

Direct Formation of Catalyst-Free ZnO Nanobridge Devices on an Etched Si Substrate Using a Thermal Evaporation Method

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ABSTRACT

Well-aligned single crystalline ZnO nanobridges have been synthesized selectively across the prefabricated electrodes on silicon substrates by a single-step thermal evaporation method without using any metal catalysts or a predeposited ZnO seed layer that was a prerequisite for such synthesis. The growth region was self-defined by the anisotropic surface of the silicon substrate as initially postulated. Careful control of the reaction time and the substrate temperature allows the nanobridges to form almost exclusively across the electrodes. The photoresponses as well as the current–voltage characteristics of the device confirm that this single-step process indeed offers a simple and a cost-effective way to integrate self-assembled nanodevices based on individual and/or a large number of ZnO nanowires with conventional circuits without using e-beam lithography techniques and/or additional costly deposition processes.

In recent years, a large number of one-dimensional nanostructures have been synthesized with precisely controlled chemical compositions, morphologies, and sizes using various synthesis methods for potential applications in a variety of nanoscale devices. These include transistors, memory devices, logics, chemical/biosensors, and lasers.^{1–4} In view of various distinctive properties of ZnO (a direct band gap of 3.37 eV at room temperature), nanodevices based on this material hold a lot of promises for, in particular, gas-sensing, electronic, optoelectronic applications.^{5–8} ZnO-based nanodevices are also promising candidates for biological applications due to easy fabrication and friendly nature to living organisms.⁹

Electrical and optical properties of nanowires are typically measured by making metallic (ohmic) contacts to the nanowires placed on an insulating substrate. To fabricate such devices, nanowires are usually separated from a substrate on which the nanowires were initially grown and then are randomly dispersed onto a desired insulating substrate after being diluted in a solution. In most cases, an electron beam lithography technique is applied to interface the nanowires with other elements of a circuit or a system.^{5,6,10,11} Although this research-based approach is suitable for a single or few

device demonstrations, it is rather complicated and time-consuming such that it may not be an economically attractive integration process for conventional complementary metal oxide semiconductor compatibility.

On the other hand, for accurate measurements of the intrinsic properties, the nanowires need to be free from a contact with any object and to be surrounded by nonconductive material to eliminate possible artifacts attributed to current paths other than those through the nanowires themselves.⁶ Placing nanowires on an insulating surface, however, cannot completely eliminate the unwanted current paths. An ideal solution to this problem is direct lateral growth of suspended nanowires between two prefabricated electrodes. Recently Islam et al. introduced a bridging technique that connects a large number of highly oriented, suspended metal-catalyzed silicon nanowires between two electrodes to design nanodevices that could be easily integrated with modern electronic fabrication technologies.¹²

Although catalysts help in the synthesis of various nanowires, they may also add impediment by becoming an impurity introduced into the nanowire structure. Often these types of impurities can hinder the performance of a device made with the nanowires. For example, one of the known issues a gold (Au) nanoparticle used for growing semiconductor nanowires is the near-center band gap ionization energy level when Au is present in silicon.¹³ Some metals

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such as Au and Cu contribute to a high level of generation-recombination currents if the metals are present in the semiconductor, even if the level of the metal is almost undetectable. Thus it is desirable to develop techniques for synthesizing nanowires without any metal catalysts.

Selective growth of ZnO nanorods on various substrates without using metal catalysts has been reported.^{14–19} Very recently Conley et al. used a predeposited thin film ZnO layer alternative to metal catalysts to define the regions of nanowire growth.¹⁸ Deposition of the seed layer on a Si substrate using an atomic layer deposition technique was thus a prerequisite to grow suspended ZnO nanowires between two electrodes in their work. This rather costly process, however, may not be necessary to selectively form ZnO nanobridges across the electrodes on Si substrates.

Surface morphology of an anisotropic crystalline substrate plays a major role in controlling the growth kinetics of low-dimensional structures.²⁰ The anisotropy of the surface often influences the growth of nanowires since it can induce an anisotropic strain and, thus, can confine the adatom diffusion to one dimension.²¹ Nucleation usually occurs in sequence at edges, at steps, and on planar surfaces in order to reduce the surface energy.^{22,23} The higher the density of broken bonds in the region, the higher the surface energy. Therefore it is expected that the edges of the prefabricated Si electrodes on a Si substrate may provide the most favorable site for a vapor to bond in a vapor–solid process since the edges of the electrodes serve as higher-energy binding sites. Consequently, the nature of structures of the electrodes on Si substrate alone may prevent random growth of ZnO on a Si substrate and define the favorable growth regions such that suspended ZnO nanobridges are expected to form preferentially across the electrodes even without a seed layer.

In this Letter we report a direct single-step method that ZnO nanowires selectively bridge prefabricated Si electrodes on a Si substrate without using any metal catalysts or a seed layer to avoid interaction of the surface of the nanowires with the surroundings. We also demonstrate that the device fabricated by using this method exhibits high photosensitivity required for optoelectronic devices.

ZnO nanowires were grown on two different types of substrates: on-axis Si(100) wafers (Si-1s) and etched Si(110) wafers with exposed Si(111) vertical planes bounding trenches (Si-2s).¹² The nanowires grown on Si-1s were to be used for the chemical and the structural characterizations (see below) while Si-2s were to form ZnO nanobridges across the trenches. The trenches are approximately 10–13 μm deep and 2–6 μm wide.

The ZnO nanowires were grown in an alumina tube horizontally placed in a conventional tube furnace. An alumina boat containing pure ZnO powders (Aldrich, 99.99%) was loaded into the center of the alumina tube. Si-1s and Si-2s were placed in pairs at the several different temperature zones nearer to the downstream end of the tube to ensure that the ZnO nanowires and the nanobridges grown on Si-1s and Si-2s, respectively, are structurally as well as chemically identical. The ZnO powders were thermally evaporated at 1450 $^{\circ}\text{C}$ with an argon flow under a constant

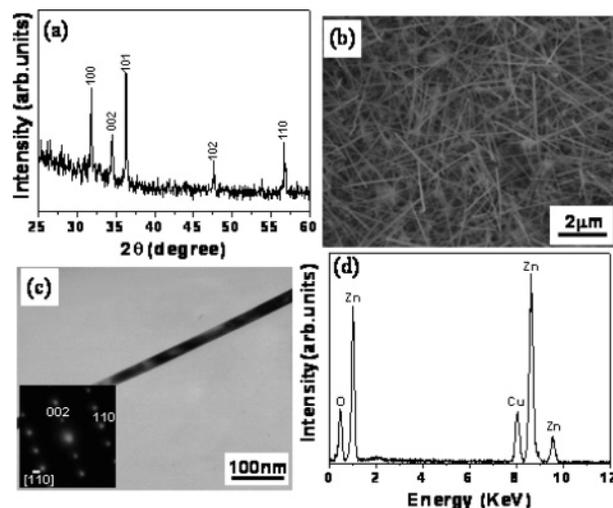


Figure 1. An XRD pattern (a), a FE-SEM image (b), a bright field TEM image (c), and an EDX spectrum (d) of ZnO nanowires synthesized on the on-axis Si(100) substrate at 850 $^{\circ}\text{C}$ for 120 min.

furnace chamber pressure of 0.7 atm. The evaporation time and the flow rate were precisely controlled. The temperature of the substrates varied from 600 to 850 $^{\circ}\text{C}$ depending upon their locations in the alumina tube.

The chemical and the structural analyses on as-synthesized ZnO nanowires on Si-1s were carried out using a X-ray diffractometer (XRD, Scintag XDS-2000) with Cu $K\alpha$ radiation, a field emission scanning electron microscope (FE-SEM, FEI XL-30 SFEG), and a transmission electron microscope (TEM, Philips CM-12).

Figure 1 summarizes the results for the ZnO nanowires grown on a Si-1 at 850 $^{\circ}\text{C}$ for 120 min with the argon flow rate of 200 standard cubic centimeters per minute (sccm). The measured XRD peaks are indexed to confirm the wurtzite hexagonal structure (Figure 1a). The diameters of the nanowires range from 20 to 150 nm, and their lengths are found to be several micrometers as shown in a FE-SEM image (Figure 1b). Parts c and d of Figure 1 reveal a representative TEM image (Figure 1c) and an energy-dispersive X-ray (EDX) spectrum (Figure 1d), respectively, of one of the nanowires shown in Figure 1b with a diameter of about 30 nm. The electron diffraction pattern of the nanowire (see the inset of Figure 1c) clearly demonstrates that the synthesized nanowires are in a single crystalline phase. The chemical composition of the ZnO nanowire was confirmed by the peaks associated with Zn and O atoms shown in Figure 1d. (The Cu-related peak in the spectrum comes from the Cu grids.)

Figure 2 shows the sequential FE-SEM images of the formation of nanobridges across the electrodes on Si-2s in 600 $^{\circ}\text{C}$ (Figure 2a–c) and 850 $^{\circ}\text{C}$ (Figure 2d,e) zones. In view of Figure 1 together with the fact that these nanobridges are formed under the identical conditions under which the nanowires shown in Figure 1 were grown on Si-1s as described above, it is reasonable to assume that these nanobridges are chemically as well as structurally identical to the nanowires shown in Figure 1. Note that neither metal catalysts nor a predeposited ZnO seed layer was used to form these nanobridges across the electrodes on a Si substrate.

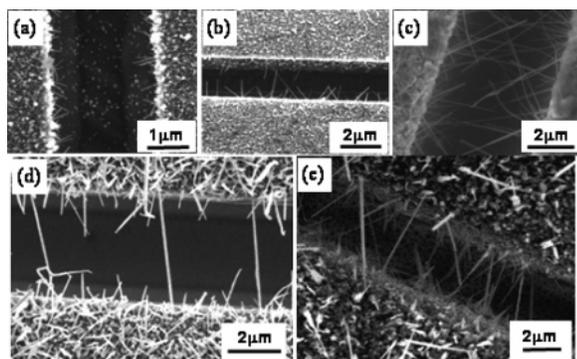


Figure 2. FE-SEM images of ZnO nanobridges formed across two electrodes at 600 °C for 20 min (a), 60 min (b), and 120 min (c) and at 850 °C for 60 min (d) and 120 min (e), respectively.

Figure 2a shows a representative image of a sample that was collected in the 600 °C zone at the reaction time of 20 min. ZnO nanowires start to laterally grow from the vertical walls (Si(111) plane) of a trench etched on a Si(110) substrate toward the opposing vertical surfaces. Nearly no sign of nanowire growth was observed before 20 min of the reaction time while nanopowders were formed on the surface of the electrodes in this temperature zone. The density of the powder was found to be distinctively higher near the edges of the electrodes as clearly seen in Figure 2a. EDX analysis confirmed that the chemical composition of these powders is ZnO. Figure 2a also demonstrates that ZnO nanowires start to preferentially grow from the edge areas. As reaction time reaches 60 min (Figure 2b), the nanowires shown in Figure 2a further grow and impinge on the opposing vertical surface to form nanobridges. A majority of nanowires are found to be still almost exclusively formed across the two electrodes. The density of the nanobridges becomes significantly higher when the reaction time was increased to 120 min (Figure 2c). At this reaction time, however, the regional selectivity of the formation of ZnO nanowires on the Si-2s starts to become lower.

On the other hand, in the 850 °C zone (parts d and e of Figure 2), within 60 min (Figure 2d), much denser and thicker ZnO nanobridges compared to those shown in Figure 2b are formed and a significant number of the nanowires have already started to grow on the top surface of the electrodes. Figure 2e shows an image obtained from a sample that was in this temperature zone for 120 min.

We have initially postulated that the evaporated ZnO preferentially nucleates near the edge area of the prefabricated electrodes on a Si substrate to self-define the growth area as schematically sketched in Figure 3a,b. Such higher density of ZnO nanopowder deposited near the edges of the electrodes is expected to allow ZnO nanowires to first grow from those areas to bridge the two electrodes (Figure 3c). Consequently, as the growth continues, the density of ZnO nanowires grown across the two electrodes becomes distinctively higher than that of ZnO nanowires grown at the plane surface (Figure 3c). Figure 2 indeed strongly supports this postulate.

Figure 4a shows ZnO nanobridges synthesized under the optimized reaction conditions (850 °C for 40 min). ZnO

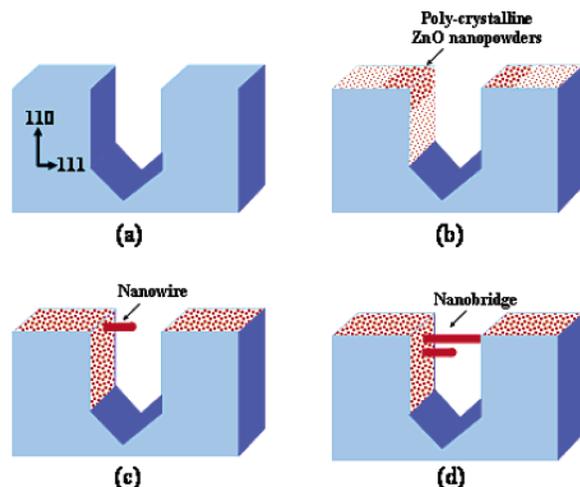


Figure 3. Schematic sketches of (a) prefabricated two electrodes on a Si substrate, (b) nucleation of ZnO nanopowders on the substrate, (c) ZnO growing across the two electrodes, and (d) a formation of ZnO nanobridges.

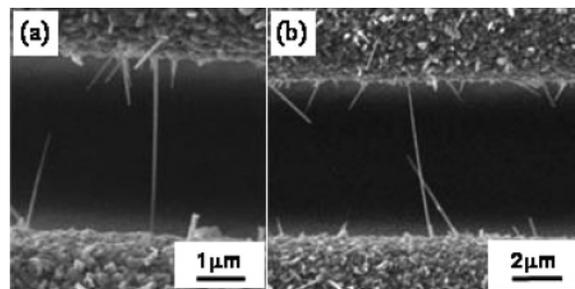


Figure 4. ZnO nanobridges formed across two electrodes with a separation of 4 μm (a) and 6 μm (b) at 850 °C for 40 min, respectively.

nanobridges were formed almost exclusively across the two electrodes. The distances between the two electrodes are 4 μm (Figure 4a) and 6 μm (Figure 4b). It is thus confirmed that ZnO nanobridges can be directly as well as selectively formed across the prefabricated electrodes on Si substrate by a single-step thermal evaporation method without using metal catalysts or a predeposited seed layer.

Figure 5 shows the current–voltage (I – V) characteristics of the synthesized ZnO nanobridges on a silicon-on-insulator (SOI) substrate in the dark and under illumination of UV light ($\lambda = 365$ nm). The measurements were performed on the device in air by probing directly on the Si electrodes without depositing metal for better contacts. The distance between electrodes was 4 μm. Figure 5 clearly demonstrates typical nonlinear and asymmetric I – V characteristics of both the dark current and the photocurrent which can be attributed to the contact barriers existing between Si and ZnO nanobridges. As seen in Figure 5, under UV irradiation, the measured current was increased from 0.014 to 2.21 μA at the applied voltage of 5.0 V. Such a high increase in the current under the UV irradiation indicates the higher sensitivity of this device to UV light compared with other ZnO nanowire devices previously reported.^{18,24–26}

Finally, the time-dependent photoresponses of the ZnO nanobridges in air at a bias voltage of 2.0 V are shown in

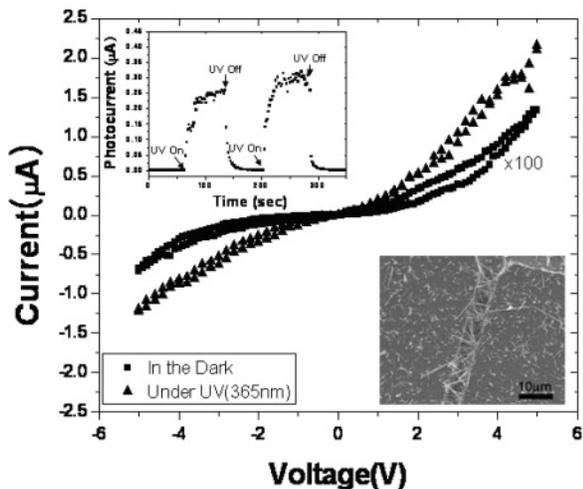


Figure 5. I - V characteristics of the dark current and the photocurrent (under 365 nm) of ZnO nanobridges on a silicon-on-insulator (SOI). (The inset shows the time-dependent photoresponses of the device in air at a bias voltage of 2.0 V.)

the inset of Figure 5. When the UV lamp was switched on, the current sharply increased to $0.20 \mu\text{A}$ at about 2.7 s and then reached the saturation value of $0.27 \mu\text{A}$ within 18 s. As soon as the UV light was turned off, the measured current drops down to $0.08 \mu\text{A}$ at about 3.0 s and then further decreased to the initial value of $0.004 \mu\text{A}$ within 50 s. The observed photoresponses of the ZnO nanobridges can be attributed to adsorption and photodesorption of oxygen on the surface of the nanobridges in addition to rapid changes in conductivity by photogenerated electron-hole pairs.²⁵⁻²⁷

In summary, chemically pure single crystalline ZnO nanowires have selectively bridged across the prefabricated electrodes on silicon substrates by a single-step thermal evaporation method without using any metal catalysts or a predeposited ZnO seed layer. The results confirm the postulate that the growth region is self-defined by the anisotropic surface of the silicon substrate used. The ZnO nanowires almost exclusively grow near the edges of the electrodes to form the nanobridges across the electrodes under precisely controlled reaction conditions. The photoresponses of a ZnO nanobridge device fabricated in this study demonstrate that this single-step method is indeed proved to be a simple and cost-effective way that one can integrate self-assembled nanodevices based on individual and/or a large number of ZnO nanowires with conventional circuits without using e-beam lithography techniques and/or additional costly deposition processes.

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