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Ultraviolet emission of ZnO film prepared by electrophoretic deposition*

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We deposited high quality ZnO film by electrophoretic deposition (EPD) using high quality ZnO powder prepared by solid-state pyrolytic reaction. X-ray photoelectron spectroscopy (XPS) and the infrared (IR) absorption spectrum clearly indicate that the ZnO phase powder has been prepared. Transmission electron microscope (TEM) imaging and x-ray diffraction (XRD) show that the average grain size of the powder is about 20nm. XRD and selected-area electron diffraction (SAED) reveal that the ZnO film has a polycrystalline hexagonal wurtzite structure. Only a strong ultraviolet emission peak at 390nm can be observed at room temperature.

Keywords: ZnO films, electrophoretic deposition, UV emission
PACC: 7820, 8115, 7855E, 7840G

1. Introduction

ZnO is a wide direct band gap II–VI semiconductor material which attracts great attention due to its unique electrical, mechanical, and optical properties. In recent years, there has been increasing interest in preparing high quality ZnO films in order to produce strong UV emission. Many techniques are used to prepare high quality ZnO films, e.g. metal–organic chemical vapour deposition (MOCVD),[1] molecular beam epitaxy (MBE),[2] sol-gel deposition,[3] spray pyrolysis,[4] pulsed laser deposition (PLD),[5] filtered cathodic vacuum arc technique,[6] vapour phase epitaxy (VPE),[7] DC reactive sputtering[8] and EPD.[9,10] The main advantages of EPD are simple instrumentation and easy operation. To the best of our knowledge, strong UV emission have not been reported for EPD prepared ZnO films. We prepared high quality ZnO powder by solid-state pyrolytic reaction and utilized the powder to deposit high quality ZnO film on indium tin oxide (ITO) by EPD. The photoluminescence (PL) spectrum shows that the ZnO film has only a UV emission peak at 390nm and no other emission bands can be observed at room temperature.

2. Experiments

2.1. Preparation of ZnO powder and electrophoretic deposition of ZnO films

Deposition solution was prepared with concentration of 0.006M of ZnO and 10^{-5}M of $Mg(NO_3)_2{\cdot}6H_2O$ in isopropyl alcohol (IPA) solvent. The preparation of ZnO powder was as follows. 2.2g (10mmol) $Zn(CH_3COO)_2{\cdot}2H_2O$(99.5%) and 2g (23.8mmol) $NaHCO_3$(99.5%) are mixed at room temperature. The mixture is pyrolytized at 300°C for 3h, then washed by deionized water and dried at 100°C for 2h. A white ZnO powder is obtained,[11] which is dissolved in ethanol solvent. A stainless steel sheet and an (ITO) coated glass slide with a deposition area of $2cm^2$ were used as the anode and cathode. The electrodes were placed parallel to each other, separated by a distance of approximately 3cm and immersed in the deposition solution. Film deposition was performed at a constant current of 10mA for 10min in ambient conditions. After deposition, the film was removed from the solution and dried at 100°C for 2h. Uniform

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white ZnO film can be obtained. Compared to other methods for synthesizing ZnO powder, the reaction condition is simple and the method is efficient.

2.2. Characterization

XPS was performed on a VG Scientific Escalb Mark II instrument, using a monochromatized AlK_α source. The pressure in the chamber was 5×10^{-8} mbar. For final calibration of the energy scale, the C1s peak was set to 284.6eV.

The IR spectrum was collected by a Shimazu FT-IR 8200D IR spectrophotometer.

TEM images and SAED patterns were obtained on a JEOL-2919 TEM operated at 200kV.

The XRD spectrum was measured on a D/max-rA XRD spectrometer (Rigaku) with a CuK_α line of 0.154nm.

The ultraviolet–visible spectrum was measured on a Hewlett-Packard 8405A diode array spectrometer with a resolution of 2nm.

In order to study the luminescence properties of ZnO films, the PL spectrum was measured on a Hitachi MPF-4 fluorescence spectrophotometer with an excitation wavelength of 325nm at room temperature.

3. Results and discussion

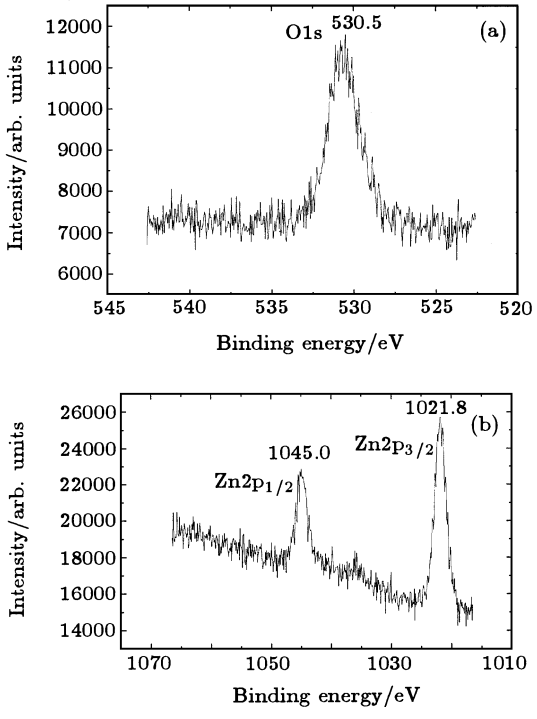


Fig.1. O^1s and Zn^2p XPS spectrum of ZnO powder.

XPS data of the sample are shown in Fig.1. The peak positions of O^1s, $Zn^2p_{1/2}$ and $Zn^2p_{3/2}$ are 531.5eV, 1045.0eV and 1021.8eV, respectively. A full survey scan did not show peaks of other elements. The result shows that the ZnO powder has been prepared.

The IR spectrum is shown in Fig.2. There are two absorption peaks, at 450cm^{-1} and 3300cm^{-1}. The peak at 450cm^{-1} comes from a stretching mode in crystalline ZnO. The peak at 3300cm^{-1} comes from water absorption on the surface of the ZnO particles. There are no other peaks in Fig.2, showing that there are no other compounds in the ZnO powder.

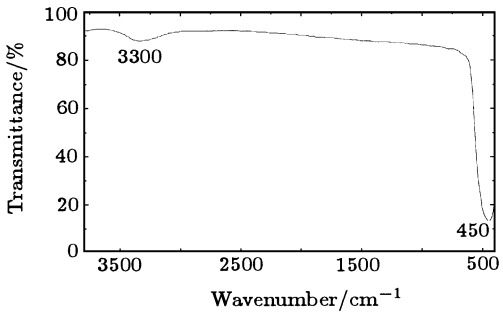


Fig.2. IR spectrum of ZnO powder.

Absorption spectroscopy can probe the crystallite internal molecular orbital and provide information concerning size and particle composition.[12] Figure 3 shows the absorption spectrum of ZnO powder. There is an absorption peak at about 371nm. According to Ref.[12], it can be attributed to exciton absorption.

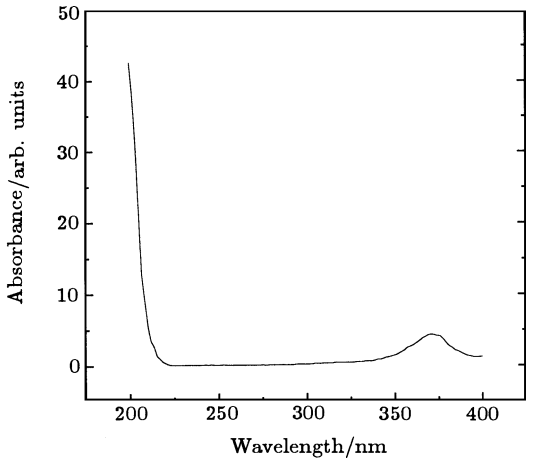


Fig.3. UV/Vis absorption spectrum of ZnO powder.

Figure 4 shows a typical TEM image of the ZnO powder. We can see that the ZnO powder is well dispersed and the particle size is about 20nm. The SAED clearly shows that the ZnO powder is polycrystalline.

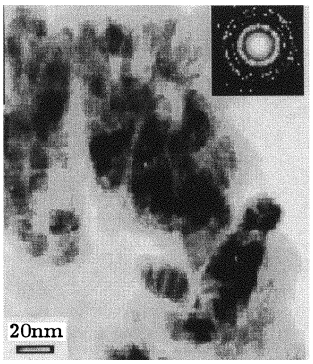


Fig.4. TEM image of ZnO powder.

The ZnO film was characterized by XRD. Three pronounced ZnO peaks, (100), (002), and (101), appear at 2θ=31.86^0, 34.68^0 and 36.46^0, respectively, as shown in Fig.5. This indicates that the ZnO film has a polycrystalline hexagonal wurtzite structure. No significant orientation can be seen from the XRD patterns due to the random arrangement of the nano-particles. The diameter of the ZnO nano-particles was calculated by the Scherrer formula: d=0.89$\lambda/B\cos\theta$. The calculated results indicate that the average size of ZnO powder is 22.3nm. This value is in good agreement with the TEM.

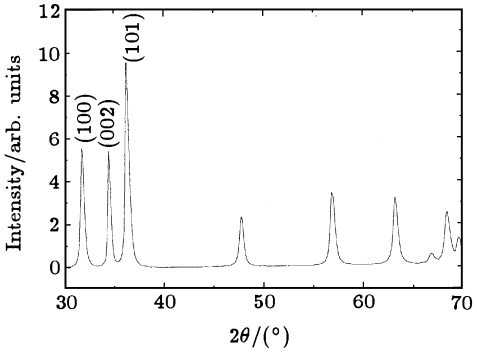


Fig.5. XRD pattern of the ZnO film deposited on ITO coated glass substrate.

The room temperature PL spectrum of the ZnO film is shown in Fig.6. The PL spectrum exhibits a strong emission at 390nm. This peak has been attributed to exciton transition.[13] Unlike the spectrum in the ZnO films prepared by many other methods, there is neither a green emission peak nor a blue emission peak in Fig.6. As is well known, the green emission and blue emission can be attributed to vacancies or impurities in ZnO; the result indicates that there are no detectable impurities and vacancies in our ZnO film, and our film prepared by EPD has high quality. We think this is because the ZnO powder is of high quality[11] and because the decomposition process at low-temperature is strictly stoichiometrical. This means that oxygen or zinc vacancies are scarcely generated. Besides, at low-temperature, heat induced native defects during the growth can be dramatically reduced. Therefore, it is a good method for preparing high quality ZnO films, and can be expected to have wide application in materials research.

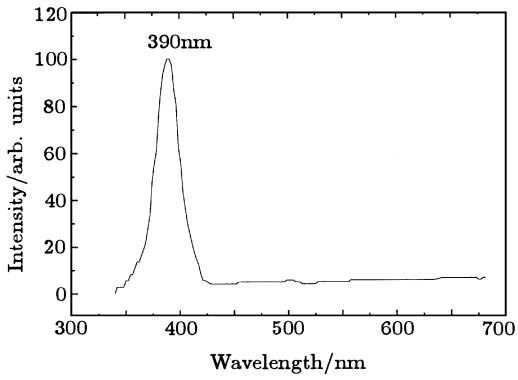


Fig.6. PL spectrum of the ZnO film deposited on ITO coated glass substrate.

4. Conclusion

XPS and the IR spectrum indicate that the ZnO powder has been prepared by solid-state pyrolytic reaction of compound of $Zn(CH_3COO)_2{\cdot}2H_2O$ and $NaHCO_3$. TEM imaging and XRD reveal that the average grain size of the ZnO powder is about 20nm. XRD pattern and SAED reveal that the ZnO film has a polycrystalline hexagonal wurtzite structure. Only a UV emission peak at 390nm is observed at room temperature. These results indicate that the ZnO film has high quality and this method may have applications in materials research.

Acknowledgment

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