

Enhanced Nucleation, Growth Rate, and Dopant Incorporation in ZnO Nanowires

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Pure and Co-doped ZnO nanowire arrays were grown on polished silicon substrates with high rates via an electrochemical technique. A negative potential applied to the substrate not only enhances the nucleation density on polished substrates more than 4 orders of magnitude but also increases the growth rate by 35 times over that obtained in the absence of the potential. Furthermore, incorporation of metallic dopants in ZnO nanowires was demonstrated in the low-temperature process. This fast growth technique provides a route to fabrication of low-cost highly oriented ZnO nanowires on polished substrate for industrial applications.

I. Introduction

Extensive studies have been conducted on wide band gap semiconducting ZnO nanomaterials due to their potential applications as light-emitting diodes,¹ photodiodes,² nanolasers,³ dye-sensitized solar cells,⁴ varistors,⁵ and gas sensors.^{6,7} Various vapor-phase methods such as the vapor–liquid–solid epitaxial (VSLE),⁸ pulsed laser deposition,⁹ and metal–organic chemical vapor deposition¹⁰ have been successfully used to grow oriented ZnO nanowire arrays at temperatures of 800–900 °C. In general, a substrate with a catalyst, such as Au-coated sapphire, is used for high-quality ZnO nanowire growth.⁸ Electrodeposition of ZnO nanorods at low temperature in the presence of bubbling O₂ has been reported, but the products contained a Zn–oxychloride impurity phase which was hard to remove.¹¹ Recently a hydrothermal approach to the growth of ZnO nanowire arrays was developed at temperatures below 100 °C.^{12–15}

Although large-scale, homogeneous, dense arrays of ZnO nanowires were produced on arbitrary substrates seeded with ZnO nanocrystals by the hydrothermal process, the typical growth rate is in the range of a few hundred nanometers per hour.^{14–16} Furthermore, nucleation density on polished substrates is low.^{15–17} To enhance the nucleation density seeded substrates were used^{15,16} to grow high-quality dense arrays of ZnO wires. The interface quality in the presence of seeds has defects leading to low adhesion, low thermal and electrical transport, and light scattering. In the absence of seeds high-quality nanowires were grown,^{12,13} but the maximum length achievable was limited to approximately 10 micrometers under the thermal conditions used for growth. Extending the growth time led to etching of the (001) face and formation of ZnO nanotubes.¹³ In the present study we used a negative electrical potential applied to the substrate in an aqueous solution to overcome these limitations and obtained dense, high-purity ZnO nanowire growth on polished substrates without seeds. We enhanced the nanowire growth rate up to 35 times over the purely thermal process. We also found that the applied potential permits incorporation of metallic dopants such as Co in the nanowires. This is promising for low-temperature growth of dilute magnetic semiconductor nanowires.

II. Experimental Details

In a typical procedure zinc nitrate hydrate (Zn(NO₃)₂·6H₂O, 10 mmol) and hexamethylenetetramine (C₆H₁₂N₄, 10 mmol) were dissolved in 200 mL of deionized water at room temperature and then heated to 90 °C on a hot plate. The reagents were used as received from Alfa Aesar. A gold wire with a diameter of 0.2 mm was used as an electrode. A negative dc potential up to −1.2 V relative to a reference electrode was applied to the substrate. At the end of the growth period (typically 1–2 h) the sample was removed from the solution and immediately rinsed in flowing deionized water to remove any residual salt from the surface.

Co-doped ZnO nanowires were grown under similar conditions where 0.1–6 mol % of the Zn salt was replaced with cobalt nitrate hydrate [Co(NO₃)₃·6H₂O] in the reaction solution.

The samples were characterized using a scanning electron microscope (SEM; FEI XL-30 at 15 kV) equipped with energy-dispersive X-ray spectroscopy (EDX), an X-ray diffractometer (XRD; Siemens D5000, with Cu Kα radiation, λ = 1.5418 Å at 40 kV and 30 mA), and X-ray photoelectron spectroscopy (XPS, Perkin-Elmer ESCA, Mg Kα, hν = 1253.6 eV).

III. Results and Discussion

Figure 1 displays SEM images of ZnO nanowires grown on polished Si substrates under potentials of −0.15 and −1.0 V relative to a reference electrode. The nucleation density of the sample grown with a potential of −0.15 V is about 5 × 10⁶/cm², whereas it was increased to 1 × 10⁹ cm^{−2} at a potential of −1.0 V.

The quantitative change of nucleation density as a function of applied potential relative to the reference electrode is shown in Figure 2. The nucleation densities were obtained from the SEM images. For comparison, the nucleation densities on both polished and substrates seeded by 10 nm ZnO nanoparticles are plotted in Figure 2. Although the applied potential has little effect on the nucleation density with a seeded substrate, it significantly enhances nucleation on the polished silicon surface. At lower potentials the nucleation density increases exponentially with the increase of the magnitude of the applied potential. At potentials higher than −0.6 V the nucleation density becomes saturated at the value of a seeded substrate. Since the nucleation

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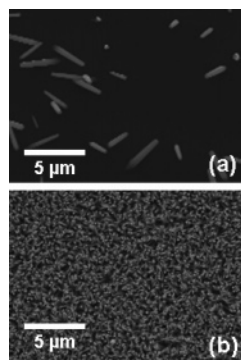


Figure 1. SEM images of ZnO nanowires grown on polished Si at applied potentials of (a) -0.15 and (b) -1.0 V relative to a reference electrode. The growth times for a and b are 1.5 and 2 h, respectively.

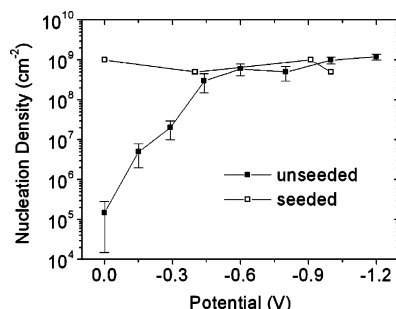


Figure 2. Nucleation density of ZnO nanowires on polished Si substrate as a function of applied potential.

density on seeded substrate is already very high, additional potential applied to the substrate does not seem to further increase the value.

Seeds have been popular for ZnO nanowire growth in conventional hydrothermal processes due to the very low nucleation density on a polished surface. The typical nucleation density of ZnO nanowires on a clean polished Si surface was found to be below 10^6 cm^{-2} . Using ZnO nanocrystals as seeds the nucleation density can be increased to 10^9 cm^{-2} . Enhancement of the nucleation density can also be obtained by applying the potential for a short time (typically about 1 min) at the start of unbiased growth.

The electrochemical process provides a new method to enhance the nucleation density of ZnO nanowires on polished surfaces and makes it possible to grow dense ZnO nanowires directly on substrate without an intermediate material. The absence of an alien material deposition between ZnO nanowires and the substrate improves the interface qualities, such as thermal and electrical transport, which are important for many applications.

Comparison of ZnO nanowires growth without (sample A) and with (sample B) an applied potential is shown in Figure 3. Sample A was grown on a ZnO nanocrystal-seeded Si substrate at $V_{\text{appl}} = 0$ V for 8 h. Sample B was grown on an unseeded, polished silicon wafer at $V_{\text{appl}} = -1.2$ V for 2 h. The insets of Figure 3a and b show the corresponding cross sections of the two samples.

The nanowires of sample B have an average diameter of 400 nm and grow at $6 \mu\text{m/h}$ perpendicular to the substrate. The nanowires of sample A are 70 nm in diameter and $1.3 \mu\text{m}$ in length after 8 h of growth. The corresponding growth rate is ~ 35 times smaller than that of sample B. Systematic study reveals that the growth rate is strongly dependent on the magnitude of the applied potential.

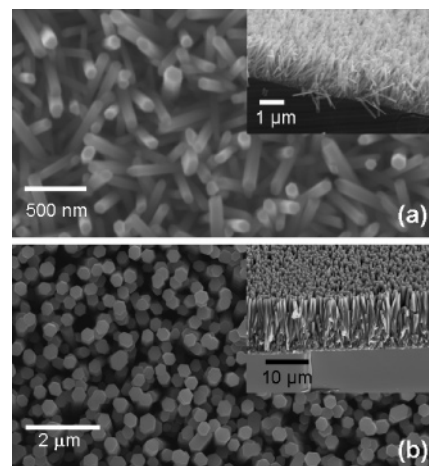


Figure 3. SEM images of ZnO nanowire arrays deposited on Si substrate with applied potentials of 0 V for 8 h (a) and -1.2 V for 2 h (b). Ten nanometer diameter ZnO nanocrystals were used as seeds for a; the growth in b was unseeded.

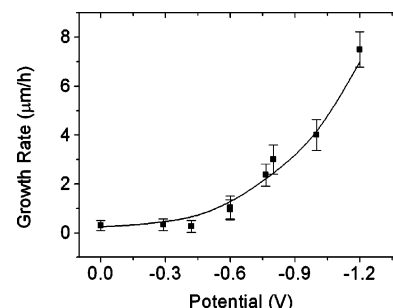


Figure 4. Growth rate of ZnO nanowires on seeded Si substrate as function of applied potential. The solid line is a guide for the eye.

Figure 4 shows the growth rate in length as a function of applied potential. Due to the low nucleation density on polished substrates at lower potentials, seeded substrates were used in order to grow ZnO nanowire samples with similar nucleation densities at different applied potentials. The growth rate increases rapidly with the magnitude of the applied negative potential. Under an applied potential of -1.2 V the growth rate in length is about 35 times higher than that without an applied electric potential. It is demonstrated that both nucleation density and growth rate were significantly enhanced by applying a negative electrical potential to the polished substrate.

X-ray diffraction patterns from samples A and B were obtained in order to check the effect of applied potential on crystalline structure. The patterns shown in Figure 5 are similar with a strong (002) peak and a number of weaker peaks with indices of (101), (102), (110), (112), and (004), indicating that both samples consist of well-aligned ZnO nanowires on the substrate. The width of the (112) diffraction peak is similar to that observed for ZnO nanocrystal seeds dispersed on a substrate. The XRD data suggest that the applied negative electric field does not noticeably reduce the nanowire quality. This was further confirmed by electron diffraction, which confirmed that the nanowires are single crystals.

The composition of ZnO nanowires was analyzed by EDX and XPS. Figure 6a shows an XPS spectrum measured from sample B. The emission peaks at 1023 and 1047 eV are, respectively, from the Zn $2p_{1/2}$ and $2p_{3/2}$ core levels. The emission peak at 533 eV is from O 1s, and that at 286 eV is from C 1s. The other peaks between 200 and 400 eV are the emissions from Zn (LMM). The electron emissions from Zn 3s, 3p, and 3d core levels are also observed. The XPS data confirm that the

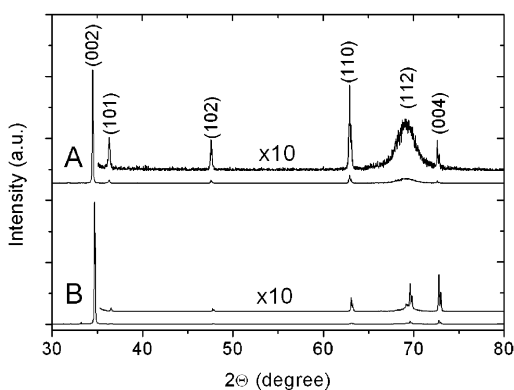


Figure 5. X-ray diffraction patterns of ZnO nanowires grown in solution with an applied potential of 0 (A) and -1.2 V (B). The (400) peak of the silicon substrate (at 69.5°) is obscured.

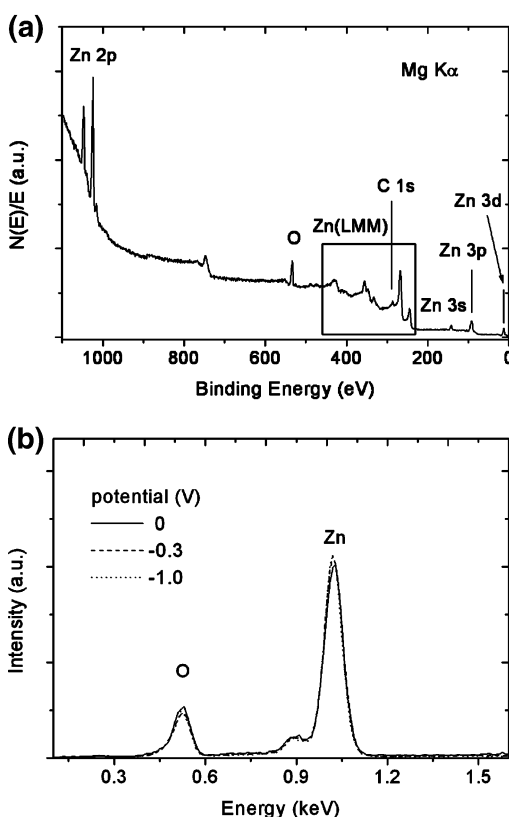


Figure 6. (a) X-ray photoelectron spectroscopy of ZnO nanowires grown with an applied potential of -1.2 V. (b) Energy-dispersive X-ray spectroscopy of ZnO nanowires deposited on polished Si by the electrochemical process. The intensity of the Zn peak has been normalized so that the oxygen intensities for the different growth conditions can be compared.

nanowire grown under a potential is ZnO. The appearance of C 1s signal in the XPS spectrum results from hydrocarbon contamination on the sample surface after exposure in air. The carbon signal can be significantly reduced through Ar ion etching since the hydrocarbon groups are removed from the surface.

Figure 6b shows the effect of the applied potential on the composition of ZnO nanowires, as determined by EDX. Both the oxygen signal at 0.53 keV and the Zn signal at 1.01 keV were observed in all samples. Note that the intensity of the Zn peak has been normalized so that the oxygen peaks from different samples are comparable. Within the accuracy of our measurements, the atomic ratio of oxygen to zinc is 1:1 for the samples grown with and without a negative potential applied to the substrate. Although the applied potential strongly affects

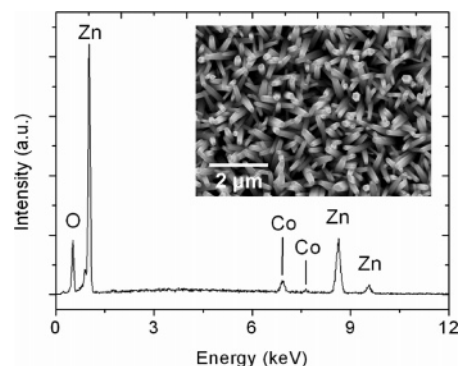


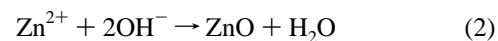
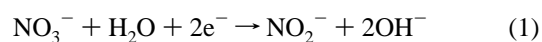
Figure 7. Energy-dispersive X-ray spectrum of Co-doped ZnO nanowires grown for 1.5 h. The applied potential was 0.7 V. (inset) SEM image of the sample.

the growth rate and nucleation density, it does not change the composition of ZnO nanowires.

Transition-metal-doped ZnO thin films which exhibit room temperature ferromagnetic properties have been extensively studied recently due to their potential application in spin-related electronics.¹⁸ In this study the growth of doped ZnO nanowires was demonstrated using Co as a test dopant. In the absence of an applied electric potential, no measurable incorporation was observed even when 10 mol % of the zinc nitrate was replaced with cobalt nitrate in the growth solution. Figure 7 presents a typical EDX spectrum of a Co-doped ZnO sample which was grown at an applied potential of -0.7 V for 1.5 h. In addition to the Zn and O signals, cobalt peaks at 6.92 and 7.63 keV were observed. Quantitative analysis of the EDX data yields a Co concentration of 5% in the sample. Clearly, electrochemical processes play a key role in the doping process, reducing the energy barrier for incorporation of Co into the ZnO structure. While there is a weak dependence of the Co content on the concentration of Co nitrate in solution, we found that the applied bias provided better control of the Co content.

The inset of Figure 7 is an SEM image showing that aligned nanorods of Co-doped ZnO were obtained. The nanowires have an average diameter of 100 nm and length of $3 \mu\text{m}$. X-ray diffraction data revealed that the diffraction pattern of the doped ZnO nanowires is similar to that from the pure ZnO nanowires as shown in Figure 5. The diffraction peak position of the doped ZnO nanowires was found to shift to a low angle. This reveals changes in the lattice constant of Co-doped ZnO, confirming incorporation of Co in ZnO nanowires.¹⁸ Vibrating sample magnetometry indicates that the material is ferromagnetic at room temperature.

The growth mechanisms of ZnO in solution have been investigated by a number of groups.^{12,19,20} In general, growth of quasi-one-dimensional ZnO is affected by both its intrinsic crystal anisotropy and the external chemical conditions. Diffusion of reactants in the solution and the interfacial free energy determine the growth rates on the different crystal faces. The concentration of the reaction agent and solution viscosity play a key role in diffusion, while an applied potential adjusts the interfacial free energy and induces electrochemical reactions in the aqueous solution. The reduction of nitrate ions, which is dependent on the applied potential, was found to play an important role in the electrochemical deposition of ZnO films.^{21,22} The reaction can be expressed as



Hydroxide ions are produced during the electroreduction of nitrate to nitrite ions. The concentration of OH^- was increased at the sample surface (cathode), resulting in formation of ZnO. The increased potential helps increase the concentration of OH^- ions, which increases the growth rate of ZnO. This accounts for the enhancement of both growth rate and nucleation density on the polished surface for applied negative potentials in our ZnO nanowire growth.

The applied bias may control incorporation of Co through two mechanisms. A study of Co films has shown that nitrate ions tends to react with a Co deposit to reform Co ions.²³ Reduction of nitrate ions in the electrochemical reaction helps stabilize Co that deposits on the growing ZnO surface, resulting in inclusion of Co dopants in the nanowires. Another factor is that the applied bias drives the deposition process away from equilibrium, where the energetics favor only Zn incorporation, to a mass-transport-limited regime, where available Co is included because of its availability despite the higher energy barrier for its incorporation. Both of these mechanisms are consistent with the observed increase in Co incorporation, where both Co concentration in the bath (weak dependence) and the magnitude of the bias (strong dependence) in the electrochemical process determine the final composition of Co:ZnO.

IV. Summary

In brief, we report here a straightforward and inexpensive method for rapid growth of pure and doped ZnO nanowire arrays in an aqueous solution. Applying a negative potential to the substrate increases the growth rate up to 35 times without deleterious effects on the nanowire quality. ZnO nanowires could be doped by applying negative potentials to the substrate, and Co:ZnO nanowires exhibited soft ferromagnetic properties at room temperature. Furthermore, an applied negative potential makes it possible to grow dense wafer-scale, homogeneous ZnO nanowire arrays directly on polished surfaces without a seeding process. The absence of seeding layer between substrate and ZnO helps improve the interface quality which is important for many applications. Although the growth kinetics of the electrochemical process requires further detailed investigation, this

fast growth technique provides a route to fabrication of low-cost highly oriented ZnO nanowires directly on polished substrate surface for industrial applications.

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