Control of grain-boundary tunneling barriers in polycrystalline silicon

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The effect of oxidation and annealing on the electrical properties of grain boundaries (GBs) in heavily doped polycrystalline silicon is characterized using bulk films and 30-nm-wide nanowires. Oxidation at 650–750 °C selectively oxidizes the GBs. Subsequent annealing at 1000 °C increases the associated potential barrier height and resistance. These observations can be explained by structural changes in the Si–O network at the GBs and the competition between surface oxygen diffusion and oxidation from the GBs in the crystalline grains. A combination of oxidation and annealing may provide a method that can better control the GB potential barriers. © 2002 American Institute of Physics. [DOI: 10.1063/1.1509853]

The structural and electrical properties of polycrystalline silicon (poly-Si) thin films are of great interest in the design of ultralarge-scale integrated (ULSI) circuits and thin-film transistors for flat panel displays.^{1,2} As ULSI design rules are reduced to the nanometer scale, the poly-Si microstructure can strongly influence the device characteristics. If poly-Si grains are a few tens of nanometer in size, the material is of considerable interest for the fabrication of nanometer-scale devices such as single-electron transistors.^{3,4} Variation between individual grains and grain boundaries (GBs) causes nonuniformity in the electrical characteristics of different devices. It has also been reported that individual GBs have different structural and electrical properties.^{5,6} Thus control of the electrical properties of GBs is vital for nanometer-scale devices, in which only a few grains and GBs may exist in the active region.

In this letter we discuss the effect of oxidation and thermal annealing on the electrical and structural properties of poly-Si thin films and on nanowires fabricated in these films. We observe that the film electrical conductivity (σ) decreases nonmonotonically with an increase in oxidation temperature and that a two-stage oxidation process, followed by annealing, reduces variation in the activation energy of the conductivity (E_a) and tunnel resistance (R_T) in nanowire devices. We propose that oxygen atoms are incorporated selectively into the GBs and that this effect determines the electrical characteristics.

Our poly-Si film was prepared by solid-phase crystallization of 50-nm-thick amorphous silicon at 850 °C for 30 min.⁶ The films were doped n type to $10^{20}/\text{cm}^3$ using phosphorus ion implantation. Transmission electron microscopy (TEM) indicated that the grains were columnar with lateral size of 20–150 nm and that the GBs were no thicker than 1 nm.⁷

The bulk film was characterized electrically using a large-area (100 μm contact spacing) transmission-line mode (TLM) test structure. Nanowire structures (30 nm wide and

20 nm–80 nm long) were used to investigate the microscopic properties over a few GBs. The nanowires were defined by electron-beam lithography in polymethyl methacrylate resist, followed by reactive-ion etching (RIE) in a 1:1 plasma of SiCl_4 and CF_4 .⁶ Ohmic contacts were formed by depositing aluminum contact pads by thermal vacuum evaporation.

We have used these test structures to characterize the effect of thermal treatment of the film. As-prepared, oxidized, thermally annealed, or oxidized and subsequently thermally annealed poly-Si films were investigated. The thermal treatment was performed after fabrication of the test structures. The oxidation was performed in a dry O_2 ambient at temperatures from 600 to 1000 °C for 1 h, except for at the 1000 °C temperature, where the process was 15 min. All samples were dipped in a HF solution before oxidation. This was necessary to obtain the oxidation effects that we report here. It may be because RIE etching forms an amorphous layer on the poly-Si nanowire surface, and the amorphous coverage results in slower oxygen diffusion than that through poly-Si GBs. The annealing was performed in an Ar ambient at 1000 °C for 15 min. The electrical characteristics were measured at 25–300 K to extract E_a and R_T values.

The effect of oxidation on the film structure was characterized by measuring oxygen depth profiles with secondary ion mass spectroscopy (SIMS). This used a Cs^+ primary ion source and detected O^- negative secondary ions. The oxygen composition was averaged over the entire film, although the local oxygen concentration may vary.

Figure 1 shows the room temperature conductivity of the films after various thermal treatments. The σ value was estimated assuming a nominally 50-nm-thick film. When the film is annealed only, the σ reduces slightly from 65 to 61 S/cm. TEM images show that the grain size increases during thermal annealing,⁷ which would usually be expected to increase the conductivity. However, it is also likely that the dopant diffuses out of the film surface and segregates into the silicon–oxide interface and the GBs, thereby lowering the carrier concentration and reducing the conductivity.

When the film is oxidized without subsequent annealing, σ gradually decreases to 43 S/cm as the oxidation temperature increases. This may be associated with a reduction in the

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FIG. 1. Apparent conductivity of bulk films measured at room temperature. Circle: As-prepared film, open triangle: film annealed at 1000 °C, diamonds: film oxidized at 650–850 °C without subsequent annealing, closed triangles: film oxidized at 500–800 °C, followed by annealing at 1000 °C.

silicon layer thickness, e.g., SIMS measurements show a film oxidized at 800 °C has a 39-nm-thick silicon layer. Therefore the actual conductivity, estimated using this value, is 64 S/cm, which is almost the same as that of the as-deposited film.

If we anneal the films after oxidation, the conductivities are reduced significantly. At even the lowest oxidation temperature of 500 °C, the conductivity (58 S/cm) is lower than in films oxidized only at 650 °C, or annealed only at 1000 °C. This cannot be explained by the reduction in dopant concentration or the silicon layer thickness alone. Unusually, the conductivity behaves nonmonotonically with the oxidation temperature, falling rapidly at 650 °C and then rising as the oxidation temperature is increased up to 800 °C.

The microscopic properties of the film can be investigated using the nanowire devices. Figure 2 shows E_a values, estimated from the slopes of Arrhenius plots of the conductance at temperatures greater than 180 K where thermionic emission dominates, and R_T values estimated at temperatures less than 100 K, where tunneling through GB potential barriers dominates since the conductance does not show tem-

FIG. 2. Effect of oxidation and annealing on the activation energy of the conductivity (a), (b), (c) and tunnel resistance (d), (e), (f). The data at 0 °C correspond to those of as-deposited nanowires, the middle data points correspond to those of the oxidized nanowires, and the data points on the right correspond to those of the oxidized and annealed nanowires. The nanowire lengths are 20 (squares), 40 (circles) and 80 nm (diamonds). The oxidation temperatures are 650 (a), (d) and 750 °C (b), (e) and two-step oxidation at 650 and 750 °C (c), (f).

FIG. 3. Depth profile of the oxygen composition as a function of the oxidation temperature. Triangles: As-prepared film, diamonds: film oxidized at 650 °C for 1 h, circles: film oxidized at 750 °C for 1 h, inverted triangles: film oxidized at 800 °C for 1 h.

perature dependence. We show measurements from as-deposited, oxidized, and oxidized/annealed nanowires. In the measurements in Fig. 2, the Arrhenius plots are straight lines at >180 K and the E_a value reflects the GB potential barrier height (V_B).

The E_a and R_T values in as-deposited nanowires vary due to differences in the GB structure and V_B along the conduction path in different devices.⁶ The R_T value does not change significantly after simple oxidation. However, subsequent annealing at 1000 °C increases the R_T value, and this effect is larger for the 650 °C oxidation than for the nanowires oxidized at other temperatures. There is greater scatter in the R_T value in nanowires annealed after 650 °C oxidation. Most E_a values do not increase significantly with simple oxidation at 650 °C although there is an increase in some samples with simple oxidation at 750 °C. After annealing, the values mainly tend to increase, and this is clearer for oxidation at 650 °C. There is significant scatter in the values after annealing for oxidation at 750 °C. If the nanowires are oxidized at 1000 °C (not shown) the behavior is similar to oxidation at 750 °C. However, two-step oxidation at 650 °C for 1 h and at 750 °C for 1 h before annealing narrows the distribution of E_a and R_T even compared within as-deposited nanowires.

Figure 3 shows a SIMS depth profile of oxygen composition x of SiO_x in the film. There is an increase in x with the oxidation temperature. Gradient changes in each profile form three distinct regions: (1) surface oxide, where x is greater than the stoichiometric value in SiO_2 of 2 due to surface contamination, (2) oxygen diffusion from the surface oxide, where the gradient is large, and (3) a deep region with a small gradient. The change in gradient cannot be explained by a simple oxygen diffusion model,⁸ implying that other oxygen diffusion paths exist. It is known that impurity diffusion in GBs is greater than in crystalline grains.^{7,9,10} We therefore attribute the third region to oxygen diffusion in the GBs.

Table I shows the silicon thickness consumed by the surface oxide (d_s) and the GB oxygen diffusion length (l_{GB}). l_{GB} corresponds to the length in region (3), Fig. 3, where x falls to half of the initial value. l_{GB} does not change markedly with the oxidation temperature whereas d_s increases. It is known that either the parabolic or linear constants in the standard oxidation model for crystalline silicon AIP license or copyright, see <http://apl.aip.org/apl/copyright.jsp>

TABLE I. Thickness of the silicon consumed by the surface oxide (d_s) and diffusion length in GBs (l_{GB}) as a function of the oxidation temperature (T_{ox}). No subsequent thermal annealing is used.

T_{ox} (°C)	d_s (nm)	l_{GB} (nm)
650	2.7	7.1
750	5.0	7.2
800	11.3	6.9

exhibit thermally activated behavior with large activation energies of 1.2–2.0 eV.⁸ However, in disordered phases like amorphous silicon or GBs, the impurity diffusion constant varies according to the structure,¹¹ and almost zero activation energy is possible.¹² The interstitial and defect states in the GBs in our film can result in a low activation energy for impurity diffusion. The GBs are then oxidized selectively at lower temperatures where the growth of surface oxide is suppressed.

We propose the following oxidation model for our poly-Si films. Simple oxidation forms a surface oxide and diffuses oxygen atoms into the GBs. This does not form silicon oxide at the GBs with a potential barrier high enough to effect conduction (Fig. 2). However, subsequent high-temperature annealing may reconfigure the oxidized GB structure. This has been observed in silicon suboxide, where the silicon-rich bonding structure $\text{Si-Si}_{4-n}\text{O}_n$ ($n < 4$) forms the major portion of the suboxide. High-temperature annealing can convert some parts of this to a Si-O_4 tetrahedral structure¹³ or cause phase separation into nanocrystalline silicon and silicon dioxide.¹⁴ In our films, the GB volume may be limited for nanocrystalline silicon formation, and a Si-O_4 structure may form locally. In addition, such suboxide structures can persist even at 1000 °C.¹³ We suggest that the GBs are a mixture of Si-O_4 and silicon-rich structures, the former with an energy gap close to silicon dioxide and the latter with a lower energy gap. These energy gaps and the local trapped charge create potential barriers at the GBs, and a mix of these structures leads to a local distribution in V_B . Carriers flow over the lowest potential barrier region. Therefore, the E_a value after oxidation/annealing depends ultimately on the oxygen concentration in the GBs, which is controlled by the oxidation temperature.

The drop in the σ around 650 °C for oxidized and annealed films (Fig. 1) is explained as follows. If the oxidation temperature is <650 °C, low oxygen diffusivity causes a low oxygen concentration in the GBs and the film conductivity is unaffected. At ~750 °C, the activation energy for crystalline silicon oxidation is overcome, and the grains are

oxidized from the GBs. This increases the oxidized GB volume and reduces x in the GB, lowering V_B and increasing σ . This is supported by the larger E_a and R_T values after annealing in the nanowires oxidized at 650 °C, compared to at 750 °C (Fig. 2), and implies that V_B is higher even though the average oxygen concentration is lower (Fig. 3). At an intermediate oxidation temperature, oxygen can diffuse into GBs from the atmosphere while the increase in the thickness of the oxidized GBs is not large. Consequently, the highest GB potential barrier is formed at temperatures between 650 and 750 °C, with a corresponding fall in the film conductivity.

In conclusion, we have observed enhancement of the GB potential barriers in poly-Si thin films by oxidation and annealing. The selectivity of GB oxidation is increased at lower oxidation temperatures. Subsequent high-temperature annealing is necessary to form high potential barriers. This behavior is explained by structural changes in the Si–O network and the competition between oxygen diffusion from the film surface and oxidation from the GBs in the crystalline grains. The process may provide a means by which to obtain consistent properties of GBs in poly-Si.

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