

A Simple Route to Porous ZnO and ZnCdO Nanowires

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Porous ZnO nanowires were obtained in an inexpensive and simple way by thermally oxidizing ZnSe nanowires in air. The morphologies of the precursor and resulted nanowires are almost identical. X-ray diffraction and energy-dispersive X-ray spectroscopy reveal that the zinc blende ZnSe nanowires were transformed into wurtzite ZnO nanowires after oxidation. Transmission electron microscope measurements indicate that the ZnO nanowires are polycrystalline and are composed of nanoparticles and nanopores. ZnCdO nanowires, which were seldom reported previously, have also been prepared in this way. Just like the ZnO nanowires, the ZnCdO nanowires also show the porous structure. Photoluminescence studies on both ZnO and ZnCdO nanowires show intense near-band edge emissions at room temperature. The transition from one kind of nanowires to another by simple thermal oxidation described in this paper may be applicable to some other compound semiconductors and may open a practical route to yield nanowires.

Introduction

ZnO nanowires have attracted quite a large amount of attention in the near past because of both the unique properties of ZnO materials and one-dimensional (1D) nanostructures.^{1–4} Many methods have been employed to fabricate ZnO nanowires; these include metalorganic chemical vapor deposition (MOCVD),⁵ thermal evaporation,⁶ chemical vapor deposition,⁷ etc. An alternative method to obtain 1D nanostructures is the transformation from one kind of nanowire to another, which is of significance if the transformation can be achieved in a very simple and inexpensive way. However, only a few papers have demonstrated this fabrication route so far.^{8–12} Nanowires with a porous structure have a very high surface-to-volume ratio, and gas sensors based on porous nanowires have higher sensitivity than those based on single-crystalline ones.^{13,14} Furthermore, porous nanowires also find applications in the fields of catalysis, environmental engineering, and photonic crystals. However, they are much less explored up to date.^{13–19}

In this paper, we demonstrate the preparation of porous ZnO nanowires by thermally oxidizing ZnSe nanowires. Scanning electron microscope (SEM) analysis indicates that the morphology of the ZnSe precursor and the ZnO product is identical. Transmission electron microscope (TEM) investigation shows that the ZnO nanowires are polycrystalline with porous structure. We also prepared ZnCdO nanowires in the same way by oxidizing ZnCdSe nanowires. ZnCdO is an important band gap engineering material to ZnO and has been studied in the thin film form,²⁰ while in its nanowire form, only very few reports can be found.^{21–23} Optical properties of the nanowires are characterized by photoluminescence (PL) measurements, and both the ZnO and ZnCdO nanowires show intense near-band edge (NBE) emissions at room temperature.

Experimental Section

The growths of the ZnSe and ZnCdSe precursor nanowires on Si substrate were carried out in an MOCVD system, employing Au as catalysts. The detailed preparing conditions can be found elsewhere.²⁴ For the oxidation process, nanowires were placed in a quartz tube, which was in turn loaded into a furnace. Oxidation was carried out at 700 °C for 1 h. Afterward, the color of the sample was found changed from yellow to white. The morphology of the nanowires was examined by an LEO 1450VP SEM, and their composition characterized by an energy-dispersive X-ray (EDX) microanalyzer attached to the electron microscope. The structure of the nanowires was determined by a Rigaku X-ray diffractometer (XRD) and a Philips C120 TEM system. The radiation source used in the XRD measurement was the 1.5406 Å Cu K α line. PL studies were performed using the 325 nm line of a He–Cd laser as the excitation source.

Results and Discussion

Figure 1a and 1b show the plan-view SEM images of ZnSe precursor and ZnO product nanowires. The as-synthesized, high-density ZnSe nanowires are yellow in color. The dimensions of the nanowires are about 80 nm in width and over 20 μ m in length on average. Despite the color change to white, the morphology and size of the nanowires are nearly retained after oxidation, as shown in Figure 1b. EDX spectra shown in Figure 1, parts c and d, confirm the transformation from ZnSe to ZnO nanowires. The spectrum of the ZnSe precursors shows only signals from zinc and selenium, whereas after the oxidation process, the corresponding spectrum shows signals from zinc and oxygen. The Si signal in the spectrum is from the substrate, and the selenium signal is below detection limit. The appearance of the Si signal in the EDX spectrum of ZnO nanowires while not in that of the ZnSe nanowires may be due to the lighter molecular weight of O compare to Se. The transformation was also verified by XRD patterns, as shown in Figure 2. In both patterns, the diffraction peak located at 69.20° comes from the

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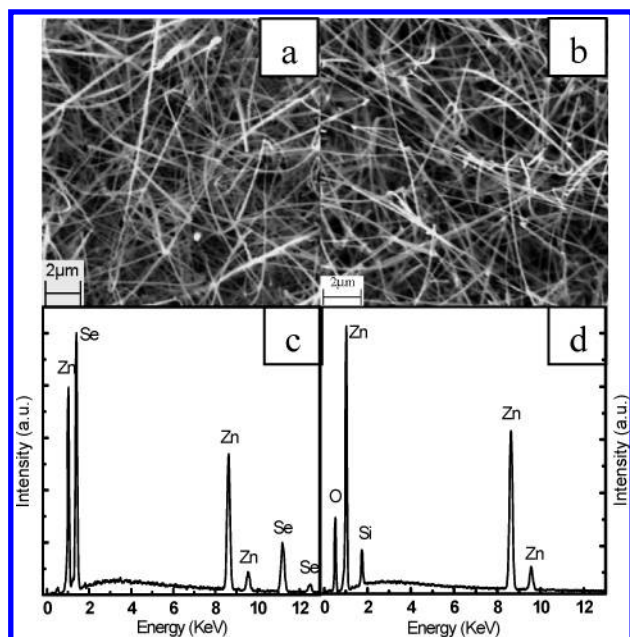


Figure 1. SEM images of the ZnSe precursor nanowires (a) and resulting ZnO nanowires (b) after annealing in air. Panels c and d are the EDX patterns of the ZnSe and ZnO nanowires.

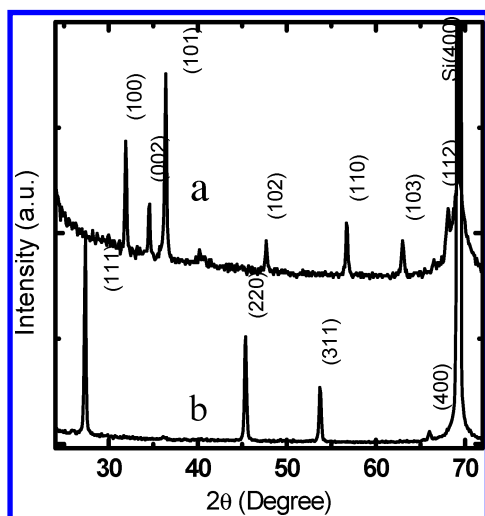


Figure 2. X-ray diffraction patterns of the ZnSe (a) and ZnO (b) nanowires, indicating the ZnSe nanowires are converted to ZnO after the oxidation process.

Si substrate. All other diffraction peaks of the sample before oxidation can be indexed to zinc blende structured ZnSe (JCPDS: 37-1463), revealing the crystal structure of the precursor nanowires. After oxidation, no peaks from other phases but only those from wurtzite ZnO (JCPDS: 80-0075) were detected, indicating that ZnSe is totally transformed to ZnO. We remark that the widths of the patterns are dominated by instrumental widths, which were checked by using a powder sample containing micrometer size silicon crystallites. Nevertheless, a slight broadening of the peaks in comparison with those of silicon powder is noticed. From the excess half width, we estimated a characteristic particle size of about 60 nm for the ZnSe precursor and 50 nm for the ZnO nanowires.

A typical TEM image of the transformed ZnO nanowires is shown in Figure 3. The size of the nanowire is clearly revealed to be 60–70 nm, consistent with the data observed in SEM. The nanowire consists of nanoparticles and nanopores, whose size is between 5 and 10 nm. The size of the particles revealed by TEM is significantly smaller than the characteristic particle

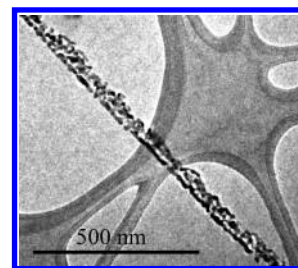


Figure 3. TEM image of the ZnO nanowires, revealing their porous structure.

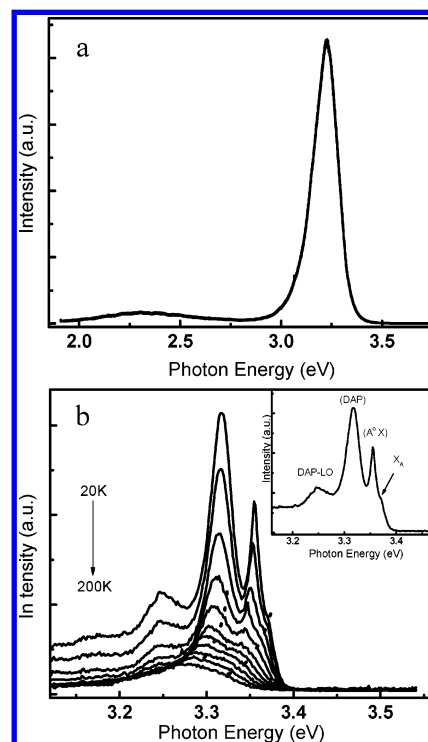


Figure 4. (a) Room-temperature PL spectrum of the ZnO nanowires, (b) PL spectra of the ZnO nanowires measured at different temperature. The inset shows the spectrum taken at 20 K. The dot lines are guidance to the variation of the two shoulder peaks with temperature.

size deduced from the width of the XRD pattern. We think this discrepancy is only an apparent one, as it reflects the differences between these two experimental techniques in measuring the particle size. XRD measures an average particle size of a distribution, whereas TEM tends to measure a selected narrow range of sizes within a wide distribution. During TEM observations, there is an unaware natural tendency to select the fine nanowires and small particles. The electron diffraction pattern (not shown here) indicates the polycrystalline nature of the nanowire. The surface-to-volume ratio for the porous nanowires ought to be much larger than that of single crystalline nanowires. This is favorable in some applications, such as in sensors, waste-absorbers, and catalyst carriers, etc.

Figure 4a shows a typical PL spectrum of the ZnO nanowires taken at room temperature. As frequently observed in ZnO thin films, the spectrum consists of two emission bands: one intense peak at about 3.227 eV, and another weak, broad peak at 2.305 eV. The intense peak is attributed to the NBE emissions of ZnO. The energy of the second peak is lower than what is frequently observed for defect-related emissions in ZnO (about 2.38 eV).²⁵ The origin of the red shift is not clear, it may be related to the possible incorporation of Se. Reynolds et al. reported that Se may incorporate into the ZnO lattice when grown from ZnSe

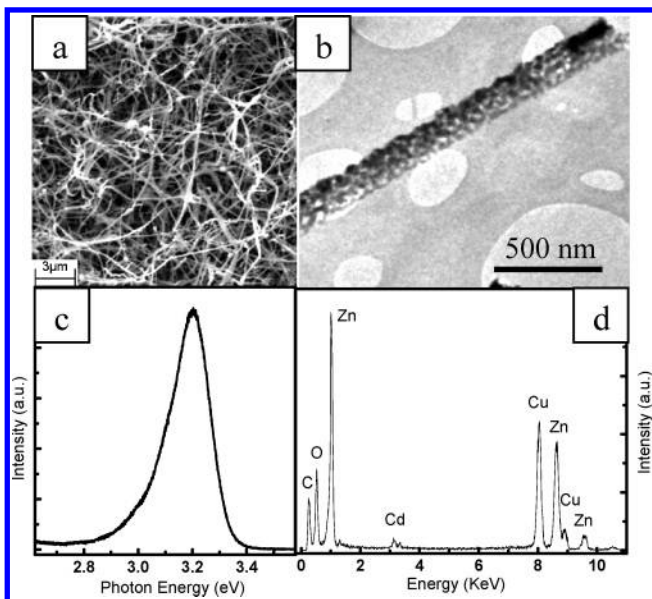


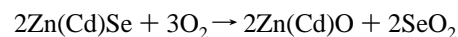
Figure 5. SEM (a) and TEM (b) images of the ZnCdO nanowires; Panel c is the room-temperature PL spectrum of the ZnCdO nanowires, and panel d is the EDX pattern of the nanowires, indicating the incorporation of Cd.

starting materials, and the trace incorporation may influence the optical properties of ZnO.²⁶ Figure 4b shows the PL spectra of ZnO nanowires taken at temperatures ranging from 20 to 200 K, and the inset is a magnified PL spectrum at 20 K. The emission at 20 K is dominated by two peaks at 3.316 and 3.355 eV in addition to a steplike peak at 3.247 eV. Careful examination reveals a weak shoulder located at 3.370 eV, which is labeled X_A . The energy of the shoulder is close to the reported A-exciton emission (3.378 eV at 4.2 K,²⁷ 3.375 eV at 13 K²⁸). Moreover, it gradually becomes more prominent with increasing temperature. Therefore, the shoulder is attributed to the free exciton emission in ZnO. The peak at 3.355 eV is frequently observed in ZnO, and is attributed to the emissions from the neutral acceptor bound exciton (A° , X).^{29,30} The origin of the peak at 3.316 eV is controversial, some attributed it to the exciton transition bound to neutral acceptors,^{31,32} while others thought it comes from donor–acceptor pair (DAP) emissions.^{30,33} We favor the latter, for there appears to be a shoulder at the high energy side of this peak at 80 K, and it prevails with increasing temperature, as shown in the temperature-dependent PL spectra. This is a typical feature for DAP transitions, and the shoulder originates from a band-to-impurity emission.³³ The steplike peak at 3.247 eV can be attributed to the phonon replica of the DAP emission, as their energy difference (69 meV) is very close to the longitudinal optical phonon energy of ZnO (~ 72 meV).

We have reported growing ZnCdSe alloy nanowires in a previous publication.²⁴ This procedure enables us to obtain ZnCdO nanowires by the same oxidation method. Figure 5a shows the general morphology observed by SEM, and Figure 5b is a TEM image of a typical ZnCdO nanowire obtained by us. The width of the nanowires is about 80–200 nm, and the length is several micrometers. Just like our ZnO nanowires, the ZnCdO nanowires are also polycrystalline and composed of nanoparticles and nanopores. Compositional analysis of the nanowire is shown in Figure 5d, in which the Cu and C signals come from the TEM grid supporting the sample. The distinct Cd signals show unambiguously the incorporation of Cd into the nanowire. PL measurement also confirms the incorporation, as shown in Figure 5c. The room temperature PL spectrum of

the ZnCdO nanowires shows an intense emission at 3.199 eV, which is about 28 meV smaller than the NBE of the ZnO nanowires shown in Figure 4. It is accepted that doping can effectively influence the band gap of a semiconductor;³⁴ the red shift in this case is thus thought to be caused by the incorporation of Cd into ZnO. Admittedly, the ZnCdO nanowires obtained in our experiment may not be a monocomposition alloy, since there appears to be a tail in the low energy side of the PL spectrum revealing that Cd-rich regions may be included in the nanowires. This phenomenon can be corroborated by the fact that ZnCdO is easily phase-separated because of the different crystal structures of ZnO and CdO.²⁰

As for the mechanism of transformation from Zn(Cd)Se to Zn(Cd)O nanowires, we think that at the oxidation temperature of 700 °C, the following reaction occurs:



in which the O_2 comes from air. The SeO_2 is quite volatile and will easily vaporize at about 315 °C, leaving only ZnO as the product of oxidation. ZnO plates have been obtained in a very similar way.³⁵ As for the formation of porous nanowire composed of nanoparticles and nanopores, we think the most rapid oxidation process occurs at the boundary or where there are defects, just like that proposed by Kolmakov et al.⁸ Therefore, the continuous nanowires are broken into small particles, and where there are defects or boundaries, nanopores appear. Consequently porous Zn(Cd)O nanowires are resulted.

Conclusions

In summary, porous ZnO and ZnCdO nanowires were obtained from ZnSe and ZnCdSe precursor nanowires in a very simple oxidizing method. Compositional, structural, and morphological characterizations reveal that the morphology of the precursor nanowires was retained after the transformation, despite the changes in crystal structure and chemical composition. The obtained ZnO and ZnCdO nanowires are polycrystalline, composed of nanoparticles and nanopores. Both kinds of nanowires show intense NBE emissions, a sign of good optical quality. We think this simple method can be readily extended to transforming other nanowires to their corresponding oxide nanowires.

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