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Aging effects on the optical properties of an individual Zn-rich ZnO nanowire

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ABSTRACT

Zn-rich ZnO nanowires are fabricated by a facile thermal evaporation method. The aging and post-annealing effects on an individual nanowire are investigated by cathodoluminescence (CL) spectra. For the nanowire aged in air, the intensity of deep-level (DL) emission is gradually strong with aging time, while are almost unchanged if aged in Ar atmosphere. Whether the individual nanowire was post-annealed in air or Ar atmosphere, the intensity of DL emission was gradually enhanced with temperature. Moreover, blue-shift of the DL emission is detected in the nanowire annealed in air. Nevertheless, for the nanowire annealed in Ar, the DL emission is first blue-shift at temperature of 400 °C, then red-shift at 500 and 600 °C. It is found that different defects can induce different DL emission, and the type of defects varies in the products depending on the experimental conditions.

1. Introduction

One-dimensional (1D) ZnO nanowires have been regarded as one of the most promising candidates for nanoscale electronic and optoelectronic devices including nanogenerators, nanolasers, field-effect transistors, optical switches and UV photodetectors due to its wide direct band gap of 3.37 eV and large exciton binding energy of 60 meV [1–10]. The optical properties of ZnO nanowires have attracted considerable attention because of its near-band-edge (NBE) ultraviolet (UV) emissions and potential applications in nanolasers and UV detectors [11–17]. Most of the researches have focused on the enhancement of UV emissions and decrease of deep-level (DL) emissions. As is well known, DL luminescence, typically centered at 500–530 nm, can result in a decrease in carrier/exciton lifetime and emission efficiency in the UV emission. Moreover, nanostructures are metastable and some physical properties can be gradually degraded with time and storage conditions. Up to now, aging and annealing effects on luminescence degradation of ZnO thin films had been intensively investigated [18–21], which presents some different experimental results. It is thought that the DL-related defects are deeply dependent on the experimental conditions such as synthesis methods, temperatures, and substrates. Nevertheless, the luminescence degradations of ZnO nanoparticles and nanowires, especially individual nanowire, are rarely investigated [22–24]. In this study, we first fabricated Zn-rich ZnO nanowires by a facile thermal evaporation method using high-purity Zn powder as source materials. Then we employed cathodoluminescence (CL) instrument inserted in the scanning electron microscope to investigate the optical degradation of an individual nanowire aged and annealed at different conditions. Some new features were presented, which has not been reported yet.

2. Experimental

ZnO nanowires were produced by direct thermal evaporation of pure Zn powder in tube furnace without using any catalyst. In the experiment, when the furnace was heated up to 1300 °C, the Zn powder is fast placed at the center of an alumina tube. The two ends of the alumina tube were open to air. Then the ZnO nanowires were deposited in regions at temperature of 750 °C. The ZnO nanowires dispersed on the Si substrates were aged in air and Ar atmosphere for 6 and 12 months, and then taken out for cathodoluminescence (CL) investigations. Moreover, the ZnO nanowires were post-annealed in air and Ar atmosphere at 400, 500 and 600 °C, respectively. The samples were also taken out for further CL studies.

Powder X-ray diffraction (XRD) data used for structural analysis were collected on PaNalytical X'Pert Pro MPD X-ray diffractometer with Cu Kα radiation. The morphology of product was examined by field-emission scanning electron microscope (FEI XL30 S-FEG). The transition electronic microscopy (TEM) and high-resolution TEM (HRTEM) images of samples were collected on the JEOL 2010F transmission electron microscope. The cathodoluminescence (CL) studies of individual nanowire were performed in the scanning electron microscope equipped with an Oxford Instruments MonoCL2 spectrometer at room temperature.

3. Results and discussion

Fig. 1a shows the XRD pattern of the products deposited in the region at temperature of 750 °C. All indexed diffraction peaks are well consistent with those of the standard wurtzite ZnO patterns (JCPDS card no. 36-1451), revealing the products are pure ZnO with wurtzite structure. SEM image of the products is shown in Fig. 1a, indicating that the product is composed of a large amount of nanowires with uniform size in diameter and length. Fig. 1c shows

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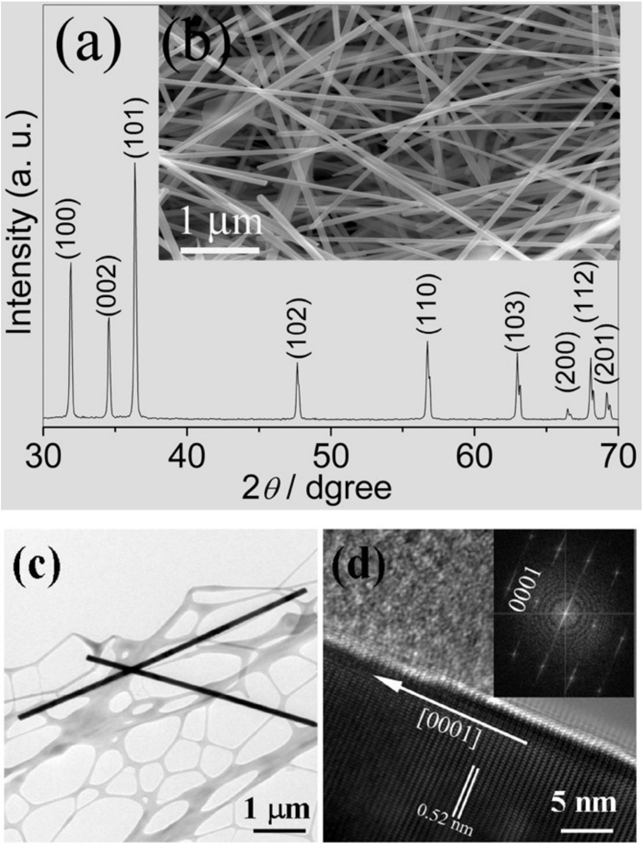

Fig. 1. (a) XRD pattern of the ZnO nanowires. (b) SEM image of the ZnO nanowires. (c) TEM image of the ZnO nanowires. (d) HRTEM images of the ZnO nanowires. The inset is the FFT pattern of the ZnO nanowires.

a typical morphology of the ZnO nanowires, clearly revealing the nanowires are of smooth surface and are straight along their growth direction. The HTREM measurement and fast Fourier transformation (FFT) pattern clearly indicates that the nanowires are well crystalline and no bulk defects such as stacking faults, dislocations and twinning defects are detected.

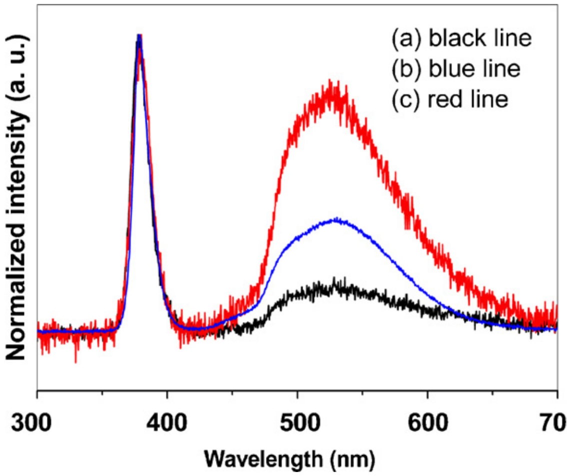

Fig. 2. Normalized room-temperature CL spectra taken from (a) an individual fresh nanowire; and the aged nanowire exposed to air for (b) 6 and (c) 12 months.

Fig. 2a–c shows the normalized CL spectra taken for an individual nanowire before and after its exposure to air for 6 and 12 months, respectively. A sharp and strong NBE emission centered at 379 nm (3.25 eV) and a weak deep-level (DL) green emission at 528 nm (2.35 eV) are observed in the fresh sample, as shown in Fig. 2a. The NBE emission is in good agreement with the well-known exciton emission, and the DL emission is related to the complex defects oxygen vacancies (V_o)/zinc interstitials (Zn_i) [25–27] due to the O-deficient experiment condition and Zn-rich formation of the nanowires. For the nanowire exposed to air, the aging effects are observed. The integrated intensity of DL emission gradually increases with aging time, as shown in Fig. 2b and c. This may suggest that the defects in the nanowires increase slowly in the aging process. Fig. 3a and b shows the TEM images of the nanowire exposed to air for 6 and 12 months, respectively. The surface of the nanowire is gradually rough with aging time. The rough sheath layer is confirmed as ZnO that is second grown on the surface during aging process. It is suggested that excess Zn originating from Zn_i on the surface of the nanowires will further react with O_2 to form a thin ZnO film. Thus, surface defects in the rough surface of the ZnO nanowire are the main reason for the enhanced DL emissions

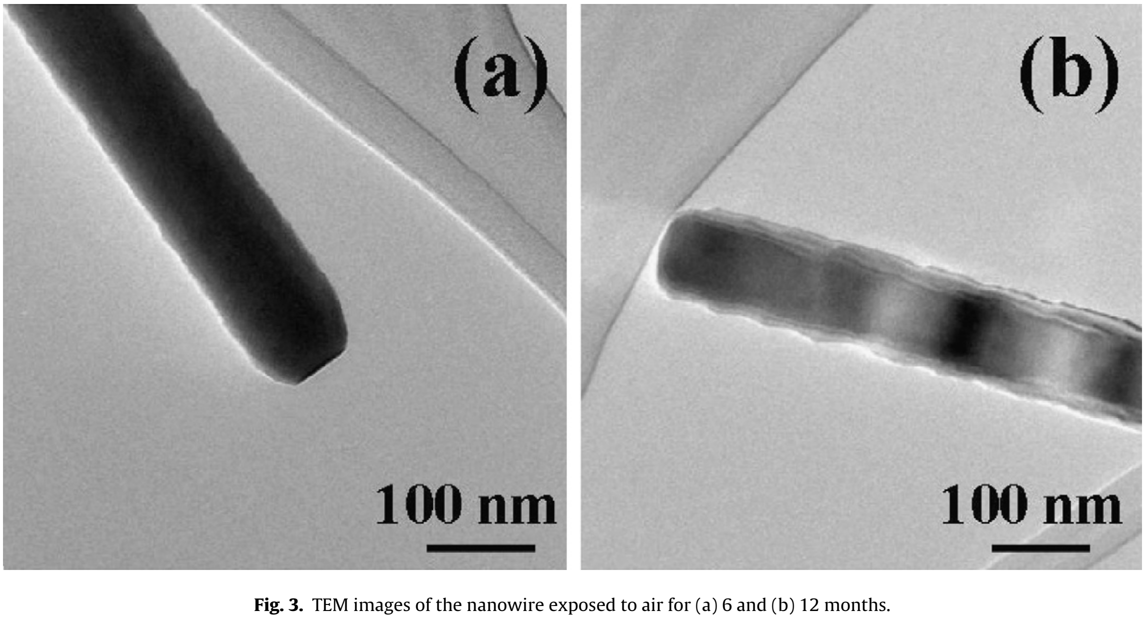

Fig. 3. TEM images of the nanowire exposed to air for (a) 6 and (b) 12 months.

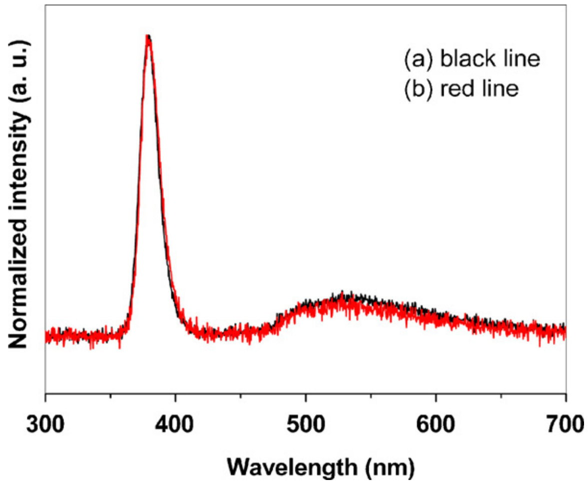

Fig. 4. Normalized room-temperature CL spectra taken from (a) an individual fresh nanowire; (b) the aged nanowire protected in Ar atmospheres 12 months.

in the ZnO nanowire exposed to air. The result is different from those reported before. Shan et al. [21] and Keem et al. [24] reported that DL emission in ZnO thin film and nanowires decreased with aging time, respectively, and attributed to oxygen vacancies (V_o) which would decrease slowly in ZnO films and nanowires exposed to air. According to these studies, it seems that different defects can induce different DL emission, and the type of defects varies in the products prepared in different experimental conditions. If the fresh nanowire is exposed to Ar atmosphere for 12 months, the DL emission is almost same to that of the fresh sample, as shown in Fig. 4a and b. We deduce that the structure of the ZnO nanowires keeps stable and new surface defects cannot form due to the inert atmosphere. Moreover, the number of the original complex defects V_o/Zn_i is not changed, which results in the almost same CL properties detected in both the fresh sample and the aged nanowire.

In order to investigate the degradation of DL emission in the nanowire, the fresh nanowires are annealed at different temperatures in air and Ar atmosphere, respectively. The interesting effects of the annealing are observed in the changes of their optical properties. Fig. 5 shows the CL spectra of an individual nanowire annealed at the temperatures ranging from 400 to 600 °C in air. It is found that the intensity of the DL emission of the nanowire is increased with extending temperatures. Moreover, large blue-shift from 525 nm to 510 nm is detected in the DL emission of the nanowire annealed at the temperatures of 400–600 °C. The DL emission centered at *ca.* 510 nm is induced by V_o, as confirmed by numerous literatures [15–17]. In this work, we deduce that large amount of Zn_i are oxidized to new ZnO products and V_o may be the main defects in the re-oxidized products. The 510 nm DL emission is attributed to the integration of the V_o in both the ZnO nanowires and re-oxidized ZnO products.

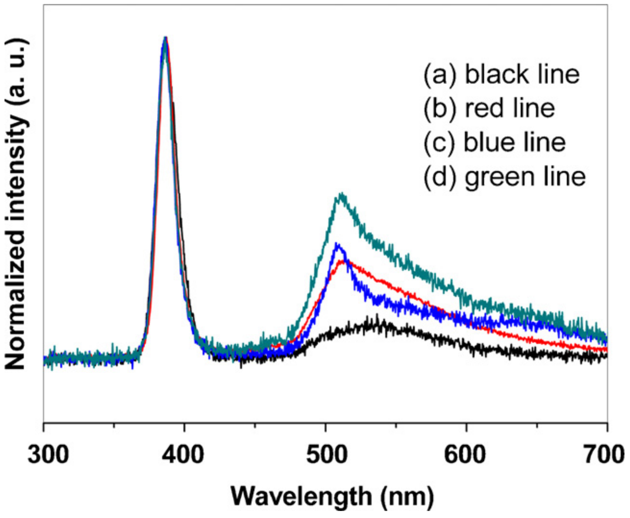

Fig. 5. Normalized room-temperature CL spectra taken from an individual fresh nanowire annealing in air at (a) room temperature, (b) 400 °C, (c) 500 °C and (d) 600 °C.

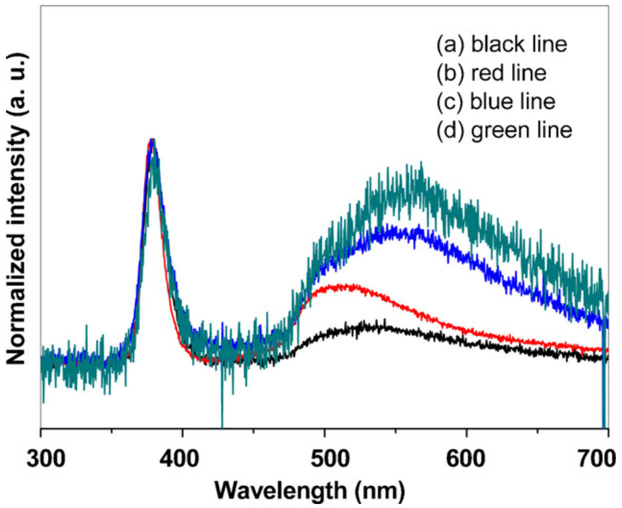

Fig. 6. Normalized room-temperature CL spectra taken from an individual fresh nanowire annealing in Ar atmosphere at (a) room temperature, (b) 400 °C, (c) 500 °C and (d) 600 °C.

Fig. 6 reveals the CL spectra of an individual nanowire annealed at room temperature, 400, 500 and 600 °C in Ar atmosphere. The intensity of DL emission is also increased with the temperature. However, the DL emission of annealing sample is first blue-shift at 400 °C, then red-shift with the annealing temperature at 500 and 600 °C. ZnO has a tendency to lose oxygen and become nonstoichiometric. The V_o are increased during the annealing process because of the absence of ambient O_2. The V_o will migrate and diffuse in the surface and inner of nanowire, resulting in increase of complex defects V_o/Zn_i. These increasing complex defects should be responsible for the increase of the intensity of DL emission of the annealed nanowires. The red-shift is also related to the complex defects V_o/Zn_i. More V_o/Zn_i are accumulated on the surface of the annealing nanowire with temperature, resulting in the red-shift of the nanowire annealed at 500 and 600 °C. However, the reason for the blue-shift of DL emission observed in the nanowire annealed at 400 °C is unknown and needs to be further investigated.

4. Conclusions

Zn-rich ZnO nanowires are fabricated by thermal evaporation of Zn powders in the tube furnace of which two ends were open to air. The aging and annealing effects of on an individual nanowire are investigated by CL spectra. The intensity of DL emission is gradually strong with aging time in air, but is almost unchanged if aged in Ar atmosphere. It is found that the integration of complex defects Zn_i/V_o and surface defects originating from reoxidization of excess Zn in the surface of the nanowire should be responsible for the enhancement of DL emission for the nanowire aged in air. Post-annealing processes have significant effects on the CL properties of the nanowire. Whether individual nanowire is post-annealed in air or Ar atmosphere, the intensity of DL emission was enhanced with temperature ranging from 400 to 600 °C. Moreover, blue shift of the

DL emission is detected in the nanowire annealed in air, which is attributed to integration of the oxygen vacancies originating from the ZnO nanowires and re-oxidized ZnO products. Nevertheless, for the nanowire annealed in Ar, the DL emission is first blue-shift at temperature of 400 °C, then red-shift at 500 and 600 °C. The red-shift was also related to the more complex defects V_o/Zn_i accumulated on the surface of the annealed nanowire.

Acknowledgements

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