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Luminescence Property and Synthesis of Sulfur-doped ZnO Nanowires by Electrochemical Deposition[†]

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Sulfur-doped zinc oxide (ZnO) nanowires were successfully synthesized by an electric field-assisted electrochemical deposition in porous anodized aluminum oxide template at room temperature. The structure, morphology, chemical composition and photoluminescence properties of the as-synthesized ZnO:S nanostructures were investigated. X-ray diffraction and the selected area electron diffraction results reveal that the as-synthesized products are single phase with hexagonal wurtzite structure with a highly preferential orientation in the (101) direction. Transmission electron microscopy observations indicate that the nanowires are uniform with an average diameter of 70 nm and length up to several tens of micrometers. X-ray photoelectron spectroscopy further reveals the presence of S in the ZnO nanowires. Room-temperature photoluminescence is observed in the sulfur-doped ZnO nanowires which exhibits strong near-band-edge ultraviolet peaks at 378 and 392 nm and weak green emissions at 533 and 507 nm. A blue emission at 456 nm and violet emissions at around 406, 420, and 434 nm were also observed in the PL spectrum for the as-synthesized ZnO:S nanowires. The PL spectrum shows that S-doping had an obvious effect on the luminescence property of typical ZnO nanowires.

Key words: ZnO nanowires, Electrochemical deposition, Photoluminescence

I. INTRODUCTION

In the late 1990s, interest in the II-VI semiconductor zinc oxide (ZnO) was renewed when room-temperature, optically pumped lasing was demonstrated for ZnO thin films [1-5]. Since that time the optical properties of ZnO bulk single crystal, thin films, and nanostructures have been studied extensively. In order to obtain different ZnO nanostructured materials, varieties of methods have been developed, for example, high-temperature physical evaporation [6], the microemulsion hydrothermal process [7], the template induced method [8-10], or the reduction and oxidation of ZnS [11]. Although controlling the size of the nanowires can bring about changes in their optical and electronic properties, doping of the nanowires either through in-situ or postprocessing techniques will provide a far more favorable approach to modulate their properties. Efficient impurity incorporation including Mg and transition metals in ZnO has been carried out in order to obtain novel properties and broaden possible applications [12-15]. However, little attention has been paid to S doping in ZnO because of the difference between the low stability of sulfur and the high growth temperature of ZnO. Sulfur has a much smaller electronegativity (2.58) than that of oxygen (3.44) and the atom radius of sulfur (1.09 Å) is much larger than that of oxygen (0.65 Å). The dif-

ference between S and O makes it possible to obtain some novel properties of ZnO via S doping. Yoo *et al.* have reported that the band gap of ZnO could be tuned via S dopant [16]. S impurities are also expected to increase the electrical conductivity of ZnO by supplying excess carriers [17]. Usually, an anodized aluminum oxide (AAO) template with hexagonally ordered pores is used as one of the most important media in fabrication of metals and their alloy nanowires. But it is difficult to synthesize compound nanowires in the porous alumina. In this research, we improved the traditional experimental method and directly obtained the sulfur-doped ZnO nanowire in AAO template synthesis (by electrochemical deposition). The transmission electron microscopy (TEM), the selected area electron diffraction (SARD) images and X-ray diffraction (XRD) pattern are reported in this letter. The X-ray photoemission spectroscopy (XPS) curve is used to confirm the formation of the doped compound. The optical property of sulfur-doped ZnO nanowires was investigated by room-temperature photoluminescence (PL). Generally, photoluminescence spectrum of a single crystal ZnO consists mainly of two bands [18]. The as-synthesized sulfur-doped nanowires exhibit broad visible emission. This special characteristic suggests that the S-doped ZnO nanomaterial may be used for visible light emitter.

II. EXPERIMENTS

The AAO templates with ordered nanopore were prepared by using a two-step anodization process. Briefly, a 99.999% pure Al foil was degreased and electropol-

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ished in a solution of perchloric acid, ethanol, and distilled water to produce a mirror-like surface [19]. This film was then washed in distilled water, air dried, and anodized in 0.3 mol/L oxalic acid at room temperature using a constant anodizing voltage of 40 V. The anodization was carried out for 0.5 h to form a thick porous alumina film on the surface. This film was stripped off in hot chromic/phosphoric acid and the anodization repeated again for 10 h to form another porous alumina film of thickness about several microns. The two-step anodization process [20] yielded an anodic alumina film with a well ordered array of about 50 nm diameter pores. After the anodization, the remaining aluminum was etched by a saturated HgCl solution. Finally, the barrier layer was dissolved using 0.5 mol/L H₃PO₄ at a constant temperature of 60 °C for 50 min. The AAO template to be used in the following experiment was obtained.

ZnO:S nanowires were synthesized by an electric field-assisted electrochemical deposition in porous anodized aluminum oxide template at room temperature. The device used in the experiment was reported recently by the group Yue *et al.* [21]. The Na₂S aqueous solution prepared was 12.5 mmol/L. The consistency of the Zn(NO₃)₂ aqueous solution was 1.25 mmol/L. The cathode connects the aqueous solution of Na₂S and the anode connects the aqueous solution of Zn(NO₃)₂. The transverse electric field was added with a voltage of 12.5 V_{AC} and a frequency of 50 Hz.

In the experiment, the doped ZnO nanowires were obtained at a constant voltage of 20 V_{DC} for 20 min. The current density was about 10 mA/cm² at first. It decreased gradually to about 1 μA/cm² after 20 min, and then it nearly did not change.

For a reference purpose, a sample of undoped ZnO nanowires was prepared under almost the same conditions but with 12.5 mmol/L NaNO₃ aqueous solution substituting for Na₂S.

Structural characterization was performed by means of XRD using a Rigaku/Max-2400 diffractometer with Cu K α radiation ($\lambda=1.54056$ Å). The bright field image of nanowires and selected area electron diffraction pattern (SAED) were taken by an EM-400T TEM. The XPS data were collected on a PHI-5702 X-ray photoelectron spectrometer using a monochromatic Al K α X-ray sources. PL spectra excited with 325 nm UV light at 295 K were collected with an FLS920T combined fluorescence lifetime and a steady state spectrophotometer.

III. RESULTS AND DISCUSSION

Figure 1 show the TEM images of dispersed nanowires with an average diameter of 70 nm obtained by electrochemical deposition in the AAO templates. The dispersed nanowires were obtained by dissolving AAO templates in 1 mol/L H₂SO₄ solution for 24 h at 30 °C. The detailed information of the ZnO:S nanowires

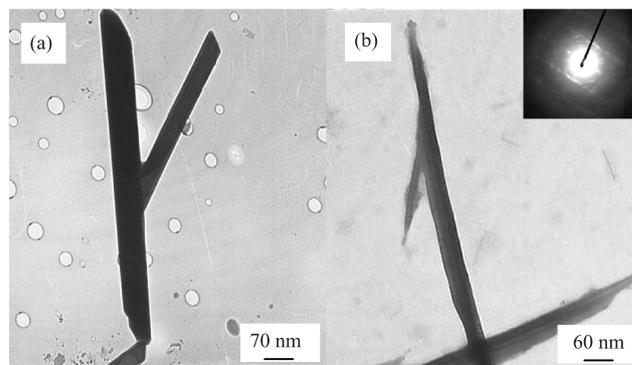


FIG. 1 TEM image of the ZnO:S nanowires. (a) and (b) images of the ZnO:S nanowires. The inset is the SAED pattern of as-synthesized products.

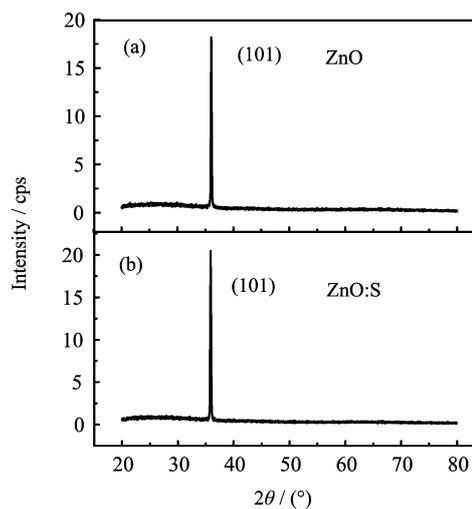


FIG. 2 XRD patterns of ZnO and ZnO:S nanowires.

was studied by SAED. The SAED pattern shown in the inset of Fig.1(b) suggests that the as-synthesized nanowires are single-crystalline with wurtzite structure.

Figure 2 illustrates the XRD patterns of doped and undoped ZnO nanowires, which revealed that the lower Bragg angle peaks are located at 36.09° and 35.85° respectively. Except for ZnO (101) orientations, no extra diffraction peaks from S-related secondary phases or impurities were observed. This indicates that both the as-grown products are single phase and (101) preferred orientation. It is known that the ionic radius of the substitute S²⁻ (184 pm) is larger than that of O²⁻ (124 pm). Thus, doping with S ions causes a slight shift of about 0.24° of XRD peaks toward the lower diffraction angle. The slight variation of the doped sample compared to the undoped sample is an indication of incorporation of S ions in the ZnO lattice. The ultra strong intensities relative to the background signal indicate the high purity of the resulting products.

Figure 3 (a), (b), and (c) show Zn2p, O1s, and S2p XPS spectra of ZnO:S nanowires, respectively. The

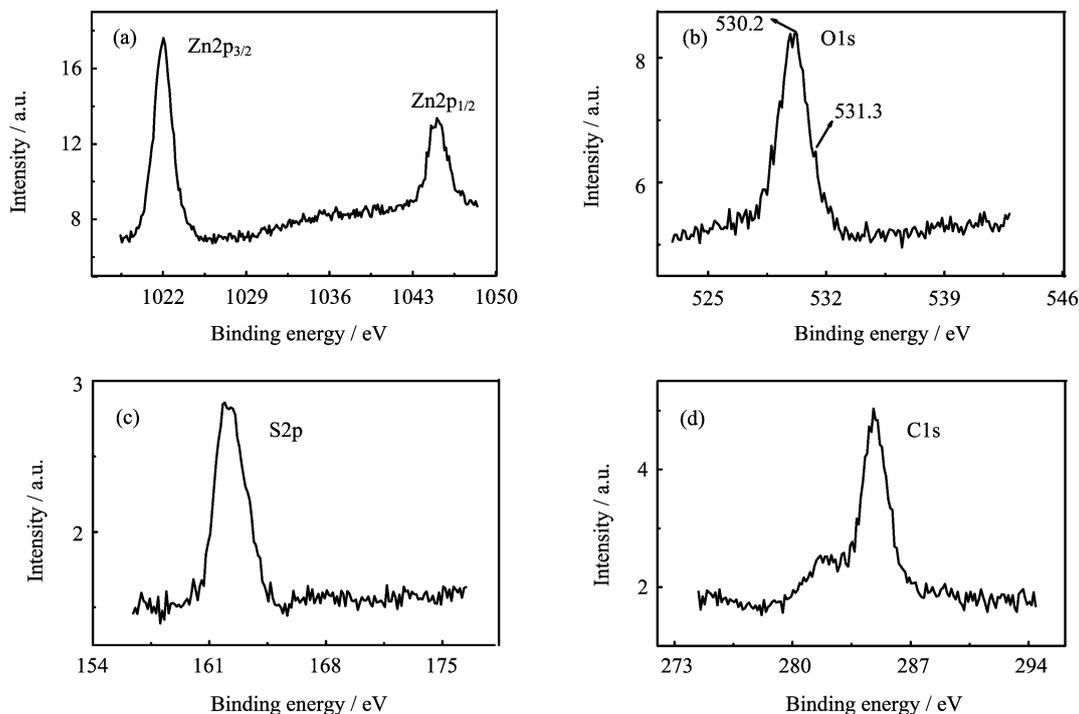


FIG. 3 XPS spectra of (a) Zn2p, (b) O1s, (c) S2p, and (d) C1s core levels for ZnO:S nanowires.

binding energies in all the XPS spectra have been calibrated using C1s at 284.6 eV as shown in Fig.3(d). The binding energy of Zn2p_{3/2} is located at 1022.2 and 1021.8 eV, showing that the Zn2p_{3/2} peak consists of ZnO and ZnS respectively [22,23]. Figures 3(b) shows O1s XPS spectrum, the stronger O1s peak at 530.2 eV may be attributed to O²⁻ in Zn–O bond [24]. While another peak at 531.3 eV is usually associated with the loosely bound oxygen (e.g., adsorbed O₂, –OH) [25]. Figure 3(c) shows the S2p core level peak. The 2p_{3/2} component is located at about 162.0 eV. This binding energy is smaller than those of sulfur and related compounds, namely, elemental sulfur (164.0 eV), chemisorbed SO₂ (163–165.5 eV), sulfite (–SO₃) (166.4 eV), and sulfate (–SO₄) (168–170 eV) [26]. This implies that the peak can be assigned to that of ZnS [27]. These results indicate that pure ZnO:S nanocrystals have formed. The full XPS spectrum (not shown here) indicates that there is no impurity detected other than the Zn, O, S, and adsorbed carbon signals.

As a wide-band-gap semiconductor, ZnO is of interest in low-voltage and short wavelength electron-optical devices, such as light-emitting diodes and diode lasers. The luminescence and conductivity of ZnO are influenced by the point defect (e.g, oxygen vacancy) content. PL study is an effective way because it provides valuable information about the structural defects. The Gaussian-fitted emission peaks from 350 nm to 650 nm are shown in Fig.4. The as-grown ZnO:S nanowires show strong UV emissions at 378 and 392 nm and weak green emissions at 533 and 507 nm. A blue emission

at 456 nm and three violet emissions at around 406, 420, and 434 nm are also observed in the PL spectrum for the as-synthesized ZnO:S nanowires. The UV emission corresponds to the near band-edge emission due to an exciton-related activity. The green emission peak is generally referred to as a deep-level or trap-state emission. To explain the green emission, various models have been proposed, including the involvement of O vacancies [28], interstitial O [29], Zn vacancies, and Zn interstitials [32]. For the sample prepared by solution-based chemical method, a two-step process model has been proposed to explain the green emission kinetics. The first step is an efficient surface trapping of photogenerated hole. Then the hole tunnels to a singly ionized oxygen vacancy and generates green emission [34]. Recently, Norberg and Gamelin proposed that the surface-trapping center is OH⁻ because green emission intensities show a direct correlation with surface hydroxide concentrations [35]. Therefore, we consider that the origins of green emission and peaks are correlated with surface OH⁻ and the structural defects caused by S incorporation. The inconspicuous green emissions in the PL spectrum reveal that the as-synthesized ZnO nanowires have a few such defects and surface OH⁻. The blue emission of the sample is likely linked to the radiative defects at the interface of the components of ZnO urchins [33,34], or the existence of interstitial zinc in ZnO lattices [35]. Therefore, we consider that the origins of blue emission are correlated with defects at the interface defects caused by doping of S ion. The prominent violet peaks can be assigned as the exciton

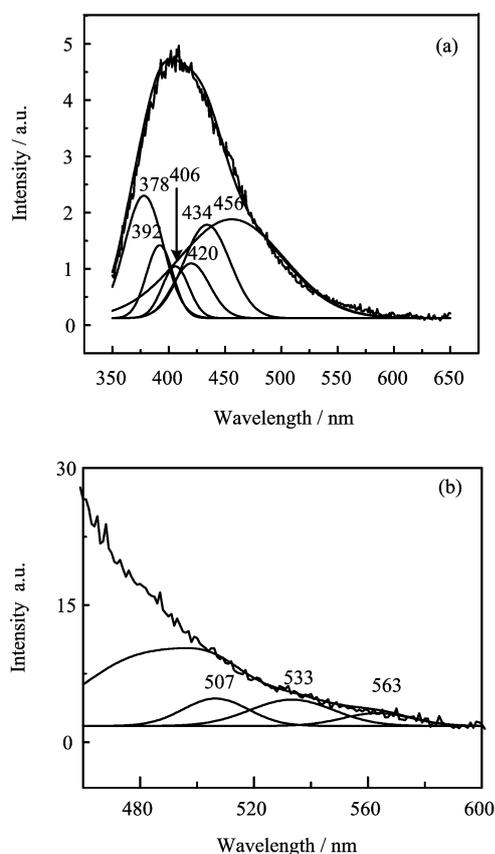


FIG. 4 Room temperature photoluminescence spectrum for the ZnO:S nanowire.

recombination between the electron localized at the Zn interstitials (Zn_i) and the holes in the valence band. [36] We believe that the violet emissions are associated with the defect-related levels in the ZnO:S nanowires, such as, intrinsic (Zn_i) and doped sulfur. The ZnO:S nanowires can be used as UV light-emitting materials, and have the potential for blue emission.

IV. CONCLUSION

To conclude, we have reported the synthesis of ZnO:S nanowires via electric field-assisted electrochemical approach in AAO template at room temperature. The structure and morphology were characterized by XRD, TEM and SAED. The chemical composition was analyzed by XPS. The photoluminescence properties of the as-synthesized ZnO:S nanostructures were also investigated. XRD and the SAED results reveal that the as-synthesized products are single phase with hexagonal wurtzite structure with a highly preferential orientation in the (101) direction. The TEM observations indicate that the nanowires are uniform with an average diameter of 70 nm and length up to several tens of micrometers. XPS further reveals the presence of S in the ZnO nanowires. Broad-band luminescence in the

region of 350-650 nm is observed by PL spectrum of the as-grown products. Strong near-band-edge (NBE) ultraviolet peaks at 378 and 392 nm and weak green emissions at 533 and 507 nm were observed. A blue emission at 456 nm and violet emissions at around 406, 420, and 434 nm were also observed in the PL spectrum for the as-synthesized ZnO:S nanowires. The PL spectrum results showed that S-doping had an obvious effect on the luminescence property of typical ZnO nanowires. Visible emission in the sulfur doped ZnO nanowires can be attributed to the increase in oxygen vacancies caused by the sulfur substitutes for oxygen within the ZnO lattice, Zn interstitials (Zn_i) and surface OH^- . These experimental results are very useful for the application of advanced optoelectronic devices of ZnO:S nanowire. The experimental results also indicate that the AAO template synthesis (by an electric field-assisted electrochemical deposition) is a versatile and particularly simple approach, especially in the preparation of ionic doped compound nanowires.

V. ACKNOWLEDGMENTS

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