Journal of Alloys and Compounds 509 (2011) 5765–5768

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Structure and photoluminescence properties of Ag-coated ZnO nano-needles

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ARTICLE INFO

Article history:
Received 15 November 2010
Received in revised form 10 January 2011
Accepted 19 January 2011
Available online 28 January 2011

Keywords:
Ag-coating
ZnO nano-needles
Pulse electro-deposition
Photoluminescence

ABSTRACT

A large number of zinc oxide (ZnO) nano-needles were synthesized by thermal oxidation of pure zinc. The surfaces of ZnO nano-needles were coated with a layer of Ag by pulse electro-deposition technique. The uncoated and coated ZnO nano-needles were characterized by using the X-ray diffraction and the scanning electron microscope (SEM). The results showed that the uncoated samples were close-packed hexagonal structure, which showed needle-like morphology. Their average diameter is about 40 nm, lengths up to 5 μm. At the same time we observed that the prepared ZnO nano-needles have been coated with Ag successfully. The photoluminescence spectrums of ZnO nano-needles with Ag-coated and uncoated were analyzed, finding that the uncoated ZnO nano-needles have two fluorescence peaks at 388 nm and 470.8 nm, respectively, the relative intensity of 143.4 and 93.61; and the Ag-coated ZnO nano-needles showed a pair of strong peaks at 387.4 nm and 405.2 nm, the relative intensity of 1366 and 1305, respectively, indicating that the Ag-coated ZnO nano-needles can increase the absorption of UV light.

1. Introduction

Zinc oxide (ZnO) is an excellent wide band gap semiconductor functional material because of its wide band gap (3.37 eV) at room temperature, and large exciton binding energy (60 meV). ZnO with a strong free exciton transition luminescence characteristic in the UV band has been widely used in the fields of antibacterial, antistatic, absorption of ultraviolet light and electrical conductivity, etc. Furthermore, one-dimensional ZnO nano-materials have practical value in the UV detection due to their faster response to ultraviolet light, good thermal stability, structure easy to control and low-cost. Since Yang et al. [1] synthesized ultraviolet diode based on single ZnO nanowire, one-dimensional ZnO nano-materials have attracted widely attention in the UV optoelectronic applications. However, the photosensitivity of one-dimensional ZnO nano-materials is always limited due to its surface states, the photon capture efficiency, defecting distribution of photoelectric sensitivity factors, so that it can not fully reflect the nano-effect, and greatly limited the application of one-dimensional ZnO nano-materials. Therefore, it is necessary to optimize zinc oxide nanostructures, such as doping, coating and surface modification. Zhang et al. [2] have reported the ultraviolet of silver (Ag) doped ZnO thin films were enhanced; Sun et al. [3] have found the light absorption ability of Ag-doped ZnO thin films were enhanced, and the UV absorption edge of the films have a obvious red shift. Fan et al. [4] have reported the gas sensing properties of the Ag-doped ZnO nanowires were greatly improved as reducing the diameter of the nanowires and their surface area increase; Li et al. [5] have found that the UV emission properties of ZnO nanowires were enhanced which were coated by ZnS, due to the surface oxygen vacancies were filled by the S element; it is showed that the surface modified or doped nano-ZnO have become the research hotspot in recent years. In this paper, the process were introduced that ZnO nano-needles were prepared by thermal oxidation and the Ag-coated ZnO nano-needles by pulsed electro-deposition means, and micro-structure and optical performance of these Ag-coated ZnO nano-needles have been investigated.

2. Experimental

2.1. Preparation of ZnO nano-needles

Large areas of pure zinc (purity of 99.9%, mass fraction) was slit into the small pieces of 1 cm × 1 cm, After the mechanical grinding and polishing of the substrate surface; mirror-like small zinc foil was washed by distilled water, absolute alcohol, respectively, and it was further cleaned using ultrasonic cleaner for 10 min to remove impurities, dried. The cleaned zinc foil was then placed into a alumina boat that was put in a box-type furnace. The heating was done at 450 °C for 10 h, and then naturally cooled to room temperature. An off-white substance can be obtained on zinc foil, placing it under scanning electron microscope. A layer of hairy needle-like nano-material can be seen on the zinc surface.

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doi:10.1016/j.jallcom.2011.01.118

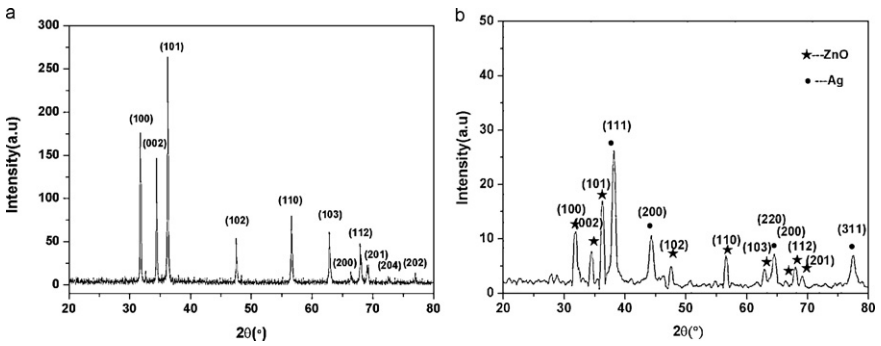

Fig. 1. X-ray diffraction patterns of uncoated and Ag-coated ZnO nanoneedles: (a) uncoated; (b) Ag-coated.

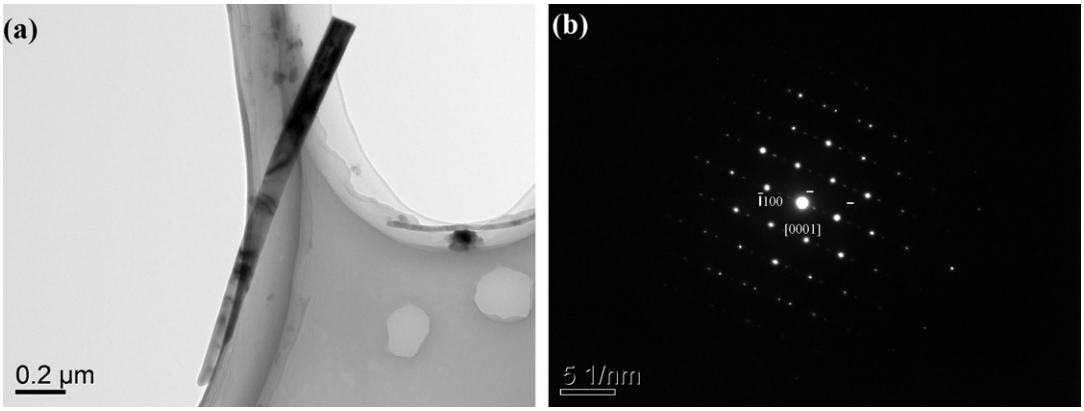

Fig. 2. The TEM and SEAD diffraction pattern of ZnO nano-needles.

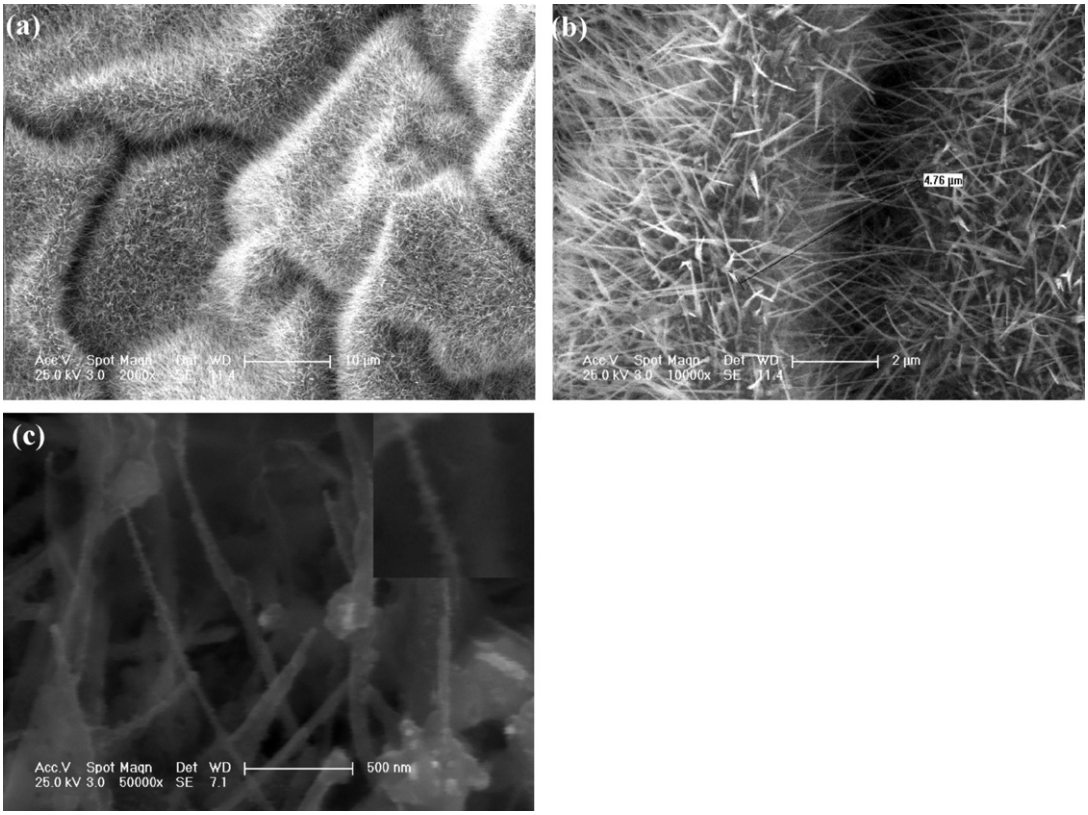

Fig. 3. SEM morphologies of ZnO nano-needles before and after Ag- coated: (a) (b) the uncoated; (c) Ag-coated, the closeup view is on the upper right corner.

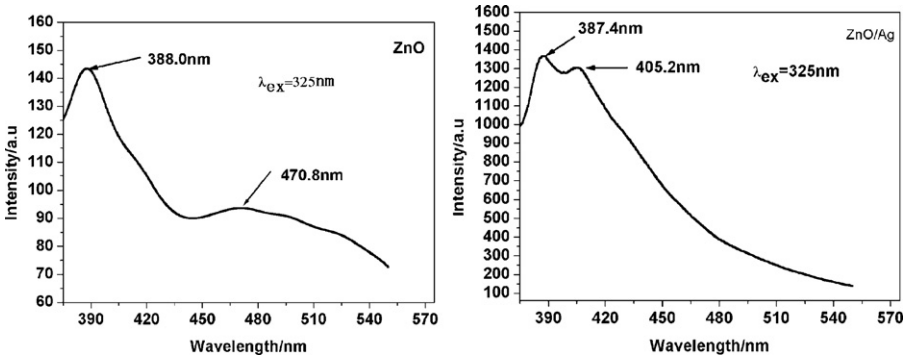

Fig. 4. Comparison of photoluminescence spectra of uncoated Ag and Ag-coated ZnO nano-needles at room temperature.

2.2. Preparation of Ag-coated ZnO nano-needles

The surface of ZnO nano-needles was coated with Ag by using pulsed electro-deposition technique. Process as follows: silver iodide (AgI) solution was used as electro-deposition solution. The addition of potassium iodide (KI) was to dissolve insoluble silver iodide. Electro-deposition liquid ingredients are shown in Table 1.

During pulsed electro-deposition, the anode was a standard graphite electrode (mass fraction is 99.9%) sized 50 cm × 50 cm, and the cathode was a zinc sheet substrate which was covered with nanoneedle-shaped material. Both electrode and substrate were placed in a standard Hull cell, and the electrolyte was mixed using a magnetic stirrer with a digital thermostat for preventing the precipitation. The power supply was a numerical control double-pulse (square-wave pulse) plating electric source (GKDM 30-15, Xin Du, China), and the power supply adopted rectangular wave output current. The plating parameters includes output pulse frequency (f = 100 Hz) and duty cycle (r = 10%). The plating was carried out at 60 °C with a plating time 5 min. The pH value of the electrolyte was measured by a PHS-25 type pH meter, and adjusted to pH 2.0 by adding sulfuric acid (H2SO4).

2.3. Characterization and testing

The phase of samples were analyzed by power X-ray diffraction (XRD) on German Bruker AXS/D8 advanced X-ray diffractometer with Cu Ka radiation (λ = 1.5418Å). The morphologies and the lengths of the samples were observed by using a scanning electron microscope (SIRION SEM, FEI the Netherlands) and a transmission electron microscope (JEOL JEM 2010 TEM, Japan). The photoluminescence spectrums of ZnO nano-needles with Ag-coated and uncoated were measured by using fluorescence spectrophotometer at room temperature (HITACHI F-4600, using Xe lamp as excitation source).

3. Results and discussion

3.1. XRD analysis

Fig. 1 shows the XRD pattern of Ag-coated and uncoated ZnO nano-needles. Fig. 1(a) shows the XRD pattern of ZnO nano-needles synthesized by thermal oxidation method. All the peaks can be indexed to ZnO. It is fully consistent with the standard spectrum of ZnO (JCPDS 79-0205), no other peaks of impurities can be detected. Fig. 1(b) shows the XRD patterns of the Ag-coated ZnO(ZnO/Ag) nano-needles. A strong diffraction peak corresponding to Ag(III) plane can be seen in the $2\theta = 38.088^\circ$ from the figure, and the corresponding diffraction peaks of Ag have been emerged in 44.2720°,64.3960° and 77.3370°. While the corresponding diffraction peaks of ZnO also still exist, but their intensities are significant weakening. It indicates that the ZnO nano-needles have been successfully achieved Ag coating by using pulsed electro-deposition technique.

Table 1
Bath compositions and pulse plating conditions.

Composition or parameter	Data
Silver iodide (AgI)	0.05 mol/L
Potassium iodide (KI)	0.05 mol/L
pH value	2.0
Positive pulse work time	8T(T = ton + toff)
Negative pulse work time	2T(T = ton + toff)
Positive pulse peak value current	0.5 A
Negative pulse peak value current	0.3 A

3.2. TEM analysis

Fig. 2(a) and (b) shows the TEM and SEAD diffraction patterns of ZnO nano-needles. According to the TEM photographs of a single nano-needle, we found that the surface of nano-needle is smoothed from bottom to top, gradually reduced in diameter, showing acicular form. Draw according to SEAD diffraction pattern, the distance between planes is 0.28 nm, corresponding to (0 0 0 2) plane of the hexagonal wurtzite ZnO. It shows that the ZnO nano-needles grow along [0 0 0 1] direction. It is illustrate that pure ZnO nano-needles can be obtained by the method of thermal oxidation. The result is consistent with that of XRD.

3.3. SEM analysis

Fig. 3 shows the SEM photographs of the uncoated and Ag-coated ZnO nano-needles. It can be seen from Fig. 3(a) and (b), when no Ag-coated, the surface of ZnO nano-needles is smoothed, showing acicular form. The length is estimated about 2–5 μm according to Digitalmicrograph Test Software. Fig. 3(c) shows the SEM photographs of ZnO/Ag nano-needles. It can be clearly seen that the closeup view on the upper right corner, the ZnO nano-needles have been buried by Ag. It is obviously that the surfaces of ZnO nano-needles have been successfully achieved the Ag coating.

3.4. The test and analysis of the photoluminescence (PL) spectra

In order to understand the optical properties of these products, we have carried out their photoluminescence spectra test. Fig. 4 shows the photoluminescence of uncoated Ag and Ag-coated ZnO nano-needles under excitation at 325 nm at the room temperature. It exhibits two fluorescence peaks at 388 nm and 470.8 nm, the relative intensity of 143.4 and 93.61, respectively. Ag-coated ZnO nano-needles showed strong double peaks, which were located at 387.4 nm violet luminescence peak and 405.2 nm blue–violet peak, the relative intensity of 1366.0 and 1305.0, respectively. Compared with the non-coated Ag ZnO nano-needles, the UV light intensity of Ag-coated ZnO nano-needles was more intense than that of uncoated ZnO nano-needles, just enhances nearly ten times. The blue-shift of the near band edge emission peak of the ZnO nanoneedles was observed comparing to that of no-coated Ag. It can be concluded that the Ag-coated affected the photoluminescence of ZnO nano-needles. Its spectrum consists of a wide and strong deep-level blue-green emission belt at 450–500 nm, a weak and narrow UV emission bands at 375 nm. Where the UV light was stimulated by radiant combination from the exciton; the blue–green belt is

attributed to the oxygen vacancy and interstitial zinc [6]. Through the PL spectrum test, we found that the relative intensity of blue emission peak at 470.8 nm is 93.61 for pure ZnO nano-needles. The association point defects in ZnO thin films and the energy levels of co-introduction defects can be calculated according to full-potential linear muffin-tin orbita1, that is FP-LMTO method [7], and 470 nm peak derived from the transitions between the Zn gap and the Zn vacancy. It could be deduced that there is Zn interstitial donor-type defects in the eigen ZnO nano-needles. The light emission peaks of Ag-coated ZnO nano-needles are at 387.4 nm and 405.2 nm. Fig. 4 shows that the near-band-edge emission peak at about 375 nm greatly strengthened, and the deep-level green emission peak at 450–500 nm disappeared. So the quality of Ag-coated crystal is improved. UV light enhancement is due to metallic Ag was electrodeposited on the surface of ZnO nano-needles. On the one hand the exciton was formed at the interface between Ag nano-crystalline and ZnO nano-needles, and the performance of ultraviolet light emission was enhanced; The other hand, Ag nano-crystalline coating in the surface of the ZnO nano-needles interacts with the ever-increasing ultraviolet light by ZnO nano-needles issued. When the interact is to achieve a certain degree, plasma resonance is generated in the surface of Ag nano-crystals, making the local field intensity surrounding Ag nano-crystals dramatically increased, which led to enhancement of ZnO ultraviolet light.

4. Conclusions

ZnO nano-needles were prepared at 450 °C by the thermal oxidation of pure Zn film. Further Ag-coated ZnO nano-needles were successfully prepared by using the electro-deposition technique in AgI bath. Comparing the photoluminescence spectrums of uncoated and Ag-coated ZnO nano-needles, the results showed that the UV light emission peak intensity of Ag-coated ZnO nano-needles significantly increased, increased nearly 10 times. The results indicated that Ag-coated ZnO nano-needles improved the luminous efficiency of ZnO nano-needles; the near band-edge emission peak of Ag-coated ZnO nano-needles greatly strengthened, and the deep level green emission peak disappeared, these indicated that the ZnO nano-needles crystal quality improved after Ag-coated.

Acknowledgement

This study is supported by the National Nature Science Foundation, no. 10747146.

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