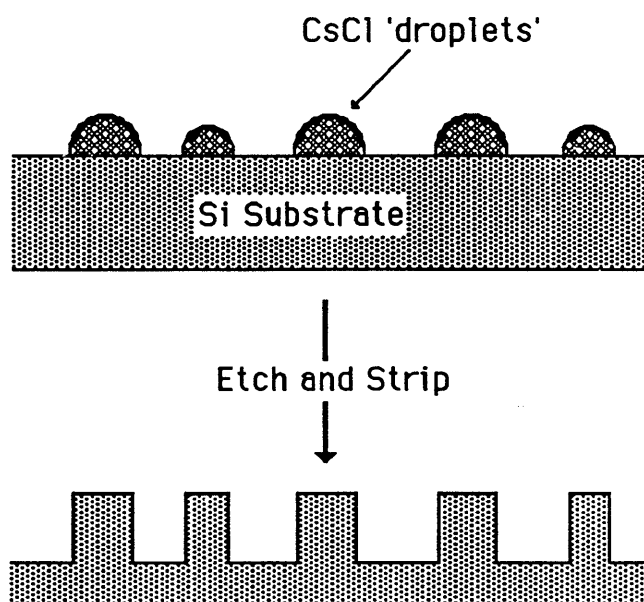


Fig. 7.2. 'Dot' structures formed in Si from the unique film properties of CsCl.

7.1. Experimental Results

7.1.1. CsCl Films of Mean Thickness 7,000 Å

Initially Analar CsCl in powder form (Hopkin & Williams) was evaporated from a molybdenum boat at a controlled rate of deposition. Deposited samples were removed from the evaporation unit and exposed to laboratory air for several minutes during transfer to the JEOL T100 SEM for examination. All samples thereafter were stored in a cupboard having an approximate relative humidity of 35% at a temperature of 21°C.

SEM micrograph of a deposited film on Si after evaporation without Au coating is shown in Fig. 7.3: it gave a talystep measurement of 6400 Å. The structure of the film after being left in laboratory air for about 2 months is shown in Fig. 7.4. The film has 'balled' up giving hemispherical structures which might be attributed to the transport of material via an adsorbed water

phase, or to the coagulation of small droplets. The effect of this structure has caused the mean film thickness to grow from 6400 Å to 10,000 Å measured using the talystep.

CsCl was deposited at a slower rate on a silicon sample coated with approximately 1400 Å of thermal oxide and the film after several minutes exposure to air is shown in Fig. 7.5. Following ripening in laboratory conditions for two months, the film has formed hemispherical structures (Fig. 7.6). An increase in the film thickness was not observed which is possibly due to the partial 'networking' and the sporadic nature of this film compared to the previous film (cf Figs. 7.3 & 7.5).

Analysis of the films shown in Figs. 7.3 and 7.4. indicated that as expected, no significant changes in the volume had occurred during ripening. The change in thickness of the two films can be calculated from the equation,

Volume of CsCl 'dots' per cc = Volume of initial film thickness per cc
ie.,

$$2\pi R^3 N / 3 = t_1 \cdot B \quad (7.1)$$

where N is the number of dots per cc, R is the average radius, t_1 is the initial film thickness (Fig. 7.3) and B is the fractional coverage of the initial film. For a film which is continuous and flat in the vacuum system, this relation can be simply stated as,

$$2\pi R^3 N / 3 = t \quad (7.2)$$

where t is the thickness of the film deposited.

The percentage area of coverage of the dots after ripening can be calculated from the equation,

$$\pi R^2 N = C \quad (7.3)$$

where C is the fractional coverage.

Dividing Eqn. 7.1 by Eqn. 7.3 gives the expression for R,

$$R = 3t_1 \cdot B / 2C \quad (7.4)$$

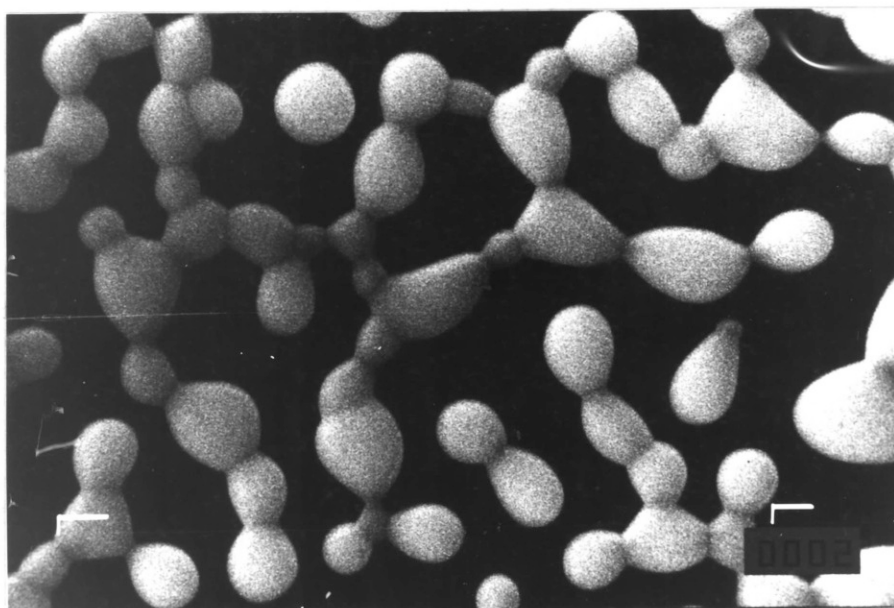


Fig. 7.3. CsCl film structure after exposure to laboratory air for several minutes ('average' thickness 6400 Å (Talystep)). Substrate Si, Rate ~ 1620 Å/min.

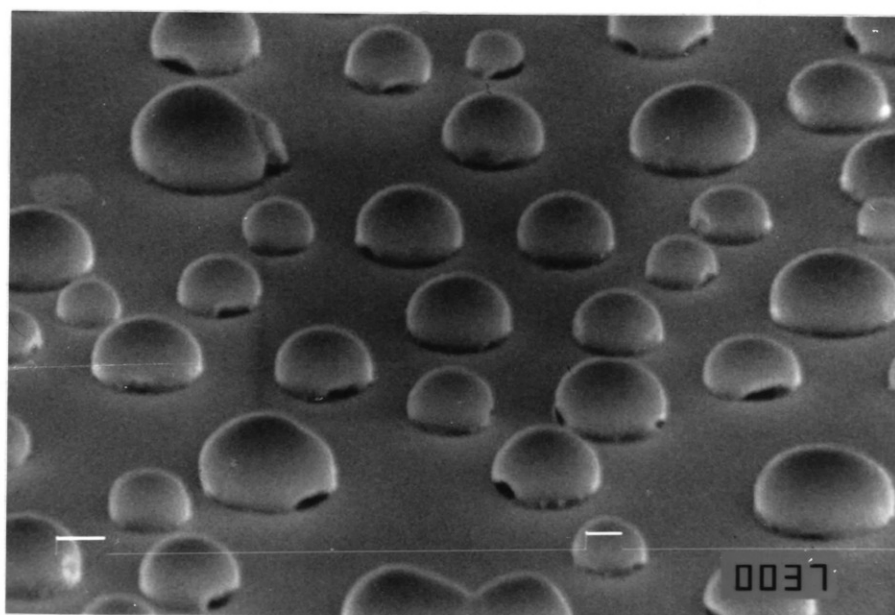


Fig. 7.4. CsCl film of Fig. 7.3. after storage in laboratory conditions for approximately two months.



Fig. 7.5. CsCl film structure after exposure to laboratory air for several minutes (average thickness 6800 Å (Talystep)). Substrate Si (1400 Å SiO₂), Rate ~ 340 Å/min.

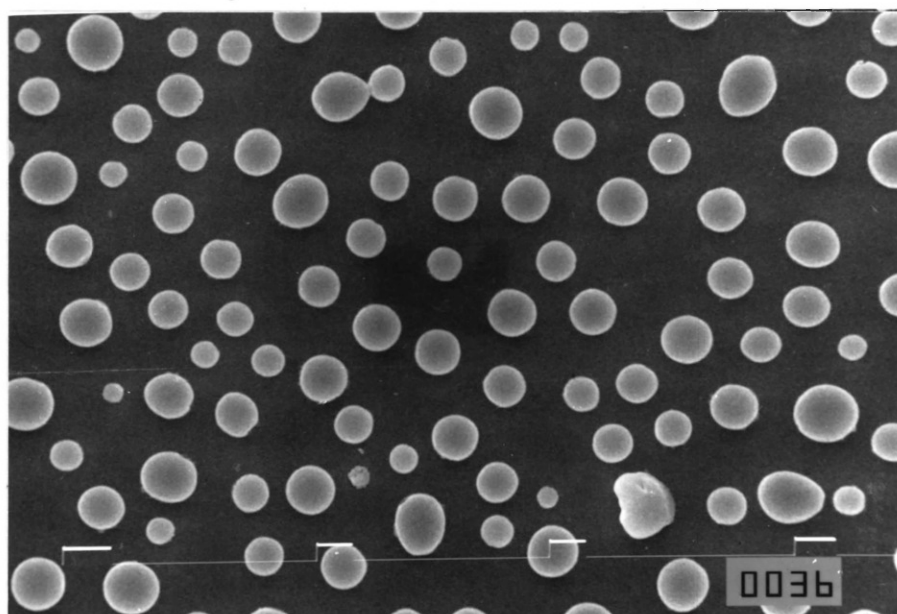


Fig. 7.6. CsCl film of Fig. 7.5 after storage in laboratory conditions for 2 months.

For the films shown in Fig. 7.3 and 7.5, R is calculated to be about 14,000 Å and 7,800 Å respectively. The average thickness of the two samples measured using the talystep after ripening was found to be 10,000 Å for the sample shown in Fig. 7.4 and 6,800 Å for the sample shown in Fig. 7.6. These values corresponds roughly to the calculated results obtained previously using Eqn. 7.4. Since the weight of the tip during the talystep measurement would flatten the structures, the measured value is almost certain to be less than the actual radius which is in agreement with the theoretical value.

An accurate assessment of the amount of CsCl deposited may be arrived at from a calibration measurement of the quartz crystal with a material of known density eg. CdF_2 . In this way, the original thickness t (Eqn. 7.2) assuming the film is continuous in vacuum may be compared to the measurement obtained using Eqn. 7.4.

Etching of the sample shown in Fig. 7.4 was carried out at 105 W, 50 mT, 20 sccm Cl_2 , 20 sccm Ar on a graphite table in the Plasmalab 80. Fig. 7.7 shows the etched profiles immediately after etching and Fig. 7.8 shows the profile after stripping the CsCl in deionised water. At these conditions, resputtered CsCl have acted as secondary masks to produce the smaller features around the base of the larger structures. Talystep measurements were carried out after each stage of the process ie. etching and stripping and a selectivity figure for Si/CsCl was found to be about 6.

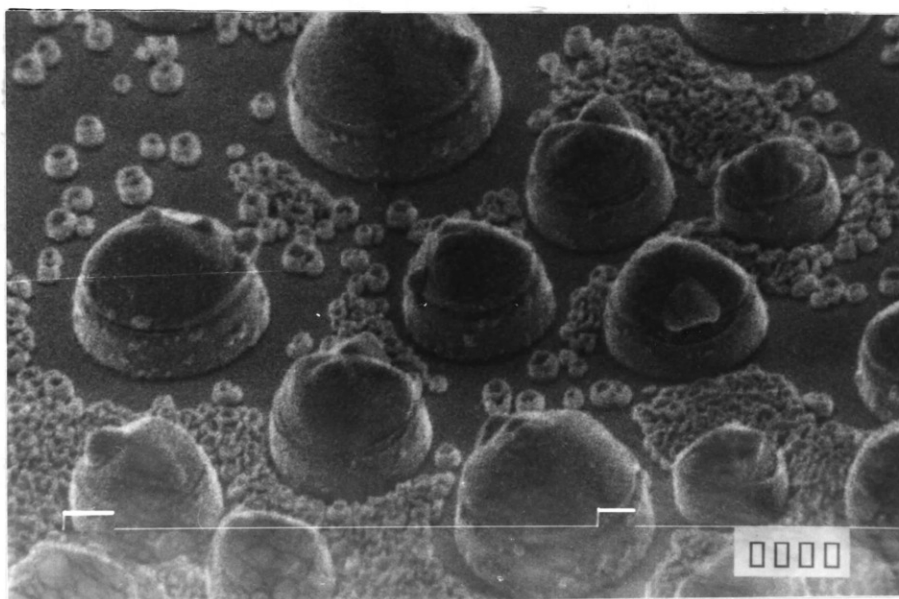


Fig. 7.7. Etched sample of the specimen shown in Fig. 7.4 before stripping.

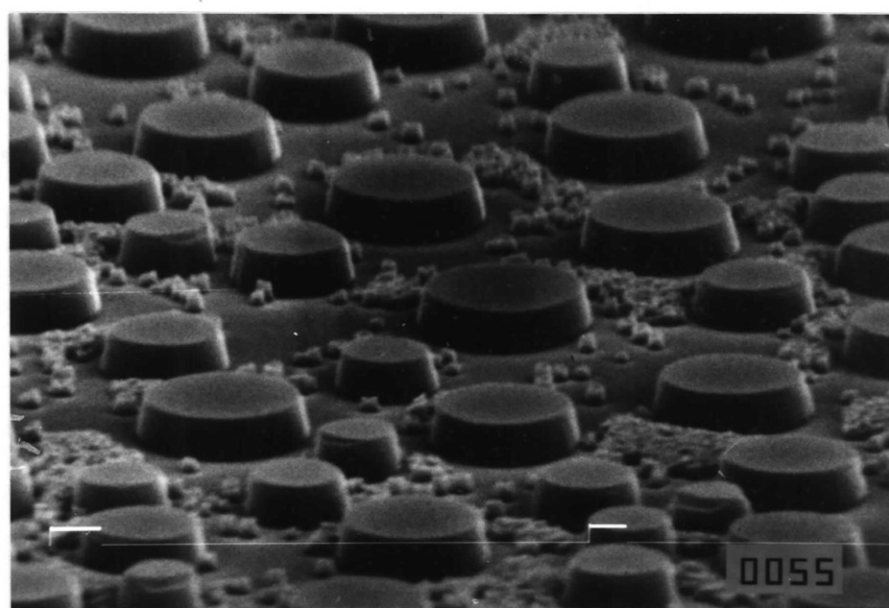


Fig. 7.8. Stripped sample of Fig. 7.7 after rinsing in deionised water.

7.1.2. CsCl Films of Mean Thickness 1000 Å

CsCl film of mean thickness 1000 Å was deposited at a rate of 2100 Å/min and left in laboratory conditions similar to the previous samples. The etched sample using the same previous conditions for RIE is shown in Fig. 7.9. It is interesting to note that the resputtered material has not been formed on the substrate which is possibly due the differences in the composition of CsCl for the two types of film structures.

A distribution of the diameters of the etched specimen (Fig. 7.11) was carried out giving two peaks at 0.32 µm and 0.63 µm. This has been calculated from the plan view of the specimen (Fig. 7.10) and measuring the outer diameter which is the top surface. The height of the etched features associated with the larger set are constant at 0.35 µm which would be suitable to the fabrication of contacts after laying an insulator layer (eg. polyamide) within the dot array.

The smaller pointed structures have been formed due to the complete erosion of the CsCl film since the etch selectivity under the RIE conditions was calculated to be about 6. The rough surface is due to the incomplete stripping of the CsCl after only a short time rinse in deionised water.

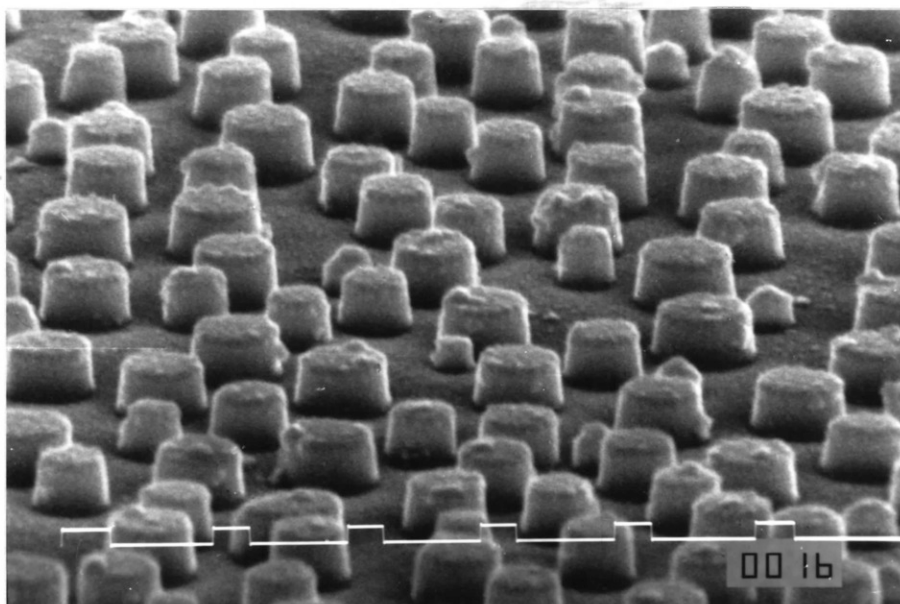


Fig. 7.9. Etched samples of CsCl after partial stripping (70° tilt).

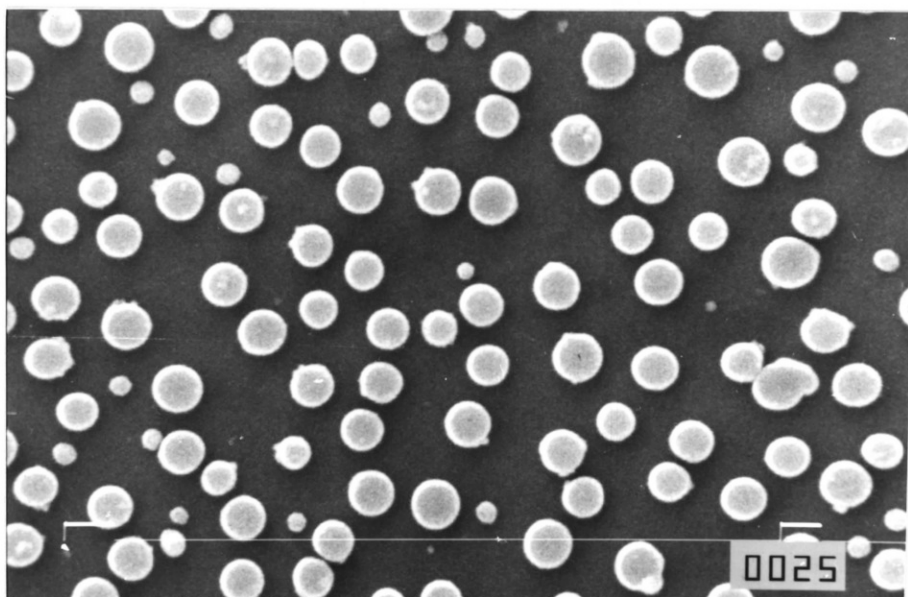


Fig. 7.10. Plan view of the etched specimen shown Fig. 7.6.

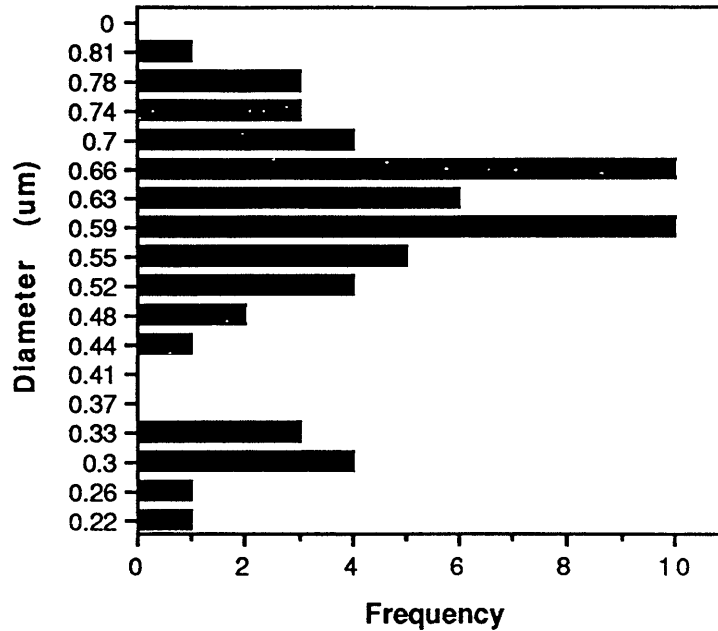


Fig. 7.11. Distribution of the diameters of the etched profiles shown in Fig. 7.10.

7.1.3. Orthogonal Table for Etch Characteristics.

A four run process optimisation was carried out (Table 7.1) on the sample shown in Fig 7.12 to examine the etching characteristic of Si and CsCl with variation in power, pressure and gas flow of Ar. A fixed etch time of 5 minutes and Cl_2 gas flow of 20 sccm was used for all the runs. Etched samples of all four runs are shown in Figs. 7.13(a) to 7.16(a) and the stripped samples shown in Figs. 7.13(b) to 7.16(b).

Comparing runs 1 and 3, the etch selectivity in the former case is greater leading to more vertical wall angles. This would therefore appear to be the optimum setting for fabricating structures less than 1000 Å in diameter since the selectivity is also very high (cf Figs 7.13 & 7.15). For run 3, most of the CsCl has been sputtered off (dc bias of 300 V) leading to the 'skirt' around the base of the structures.

Table 7.1.

Four run orthogonal table to examine etched profiles.

RUN	POWER (W)	PRESSURE (mT)	GAS FLOW (sccm Ar)	DC Bias (V)
1	80	50	10	205
2	80	100	20	120
3	100	50	20	300
4	100	100	10	150

In the high pressure conditions of runs 2 and 4 the resputtered CsCl has been deposited on the the Si substrate with the effect being greater at the low power condition (run 2). The smaller structures formed around the big features in run 4 are almost uniform in size, suggesting the possibility of fabricating quantum structures in this mode of operation. But since this process is highly dependent on many factors such as the system parameters and possibly the CsCl compositional form, the method of direct deposition and control of humidity followed by etching should give a more systematic approach to the size of the features etched.

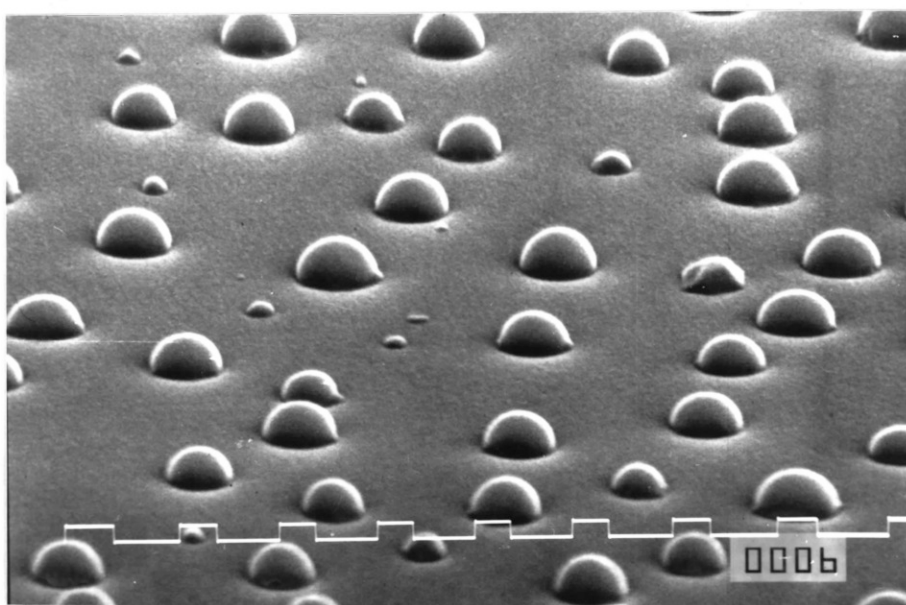
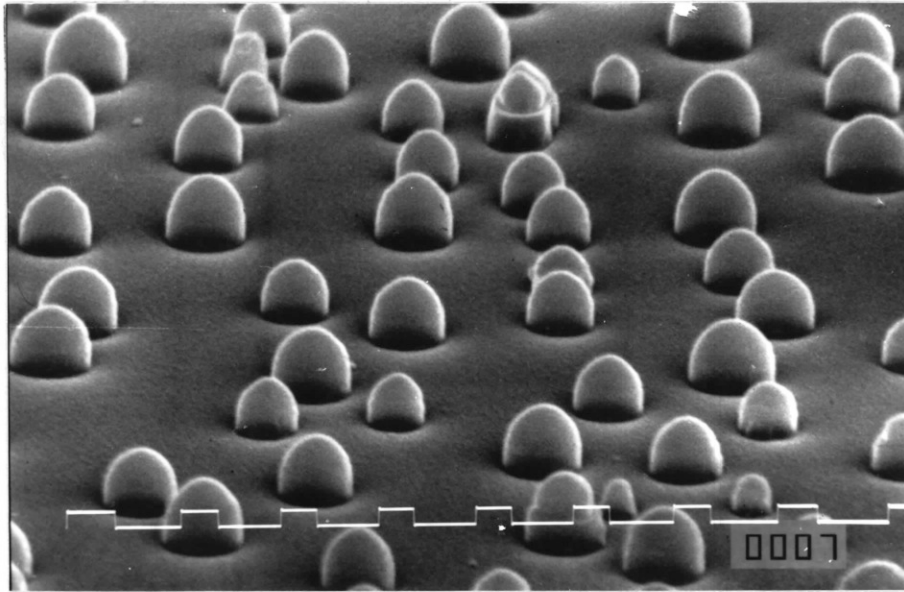
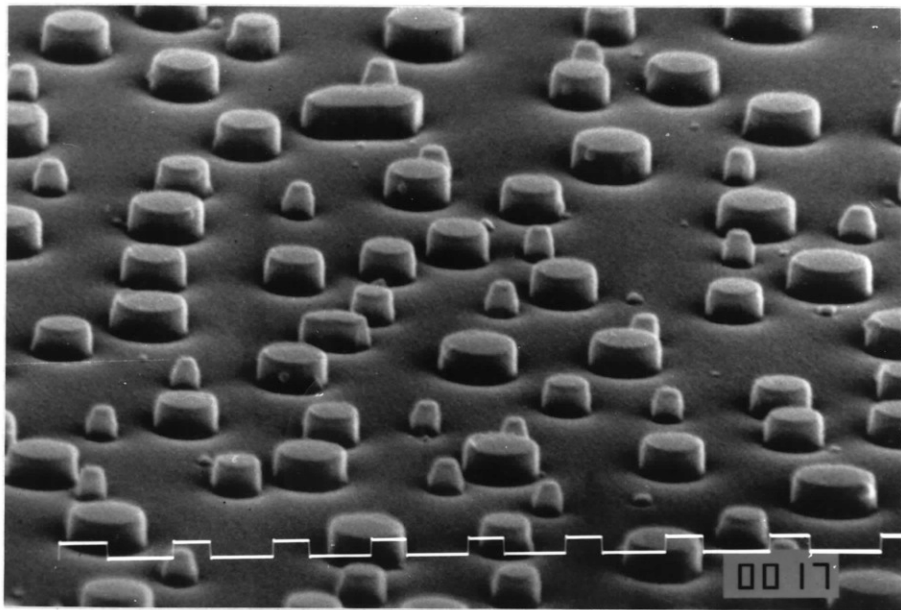


Fig. 7.12. CsCl structures on silicon substrate for the four run process.

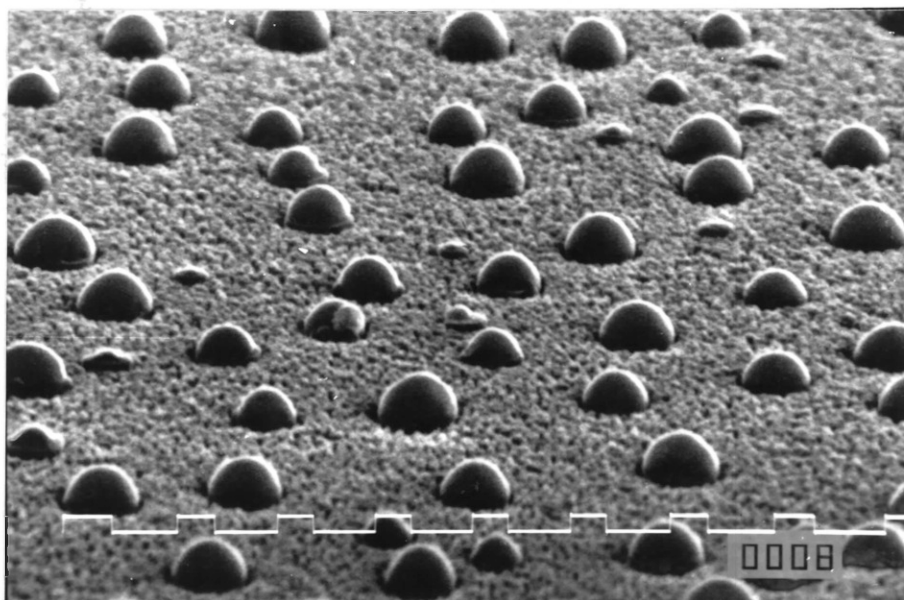


(a)

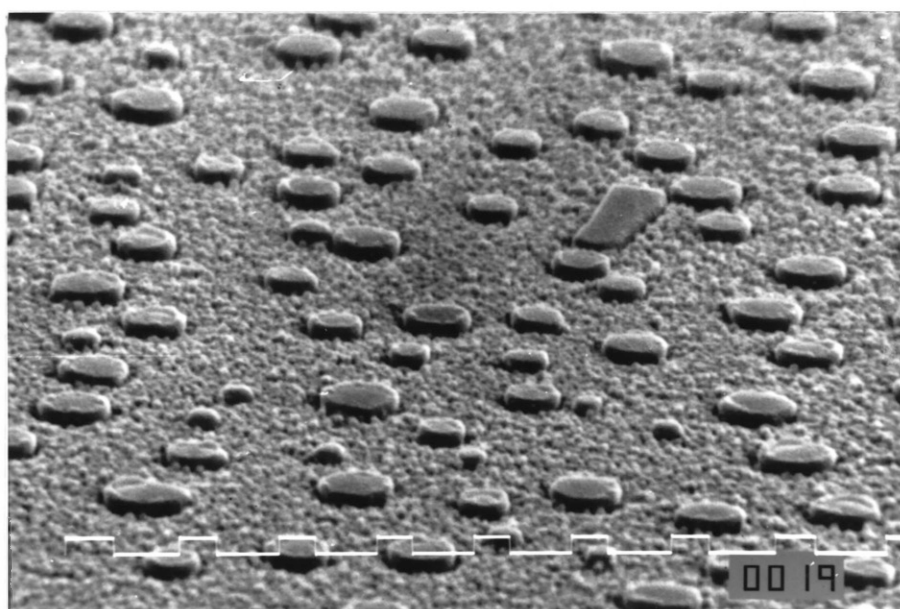


(b)

Fig. 7.13. (a) Si and CsCl profiles after RIE for *run 1* and (b) after stripping of CsCl.

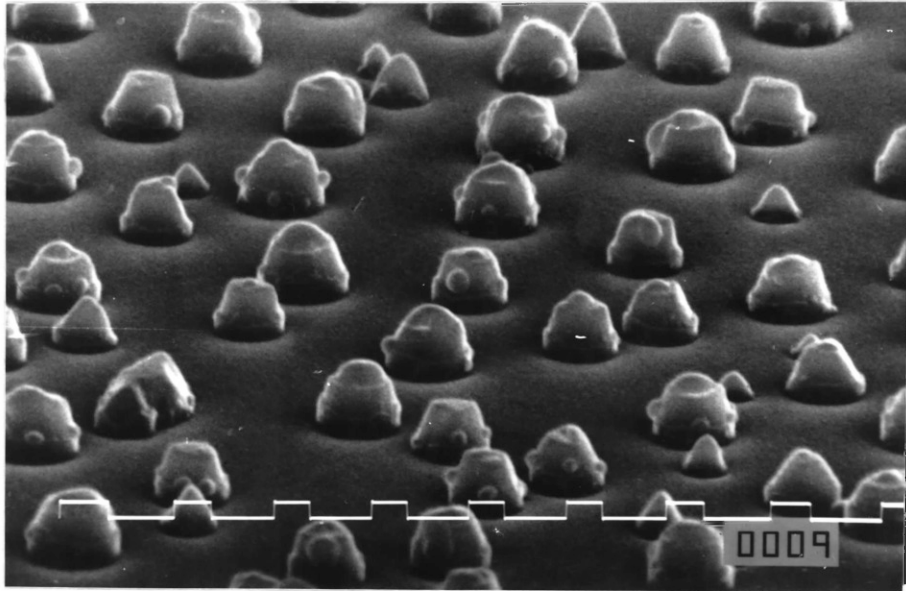


(a)

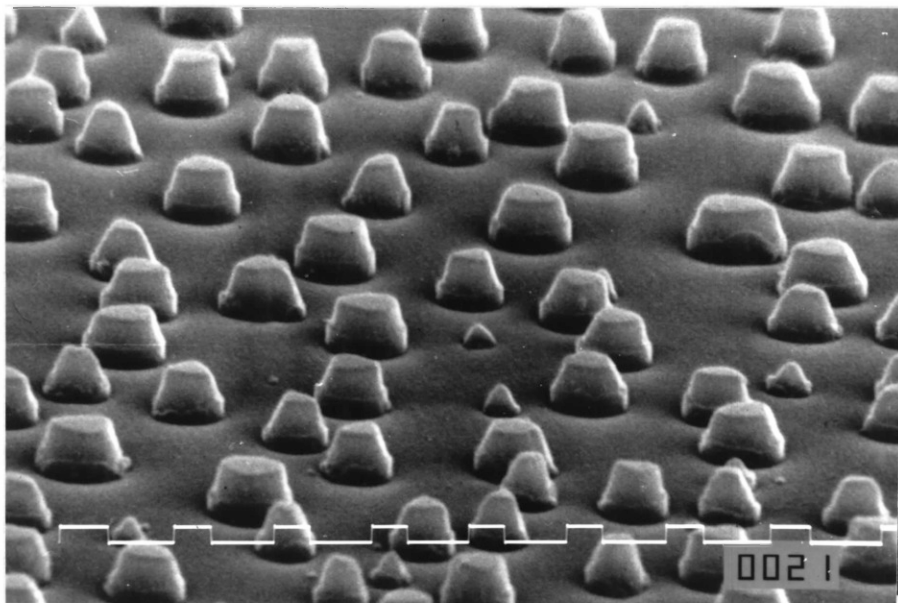


(b)

Fig. 7.14. (a) Si and CsCl profiles after RIE for *run 2* and (b) after stripping of CsCl.

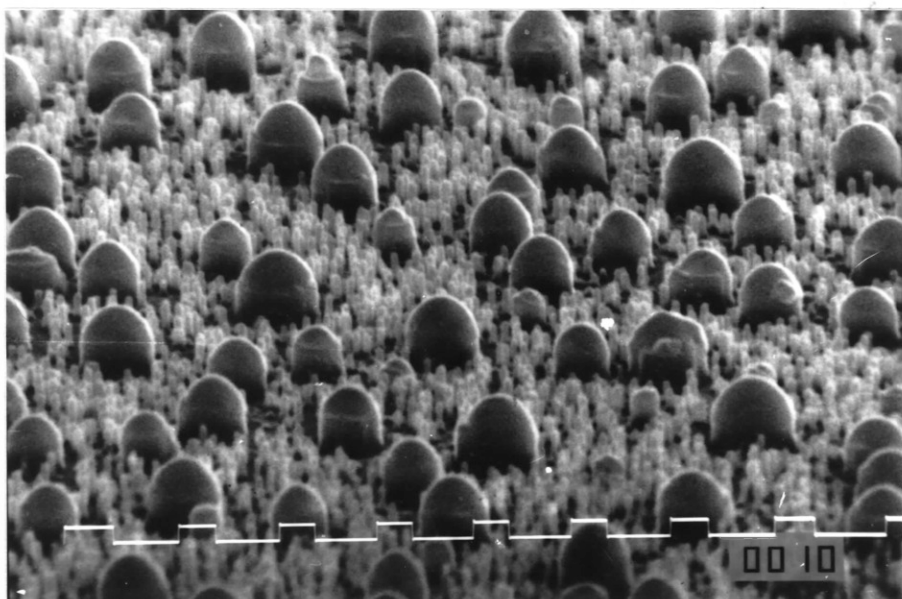


(a)

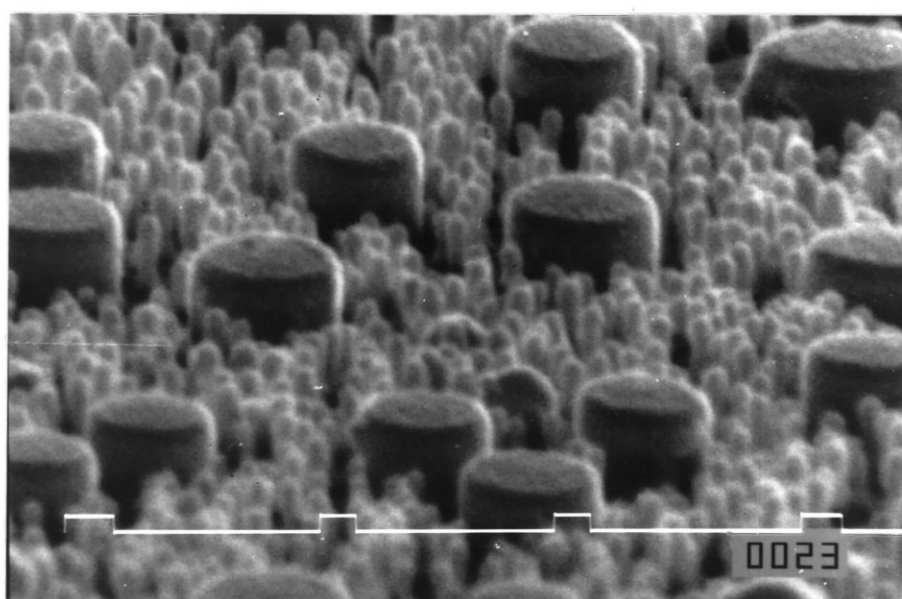


(b)

Fig. 7.15. (a) Si and CsCl profiles after RIE for *run 3* and (b) after stripping of CsCl.



(a)



(b)

Fig. 7.16. (a) Si and CsCl profiles after RIE for *run 4* and (b) after stripping of CsCl.

7.1.4. Features Below 3000 Å

Silicon samples were deposited with CsCl in the evaporator and placed immediately in a box with humidity of 30 % at room temperature. Two samples of silicon substrates were deposited with the material at rate of about 4,800 Å/min having mean film thicknesses of 820 Å and 280 Å. Both silicon samples were etched after 24 hours of the deposition using the RIE conditions of run 3 (optimisation was actually carried out after these two runs) mentioned previously. Figs. 7.17 and 7.18 show the etched and stripped samples (gold coating) for the two films respectively.

The measured average dimensions of the structures in Fig. 7.18 is approximately 900 Å in diameter. Owing to the resolution limits of the JEOL T100 SEM the structures appear rounded, so effectively the diameter is possibly less than this. An etch time of 45 seconds was used giving an etch depth of about 800 Å. It should be possible to use the conditions of run 1 described in the previous section to give deeper profiles.

Fig. 7.17 shows structures in Si with diameters less than 3000 Å. Some of the CsCl around the edges have been eroded during the etch leading to the pointed structures on the substrate. The 'dots' produced have a distribution similar to the other etched specimens and the heights are relatively constant provided the CsCl is not completely eroded.

Preliminary experiments on the size of the CsCl 'balls' deposited on GaAs and Si suggests a diameter smaller on GaAs than on Si all other conditions being identical, which would be advantageous to the fabrication of quantum 'dots'.

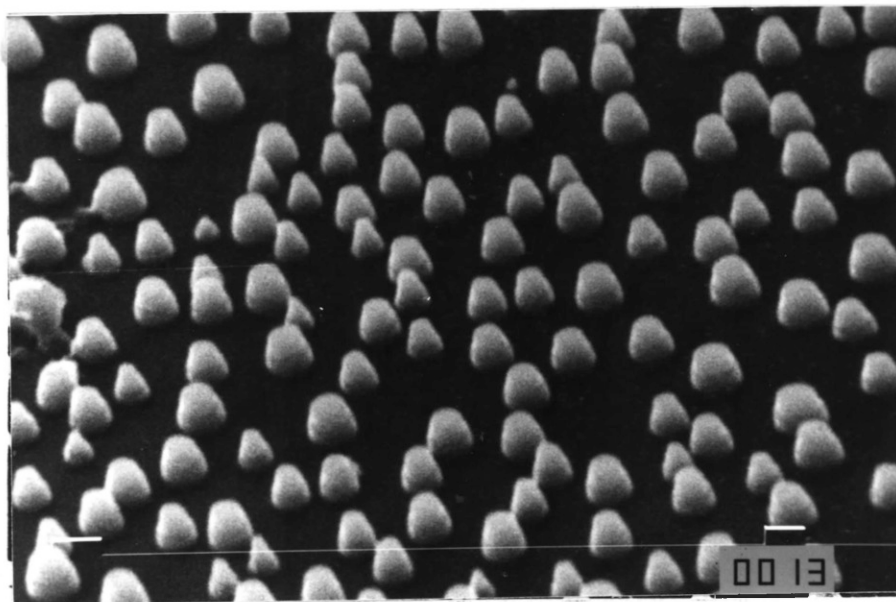


Fig. 7.17. Etched and stripped silicon sample with initial CsCl film thickness of 820 Å. Average diameter of the dots is 0.3 μm and an etch time of 3 mins. was used. (6 μm bar from weighting)

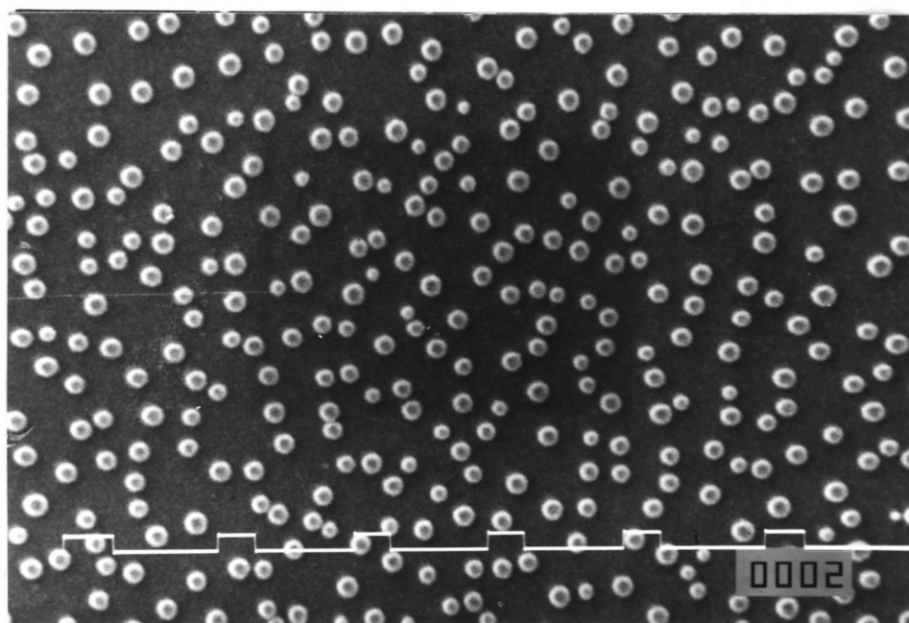


Fig. 7.18. 800-900 Å 'dots' in Si with an etch depth of about 800 Å. (1 μm bar)

7.2. Further Work

It has been shown that by depositing a very thin film of CsCl, hemispherical structures below 1000 Å can be formed on a silicon substrate. To have any understanding of the radius, percentage coverage of the dots in relation to the film thickness or deposition rate requires proper experimental procedure where the film can be deposited and possibly examined in-situ in vacuum. By opening up the system to dry air and storing the sample in a dry box, could eliminate some of the uncertainties encountered when transferring to the SEM for examination.

The relationship between the film thickness and the mean radius of dots will be a function of the humidity, temperature, deposition rate and time of ripening. To examine how these variables affect the distribution, a 9 run orthogonal table may be employed (Appendix I) with the input parameters being all of the above and the output functions being the distributions of the diameters and the percentage coverage.

7.3. Applications

7.3.1. Quantum Dots

Scientists searching ways to create zero dimension (OD) structures have used the term 'quantum dots' [7]. A typical sequence for fabricating quantum well diodes using the CsCl technique is shown in Fig. 7.19. The fully localised electron wave functions are present in the OD quantum dot.

Fig. 7.20 illustrates the current-voltage-characteristic of a 100 nm, dot structure [8]. At low temperature, the splitting between the emitter states is evidence of discrete OD states. By making even smaller structures the energy shift would be observed at room temperature.

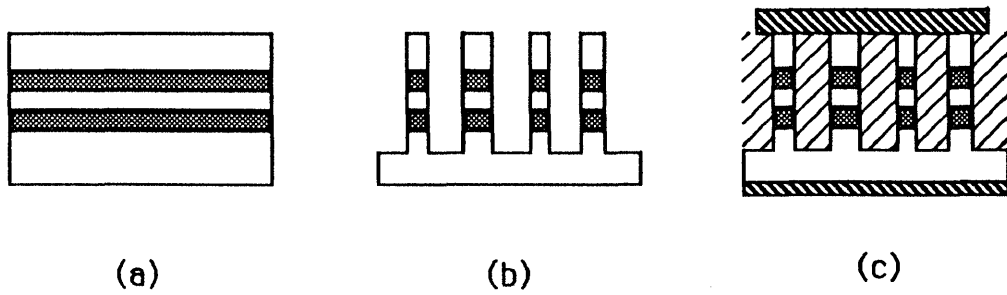


Fig. 7.19. (a) GaAs/AlGaAs double barrier carrier structure with n^+ GaAs contacts on top and bottom; (b) pillars defined using the technique of CsCl deposition and etching; (c) planarisation with polyamide and etchback followed by deposition of Au bonding pads.

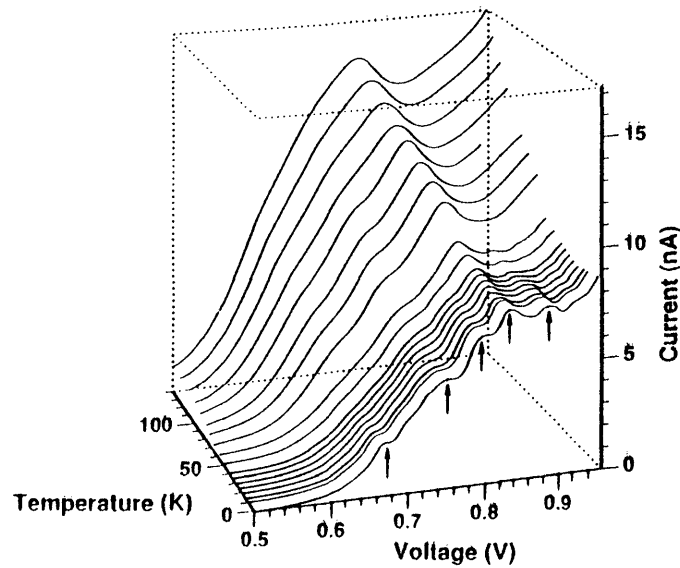


Fig. 7.20. Current-voltage effect observed in the the quantum dot structure as a function of temperature showing discrete states at the $n=2$ quantum well resonance. (After Bate [1])

7.3.2. Field Emission Tips.

The advantage of microfabricated field emission cathode sources [9, 10] is the small radius of tips ($\sim 500 \text{ \AA}$) which reduces the voltage to 50-100 V required for emission thus producing long-life devices. Fabrication of the tips requires expensive lithography steps with typical cathode arrays having over 20,000 tips in an area of about 1mm^2 .

Using the method of CsCl deposition on tungsten substrates and then etching, tips as small as $100 \text{ \AA}$ could be constructed with geometry similar to the ones shown in Fig. 7.17. The common practice of shaping the tips using several stages of the etching process could also be utilised.

7.3.3. Fast Discrete Bipolar Transistors

One of the applications suggested by my supervisor M. Green is to fabricate discrete transistors in one single wafer. The main advantage of employing this technique (Fig. 7.21) is that the base width is extremely narrow thus allowing very fast switching capabilities. The process for producing these transistors involves etching using conditions similar to run 1 (section 7.1.3) to produce the well structures as shown. This is followed by three metallisation processes for the contacts and the deposition of the silicon dioxide insulating layer. The metallisation for the base contact could lead to coverage around the sidewalls, but this could be removed by non-directional etching (for example in the high pressure conditions). The wafer can be diced to produce many of these transistors from just the one single wafer of silicon.

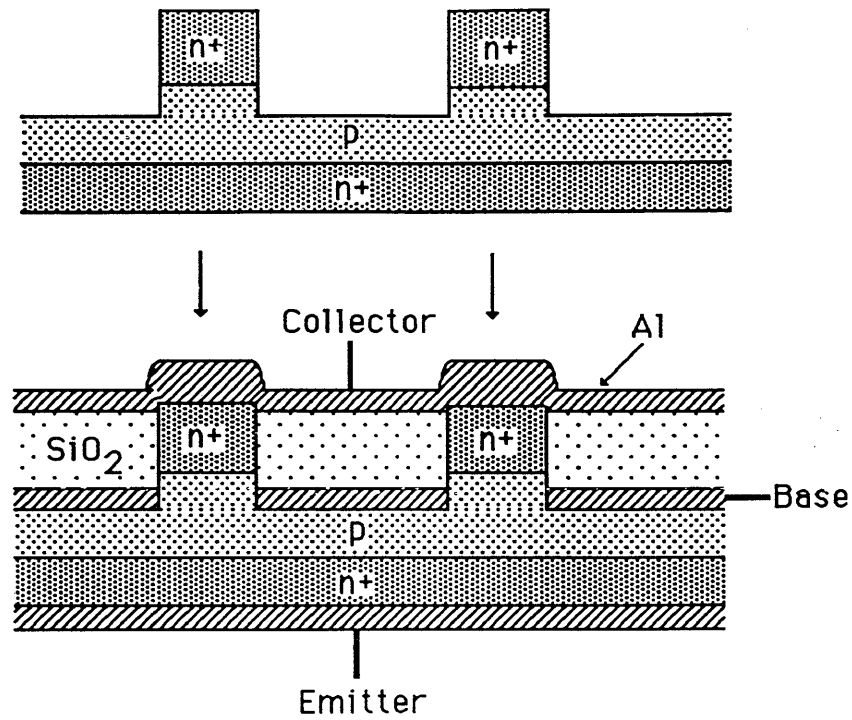


Fig. 7.21. Discrete transistor fabricated from a silicon wafer doped n^+ and p type.

CONCLUSION

E-beam lithography is the only real solution today for patterning submicron structures on a range of substrates. The image reversal technique is a very attractive method for replicating patterns onto a variety of substrates, since CdF_2 is compatible with fluorine and chlorine hydrocarbon gases and is highly etch resistant. This has been demonstrated for the case of SiO_2 and Cr films where linewidths of $0.3\text{ }\mu\text{m}$ have been obtained using the T220 and the EBMF6-5 systems. Quantum devices, on InSb substrate, are now being fabricated in this department using this technique of lift-off.

Direct writing of CdCl_2 requires high dosages of around 10 mC/cm^2 at a beam energy of 2 keV and this leads to considerable backscattering and hence broadening of the lines. Heating the substrate to an elevated temperature ($\sim 120^\circ\text{C}$) and the long periods of exposure makes this technique an unattractive proposition for e-beam lithography. One possible scheme is to use very thin films of inorganic resist ($\sim 300\text{ }\text{\AA}$) and do a 'cold beam' writing on the substrate but this will require a high intensity beam so the material might simply be evaporated off. Employing a 'cap' scheme did not improve the sensitivity sufficiently to justify its use but it has been shown to be useful for some specialised needs.

The thin film properties of CsCl were put to good use for the fabrication of quantum dots in Si. Thus far four diameter ranges have been made investigated of $600\text{ }\text{\AA}$, $800\text{ }\text{\AA}$, $3000\text{ }\text{\AA}$ and $6500\text{ }\text{\AA}$ with pillar density of about 20% of the surface area. Continued work is being undertaken in the laboratory to make dots of $100\text{ }\text{\AA}$ in diameter so that quantum effects can be readily examined at room temperature. The possibility of transferring this technique to other direct band-gap semiconductor substrates will also be examined.

REFERENCES

CHAPTER 1

Section 1.1

- [1] D. R. Herriott et al., IEEE Trans. Electron Devices, vol. **ED-22**, 385 (1975).
- [2] F. S. Oxdemir et al., in Proc. 13th Symp on Electron Ion and Photo Beam Tech., J. Vac. Sci. Technol., 1246 (May 1975).
- [3] T. P. C. Chang et al., in Proc. 7th Int. Conf. on Electron Ion and Photon Beam, Sci. and Technol. (Electrochemical Soc.), R. Bakish, Ed. 392 (1976).
- [4] G. L. Varnell et al., in Proc. 12th Symp. on Electron Ion and Photon Beam Tech., J. Vac. Sci. Technol., 1048 (May 1973).
- [5] J. Trotel, in Proc. 14th Symp. on Electron Ion and Photon Beam Tech., J. Vac. Sci. Technol., 872 (1977).
- [6] Private communication
- [7] R. D. Moore et al., in Proc. 16th Symp. on Electron Ion and Photon Beam Technol., J. Vac. Sci. Technol., vol **19**, 950 (Nov/Dec 1981).
- [8] G. A. C. Jones, G. Owen, J. Vac. Sci. Technol., **15**, No. 3, 896 (1978).
- [9] C. W. Oatley: 'The Scanning Electron Microscope ', Part 1, Chaps. 2 and 3, Cambridge Univ. Press., (1972).
- [10] O. C. Wells, ' Scanning Electron Microscopy,' Chapt. 4, 69-88, McGraw Hill (1974).
- [11] Private communication from Cambridge Instrument Ltd.
- [12] M. E. Jones, C. Dix, Br. Telecom. Technol. J., **7(1)**, 25 (1989).
- [13] C. Oshima, M. Aono, T. Tanaka, S. Kawaii and T. Tanaka, J. Vac. Sci. Technol., **15 (3)**, 933 (1978).

Section 1.2

- [1] S. A. Rishton, S. P. Beaumont, C. D. W. Wilkinson, J. Phys. E. **117**, 296 (1984).
- [2] T. Chisholm, J. Vac. Sci. Technol. **B6 (6)**, 2066 (1988).
- [3] J. R. A. Cleaver, K. C. A. Smith, Scanning Elec. Microscopy: Syst. & App. (Inst. Phys. Conf. Ser. 18), 6 (1973).

Section 1.3

- [1] D. M. Rickey, Semicon. Intern., 230 (April 1985).
- [2] "Line Measurement Audit", National Physical Laboratory.
- [3] D. A. Sywt, Solid State Technol., 55 (April 1976).
- [4] D. A. Sywt, Solid State Technol.,

CHAPTER 2

- [1] W. Bothe, *Hanb. Phys* 22/2 1 (Berlin : Springer-Verlag), (1933).
- [2] W. Bothe, *Ann. Phys. Lpz.* 6, 44-52 (1949).
- [3] H. A. Bethe, *Hanb. Phys.* 24, 519 (Berlin : Springer-Verlag) (1933).
- [4] H. A. Bethe, M. E. Rose and L. P. Smith, *Proc. Am. Phil. Soc.* 78, 583-5 (1938).
- [5] G. Wentzel, *Ann. Phys. Lpz.* 69, 335-68 (1922).
- [6] G. Wentzel, *Z. Phys.* 40, 590-3 (1927).
- [7] H. Moliere, *Z. Naturf.* 2a, 133-45 (1943).
- [8] H. Moliere, *Z. Naturf.* 3a, 78 (1948).
- [9] F. Lenz, *Z. Naturf.* 99, 185-204 (1954).
- [10] L. Marton, J. A. Simpson, H. Fowler, N. Swanson, *Phys. Rev.* 126, 182-92 (1962).
- [11] G. H. Smith and R. E. Burge, *Proc. Phys. Soc.* 81, 612-32 (1963).
- [12] V. E. Coslett and R. N. Thomas, *Br. J. Appl. Phys.* 15, 883-907 (1964).
- [13] V. E. Coslett and R. N. Thomas, *Br. J. Appl. Phys.* 15, 1283-300 (1964).
- [14] V. E. Coslett and R. N. Thomas, *Br. J. Appl. Phys.* 16, 779-96 (1965).
- [15] S. Goudsmit and J. L. Saunderson, *Phys. Rev.* 57, 24-9 (1940).
- [16] L. V. Spencer, *Phys. Rev.* 98, 1597-615 (1955).
- [17] F. Lenz, *Z. Angew. Phys.* 10, 31-4 (1958).
- [18] H. Meister, *Z. Naturf.* 3a, 809-20 (1958).
- [19] G. D. Archard, *J. Appl. Phys.* 32, 1505-9 (196).
- [20] T. E. Everhart, *J. Appl. Phys.* 31, 1483-90 (1960).
- [21] A. E. Makhov, *Sov. Phys-Solid St.* 2, 1934-41 (1960).
- [22] A. E. Makhov, *Sov. Phys-Solid St.* 2, 1942-4 (1960).
- [23] A. E. Makhov, *Sov. Phys-Solid St.* 2, 1945-51 (1960).
- [24] R. Shimizu and G. Shinoda, *X-ray Optics and X-ray Microanalysis*, ed. H. H. Pattee, V. E. Coslett and A. Engstrom (N. Y. Academic Press) 419-30, (1963).
- [25] R. F. Dasher, *Phys. Rev.* 134, A1026-32 (1964).
- [26] R. D. Birkhoff. In "Handbuck der Physik" (E. Fluegge, ed.), 53, Springer, Berlin and New York, (1958).
- [27] M. J. Berger, S. M. Seltzer, *Nat. Acad. Sci, Nat-Res. Council. Publi. No.* 1133, 205 (1964).
- [28] J.S.Greeneich, "Electron-Beam-Processes" in G.R.Brewer(ed), *Electron-Beam Technology in Microelectronic Fabrication*, Academic, New York (1980)
- [29] A. E. Gruen, *Z. Naturforsch.* 12A, 89 (1957).
- [30] T. E. Everhart and P. H. Hoff, *J. Appl. Phys.* 42 (13), 5837 (1971).

CHAPTER 2 cont.

- [31] J. S. Greeneich and T. Van Duzer, IEEE Trans. Elect. Devices **ED-20**, 6, 598 (1973).
- [32] E. H. Darlington and V. E. Cosslett, J. Phys. D: Appl. Phys. **5**, 1969 (1972).
- [33] D. F. Kyser and K. Murata, Proceed. 6th Int. Conf. Electron and Ion Beam Science and Technology, The Electrochem. Soc., Princeton, N. J. (1974).
- [34] K. Kanaya and S. O. Okayama, J. Phys. D: Appl. Phys. **5**, 43 (1971).
- [35] K. Kanaya and S. Ono, Electron Beam Interactions with Solids, SEM Conference (Chicago), 69 (1984).
- [36] J. Lindhard, M. Scharff, H. E. Schiott, K. danske Vidensk. Selsk., Math.-fy. Meddr. **33** 1-4 (1963).
- [37] K. Kanaya, H. Kawakatsu, J. Phys. D: Appl. Phys., **5**, 1727 (1972).
- [38] J. R. Young, J. Appl. Phys. **27**, 1 (1956).
- [39] J. E. Holliday, E. J. Sternglass, J. Appl. Phys., **30**, 1428 (1959).
- [40] L. E. Glendenin, Nucleonics, **2**, 12 (1948).
- [41] L. Katz, A. S. Penfold, Rev. Mod. Phys., **24**, 28 (1952).
- [42] M. J. Berger, S. M. Seltzer, NASA, SP-3012, (1964).
- [43] V. E. Cosslett, R. N. Thomas, Br. J. Appl. Phys., **16**, 779 (1965).
- [44] G. Dupouy, P. Perrier, F. Verdier and F. Arnal, C. R. Acad. Sci. Paris, **258**, 3655 (1964).
- [45] A. Ya. Vyatskin, V. V. Trunev, Radioteknika i Elektronika, **12**, 1636 (1967).
- [46] H. Niedrig, P. Seiber, Ruckstreuung mittelschneller Elektronen an dunnen Schichten, Z. angew. Phys. **31**, 27 (1971).
- [47] J. S. Greeneich and T. Van Duzer, J. Vac. Sci. Technol. **10**, 1056 (1973).
- [48] E. D. Wolf, F. S. Ozdemir, W. E. Perkins, P. Coane, Rec. Symp. Electron. Ion Laser Beam Tech., 11th. San Fransisco Press, San Fransisco, California (1971).
- [49] J. S. Greeneich and T. Van Duzer, IEEE Trans. Elect. Devices **ED-21(6)**, 286 (1974).
- [50] R. D. Heidenrich, J. P. Ballantyne and L. F. Thompson, J. Vac. Sci. Technol. **12**, 1284 (1975).
- [51] A. Sujita and T. Tamamura, J. Electrochem. Soc. **135**, 1741 (1988).
- [52] T. H. P. Chang, J. Vac. Sci. Technol. **12**, 1271 (1975).

CHAPTER 3

- [1] A. Yoshikawa, O. Ochi, H. Nagai and Y. Mizushima, *Appl. Phys. Lett.* **31**, 161 (1977).
- [2] K. L. Tai, R. G. Vadimsky, C. T. Kemmerer, J. S. Wagner, V. E. Lamberti, and A. G. Timko, *J. Vac. Sci. Technol.* **17**, 1169 (1980).
- [3] A. N. Broers, J. M. E. Harper and W. W. Molzen, *Appl. Phys. Lett.* **33(5)**, 392 (1978).
- [4] B. Singh, S. P. Beaumont, P. G. Bower and C. D. W. Wilkinson, *Appl. Phys. Lett.* **41**, 1002 (1982).
- [5] G. W. Kammlott, and W. R. Sinclair, *J. Electrochem. Soc.* **121**, 929 (1974).
- [6] A. Murray, M. Scheinfeir, M. Isaacson, I. Adesida, *J. Vac. Sci. Technol.*, **B3(1)**, 367 (1985).
- [7] M. Isaacson, A. Murray, *J. Vac. Sci. Technol.* **19**, 1117 (1981).
- [8] T. R. Harrison, P. M. Mankiewich and A. H. Dayem, *Appl. Phys. Lett.* **41**, 1102 (1982).
- [9] P. M. Mankiewich, H. G. Craighead, T. R. Harrison and A. H. Dayem, *Appl. Phys. Lett.* **44**, 1289 (1984).
- [10] I. G. Salisbury, R. S. Timsit, S. D. Berger, C. J. Humphreys, *Appl. Phys. Lett.* **45**, 1289 (1984).
- [11] M. Green, C. J. Aidinis and O. A. Fakolujo, *J. Appl. Phys.* **57**, 631 (1976).
- [12] M. Green and C. J. Aidinis, O. A. Fakolujo, *Emerging Technologies for In Situ Processing*, Pub. Martinus Nijhoff (NATO Science Affairs Division), 131 (1988).
- [13] C. J. Aidinis, M. Green, *J. Appl. Phys.* **63**, 4397 (1988).
- [14] M. G. Albecht, M. Green, *J. Phys. & Chem. Solids* **38**, 297 (1977).
- [15] Vapour Pressure Tables, *Handbook of Chemistry & Physics*, D-199 (1980).
- [16] K. L. Chopra, McGraw Hill, 'Thin Film Phenomena', **Chapt 4**, 185 (1969).
- [17] C. J. Aidinis, PhD Thesis, University of London, (1987).
- [18] O. A. Fakolujo, PhD Thesis, University of London, (1988).
- [19] R. D. Bringans and W. Y. Liang, *J. Phys. C* **14**, 1065 (1981).

CHAPTER 4

- [1] H. Yamaguchi, A. Shimase, S. Haraichi and T. Miyauchi, *J. Vac. Sci. Technol.* **B3**, 71 (1985).
- [2] L. R. Harriot and M. J. Vasile, *J. Vac. Sci. Technol.* **B6(3)**, 1035 (1988).
- [3] P. J. Heard, P. D. Prewett, *Microcircuit Engineering* **89**, Programme and Abstract B3-1 (1989).
- [4] S. J. Fonash, *Solid State Technol.* **28 (No.1)**, 150 (Jan. 1985).

CHAPTER 4 cont.

- [5] J. W. Coburn, H. F. Winters, J. Appl. Phys. 50, 3189 (1979).
- [6] D. J. Ehrlich, J. Y. Tsau, J. Vac. Sci. Technol. B1, 969 (1983).
- [7] H. F. Winters, J. W. Coburn, J. Vac. Sci. Technol. , 1376 (1985).
- [8] J. W. Coburn, H. F. Winters, Ann. Rev. Mater. Sci., 13, 95 (1983).
- [9] C. J. Mogab, "Dry Etching," in "VLSI Technology (S. M. Sze ed.), McGraw-Hill, New York (1983).
- [10] H. W. Lehmann, L. Krausbauer, R. Widmer, J. Vac. Sci. Technol. 14, 281 (1977).
- [11] J. L. Vossen, J. J. O'Neill, K. M. Finlayson, L. J. Roye, RCA Rev, vol 31, 293 (1970).
- [12] P. D. Townsend, J. C. Kelly, N. E. W. Hartley, "Ion Implantation, Sputtering and their Application," Academic Press, New York (1976).
- [13] J. W. Coburn, H. F. Winters, J. Vac. Sci. Technol. 16, 391 (1979).
- [14] D. Bollinger, S. Iida, O. Matsumoto, Solid State Technol. , May 1984.
- [15] J. L. Mauer, J. S. Logan, L. B. Zielinski, G. S. Schwartz, J. Vac. Sci. Technol. 15, 1734 (1978).
- [16] D. L. Flamm, V. M. Donnelly, Plasma Chem. Plasma Process, 1, 317 (1981).
- [17] Y. -Y. Tu, T. J. Chuang, H. F. Winters, Phys Rev. B23, 823 (1981).
- [18] S. Matsuo, J. Vac. Sci. Technol. 17, 587 (1980).
- [19] B. Garowitz, R. J. Saia, 'Reactive Ion Etching,' in 'VLSI Electronics,' N. G. Einspruch and D. M. Brown (Eds.), Microstructure Science 8, Chapt. 10, Academic Press Inc. (1984).
- [20] L. M. Ephrath, D. J. DiMaria and F. L. Pesavento, J. Electrochem. Soc. 128, 2415 (1981).
- [21] J. L. Vossen, J. Electrochem. Soc. 126, 319 (1979).
- [22] J. W. Coburn and E. Kay, J. Appl. Phys. 43, 4965 (1972).
- [23] D. K. Lam, Solid State Technol., vol.25, no. 4, 215 (Apr. 1982).
- [24] D. Bollinger, S. Iida, O. Matsumoto, Solid State Technol. 167 (June 1984).
- [25] C. J. Mogab, J. Electrochem. Soc., 124, 1262 (1977).
- [26] G. Z. Yin, D. W. Jillie, Solid State Technol., 127 (May 1987).

CHAPTER 5

- [1] O.A.Fakolujo, PhD. Thesis, University of London, 1988.
- [2] G. O. Fior, L. N. Giffen, W.W.Palmer, Solid State Technol., 109 (April 1988).
- [3] C.J.Mogab, A.C.Adams, D.L.Flamm, J. Appl. Phys., vol. 49, 3796 (1978).

CHAPTER 5 cont.

- [4] L. M. Ephrath, J. Electrochem. Soc., **126**, 1419 (1979).
- [5] K. Hirata, Y. Ozaki, M. Oda and M. Kimizuka, IEEE Trans. Electron Devices, **ED-28**, 1323 (1981).
- [6] J.W.Coburn, H.F.Winters, J. Vac. Sci. Technol. **vol. 16**, 391 (1979).
- [7] R. N. Costellano, Solid State Technol. 203 (May 1984).
- [8] M. Bowden, J. Electrochem. Soc. **128**, 1956 (1981).
- [9] A. Broers, IEEE Trans. Electron. Devices **ED-28**, 1268 (1981).
- [10] D.Bollinger, S.Iida, O.Matsumoto, Solid State Technol., **part 11**, 167, (June 1984).
- [11] Ch.Steinbruchel, H.W.Lehmann, K.Frick, J.Electrochem. Soc. (Solid State Science & Technol.), 186 (Jan 1985).
- [12] W.S.Pan, A.J.Steckl, J. Vac. Sci. Technol., **B6(4)**, 1073 (1988).
- [13] M. Green, O. A. Fakolujo, Thin Solid Films, **L 93**, 150 (1987).

CHAPTER 6

- [1] D. Shernock, Solid State Technol., 150 (May 1988).
- [2] A. Murray, M. Scheinfein, and M. Isaacson, J. Vac. Sci. Technol. **B3(1)**, 367 (1985).
- [3] F. Khaleque, M. Green, "Application of Inorganic Resists to Submicron Fabrication," (accepted for publication, see Appendix III).
- [4] A. Scherer, H. G. Craighead, J. Vac. Sci. Technol., **B5(1)**, 374 (1987).
- [5] D. A. Swyt, Solid State Technol., 55 (April 1976).
- [6] D. M. Rickey, M. R. Toof, Semicon. Int., 230 (1985).
- [7] D. A. Swyt, Solid State Technol., 70 (August 1977).
- [8] T. H. P. Chang, J. Vac. Sci. Technol., **12**, 1271 (1975).
- [9] J. S. Greeneich, T. Van Duzer, IEEE Trans. Electron Devices, **ED-21**, 286 (1974).
- [10] J. L. Balladore, M. Pyee, H. Camen, E. Bourdel, J. P. Martinez, N. Sekkaki, Microelect. Eng., 201 (1987).
- [11] E. D. Wolf, F. S. Ozdemir, W. E. Perkins, P. Coane, Rec. Symp. Electron. Ion Laser Beam Tech., 11th. San Fransisco Press, San Fransisco, California.
- [12] M. Parikh and D. E. Schreiber, IBM J. Res. Develop, **24**, 530 (1980).
- [13] H.Nakata, K.Nishioka, H.Abe, J. Vac. Sci. Technol. **17(6)**, (1980).
- [14] D. F. Kyser and R. Pyle, IBM. J. Res. & Develop., **24**, 426 (1980).

CHAPTER 7

- [1] R. T. Bate, Solid State Technol. , 101 (1989).
- [2] H. W. Deckman and J. H. Dursmiur, Appl. Phys. Lett. **41**, 377 (1982).
- [3] H. Fang, R. Zeller, and P. J. Stiles, App. Phys. Lett. **55(14)**, 1433 (1989).
- [4] T. H. P. Chang, D. P. Kern, E. Kratschmer, K. Y. Lee, H. E. Luhn, M. A. McCord, S. A. Rishton and Y. Vladimirsky, IBM J. Res. Dev. **32**, 462 (1988).
- [5] S. Matsui, Y. Kojima, Y. Ochiai, T. Honda, Microcircuit Engineering 89 (Programme & Abstracts), **B3-2**, (1989).
- [6] J. H. F. Scott-Thomas, M. A. Kastner, D. A. Antoniadis, H. I. Smith and S. B. Field, J. Vac. Sci. Technol. **B6**, 1841 (1988).
- [7] M. A. Reed et al. *ibid*, vol **B4**, 358 (1986).
- [8] M. A. Reed, Phys. Rev. Lett. vol **60**, 535 (1988).
- [9] C. A. Spindt, J. Appl. Phys. **39**, No **7**, 3504 (1988).
- [10] C. A. Spindt, I. Brodie, L. Hurmphyre and E. R. Westerberg, J. Appl. Phys. **47**, No **12**, 5248 (1976).

APPENDIX I

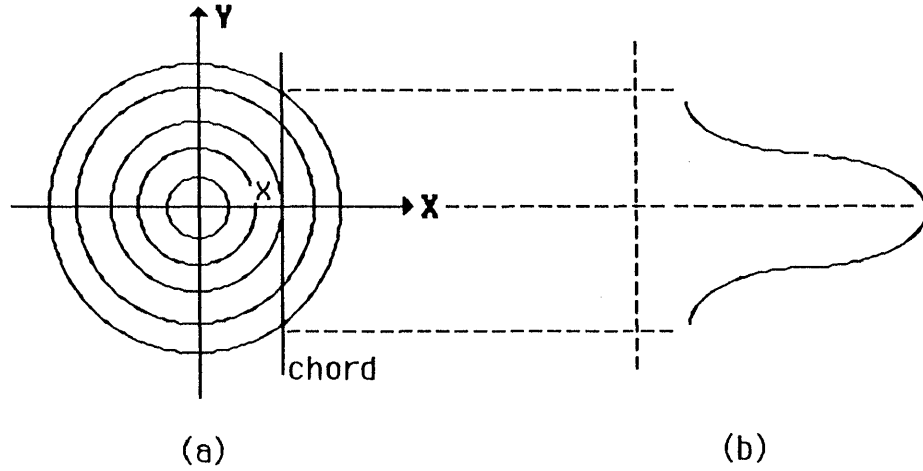


Fig. 1(a) Gaussian beam in the x, y plane with normalised axis at coordinates $(0, 0), x$ and (b) the current distribution along a chord $X=x, Y=\pm\infty$.

We consider the idealised case of an electron beam which can be represented by a Gaussian. In narrow angle, low aberration electron guns, the spot current distribution is very closely of Gaussian form.

The current density of an electron beam in terms of a Gaussian is given by,

$$J(r) = J_0 e^{-r^2/\beta^2} \quad (1)$$

where J_0 is the maximum current density at $r=0$ and β is a constant.

The beam current I_T is the integral of the Gaussian beam, ie.

$$I_T = J_0 \int_0^{2\pi} \int_0^\infty d\theta \cdot r \cdot dr \cdot e^{-r^2/\beta^2} \quad (2)$$

where $rd\theta dr$ is the element area and $e^{(-r^2/\beta^2)}$ is the relative current density of that element.

Integrating (2) gives,

$$I_T = J_0 \pi \beta^2 \quad (3)$$

The Gaussian beam is scanned over the silicon edge giving rise to a current detected in the Faraday Cup. In order to determine the equations of the output current we shall consider the chord (Fig. 1a) to represent the silicon edge.

Current density at the slice $X=x$, $Y=\pm\infty$ is also a Gaussian and the maximum value is at $X=x$, $Y=0$ (Fig. 1b).

This is given by,

$$J(y) = J_0 e^{-x^2/\beta^2} \quad (4)$$

where J_0 is the maximum value of the beam (ie. at $X=0$, $Y=0$). Therefore the Gaussian on the slice at x is given by,

$$J(y) = (J_0 e^{-x^2/\beta^2}) e^{-y^2/\beta^2} \quad (5)$$

The current in a slice dx wide is given by,

$$I(dx) = J_0 (e^{-x^2/\beta^2}) \int_{-\infty}^{+\infty} e^{-y^2/\beta^2} dy \cdot dx \quad (6)$$

$$= J_0 \sqrt{\pi} \beta e^{-x^2/\beta^2} dx \quad (7)$$

For part of the half circle from 0 to x and $y=\pm\infty$ we have,

$$I(x) = J_0 \sqrt{\pi} \beta \int_0^x e^{-x^2/\beta^2} dx \quad (8)$$

Let $t=x/\beta$ so $t=dx/\beta$, therefore

$$I(x) = J_0 \sqrt{\pi} \beta^2 \int_0^t e^{-t^2} dt \quad (9)$$

Now the integral

$$\frac{2}{\sqrt{\pi}} \int_0^t e^{-t^2} dt$$

can be solved numerically and this gives the **error function** ie.,

$$\int_0^t e^{-t^2} dt = \frac{\sqrt{\pi}}{2} [\text{error function of } t] \quad (10)$$

This has been plotted in Fig. 2.

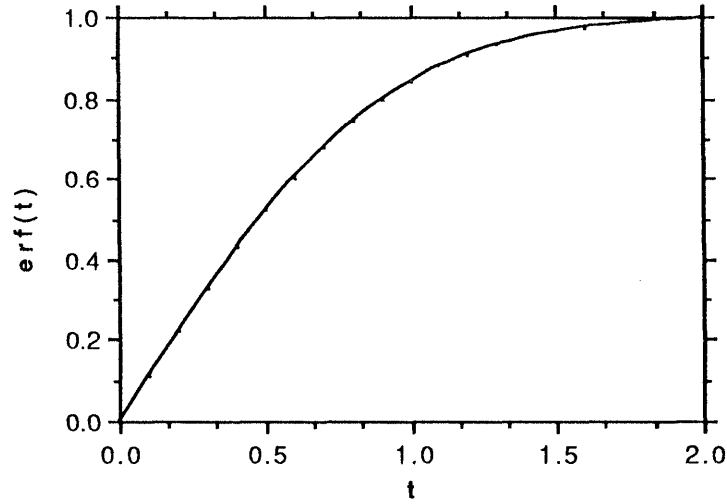


Fig. 2. Graph of the error function erf(t).

Equation 9 can thus be rewritten as,

$$I(x) = \frac{J_0 \pi \beta^2}{2} \left[\text{erf} \left(\frac{x}{\beta} \right) \right]$$

and

$$I(x) = \frac{I_T}{2} \left[\text{erf} \left(\frac{x}{\beta} \right) \right]$$

If we define $r=\sigma$ when $J(r)/J_{\max} = e^{-1/2}$ then $x/\beta = 1/\sqrt{2}$ which corresponds to 16% and 84% in the error function graph giving 68% of the total beam current within this diameter.

APPENDIX II

Optimisation based on the orthogonal tables can be efficiently used with our present RIE (Plasmalab 80). A first time user with no knowledge of the etch rate and selectivity or someone running a completely new process can utilise the L_42^3 orthogonal table. This table requires only 4 runs to be made and will provide a good insight into the effects of power, pressure and gas flow on the etch rate and selectivity. An $L_{16}4^5$ can take into account the effects of 3 different gases and this table only requires 16 runs.

Tables 1, 2 and 3 are listings of the above tables with the corresponding output calculations including the L_93^4 table. The effect of each input variable such as E_{pO} is averaged over the same setting and the difference in the maximum and minimum values determine its overall effect on the etch rate.

As we are primarily concerned with the etch rate and selectivity, these two are chosen as the outputs. It is easily possible to quantify other output functions such as anisotropy or uniformity and the calculations remain exactly the same.

Table 1.

L_42^3 matrix with two level settings for each input parameter.

RUN	INPUT PARAMETER			OUTPUT	
	POWER (W)	PRESSURE (mT)	GAS FLOW (sccm)	ETCH RATE (Å/min)	SELEC- TIVITY
1	1	1	1	E_1	S_1
2	1	2	2	E_2	S_2
3	2	1	2	E_3	S_3
4	2	2	1	E_4	S_4

Output Calculations

Etch Rate:

$$E_{Po1} = (E_1 + E_2)/2 \quad E_{Pr1} = (E_1 + E_3)/2 \quad E_{Flo1} = (E_1 + E_4)/2$$

$$E_{Po2} = (E_3 + E_4)/2 \quad E_{Pr2} = (E_2 + E_4)/2 \quad E_{Flo2} = (E_2 + E_3)/2$$

$$\Delta E_{Po} = E_{Po}(\max) - E_{Po}(\min)$$

$$\Delta E_{Pr} = E_{Pr}(\max) - E_{Pr}(\min)$$

$$\Delta E_{Flo} = E_{Flo}(\max) - E_{Flo}(\min)$$

Selectivity:

$$S_{Po1} = (S_1 + S_2)/2 \quad S_{Pr1} = (S_1 + S_3)/2 \quad S_{Flo1} = (S_1 + S_4)/2$$

$$S_{Po2} = (S_3 + S_4)/2 \quad S_{Pr2} = (S_2 + S_4)/2 \quad S_{Flo2} = (S_2 + S_3)/2$$

$$\Delta S_{Po} = S_{Po}(\max) - S_{Po}(\min)$$

$$\Delta S_{Pr} = S_{Pr}(\max) - S_{Pr}(\min)$$

$$\Delta S_{Flo} = S_{Flo}(\max) - S_{Flo}(\min)$$

Table 2.

L₉3⁴ matrix with three level settings for each input parameter.

RUN	INPUT PARAMETER				OUTPUT	
	POWER (W)	PRESSURE (mT)	GAS 1 (sccm)	GAS 2 (sccm)	ETCH RATE (Å/min)	SELEC- TIVITY
1	1	1	1	1	E ₁	S ₁
2	1	2	2	2	E ₂	S ₂
3	1	3	3	3	E ₃	S ₃
4	2	1	2	3	E ₄	S ₄
5	2	2	3	1	E ₅	S ₅
6	2	3	1	2	E ₆	S ₆
7	3	1	3	2	E ₇	S ₇
8	3	2	1	3	E ₈	S ₈
9	3	3	2	1	E ₉	S ₉

Output Calculations

Etch Rate:

$$E_{Po1} = (E_1 + E_2 + E_3)/3$$

$$E_{Pr1} = (E_1 + E_4 + E_7)/3$$

$$E_{Po2} = (E_4 + E_5 + E_6)/3$$

$$E_{Pr2} = (E_2 + E_5 + E_8)/3$$

$$E_{Po3} = (E_7 + E_8 + E_9)/3$$

$$E_{Pr3} = (E_3 + E_6 + E_9)/3$$

$$\Delta E_{Po} = E_{Po}(\max) - E_{Po}(\min)$$

$$\Delta E_{Pr} = E_{Pr}(\max) - E_{Pr}(\min)$$

$$E_{Gas11} = (E_1 + E_6 + E_8)/3$$

$$E_{Gas21} = (E_1 + E_5 + E_9)/3$$

$$E_{Gas12} = (E_2 + E_4 + E_9)/3$$

$$E_{Gas22} = (E_2 + E_6 + E_7)/3$$

$$E_{Gas13} = (E_3 + E_5 + E_7)/3$$

$$E_{Gas23} = (E_3 + E_4 + E_8)/3$$

$$\Delta E_{Gas1} = E_{Gas1}(\max) - E_{Gas1}(\min)$$

$$\Delta E_{Gas2} = E_{Gas2}(\max) - E_{Gas2}(\min)$$

Table 3.

L₁₆4⁵ matrix with four level settings for each input parameter.

RUN	INPUT PARAMETER					OUTPUT	
	POWER (W)	PRESSURE (mT)	GAS 1 (sccm)	GAS 2 (sccm)	GAS 3 (sccm)	ETCH RATE (Å/min)	SELEC- TIVITY
1	1	1	1	1	1	E ₁	S ₁
2	1	2	2	2	2	E ₂	S ₂
3	1	3	3	3	3	E ₃	S ₃
4	1	4	4	4	4	E ₄	S ₄
5	2	1	2	3	4	E ₅	S ₅
6	2	2	1	4	3	E ₆	S ₆
7	2	3	4	1	2	E ₇	S ₇
8	2	4	3	2	1	E ₈	S ₈
9	3	1	3	4	2	E ₉	S ₉
10	3	2	4	3	1	E ₁₀	S ₁₀
11	3	3	1	2	4	E ₁₁	S ₁₁
12	3	4	2	1	3	E ₁₂	S ₁₂
13	4	1	4	2	3	E ₁₃	S ₁₃
14	4	2	3	1	4	E ₁₄	S ₁₄
15	4	3	2	4	1	E ₁₅	S ₁₅
16	4	4	1	3	2	E ₁₆	S ₁₆

APPENDIX III

APPLICATIONS OF INORGANIC RESISTS TO SUB-MICRON FABRICATION

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Various materials (AlF_3 [1], CdCl_2 [2], $\text{BaF}_2/\text{SrF}_2$ [3], Ag_2Se [4]) have been used as resists in a variety of fabrication schemes. The attraction of these materials has been their usefulness in direct-write schemes as e.g. in ion beam writing; or in image reversal going from low to high etch selectivity as carried out by Scherer and Craighead [3]; or in their potential for special pattern fabrication; or in the direct writing of metal lines reported here. In each case it is only the fact that the inorganic material may have a much better or unique property which makes it useful, since it is clear that organic resists have universal acceptance

We first make some fairly general comments about the mechanism of e-beam decomposition of inorganic solids, and then follow this with their use in various schemes.

When a high energy electron traverses a thin film of inorganic, wide band gap, material its main energy loss process is the excitation of energetic electron/hole pairs. These electron/hole pairs decay to their respective band edges where they have relatively long life (10^{-10} – 10^{-6} seconds). The band edge electron/hole pairs may recombine or may participate in chemical decomposition. A variety of decomposition processes may occur. We have observed two types, namely [5] the surface anion/cation type (CdCl_2) and [6] the surface anion, bulk cation type (PbCl_2). In all inorganic decompositions temperature plays an important role, since desorption and vacancy motion both increase with temperature – while recombination is relatively temperature independent. This thermal requirement gives rise to the " $2/3$ Rule", which states that [7]: as a broad guide, electron induced decomposition will occur when the solid is about equal to or greater than $2/3$ of its melting point in °C. The mechanisms are illustrated in Figures 1 and 2.

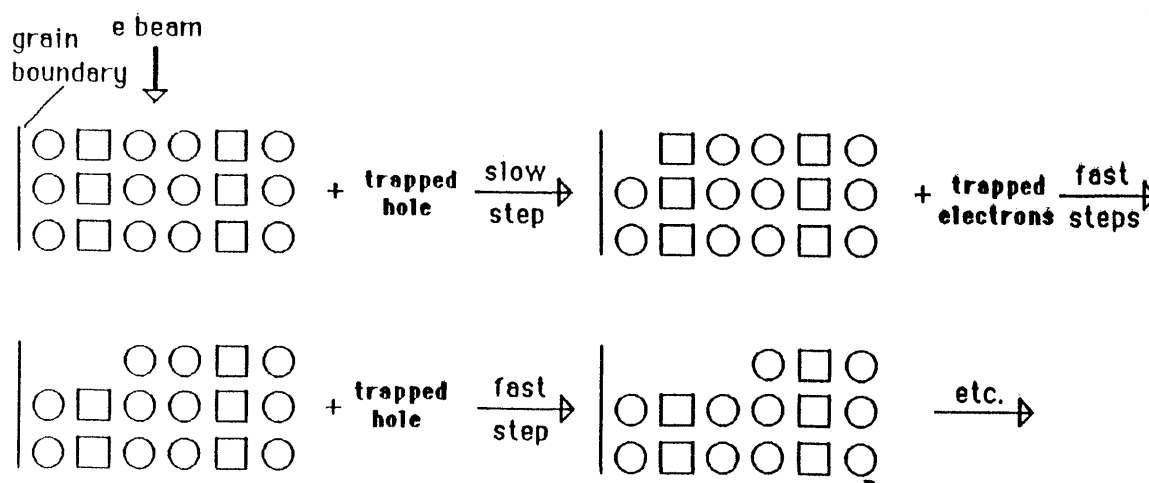


FIGURE 1
Surface anion (○)/cation (□) decomposition mechanism

We have used CdCl_2 (and CdBr_2 or CdI_2) in direct decomposition schemes: at temperatures above 90°C both elements of the molecule are volatile in the e-beam machine so that no development is necessary, since a trench with a clean bottom can be produced. Some of the characteristics of CdCl_2 as resist are listed below:

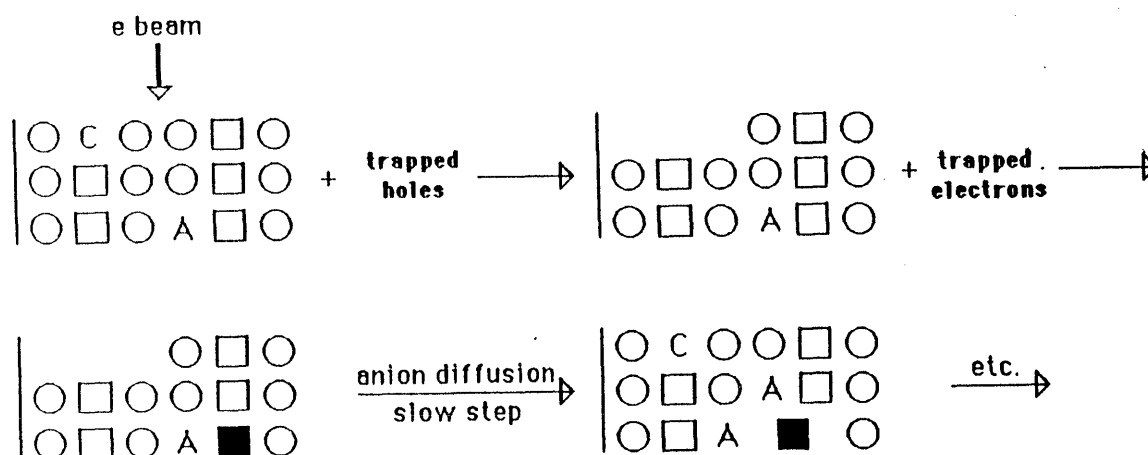


FIGURE 2

Surface anion/bulk cation decomposition mechanism. The surface anion loss is reset by bulk diffusion, which is the slow step. Cation discharge in bulk gives metal particles.

Contrast: 0.9

Sensitivity: $25 \text{ mC/cm}^2 \sim$ at 10KeV

Resolution: $\lesssim 50\text{nm}$ (grain size limited)

Sidewall angle: for film thickness equal to radius of Gaussian beam; 60°

Selectivity: with respect to SiO_2 in fluorine RIE, 20 to > 100 depending on conditions.

Stripping: highly water soluble; or evaporation $> 250^\circ\text{C}$

Inorganic resists lend themselves to various cap schemes for sensitivity improvement and for special fabrication needs. Thus Scherer and Craighead [3] have claimed that e-beam exposure of 1:1, $\text{BaF}_2\text{:SrF}_2$ produces a water insoluble material with a write sensitivity of $25\text{--}100\mu\text{C/cm}^2$. We suggest that this is due to a combination of the formation of hydrated barium/strontium oxide and grain growth under an electron beam of sufficient power density to cause local heating. CdCl_2 could also be given an oxide cap in this way, and at lower power densities, but we have not yet tried it. We have however used the difference in vapour pressure versus temperature characteristics to improve sensitivity (approximately a factor of four) and show that a tri-level scheme, such as depicted in Figure 3, should be possible.

Inorganic halides do not react chemically in halide plasmas, except to exchange to the extent of the top one or two atomic layers [8]. Thus the only mechanism of resist loss is through sputtering. We have used CdF_2 as a resist in RIE where it acts as a pattern reversal mask. The scheme is shown in Figure 4. Figure 5 shows an example of a mesa structure using CdF_2 and a fluorine etch. We are currently using CdF_2 for the fabrication of 100 nm wide quantum wire structures on InSb using a chlorine etch. Other fabricated structures, e.g. Cr lines* on glass point to a resolution of ca. 10 nm or smaller and a selectivity of ~ 40 to ~ 100 depending upon conditions. One molar phosphoric acid solution is used to remove the CdF_2 resist.

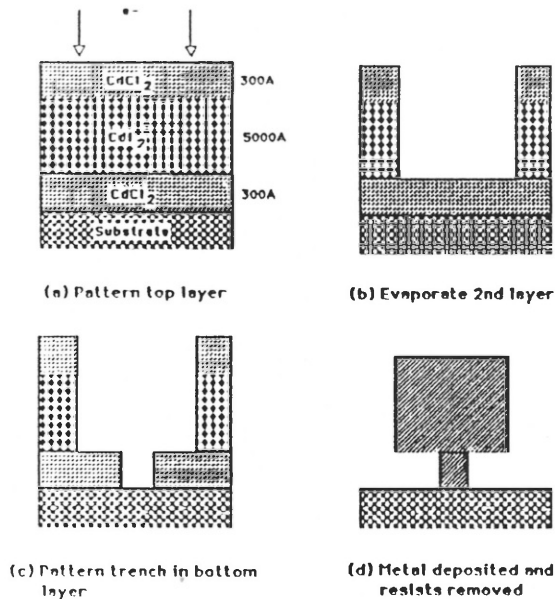


FIGURE 3
Tri-level scheme for T-bar fabrication

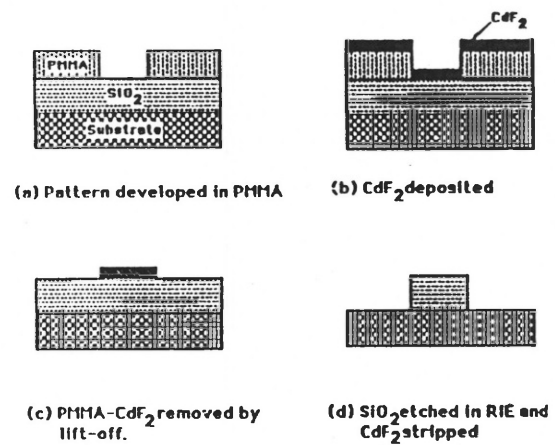


FIGURE 4
Pattern reversal using CdF_2

PbCl_2 under e-beam irradiation decomposes at temperatures $\geq 100^\circ\text{C}$ into lead and chlorine, cf Fig. 2. We find that the lead produced tends to be a discontinuous "balled-up" stripe. On the other hand, when a 80:20 $\text{PbCl}_2:\text{CdCl}_2$ film is e-beam decomposed at $\geq 100^\circ\text{C}$, the resulting alloy is continuous. We have fabricated $600\mu\text{m}$ long ribbons $2\mu\text{m}$ wide and $0.07\mu\text{m}$ thick [8]. The dose required was $14\mu\text{C}/\text{m}$ at 10KeV . The adhesion to the surface was insufficiently strong to resist the strain in the ribbon which caused the edges to roll-up to give ribbons of final width about $0.7\mu\text{m}$. The ribbons were strong and continuous as evidenced by the fact that where they become detached from the surface (during masking) they did not break-up.

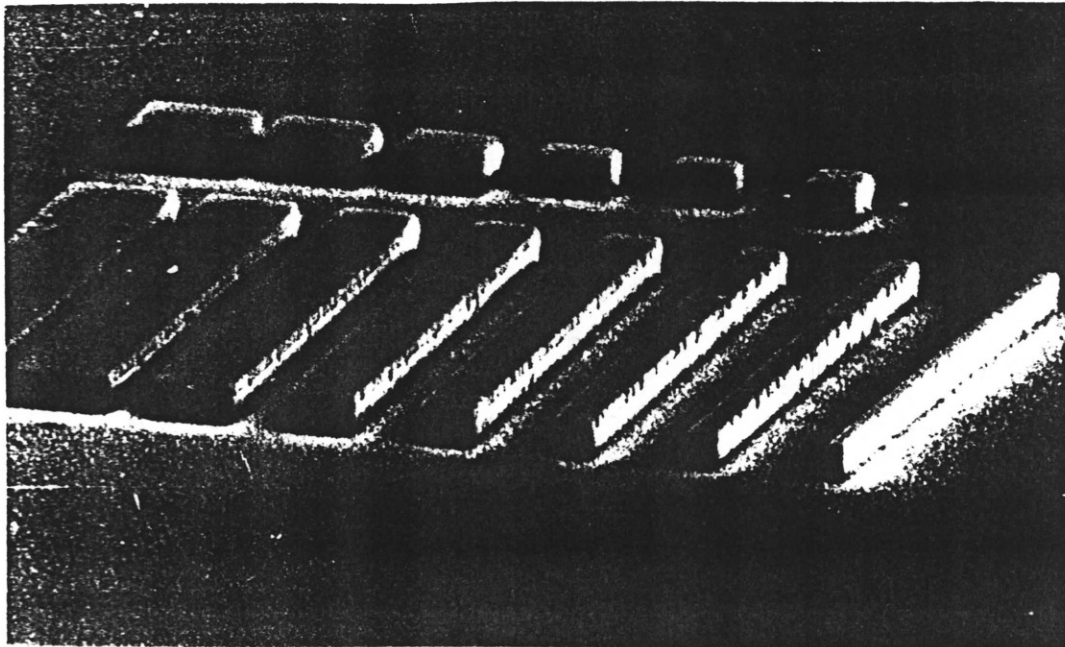


FIGURE 5
 SiO_2 pattern (on Si) produced using CdF_2 resist. Initial RIE was low pressure (rough edges produced) final RIE was high pressure (smooth sides). Smallest line (on right hand side) is $1\mu\text{m}$ high, $0.4\mu\text{m}$ wide and $40\mu\text{m}$ long.

We conclude that a combination of organic and inorganic resists for high selectivity pattern reversal using CdF_2 is going to be very useful in a range of IC fabrication schemes. The use of inorganic materials as direct write resists is more problematical: it would seem that there has to be a very strong incentive before the integrity of the internal environment of the e-beam machine is put at possible risk. This point needs further investigation. Finally, bearing in mind the environmental point, metal patterns (and local diffusion sources) can easily be made using e-beam decomposition.

REFERENCES

- [1] Murray, A., Schienfein, M. and Isaacson, M., J. Vac. Sci. Technol. B3 (1985) 367.
- [2] Green, M., Aidinis, C.J. and Fakolujo, O.A., J. Appl. Phys., 57 (1985) 631
- [3] Scherer, A. and Craighead, H.G., J. Vac. Sci. Technol., B5 (1987) 374
- [4] Singh, B., Beaumont, S.P., Webb, A., Bayer, P.G. and Wilkinson, C.D.W., J. Vac. Sci. Technol. B1 (1983) 1174
- [5] Aidinis, C.J., and Green, M., J. Appl. Phys. 63 (1988) 4397
- [6] Albrecht, M.G. and Green, M., J. Phys. Chem. Solids 38 (1977) 297
- [7] Green, M., Aidinis, C.J. and Fakolujo, O.A., Emerging Technologies for In Situ Processing, Pub. Martinus Nijhoff (NATO Science Affairs Division) (1988) 131
- [8] Fakolujo, O.A., PhD Thesis, University of London, 1988.

Thin film inorganic resists for submicron fabrication

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ABSTRACT

Submicron features have been fabricated in silicon dioxide and chromium using cadmium fluoride (CdF_2) in a lift-off mask scheme. High resolution lines are patterned by the e-beam on PMMA on a SiO_2 substrate and a thin film of CdF_2 is then evaporated. Following a lift-off stage in chloroform a pattern reversal of the PMMA image is obtained in CdF_2 which is then etched in the RIE mode providing a high selectivity with SiO_2 (>30) and giving a highly anisotropic etch in SiO_2 . In this way, high resolution submicron features in silicon dioxide with dimensions of $0.4\mu\text{m}$ (wide) and $1\mu\text{m}$ (deep) have been obtained. A similar procedure was used for chromium on glass.

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1. INTRODUCTION

Scherer and Craighead¹ have fabricated quantum well structures using a barium/strontium fluoride alloy as the lift-off mask in an image reversal scheme. The etch resistance of this material (selectivity) with respect to GaAs, glass, and Cr is high. The aim of this paper is to describe similar work that we have been doing using cadmium fluoride and PMMA e-beam resists. CdF_2 is compatible with both fluorine and chlorine plasmas.

Organic electron beam resists such as PMMA, EBR-9 and CMS² are widely used in the pattern transfer of SiO_2 on Si; chromium for mask fabrication; and various

lift-off strategies for metal gate fabrication. For high resolution, thin films of e-beam resist are favoured^{3,4} because of reduced forward and backscattering of primary electrons in the resist. Heidenrich et al⁵ used Monte Carlo methods to calculate the effects of film thickness and e-beam energy on the contour widths (effectively the linewidths) after complete development down to the substrate. The results are summarised in Fig.1. The normal working energies used in e-beam lithography today is 20keV. The data indicates two clear trends. For a given resist thickness the linewidth remains a minimum constant value beyond some incident electron energy. A decrease in linewidth occurs over a broad range of beam energies for thick films. Hatzakis and Broers⁶ have confirmed these results experimentally on thick PMMA. Thin films also allow low operating beam energies to be used without any significant loss in linewidth permitting writing time reduction of the resist because of the lower dosage required at these energies. Resist sensitivity and proximity effect are considerably improved by decreasing the beam energy⁷. It is therefore highly advantageous to have a scheme employing thin layers of e-beam resist.

Process engineers are currently restricted to thick films as they provide good adhesion, reduced pinholes and greater protection against RIE. For dry processing the thickness of the organic resist is required to be at least twice the thickness of the underlying film to be etched allowing for overetching for non-uniform films. These limitations imposed on organic resists have somewhat hindered the progress towards submicron technology. As a consequence of this, considerable research activity has gone into inorganic and multilevel resists. They offer a high etch resistance to plasma etching but their sensitivities are generally poor^{8,9,10}. By using a combination of thin organic and inorganic resists it is possible to overcome many of the associated problems related to resist processing.

11. RESULTS AND DISCUSSION

We show results of a scheme in which submicron features have been fabricated on SiO_2 . The steps required for such a process are indicated in Fig.2. A 3 inch silicon wafer with $1\mu\text{m}$ of thermal oxide is first coated with PMMA (mol. wt. approximately 500,000) in a xylene solvent and baked at 120°C for 30 minutes. Following e-beam exposure and development cadmium fluoride (Alfa Products, W. Germany, ultrapure grade) was thermally evaporated in a shuttered evaporation system (base pressure $< 10^{-6}$ torr) from a heated molybdenum boat. Rate of deposited material was approximately 3nm/s monitored on a digital (Intellemetrics) film thickness monitor. Post-baking was not required at this stage since a lift-off in chloroform at room temperature will produce the negative image in CdF_2 only. The wafer is subsequently etched in a RIE and the resist stripped by immersing in one molar phosphoric acid solution followed by flooding in distilled water. Exposure was carried out on a JEOL T220 SEM (modified for e-beam writing) and in the photo mode of a JEOL T100 SEM. Etching was carried out in a Plasmalab (Microprocessor Series 80) in the RIE mode with 170mm diameter graphite cathode and 240mm Al anode and electrode spacings of 50mm.

Cadmium fluoride grain size in the film was determined (Fig.3) by etching the film, to develop the grain boundaries. A dilute solution of H_3PO_4 was used as a developer followed by rinsing in deionised water. The grain size was determined by drawing a line across the micrograph and dividing this length by the number of grain boundaries intersecting this line. The mean grain size was found to be approximately equal to half the film thickness. Resolution of the etched profiles is

not limited by the grain size of the CdF_2 but rather by the profiles formed on the PMMA. This is depicted in Fig.4 where film growth is also seen to be faster at the steps of the PMMA wall.

Fig.5 shows the etched mesa profile obtained for the conditions indicated in the caption. The initial thickness of the PMMA used to carry out the exposure was about 160nm measured with a stylus depth measuring instrument (Talystep, Rank Taylor Hobs. Ltd UK). CdF_2 to a thickness of 54nm was deposited; measured with an ellipsometer (Rudolph Research Auto EL3). Since CdF_2 thickness on PMMA cannot be measured directly, a small test piece of the bare SiO_2/Si substrate was coated with CdF_2 at the time as the original patterned sample in order to carry out this measurement. The etching is highly selective ($\text{SiO}_2/\text{CdF}_2 > 30$) and anisotropic. The roundness at the base of the structure (cf. Fig.4) is a result of spatial non-uniformity near a feature edge. The etch rate of SiO_2 with this process is about 20nm/min.

All electron micrographs shown are tilted in the plane at right angles to the axis on which the scale is shown.

A new set of parameters were selected for the etched features shown in Fig.6. RF power of 200 watts, pressure of 50mT and gas flows of 25 sccm CHF_3 and 25 sccm Ar were employed for this process. Initial PMMA film thickness of 400nm and a CdF_2 film 182nm thickness was deposited to produce the reverse pattern. Slight tapering of the etched feature is evident for this set of conditions. This is due to the slight lateral CdF_2 resist erosion around its perimeter (Fig.2c). For these conditions, the selectivity of SiO_2 to CdF_2 is ~ 10 . Considerable ion bombardment occurs at this power and

pressure (DC Bias 210V) leading to very sharp edges at the base of the structure and high etch rate of SiO₂ (45nm/min).

The etch rate of Si was determined for the same conditions mentioned immediately above. Fig.7 shows the small degree of etching of Si (CdF₂ stripped). Clearly, the etch rate selectivity of SiO₂/Si is very high as noted by Coburn and Winters¹¹ for etching in CHF₃ where SiO₂/Si selectivity is very dependent on the C:F ratio. It should be possible to tailor the edge profiles by changing the power and pressure settings.

Chromium lines have been etched on a 2.5 inch glass plate coated in a 80nm thick film of Cr using this image reversal technique with a combination of chlorine, oxygen and argon gas (Fig.8). Edge resolution is better than 10nm and is mainly dependent on the resolution of the PMMA resist, electron scattering , and the noise on the deflected e-beam.

III. CONCLUSIONS

The above technique for producing submicron profiles has potential applications for nano-lithography. Pinholes in organic resist resulting from plasma processing are not a problem encountered when inorganic material is used. The high etch resistance offered by the inorganic resist to plasma etching allows the use of very thin films. Low e-beam writing voltages can be utilised to increase the efficiency of the writing time for higher throughput. The possibility of using other inorganic halide resists compatible with various substrates exists.

V. FIGURE CAPTIONS

Fig.1 Computed variation of contour width W as a function of incident electron energy for three resist thicknesses. The computed Bethe range of electrons in the resist is also shown. (*After Heidenreich et al. Ref 5*)

Fig.2 Patterning of SiO_2 using CdF_2 as a pattern reversal mask.

Fig.3 Grain structures of a CdF_2 film (180nm) after etching in a dilute solution of H_3PO_4 .

Fig.4 Film structure of CdF_2 at a PMMA edge.

Fig.5 SiO_2 profile obtained with RIE conditions: rf power 93 watts, pressure 270mT, 35 sccm CHF_3 , 14% O_2 , dc bias 145V, etch time 60 mins (e-beam exposure in JEOL T100, specimen tilt 80° , mark spacing $1\mu\text{m}$).

Fig.6 Line and square features in SiO_2 , minimum linewidth $0.4\mu\text{m}$. Etching conditions: rf power 200 watts, 50mT pressure, 25sccm CHF_3 , 25sccm Ar, dc bias 210V, etch time 20 mins (e-beam exposure in JEOL T220, specimen tilt 70° , mark spacing $10\mu\text{m}$).

Fig.7 Si substrate etched with the same conditions as in fig.5 to show the high selectivity obtained with the combination of CHF_3 and Ar (specimen tilt 45° , mark spacing $10\mu\text{m}$).

Fig.8 Chromium lines fabricated on a photomask with etch conditions: Pressure 30mT, RF Power 100W, Etch Time 3.5mins, 10sccm O_2 , 10sccm Ar, 20sccm Cl_2 (dust particles have collected on the substrate outside the clean room).

IV. REFERENCES

- ¹A. Scherer, H. G. Craighead, J. Vac. Sci. Technol. B **1**, 374 (1987).
- ²S. M. Sze, 'VLSI Technology,' 2nd edition, McGraw-Hill, 158 (1988).
- ³M. Bowden, J. Electrochem. Soc. **128**, 1956 (1981).
- ⁴A. Broers, IEEE Trans. Electron. Devices ED-28, 1268 (1981).
- ⁵R. D. Heidenrich, J. P. Ballantyne and L. F. Thompson, J. Vac. Sci. Technol. **12**, 1284 (1975).
- ⁶M. Hatzakis and A. N. Broers, 'Proc. 11th Symp. on Electron Ion and Laser Beam Technol.' R. F. Thornley Editor, 337, San Fransisco Press, San Fransisco, Calif. (1971).
- ⁷A. Sujita and T. Tamamura, J. Electrochem. Soc. **135**, 1741 (1988).
- ⁸P. M. Mankiewich, H. G. Craighead, T. R. Harrison, A. H. Daylem, App. Phys. Lett. **44**, 468 (1984).
- ⁹B. Singh, S. P. Beaumont, A. Webb, A. G. Bower and C. D. W. Wilkinson, J. Vac. Sci. Technol., 1174 (1983).
- ¹⁰M. Isaacson, A. Murray, J. Vac. Sci. Technol. **19**, 1117 (1981).
- ¹¹J. W. Coburn, H. F. Winters, J. Vac. Sci. Technol. **16**, 391 (1979).

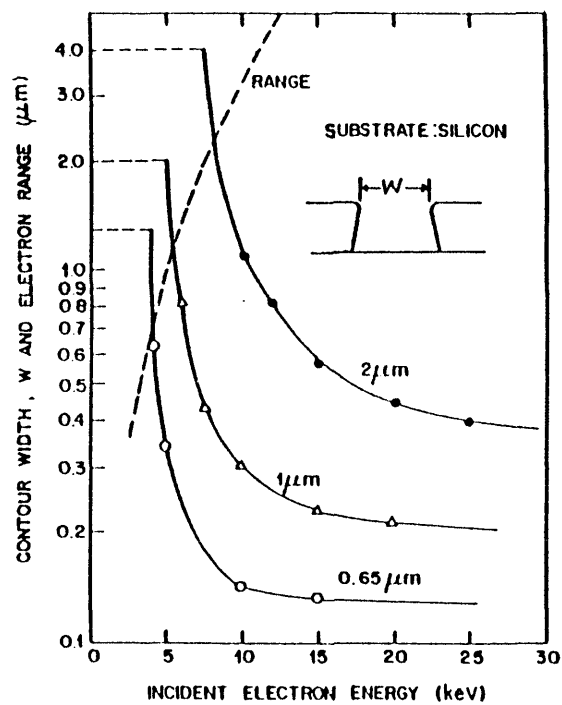


Fig.1.

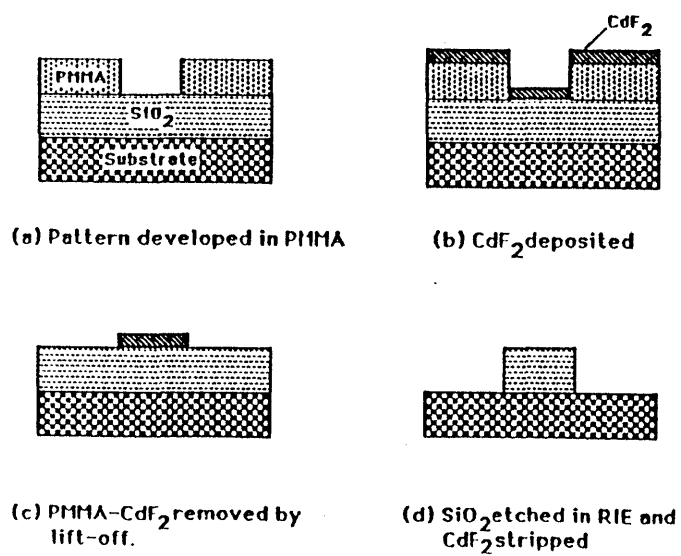


Fig.2.

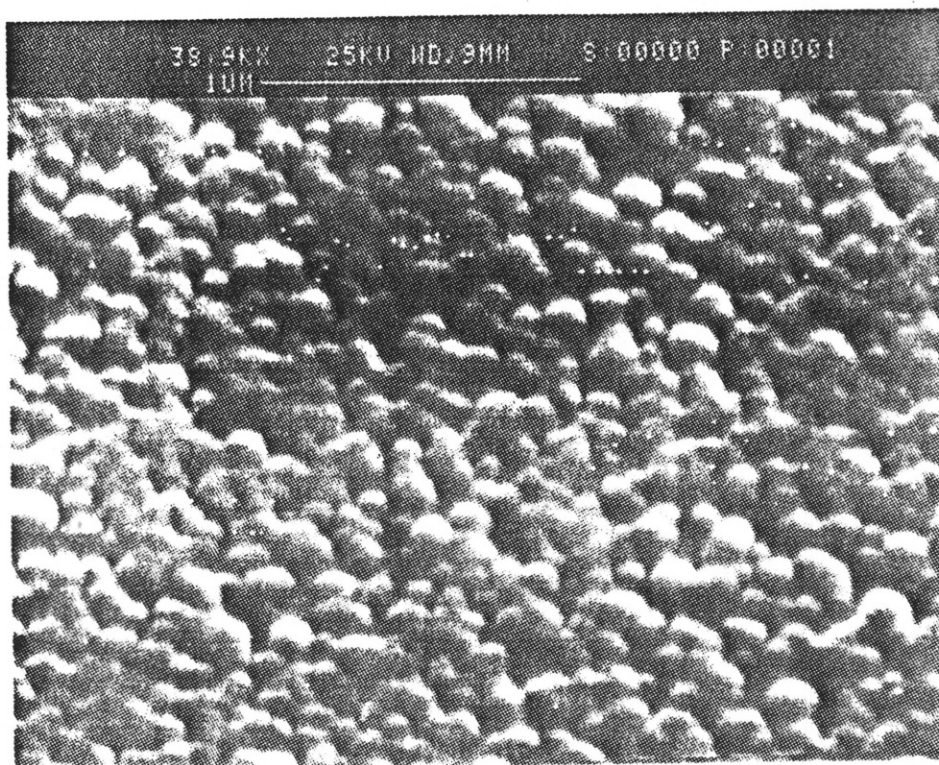


Fig.3.

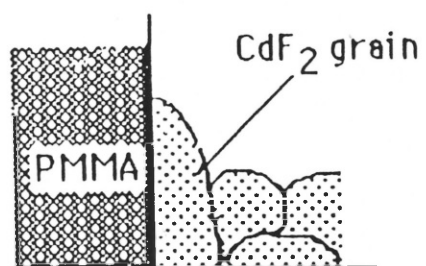


Fig.4.

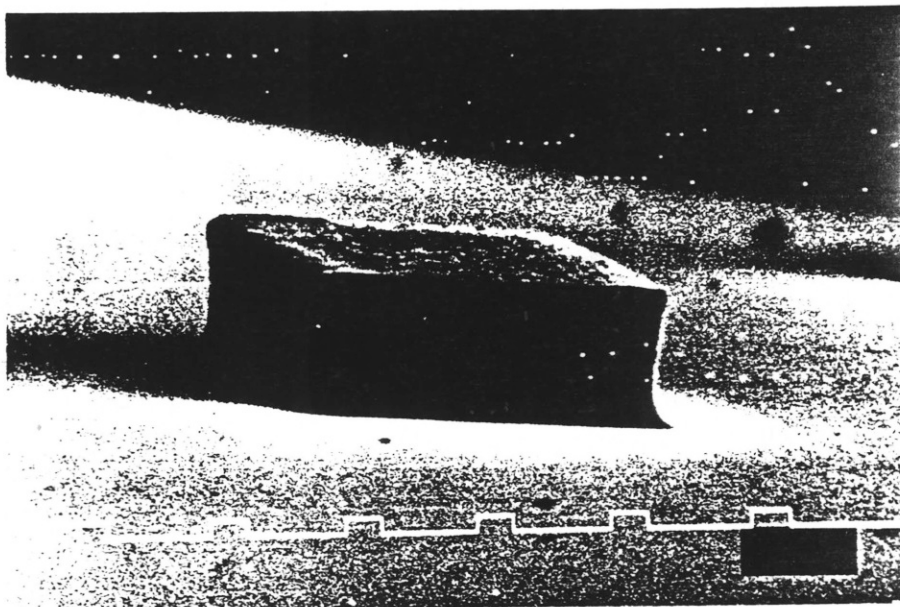


Fig.5.

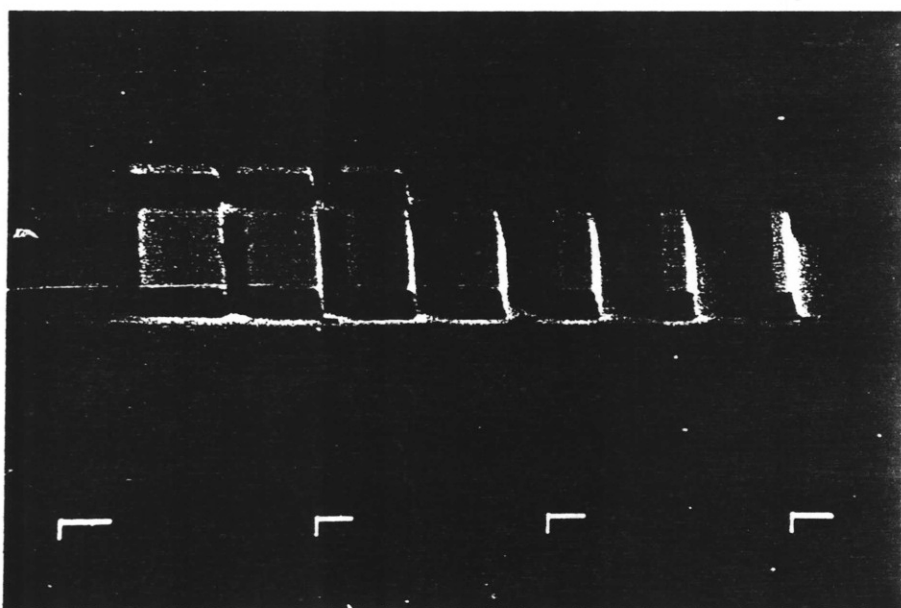


Fig.6.

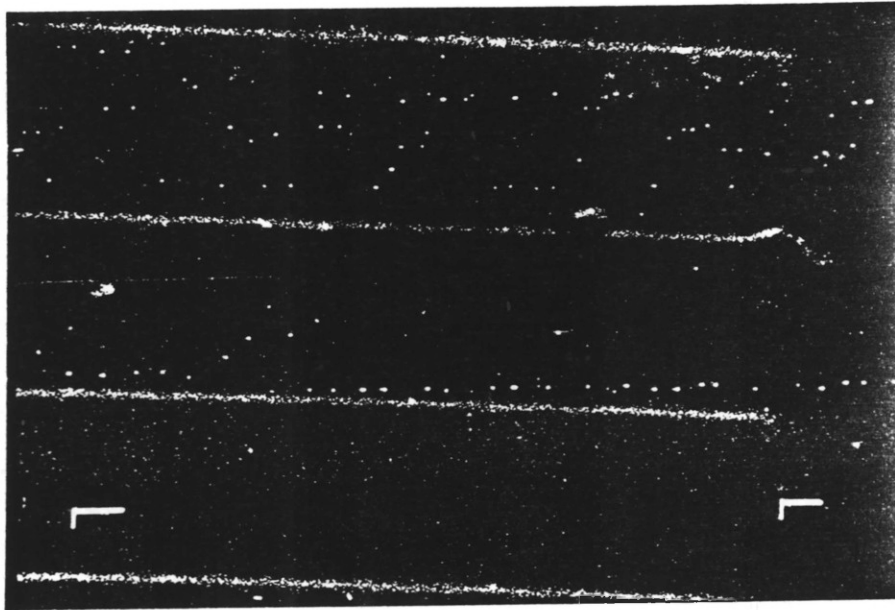


Fig.7.

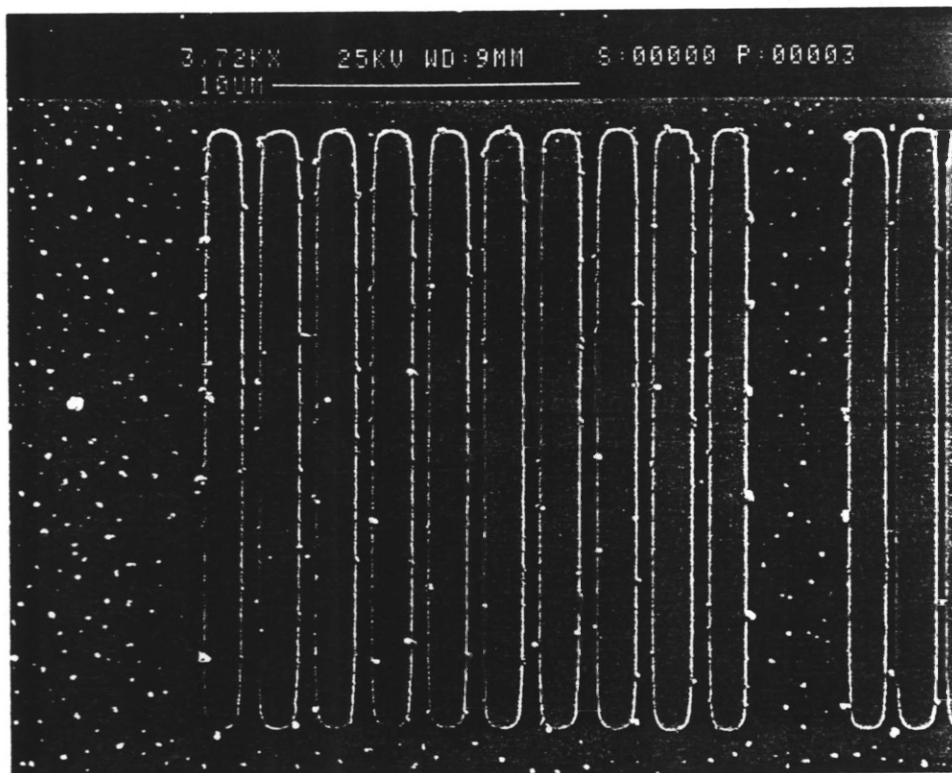


Fig.8.