Hydrothermal growth of ZnO nanorods aligned parallel to the substrate surface

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Abstract

Hydrothermal growth of ZnO nanorods with their *c*-axis aligned parallel to the surface of a Si (100) wafer substrate is demonstrated. With appropriate choice of process conditions (precursor concentrations, solution temperature, growth time), the (002) face of such nanorods is seen to support the emergence of as many as 10-20 aligned ZnO nanowires, with diameters ~ 50 nm and lengths that can extend to several microns. Similar growth of parallel nanorods/nanowires is observed on an amorphous carbon film surface. The influence of the substrate surface on the formation of such nanostructures is discussed. Such demonstrations of nanorod/nanowire growth parallel to a substrate surface could prove helpful in future nanodevice fabrication strategies.

Introduction

The last decade has witnessed major worldwide interest in the fabrication of nanodevices based on quasi one-dimensional (1-D) semiconductor nanostructures. ZnO, an important II-VI group semiconductor with many excellent properties, has been suggested for a diverse range of applications, including use as an optoelectronic and as a gas sensing material. [1,2] 1-D ZnO nanorods (NRs) and nanowires (NWs) have been synthesized using a range of techniques, [3,4,5,6,7,8] and prototype nanodevices (*e.g.* field-effect transistors [9] and electrical gas sensors [10]) fabricated.

Measurement of the electrical properties of ZnO NRs/NWs is important in fabricating such nanostructured devices, wherein it is often required that metallic (ohmic) contacts be made to the NRs on an insulating substrate. The typical fabrication procedure involves: first, transfer of the NRs/NWs into a dilute solution; second, (random) dispersion of the NRs/NWs onto an insulating substrate (typically a silica or sapphire wafer) and, finally, use of electron beam lithography [11,12,13] or photolithography [14] techniques to position individual NRs/NWs and to deposit nanometer-scale metal electrodes onto them. An alternative strategy is, first, to form the conductive metal electrodes on the insulating substrate of choice, and then to place the NRs/NWs on top of the electrodes so as to realize good ohmic contact between the ZnO and the electrodes. [15] Many prototype devices based on NRs/NWs have been reported, but the transfer and positioning of the NRs is too arduous for adoption in industrial applications. Harnack *et al.* [16] demonstrated an electrical method of aligning semiconducting ZnO NRs onto pre-defined electrodes. In this work, ZnO NRs, in suspension, were dropped onto gold electrode structures and then subjected to alternating electric fields at frequencies $f = 1\text{-}10$ kHz and field strengths $E = 10^6\text{-}10^7$ V m⁻¹. The NRs aligned parallel to the electric field lines and made electrical contact with the gold electrodes.

Most reports of ZnO NR growth either describe disordered, tangled networks of NRs/NWs or arrays of NRs directed along the substrate surface normal (*i.e.* *perpendicular* to the substrate surface). Controlled NR/NW growth *parallel* to the surface of an insulating substrate might offer a simpler device fabrication procedure. Several groups had recently reported lateral growth of ZnO NWs by a different gas phase deposition techniques. [17,18,19] Here we report growth of 1-D ZnO NRs and NWs parallel to a substrate surface using wet chemical methods. Scanning electron microscopy

(SEM), gallium focused ion beam (FIB) microscopy and transmission electron microscopy (TEM) were used to examine the resulting nanostructures, and their growth properties, and thus to infer process parameters that encourage such growth.

Experimental

For each set of experiments, two sealed Schott bottles with a volume of 135 cm³, one containing 50 cm³ of zinc nitrate (Zn(NO₃)₂, Alfa Aesar, 99%) solution, the other 50 cm³ of hexamethylenetetramine (HMT, also termed methenamine, Alfa Aesar, 99+%) solution, were placed in an oil bath maintained at 90.0±0.3°C. Both solutions were prepared with deionized water (Elgastat, resistivity > 18 MΩ cm), and their initial concentrations were chosen to be in the range 0.1-0.2 mol dm⁻³. Substrates used in this work were 1 cm² pieces of Si (100) wafer (pre-cleaned with acetone and then ethanol) or copper TEM grids pre-coated with a thin film of amorphous carbon, which were mounted on glass slides. Upon reaching thermal equilibrium the solutions were mixed and, after a user defined time τ , the substrate introduced so as to sit in the middle of the reactive solution, on the underside of its glass slide, at a tilt angle of ~80° to the horizontal. This strategy largely precludes the possibility of simple precipitation contributing to material on the substrate surface. The reaction mixture was kept sealed and maintained at 90°C throughout the full deposition run, which may be as long as $t = 24$ hrs. Post-growth, the samples were rinsed rigorously with water, then dried in air in a laboratory oven at 80°C. The as-deposited products were characterized and analyzed by SEM (JEOL 6300LV), gallium focused ion beam microscopy (FEI FIB201) and TEM (JEOL 1200EX).

Results and Discussion

Building on the pioneering work of Vayssieres, [6] we have previously reported the hydrothermal growth of ZnO nanostructures from HMT and zinc nitrate solutions, both on untreated Si substrates and on Si substrates that had been pre-coated (by pulsed laser deposition (PLD)) with a thin layer of ZnO. [20,21,22,23] Key reactions in the formation of zinc oxide nanostructure arrays are the thermal decomposition of HMT to formaldehyde and ammonia, with the latter acting as a base in aqueous solution:

and the precipitation of Zn^{2+} ions:

or

Using initial reagent concentrations in the range ~ 0.05 - 0.1 M and untreated Si substrates, we observed growth of dense assemblies of ZnO NRs that retain their hexagonal morphology at extended growth times. Samples grown on thin PLD ZnO films also comprise many hexagonal NRs at early times ($t \leq 3$ hrs), from many of which ultra-thin, single crystal ZnO nanotubes (NTs) are seen to emerge at later t (>10 hr). [21] When using much lower precursor concentrations ($\sim 10^{-3}$ M), no nucleation or subsequent ZnO growth was observed on a Si substrate, but the PLD ZnO film coated substrates were found to support dense arrays of vertically aligned thin ZnO NRs – thus demonstrating one route to selective area growth of ZnO nanostructures on Si substrates. [23]

The morphology of ZnO nanostructures formed by hydrothermal methods as above can be sensitively dependent upon the growth time, because of the evolving concentrations of OH^- (or H^+), Zn^{2+} and HMT in the reactive solution. [22] *In situ* measurements of a sealed solution that was, initially, 0.05 M in zinc, as a function of time after mixing showed a rapid (but modest) decline in pH at early t , followed by a slower recovery until $t \sim 2$ hr, after which time the pH remains constant. The Zn^{2+} ion and HMT concentrations were also found to fall rapidly until $t \sim 2$ hr but thereafter to decline more slowly via processes displaying, respectively, zero- and first-order decay kinetics before reaching asymptotic values once $t \sim 9$ hr. By this time, the initial Zn^{2+} ion concentration has dropped to $<10^{-3}$ M and, as such, is now also sufficiently low to support hydrothermal growth of ultrathin single crystal ZnO NWs on a PLD ZnO film-coated substrate.

Figure 1(a) shows a top view SEM image of a dense assembly of ZnO NRs grown on a Si substrate. This sample was formed by mixing equal volumes of 0.2 M HMT and zinc nitrate solutions at 90°C , then immediately inserting the substrate and allowing growth for $t = 24$ hr. Competition for space at such high nucleation densities (*i.e.* excluded volume effects) precludes formation of NRs aligned parallel to the substrate surface.

The present studies employed relatively high concentration (0.1-0.2 M) solutions, but the experimental procedure was altered by pre-mixing the $\text{Zn}(\text{NO}_3)_2$ and HMT solutions for $\tau = 2$ min (during which time considerable precipitation from solution occurs) prior to inserting the substrate. During this time, the Zn^{2+} ion concentration (in particular) dropped sufficiently that only a low density of ZnO NRs formed on the substrate. Extending τ to 5 min resulted in a yet lower density of NRs on the substrate surface, but no obvious morphological change. The SEM images in figs. 1(b) and 1(c) demonstrate that, by using initial solutions that were both 0.1 M (*i.e.* each was 0.05 M in the mixed solution at $\tau = 0$) and this initial delay, it is possible to observe ZnO NR growth parallel to the substrate surface, *i.e.* NRs that would be inhibited and/or hidden in samples grown with higher reagent concentrations. Morphologically, the nanostructures shown in figs. 1(b) and 1(c) sub-divide crudely into three groups: nanoflowers, NRs directed roughly perpendicular to the substrate surface, and twin-structured NRs that lie in or on the plane of the substrate. The nanoflowers are collections of NRs growing from a common origin, as can be seen clearly in those nanoflower structures that consist of just a few ‘petals’ (see inset in fig. 1(c)). The vertical NRs all appear to have grown from basal nanoparticles, as illustrated in the high-resolution tilt-view SEM images of a single NR and a pair of NRs shown as insets in fig 1(c). The basal particles are presumed to evolve from nucleation on the substrate surface, and to guide the subsequent formation of the vertical NRs, including their polarities and morphologies. Both the NRs and the basal particles exhibit near perfect hexagonal cross-sections. No NRs that grow directly from the Si substrate have been identified. Clearly, the effect of substrate surface on the growth of crystallites that seed such nucleation merits further study.

Here we concentrate on NRs that have grown parallel to the substrate surface which, as figs. 1(b) and 1(c) show, exhibit twin-like structures. The literature contains several reports of twinned ZnO nanostructures formed by precipitation from solution. [24,25,26] These have the appearance of classic contact twins, *i.e.* are likely to have grown along the same [0001] crystallographic direction, from a common nucleation point, and thus to have 180° reversed polarities. It is worth considering whether NRs observed on the substrate surface in the present work could also have precipitated from solution – notwithstanding the deposition geometry and the thorough rinsing procedures employed. The high-resolution tilt-view FIB microscopy image of NRs shown in fig. 1(d) (and its inset) serves to dispel such concerns, however. Very evidently, many of the NRs aligned parallel to the substrate

surface are ‘half’ NRs (prisms) – consistent with these NRs having grown directly from the substrate surface.

Upon extending the growth time, thin NWs emerge from the tops of pre-formed NRs. By way of illustration, fig. 2(a) shows an SEM image of a twinned NR after growth for $t=18$ hr in a reactive mixture prepared by mixing equal volumes of 0.2 M $\text{Zn}(\text{NO}_3)_2$ and 0.1 M HMT stock solutions and then waiting for $\tau=2$ min before inserting the substrate. As shown more clearly in the inset, the emergent NWs have diameters $d_{\text{NW}} \sim 50\text{-}100$ nm (*cf* $d_{\text{NR}} \sim 1\text{-}2$ μm for the parent NR formed under these conditions) and lengths $\ell \sim 500$ nm. The morphologies of the parent NRs and of the emergent NWs are both sensitive to the reagent concentrations. For example, the NR twins observed growing parallel to the substrate surface from a solution prepared by mixing 0.2 M $\text{Zn}(\text{NO}_3)_2$ and 0.2 M HMT, with $\tau=2$ min and $t=24$ hr, are much thicker ($d_{\text{NR}} \sim 5$ μm), have arrays of NWs emerging from the end of each NR and, in addition, two needle-like structures growing from the twin boundary and directed parallel to the substrate surface (fig. 2(b), which also shows a nanoflower-like structure that has nucleated and grown under the same conditions). NWs can also be observed emerging from individual NRs in the nanoflower structure, but only from those NRs that are closest to the substrate surface. We return to this observation when considering the SEM images shown in fig. 3. Much longer NWs could be obtained using lower $\text{Zn}(\text{NO}_3)_2$ concentrations, as illustrated in fig. 2(c), which shows NWs with $\ell \sim 4$ μm emerging from NRs grown from a solution prepared by mixing 0.1 M $\text{Zn}(\text{NO}_3)_2$ and 0.2 M HMT, with $\tau=2$ min and $t=24$ hr. As fig. 2(d) shows, the needle-like structures growing from the NR twin boundaries can also support NW growth parallel to the substrate surface, leading to ‘fishbone’-like nanostructures. Figures 2(b), 2(c) and 2(d) illustrate another notable feature: under the growth conditions used here, NRs that have grown in directions other than (near-) parallel to the substrate surface (*i.e.* the individual NRs that have grown normal to the substrate surface, and many of the NRs within the nanoflower structures) all retain hexagonal cross-sections and smooth, flat end surfaces.

The emergence of NWs from the end of NRs had been observed previously. Hung *et al.* [27] reported formation of dispersively self-oriented nanotip arrays on the (002) polar surfaces of pre-formed ZnO NRs when the latter were placed in a dilute $\text{Zn}(\text{NO}_3)_2$ / HMT reactive mixture. We previously reported the emergence of thin NTs from the hexagonal basal plane of ZnO NRs during

hydrothermal growth on PLD ZnO film-coated Si substrates once $t \sim 6$ hr. Growth on an uncoated Si substrate, in contrast, yielded dense assemblies of hexagonal NRs, none of which showed any evidence of emergent NTs or NWs, even at $t = 24$ hr. [21] These studies highlight the extreme sensitivity of sample morphology to the local solution phase composition when working with low reactant (particularly Zn^{2+}) concentrations. Indeed, under such conditions, even the termination of the polar surface of a ZnO NR can affect the product morphology – by influencing the cation (Zn^{2+} and ZnOH^+) to anion (OH^-) concentration ratio (*i.e.* the extent of solution super-saturation) in the double layer at the growing polar surface. Such electrostatic effects dictate that Zn-terminated, Zn-polar NRs (such as are grown on PLD ZnO film-coated substrates [28]) experience a local $\text{Zn}^{2+}/\text{OH}^-$ (and $\text{ZnOH}^+/\text{OH}^-$) ratio at their growing surface that is lower than that in the bulk solution, encouraging tapered NR growth and, as the zinc concentration falls further, the emergence of volcano-like structures from the polar surface, which seed the subsequent growth of ZnO NTs. Conversely, the O-terminated surface of an O-polar NR (such as grow on an Si substrate) will be exposed to a local $\text{Zn}^{2+}/\text{OH}^-$ concentration ratio that is higher than in the bulk solution, favouring columnar growth, the retention of hexagonal morphology and a smooth basal surface. [29,30] Given these earlier findings, we conclude that solution phase compositional changes with time, and with location (*i.e.* proximity to the substrate), account for the evolution from NR to NW growth observed in nanostructures that grow parallel to the substrate surface.

SEM images of NWs emerging from the (002) polar surfaces of a single NR growing parallel to the substrate surface and of NRs within a nanoflower structure are shown in figs. 3(a) and 3(b), respectively. In both cases, the NWs are seen to be distributed non-uniformly, being concentrated on the polar face of NRs adjacent to the substrate (fig. 3(b)), and even on the part of this (002) face that is closest to the substrate (fig. 3(a)). In the light of the foregoing discussions, such NW distributions suggest that the substrate surface must have a significant influence on the local composition of the reactive solution. Given that lower $\text{Zn}^{2+}/\text{OH}^-$ ratios favour NW growth, we conclude that the substrate surface must be promoting a local increase in the relative concentration of OH^- , and/or a decrease in the concentration of Zn^{2+} (or Zn(OH)^+). The substrate surface in our experiments will resemble silica, as the native oxide was not removed from the silicon. Studies of the isoelectric point of silica indicate that above pH 4 a silica surface exhibits a net negative charge [31]. Our previous investigations of the hydrothermal growth of ZnO under these conditions showed only a small

variation in pH, in the range 5.5 to 5.7, indicating that the substrate surface is likely to be negatively charged throughout the deposition process. Hence, electrostatic considerations are unlikely to account for a decrease in the $\text{Zn}^{2+}/\text{OH}^-$ ratio near the substrate surface and the emergence of NWs. In addition to electrostatic effects, however, the substrate will also influence the transport of reactants to the growing interface. NW formation is not observed until the Zn^{2+} concentration in bulk solution is massively depleted. At very low Zn^{2+} concentrations, the rate of reaction may be transport limited, or the system may reach equilibrium. If the reaction is transport limited, the local concentration of Zn^{2+} at the (002) surface will be proportional to the local flux of ions. For the specific case of *c*-axis growth of a ZnO NR parallel to the substrate surface, any impediment to transport to the ZnO (002) surface caused by the inert substrate will be greatest in the region immediately adjacent to the interface – leading to a decreased $\text{Zn}^{2+}/\text{OH}^-$ ratio at this location, and favouring NW growth. If the reaction is at equilibrium, there can still be localized changes in NR structure owing to continual local dissolution and re-deposition of material. Impeded transport of dissolved material adjacent to the substrate surface at very low Zn^{2+} concentrations could act to promote re-deposition in this region, possibly leading to the formation of NWs.

By judicious choice of precursor concentrations and/or growth time it is possible to grow arrays of NWs that are several microns long, parallel to one another and parallel to (or on) the substrate surface, as shown in figs. 3(c) and 3(d). Given that any Si substrate wafer will usually have a thin SiO_2 surface layer, and could thus constitute an insulating substrate in cases that the oxide layer was sufficiently thick, such NWs might be well suited to nanodevice fabrication – using, for example, focused ion beam (or other) lithography techniques to form metal lines across the NW sample on the SiO_2 layer, thereby realizing contacts between the ZnO NWs and metal electrodes on an insulating substrate.

To investigate substrate surface effects further, a copper TEM grid over-coated with an evaporated amorphous carbon (a-C) film was employed as an alternative substrate. Figure 4 shows SEM and TEM images of ZnO nanostructures formed by mixing equal volumes of 0.1 M $\text{Zn}(\text{NO}_3)_2$ and 0.2 M HMT stock solution, waiting $\tau = 2$ min prior to inserting the grid, and then growing for $t = 24$ hr. Again, we observe long and reasonably parallel NWs emerging from short NRs and growing along the carbon film surface. TEM images (figs. 4(c) and 4(d)) clearly show bundles of ~ 15 parallel NWs,

with d_{NW} of ~ 50 nm and $l \leq 7$ μm . The crystallinity and crystal structure of the NWs were confirmed by selected area electron diffraction (SAED); an illustrative SAED pattern is shown as an inset in fig. 4(c). Interestingly, we observe that most of the NWs have emerged from just one side of the parent NR. The different morphologies of nanostructures formed on the a-C coating as compared with the Si substrate, when using the same growth conditions, points to the importance of the substrate on the nucleation and subsequent growth properties of ZnO by hydrothermal methods. The physical chemistry underpinning the effects of the substrate on the growth and properties of ZnO nanostructures formed by hydrothermal methods clearly merits further study.

In summary, growth of ZnO NRs and NWs parallel to the substrate surface by hydrothermal methods has been demonstrated, for both Si(100) wafer and a-C film coated substrates. Surface induced variations in the local $\text{Zn}^{2+}/\text{OH}^-$ concentration ratio within the reactive solution are proposed in order to account for the emergence of NWs from pre-formed NRs, and for the growth of NWs along the substrate surface. This demonstration of a route to forming bundles of parallel NWs aligned parallel to a substrate surface could offer a convenient route to nanodevice fabrication.

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Figure Captions

Figure 1

SEM images of ZnO NRs grown on Si substrates at 90 °C by: (a) mixing equal volumes of 0.2 M HMT and $\text{Zn}(\text{NO}_3)_2$ solutions, then inserting the substrate immediately and leaving for $t = 24$ hr growth; (b) and (c) mixing equal volumes of 0.1 M HMT and $\text{Zn}(\text{NO}_3)_2$ solutions, inserting the substrate into the solution after $\tau = 2$ min and leaving for $t = 6$ hr. The insets in (c) show NRs that have grown vertically from basal nanoparticles. (d), and its inset, show cross-sectional views of selected NRs that have grown parallel to the substrate surface obtained by FIB microscopy. All scale bars in a given image express the same length.

Figure 2

SEM images of: (a) a NR twin that has grown parallel to the Si substrate surface from a solution prepared by mixing 0.2 M $\text{Zn}(\text{NO}_3)_2$ and 0.1 M HMT, with $\tau = 2$ min and $t = 18$ hr, with an expanded view of the NWs emerging from one end face shown in the inset. (b) NR twins formed on the substrate surface from a solution formed by mixing equal volumes of 0.2 M $\text{Zn}(\text{NO}_3)_2$ and 0.2 M HMT solutions, with $\tau = 2$ min and $t = 24$ h. The inset depicts one NR twin on an expanded scale to illustrate the needle-like structures that have grown out parallel to the twin boundary. (c) and (d) long, thin NW arrays emerging from NRs that have grown parallel to the substrate surface from a solution prepared by mixing 0.1 M $\text{Zn}(\text{NO}_3)_2$ and 0.2 M HMT, with $\tau = 2$ min and $t = 24$ hr. As in fig. 1, all scale bars in a given image express the same length.

Figure 3

SEM images from NWs growing from (a) a horizontal NR (grown for $t = 24$ h after immersion at $\tau = 2$ min in a reaction mixture formed by mixing equal volumes of 0.1 M $\text{Zn}(\text{NO}_3)_2$ and 0.2 M HMT) and (b) NRs in a nanoflower structure grown (grown for $t = 24$ h after immersion at $\tau = 2$ min in a reaction mixture formed by mixing equal volumes of 0.2 M $\text{Zn}(\text{NO}_3)_2$ and 0.2 M HMT). (c) and (d) SEM images of long, parallel NWs that have grown along the substrate surface (using the same growth conditions as in (a)).

Figure 4

SEM ((a) and (b)) and TEM ((c) and (d)) images of ZnO nanostructures grown on an a-C over-coated Cu a TEM grid for $t = 24$ h in a reactive solution prepared by mixing equal volumes of 0.1 M $\text{Zn}(\text{NO}_3)_2$ and 0.2 M HMT solutions that had been allowed to evolve for $\tau = 2$ min. A selected area electron diffraction pattern from the NW sample is (c) is shown in the inset to this figure.

Figure 1

Figure 2

Figure 3

Figure 4

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