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Research Article

Synthesis of SnO_2-ZnO Core-Shell Nanowires and Their Optoelectronic Properties

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Zinc oxides deposited on Tin dioxide nanowires have been successfully synthesized by atomic layer deposition (ALD). The diameter of SnO_2-ZnO core-shell nanowires is 100 nm by ALD 200 cycles. The result of electricity measurements shows that the resistance of SnO_2-ZnO core-shell nanowires (ALD: 200 cycles) is 925 Ω, which is much lower than pure SnO_2 nanowires (3.6×10^6 Ω). The result of UV light test shows that the recovery time of SnO_2-ZnO core-shell nanowires (ALD: 200 cycles) is 328 seconds, which is lower than pure SnO_2 nanowires (938 seconds). These results demonstrated that the SnO_2-ZnO core-shell nanowires have potential application as UV photodetectors with high photon-sensing properties.

1. Introduction

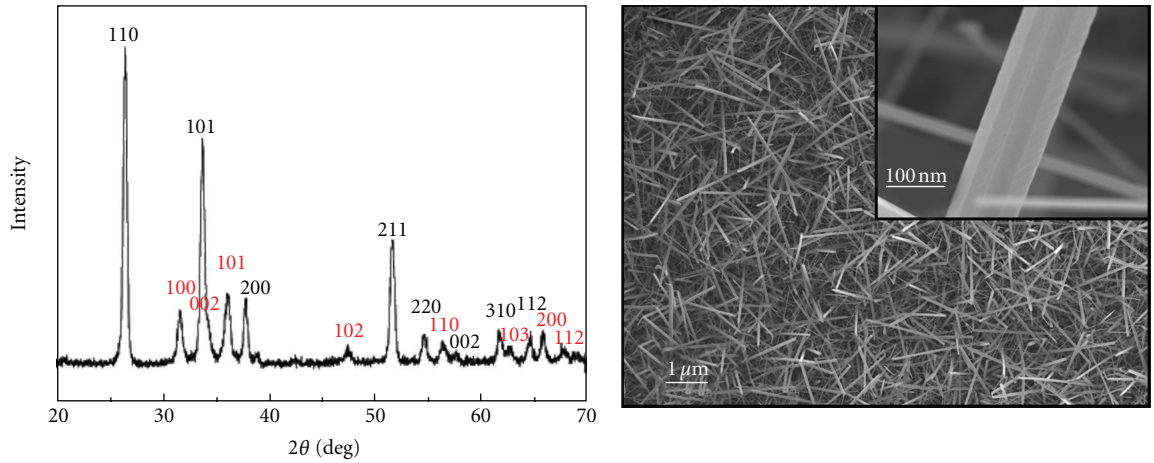
Tin dioxide (SnO_2) and zinc oxide (ZnO), world-renown n-type multifunctional semiconductors, have wide direct band-gap energy: 3.6 and 3.37 eV at 300 K, respectively. Furthermore, because of the very large length-to-diameter and surface-to-volume ratios in nanoscale regime, the gas sensing and optoelectronic properties of one-dimensional SnO_2 and ZnO nanostructures are highly sensitive to adsorbed species on their own surface. Owing to special physical and chemical characteristics of one-dimensional SnO_2 and ZnO nanowires, plenty of nanocompounds based on them have been widely applied to many industrial places, such as field emission devices [1], lithium-ion batteries [2], optoelectronic devices [3–6], and gas sensors [6–10]. However, upgrading the optoelectronic sensitivity is still a challenge for SnO_2 nanostructure-based photodetectors.

In recent years, many literatures have demonstrated that nanocompounds of SnO_2 and ZnO which belong to a hetero-combination acted with good chemical and physical properties exceeding to their individual materials [11–13]. Most of all, a synthesis of core-shell nanostructure is a considered method for strongly improving sensing properties of SnO_2 nanowires since surface states affects the sensing properties significantly.

In this study, SnO_2-ZnO core-shell nanowires were synthesized by a step-by-step manufacture. First, SnO_2 nanowires were fabricated by thermal evaporation. Second, ZnO layers were deposited on SnO_2 nanowires by atomic layer deposition. Atomic layer deposition (ALD), a chemical vapor deposition, is a cutting-edge technique for the good controllable deposition of inorganic layers and has been commonly applied to semiconductor industries. In particular, the self-limiting gas-solid growth features of the ALD growth expedites the growth of thin films and nanomaterials with pretty accurate thickness and good uniformity.A few research of SnO_2-ZnO core-shell nanowires focuses on enhancement of optoelectronic sensing, so their optoelectronic properties under UV light were investigated.

2. Experimental

There are two steps in this fabrication of SnO_2-ZnO core-shell nanowires. In advance, an Au layer (about 30 Å), a catalyst in this fabrication, was coated on aluminum substrates by sputtering. In the first step, Tin oxide nanowires were



(a) (b)

Figure 1: (a) XRD pattern (b) SEM image of SnO_2-ZnO core-shell nanowires (ALD: 200 cycles).

fabricated on aluminum substrates by thermal evaporation. High quality 0.4 g Sn powders (Aldrich, purity 99.99%) and several aluminum substrates were situated in an Al boat and then placed the Al boat in the heating area of a quartz tube. In the growth of Sn nanowires, the pressure inside the quartz tube was kept up at 1 Torr by a rotary pump. The working conditions of this process were as follows. (1) Raising the temperature to 950°C with 20°C/min was at a constant flow rate of 10 sccm Ar gas. (2) Maintaining the temperature at 950°C for 1 hour was at a constant flow rate of mixed gas of 10 sccm Ar and 1 sccm O_2. (3) Cooling to the room temperature was under a constant flow rate of 10 sccm of Ar gas.

In the second step, a ZnO layer was coated on SnO_2 nanowires by atomic layer deposition (ALD) [14–16]. The precursors were DEZ ($Zn(C_2H_5)_2$, Aldrich, purity 98%) and H_2O (purity 99.999%) in 200 ALD reaction cycles. Every single cycle, a 60 ms DEZ pulse and a 60 ms H_2O pulse were sequentially delivered into the ALD chamber by 5 s of purging with N_2 (purity 99.9995%). The pressure of chamber was maintained 1 Torr in the ALD reaction.

The morphology, crystal structure, and chemical composition of the SnO_2-ZnO core-shell nanowires were analyzed by a field emission-scanning electron microscope (FESEM, JEOL JSM-6900F), a MAC glancing incident X-ray spectrometer with an incident angle of 0.5°, a high-resolution transmission electron microscope (HRTEM, JEOL, JEM-2010), and X-ray photoelectron spectroscopy (XPS Perkin-Elmer Model PHI1600 system). In order to test the optoelectronic properties of SnO_2-ZnO core-shell nanowires, the measurements of I-V curves via a constant voltage (5 V) and photoresponse curves under UV light (λ = 365 nm and intensity is 17.1 W/m^2) were handled.

3. Results and Discussion

Figure 1(a) shows the XRD $\theta - 2\theta$ diffraction pattern of the SnO_2-ZnO core-shell nanowires obtained after 200 ALD reaction cycles. Red numbers (100), (002), and (101) are the main planes in ZnO with hexagonal wurtzite structure, and this XRD pattern corresponds with JCPDS: 89-1397. The lattice constants of hexagonal wurtzite structure are as follows: $a = b = 3.253$ Å and $c = 5.213$ Å. Black numbers are the main planes in SnO_2 with tetragonal rutile structure with lattice constants: $a = b = 4.737$ Å, $c = 3.187$ Å, and this XRD pattern matches up with JCPDS: 88-0287. Figure 1(b) is the SEM image of the SnO_2-ZnO core-shell nanowires obtained after 200 ALD reaction cycles, and the enlarged image is in the upper right corner. According to these images, the abundant SnO_2-ZnO core-shell nanowires with dimensions of 100–150 nm in diameters and several micrometers in length have been produced. These results demonstrate that the nanocompound is made of SnO_2 and ZnO without other materials, signifying that the high quality nanocompounds of SnO_2-ZnO have been successfully prepared.

To further investigate the detailed microstructure of SnO_2-ZnO core-shell nanowires, taking images by TEM was performed. Figures 2(a) and 2(b) show a low-magnification TEM image. The diameter of core-shell nanowires is 100 nm, and the thickness of ZnO shell layer is 25 nm. From Figure 2(c), the HRTEM image of core-shell SnO_2-ZnO nanowires shows that the lattice spacing between (0002) is 0.28 nm, and the structure of ZnO that has hexagonal structure is corresponding. From Figure 2(d), the growth direction is [101], the lattice space is 0.26 nm, and the angle between [101] and [−101] is 67.85, which are consistent with the SnO_2 that has tetragonal rutile structure. According to these TEM images, no doubt the core-shell nanostructure is certainly formed via two-step method.

In order to identify the chemical composition of the SnO_2-ZnO core-shell nanowires and check the quality of ZnO deposited on SnO_2 by ALD, the core-shell SnO_2-ZnO nanowires were additionally characterized by XPS. Figure 3(a) shows that the binding energy of Zn ($2p_{3/2}$) and Zn ($2p_{1/2}$) are 1021.9 eV and 1044.9 eV, respectively. Figure 3(b) shows that the binding energy of O (1 s) is

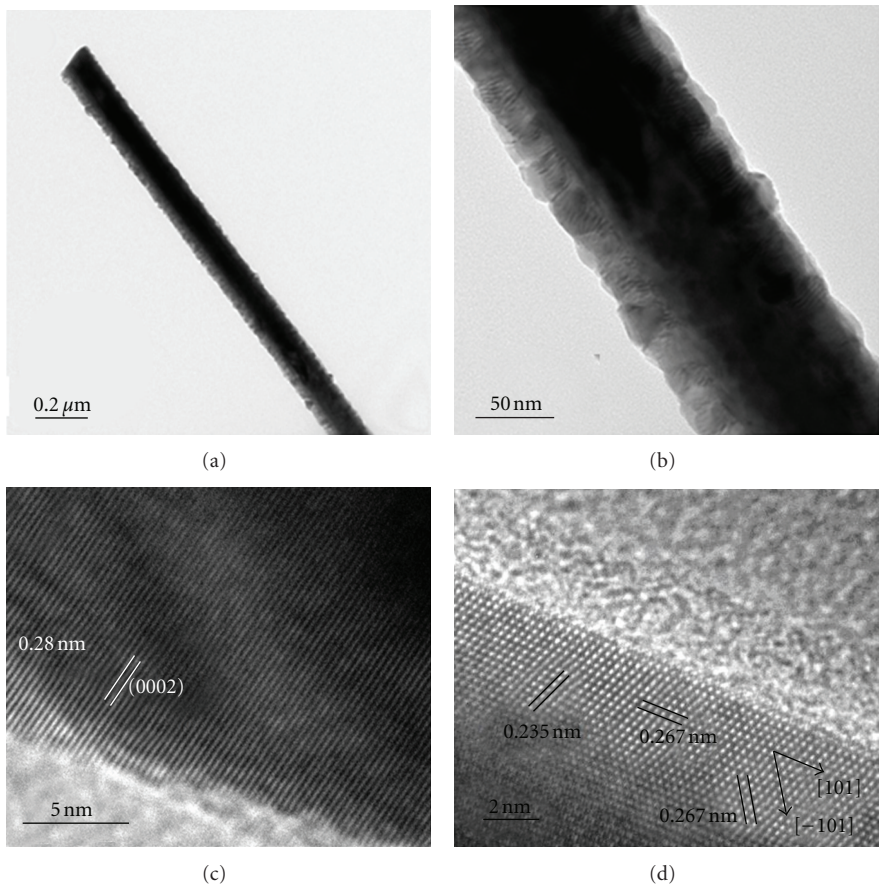


Figure 2: (a) and (b) Low-magnification TEM, (c) HRTEM image of a SnO_2-ZnO core-shell nanowires (ALD: 200 cycles), and (d) HRTEM image of a SnO_2 single nanowires.

530.9 eV. Figure 3(c) shows that binding energy of Sn ($3d_{3/2}$) and Sn ($3d_{5/2}$) is 495.1 eV and 487.5 eV. After integration of the area of three main elements "peaks by computer program", the atomic percentages of oxygen, zinc, and tin are 55.27, 41.7, and 3.03, respectively. Judging from XPS analysis, because the atomic percentage of ZnO is large in this compound, ZnO crystalline shell is definitely deposited on SnO_2 nanowires by ALD.

By above material analyses, the confirmation of SnO_2-ZnO core-shell nanowires synthesized sequentially via thermal evaporation, and ALD was done. To determine the potential applicability of SnO_2-ZnO core-shell nanowires in this study to photodetectors, their I-V curves and UV photon-sensing properties were investigated. Figure 4 shows the current-voltage (I-V) curves of SnO_2-ZnO core-shell nanowires with ALD 200 cycles reaction (red line) and pure SnO_2 nanowires (black line) at room temperature and atmospheric pressure. Two curves show a good ohmic contact between the nanocompounds and Ag electrodes. The electrical resistivity can be expressed as $R = \rho \times \mathrm{L/A}$, and the electrical resistivity of SnO_2-ZnO nanowires and pure SnO_2 nanowires can be solved as 925 Ω and 3.6×10^6 Ω, respectively. The electrical resistivity of core-shell nanostructure is much lower than pure nanowires. Because of that ZnO film of core-shell SnO_2-ZnO nanowires is more compact than SnO_2 nanowires, this effect is able to increase the film conductivity.

When setting up an electric circuit with core-shell nanostructures, there will be a strain in a heterointerface to keep from a deformation happened and decrease the total energy. Moreover, the band gap of core-shell materials will be reduced, and then the conductivity will be raised [17].

To investigate the application of SnO_2-ZnO core-shell nanostructure and pure SnO_2 nanowires for UV detectors, the optoelectronic response and recovery of the as-fabricated photodetectors were tested under emitted UV lamps (λ = 365 nm). The optoelectronic test unveils that the current very quickly rises to a steady level under UV light (UV light is on) and then increasingly recovers to the initial state in the dark (UV light is off). Figures 5(a) and 5(b) show the period photoresponse curve of pure SnO_2 nanowires and SnO_2-ZnO core-shell nanowires (200 ALD cycles), respectively. In previous studies [18], the opinion of these photoresponse curves was discussed. When the UV light is off, the species of oxygen molecular structure are chemoadsorbed on the interfaces of nanostructures because oxygen molecules catch free electrons, that is, $O_{2(g)} + e^- \rightarrow O_{2(ad)}{}^-$. Therefore, a low conductivity depletion layer is formed near the surface of nanowires, and the nonmaterial's conductivity will be decreased. When UV light is on, electron-hole

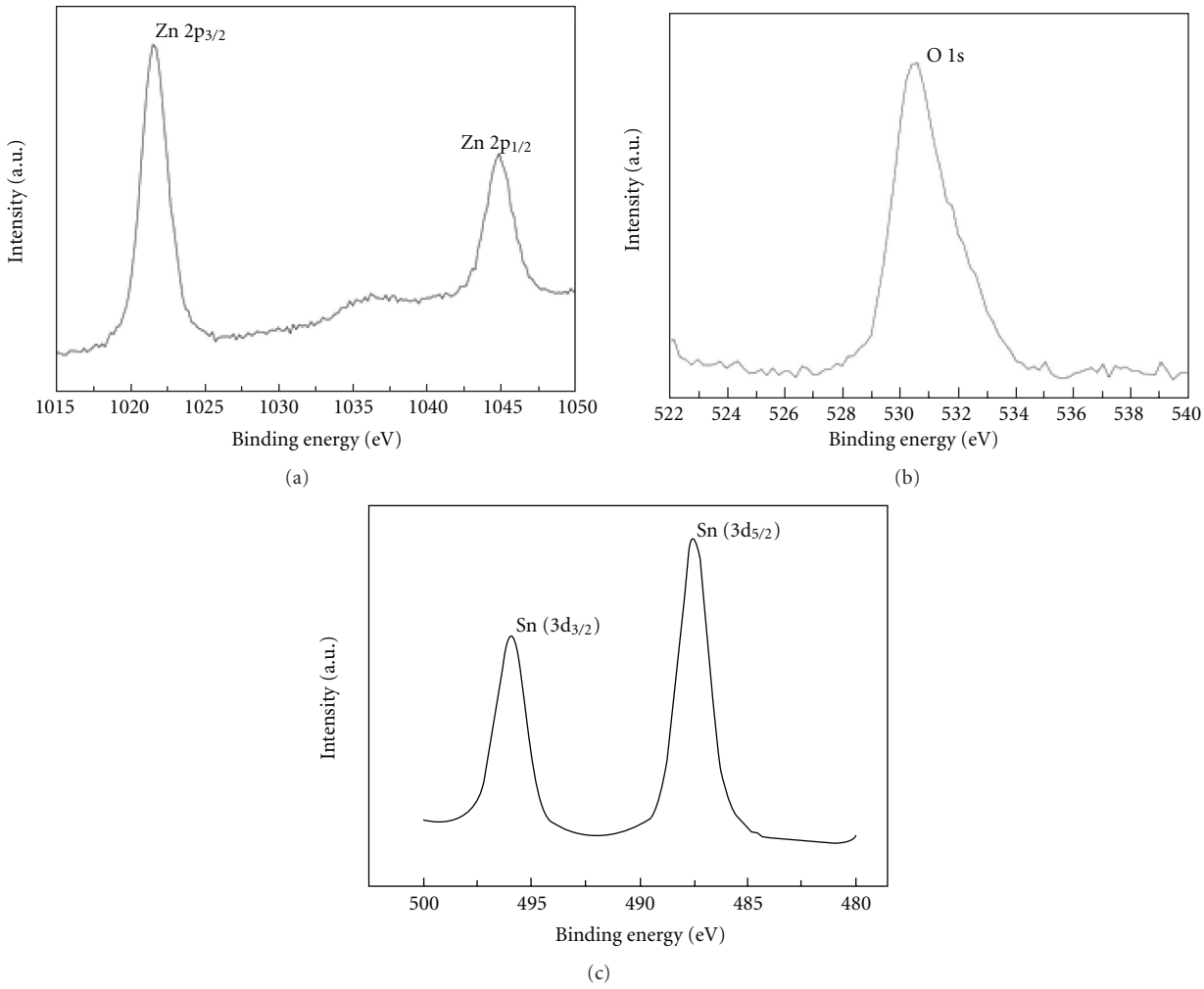


Figure 3: The XPS (a) Zn 2p (b) O 1S (c) Sn 3d spectrum.

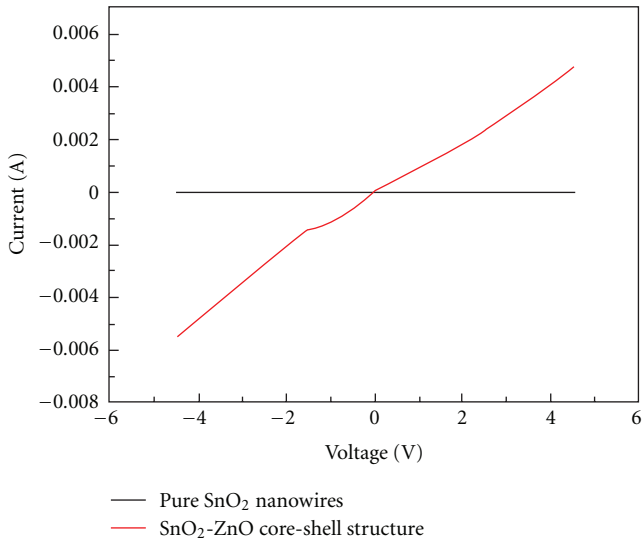


Figure 4: The I-V curve of SnO_2-ZnO core-shell nanowires (ALD: 200 cycles) and pure SnO_2 nanowires.

pairs follow this reaction, $h\nu \rightarrow e^- + h^+$, and will be happened in the nanowires. The photoinduced holes will relocate to the surface and recombine with the oxygen ions, that is, $h^+ + O_{2(ad)}{}^- \rightarrow O_{2(g)}$. At the same time, the photon-generated electronics are able to play free electrons and upgrade the electron conductance of nanowires. The photocurrent rapidly increases with the reduced depletion layer.

Figure 5(a) shows that since UV light is on, the current is 3.47×10^{-6} A. After 50 seconds, the current increases to 7.23×10^{-6} A. The slope is 0.0752. From Figure 5(b), since UV light is on, the current is 3.53×10^{-5} A. After 50 seconds, the current lifts to 5.35×10^{-5} A. The slope is 0.0364. Therefore, the device based on pure SnO_2 nanowires has a better sensitivity than based on SnO_2-ZnO core-shell nanowires. In terms of photosensitivity, the pure SnO_2 nanowires are little larger than the SnO_2-ZnO core-shell nanowires, and two depletion areas of core-shell nanostructure might be the cause for this phenomenon. However, the recovery time of core-shell SnO_2-ZnO nanowires is just 328 seconds, which is much shorter than that of pure SnO_2 nanowires

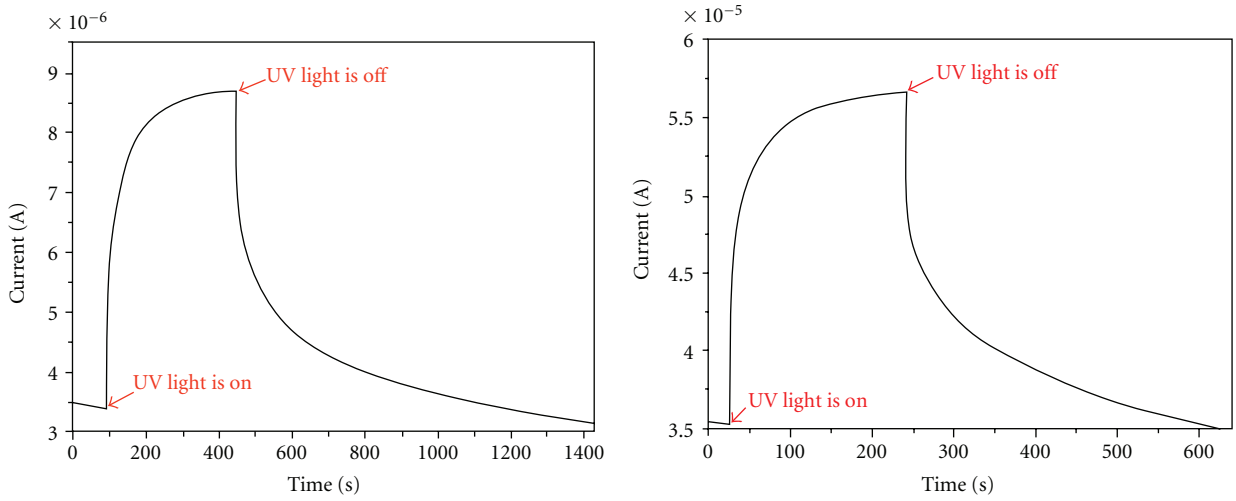


FIGURE 5: Photoresponse curves of (a) pure SnO_2 nanowires and (b) SnO_2-ZnO core-shell nanowires-based photodetectors.

(938 seconds). It is a reason that a superposition of the homo- and heterointerfaces formed at the junctions may be the root cause for the decreased recovery time compared with the detector judging from the nanowires without the shell layer [19, 20]. All in all, the SnO_2-ZnO core-shell nanowires have positive characteristics and applications in the manufacture of photodetectors.

4. Conclusion

SnO_2-ZnO core-shell nanowires have been successfully fabricated by a step-by-step process. First, SnO_2 nanowires were synthesized by thermal evaporation. Sequentially, ZnO shell layers were deposited by ALD. The SnO_2-ZnO core-shell nanowire-based photodetectors has the low electrical resistance (925 Ω) and the short recovery time (328 seconds), compared with pure SnO_2 nanowires. Thanks to excellent optoelectron abilities, the SnO_2-ZnO core-shell nanowires are the promising candidates as photodetectors.

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