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Selective Growth of Single-Crystalline ZnO Nanowires on Doped Silicon

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Selective growth of single-crystalline ZnO nanowires on doped silicon

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We report the growth of single-crystalline ZnO nanowires on *n*- and *p*-type Si wafers by electrodeposition. On strongly doped *n*-type Si high-quality nanowires can be grown under similar conditions as used for metallic substrates. For low electron concentrations occurring in weakly *n*-type or in *p*-type wafers, nanowire growth is inhibited. This difference allows selective growth in strongly *n*-type areas. The inhibited growth on weakly *n*-type and *p*-type wafers can be improved by applying stronger cathodic electrode potentials or by illuminating the growth area. The wires on *n*-Si show efficient electroluminescence covering the visible and extending into the ultraviolet spectral range. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2777133]

Low-dimensional semiconductor nanostructures are presently considered as active components in various optoelectronic devices. ZnO has attracted considerable interest due to its high exciton energy and wide band gap, which make this material a promising candidate for visible and ultraviolet light-emitting diodes (LEDs) and lasers.[1] The monolithic growth of optically active nanostructures on Si wafer surfaces is of particular relevance for on-chip optical applications. Freestanding vertically oriented ZnO nanowires can be made in a variety of processes, including chemical vapor deposition, metal-organic vapor phase epitaxy, and electrodeposition.[2–6] Growth on Si has mainly utilized catalyst-induced processes or depsition on metallized wafers.[7,8] Electrodeposition produces crystalline nanowires of excellent electronic and optical qualities in a variety of shapes.[5,6,9] The electrodeposition process is carried out at an aqueous solutions at temperatures well below 100 °C. This makes the process uniquely compatible with glass and polymer substrates and possibly with processed Si circuits. No interface layer deposition is required. As the growth process involves the transfer of electrons from the substrate, the electric contact between the grown wire and the substrate is in most cases exceptionally good, i.e., there is low contact resistance at the interface. Electrodeposition thus involves several technological advantages which are not easily obtained in other methods. Here we show that electrodeposition allows the growth of ZnO nanowires on Si and that the growth occurs at markedly different electrode potentials on areas of high electron density, such that selective growth on these areas can be obtained. The nanowires grown on *n*-Si are of high electronic quality and show excellent electroluminescence at room temperature.

ZnO nanowires were grown electrochemically from aqueous solutions on Si wafers with (100) surface orientation and differing doping levels. Strongly doped *n*-type wafers with P concentrations of 10^{18} cm^{-3}, weakly *n*-doped wafers with P concentration of 3×10^{15} cm^{-3}, and boron-doped *p*-type wafers with dopant concentration of 10^{15} cm^{-3} were used. Before deposition the wafers were rinsed in H_2O and dried under N_2 flow. Ellipsometry showed the polished (100) surfaces to be covered with natural oxides of 18–28 Å thickness. Since the electrolyte in the electrodeposition process is oxygen enriched and the deposition conditions are oxidative, the wafers were not etched prior to deposition. Instead, areas of minimal initial oxide coverage were prepared by cleaving the wafers along the (111) direction immediately before the ZnO growth or by mechanically scraping the polished (100) surface. The electrodeposition involved a standard three-electrode arrangement with Pt counter- and Ag/AgCl reference electrodes. Aqueous solutions of $5\times10^{-4}M$ $ZnCl_2$ and $0.1M$ KCl were used; the KCl solution serving as supporting electrolyte. This process has been described in some detail in Ref. 5. Depositions on *n*-Si were carried out at −1.0 V versus Ag/AgCl electrode at 80 °C with externally induced convection and oxygen bubbling. These conditions are the same as used for nanowire growth on metallic and conductive oxide substrates.[6] Deposition times of 1 h resulted in single-crystalline hexagonal ZnO columns of 50–200 nm in diameter and 2 μm in length. No ZnO deposition occurred on the naturally oxidized areas of weakly *n*-type or *p*-type substrates at electrode potentials of −1.0 V. However, filmlike coverage occurred on freshly cleaved or scraped areas at these conditions. Nanowire growth on these substrates is only obtained at electrode potentials of −1.5 V versus Ag/AgCl.

Figures 1(a) and 1(b) show a typical electron diffraction pattern and a high-resolution transmission electron micros-

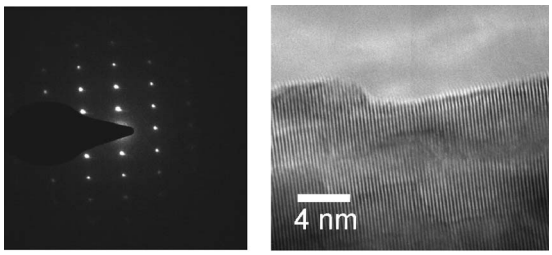

FIG. 1. Crystallinity of ZnO nanowires made by electrodeposition: (a) electron diffractogram of a single wire showing monocrystallinity; (b) high resolution TEM micrograph of a ZnO nanowire.

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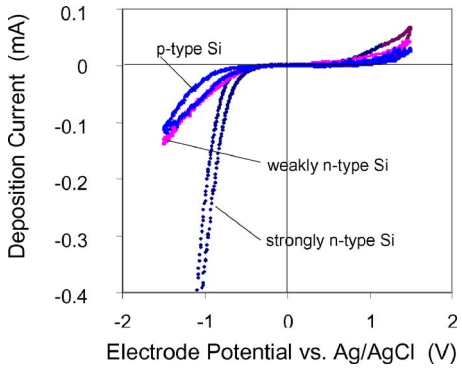

FIG. 2. (Color online) Voltammograms of ZnO deposition on Si: comparison of deposition currents on strongly *n*-doped Si, weakly *n*-doped Si, and *p*-type Si.

copy (TEM) micrograph typically obtained for ZnO wires grown in electrodeposition. The images indicate that the wires are single crystalline and of high structural quality. Infrared reflectance results on these wires have indicated electron mobilities as high as 10 $cm^2/V\,s$.[6] Ultraviolet and visible photo- and electroluminescences in these wires have been reported earlier by us.[10]

The growth on Si is challenging due to several effects. Since the electrolyte solution favors oxidation, the formation of a thin oxide layer on the Si wafer cannot be avoided, even if a stable oxide-free surface is prepared prior to the deposition process. SiO_2 formation may thus be expected as a growth-inhibiting or growth-altering effect. Secondly, there is a significantly lower electron density in many Si substrates compared to the metallic substrates that have previously been used. Since free electrons are needed in the growth process, weakly *n*- or *p*-doped substrates may not supply sufficiently high current densities for efficient growth.

Figure 2 shows voltammograms obtained for the various Si substrate types. It is noted that only low-resistivity *n*-type Si is capable of providing high deposition currents at electrode potentials of −1 V. The current density is typically 1 mA/cm^2 and comparable to that observed on metallic substrates. Weakly *n*-doped and *p*-doped electrodes conduct much smaller currents. These differences can be explained in terms of voltage loss in the semiconductor bulk and interface regions. Under cathodic polarization, as used here, the strongly *n*-type Si is not much affected by these two effects, and the voltammogram is therefore very similar to those of metallic electrodes. In weakly *n*-type and *p*-type Si electrodes, however, a sizable portion of the applied electrode potential is dropped across the semiconductor space charge layer at the interface to the electrolyte, and a significant overvoltage is needed to establish a sufficient flux of electrons to the surface where they are needed in the deposition reactions. As a consequence, not all of the applied electrode potential is dropped across the electrolyte double layer and an increased cathodic electrode potential is required to initiate and maintain the growth process. For more detailed discussion on semiconductor electrodes see, for example, Ref. 11 or the book by Sato.[12] In Fig. 3(a) we show electron micrographs of nanowires grown at −1.0 V versus Ag/AgCl on the naturally oxidized polished (100) strongly *n*-type Si. Bunched nanowire growth is observed. We attribute the bunched morphology to a low density of nucleation sites on the lightly oxidized substrate. Nanowires with similar morphology are also observed on the freshly cleaved and mechanically scratched surfaces. Application of the same electrode potential to the naturally oxidized surface of weakly *n*-doped or *p*-type surfaces produces no ZnO growth. However, Figs. 3(b) and 3(c) show that continuous thin film deposition occurs on these areas of minimal oxide thickness of the weakly *n*-type wafers. Material analysis indicates that the films are nanocrystalline ZnO. Nanowires are not formed.

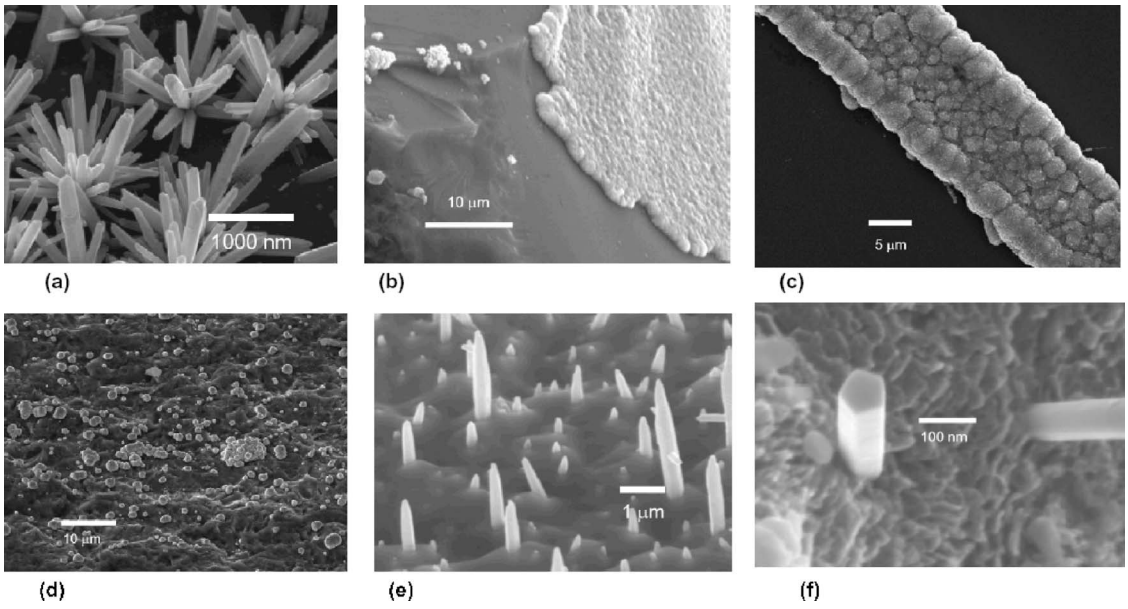

FIG. 3. (a) Strongly *n*-type Si substrate: bunched nanowire growth on Si (100) facets covered with natural oxide; (b) weakly *n*-type Si: dense layer of nanocrystalline ZnO on a freshly cleaved (111) facet. (c) Nanocrystalline ZnO deposition restricted to the deep scratch on a Si (100) surface. No ZnO deposition is found on oxidized facets. (d) *p*-type Si: islandlike clusters of ZnO on freshly cleaved (111) facets of *p*-type Si; (e) nanowires grown on a freshly cleaved surface of a *p*-type wafer at −1.5 V, (f) pentagonal nanowire grown on *p*-type substrate at −1 V with white-light illumination.

On the freshly cleaved or scratched *p*-type surfaces, the ZnO growth is even more scarce and produces only islandlike thin film coverage, as shown in Fig. 3(d). These results indicate that selective growth on *n*-doped Si regions can be achieved. The selectivity between strongly *n*-type and other surfaces is 100% on Si surfaces covered with a natural oxide of 20 Å at electrode potentials of −1.0 V.

With electrode potentials of −1.5 V, sufficient overvoltage is provided to obtain nanowire deposition on the cleaved surface of *p*-type wafers, i.e., the growth selectivity is lifted. Vertically oriented nanowires as shown in Fig. 3(e) are observed for these conditions on *p*-type substrates. In the regime between optimized growth conditions and completely suppressed growth, defective wires, continuous films, and islandlike clusters can be grown. This intermediate growth regime occurs on Si substrates with low doping levels at deposition potentials between −1 and −1.5 V and is characterized by insufficient electron supply to the surface. When illumination is used to increase the surface carrier densities the growth results can further be modified. In general, however, nanowire deposition is scarce and/or defective in this growth regime, as is illustrated in Fig. 3(f), showing wire with pentagonal cross section on a nanocrystalline ZnO island. The pentagonal cross section is likely a result of multiple twinning defects or the stabilization of high-index surface planes in nonoptimal deposition conditions.[13]

Finally, to demonstrate that under optimized conditions wires of highest quality can be grown, we show in Fig. 4 the electroluminescence spectrum of nanowires grown at −1.0 V on *n*-type Si. The used light-emitting device has a device structure as developed earlier by us for applications on SnO_2/glass substrates.[10] A band of visible luminescence and a small tail toward ultraviolet contributions are observed in this room-temperature spectrum.

Our results indicate that high-quality single-crystalline ZnO nanowires can be grown on cleaved and naturally oxidized Si surfaces of *n*-type wafers using deposition conditions very similar to those explored by us earlier on metallic and highly doped SnO_2 substrates. ZnO deposition is also possible on low conductivity *n*-type and even on *p*-type samples. But the deposition is markedly less effective at electrode potentials of −1.0 V: It only occurs on freshly cleaved surface *n*-type surfaces; there is no deposition on naturally oxidized surfaces. With additional external light bias defective pentagonal nanowires can be grown on *p*-type substrates. Regular hexagonal nanowires can be grown on weakly *n*-type and *p*-type substrates at −1.5 V. Despite the low growth temperature of only 80 °C, these wires exhibit visible electroluminescence at room temperature.

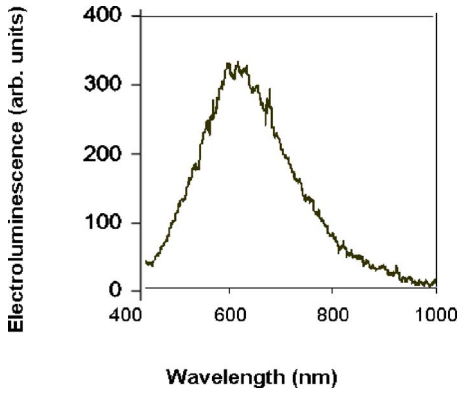

FIG. 4. Electroluminescence spectrum of ZnO nanowires on *n*-Si using the structure *n*-Si/ZnO/polystyrene/Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT)/Au.

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