

Research Result

Annealing Effect on the Photoelectric Properties of ZnO Nanocrystalline Films

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ABSTRACT

In this study, the ZnO nanocrystalline films were fabricated with varies annealing temperature to observe the photoelectric properties. The ZnO nanocrystalline films were deposited on the corning glass substrates separately by sol-gel spin-coating method at the annealing temperature (T_a) of 500, 550 and 600°C separately. The transmittance spectra of all ZnO nanocrystalline films show the same ultraviolet emission indicating the similar crystallite state. The transmittance ratio of the ZnO nanocrystalline films increases as the annealing temperature increases. Derived with the transmittance results by T_{auc} plot method, the optical bandgap (E_g) slightly increases form $E_g=3.2626\text{eV}$ for $T_a=500^\circ\text{C}$, $E_g=3.2723\text{eV}$ for $T_a=550^\circ\text{C}$, to $E_g=3.2765\text{eV}$ for $T_a=600^\circ\text{C}$, which was resulted from the enhancement of ZnO grain crystallization induced by increasing annealing temperature. Finally, the Current-Voltage curves of the ZnO nanocrystalline films were measured in the dark and under ultraviolet (UV) light illumination, respectively. The results show a gradually decrease of current variation ratio of the ZnO nanocrystalline films, defined as $(I_{UV-photo}-I_{dark})/I_{dark}$, that decreases from 141.84%, 123.53%, to 118.99% with increasing annealing temperature from 500, 550, to 600°C, respectively. The reason is that obvious increase of I_{dark} with increasing annealing temperature resulting in an apparent decrease of current variation ratio. However, the current variation ratios of all ZnO nanocrystalline films are all above 68.97% which all exhibit sufficient UV light photodetection characteristics which may be possible for future high-performance UV photodetection application.

KEYWORDS

ZnO, Annealing Temperature, Current variation ratio, UV photodetection.

1. INTRODUCTION

Ultra-violet (UV) photodetectors fabricated by compound semiconductors showed more excellent property than silicon opens new possibilities for commercial applications [1]. Compared with traditional Si-based devices, UV photodetectors with wide bandgap compound semiconductors are attracted attention by the related researchers due to solar-blind UV photodetection property [2]. The II-VI compound semiconductor ZnO with a wide bandgap of 3.37 eV along with the advantages of high thermal stability, low-cost, simple fraction process and Silicon process compatibility makes itself becoming one of the most important photonic materials for UV photodetection application [3]. For the past few years, researchers further declared that synthesis, characterization, and practice applications of the ZnO compound including nanoparticles, nanocrystalline films and other structures have been important objects due to their brilliant electrical, optical, and chemical properties [4]. A great deal of research has been focused their research on the ZnO-based UV photodetectors with nano-scale thin films. In this study, the ZnO nanocrystalline films are fabricated on the Corning glass substrates separately by the sol-gel spin-coating method with various annealing temperature, which are designed to grow the ZnO

nanocrystalline films with different heating conditions for the investigation of the structural induced optical properties variation. Besides, the application of the ZnO nanocrystalline films for UV photodetection is also discussed.

2. EXPERIMENTAL PROCEDURE

The ZnO nanocrystalline films were deposited on the Corning glass substrates separately by sol-gel spin-coating method. The precursor solutions were prepared by zinc acetate dihydrate $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$, 2-methoxyethanol $\text{C}_3\text{H}_8\text{O}_2$, and 2-aminoethanol $\text{C}_2\text{H}_7\text{NO}$. Zinc acetate dihydrate was firstly dissolved in 2-methoxyethanol with Zn ion concentration keeping at 0.5 M. Then, 2-methoxyethanol as a stabilizer was added into the solutions to form stable precursor solutions. Transparent solutions were obtained after stirring at 150°C for 1 hour on a hotplate. Then, the solution was left at room temperature for 72 hours to obtain a clear solution. After that by spin-coating method, the precursor solution was dropped on the Corning glass substrate and then spun at 1000 rpm for 10 seconds and following 3000 rpm for 30 seconds. After the spin-coating process, the ZnO nanocrystalline film samples were preheated on the hotplate at 300°C and following repeated this coating step for 8 times to fabricate samples of

ZnO nanocrystalline films with thickness of 160 nm. After that, the samples of ZnO nanocrystalline films were annealed by a high temperature quartz tube furnace at 500, 550 and 600°C separately in air for 5 hours.

The transmittance spectrometer was used to measure the optical properties of all ZnO nanocrystalline films with a UV-VIS-NIR Spectrometer with model Jasco V-670. Finally, the current-voltage (I-V) curves of all ZnO nanocrystalline films with the bias voltage from -5 V to +5 V were performed to measure the in the I-V curves under dark and UV illumination using the two-point probe holder in a black isolated black box with a Keithley 2400 source meter.

3. RESULTS AND DISCUSSION

The transmittance spectra from 300 to 800 nm of the ZnO nanocrystalline films grown on the Corning glass substrate with annealing temperature at 500, 550 and 600°C separately were measured to observe the transmittance ratio from UV (ultra-violet light), VIS (visible light) to NIR (near infrared light). As shown in Fig. 1, the transmittance ratio of the ZnO nanocrystalline films increases as the annealing temperature increases. The transmittance ratio is all above 80% within VIS-NIR wavelength range which shows transparent nature for visible and infrared light.

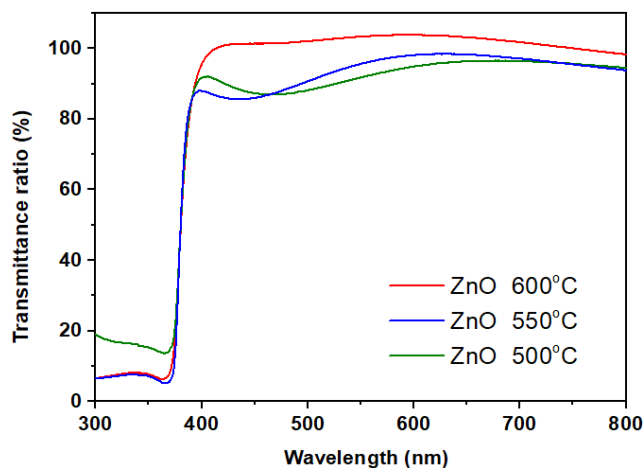


Figure 1. The transmittance spectra from 300 to 800 nm of the ZnO nanocrystalline films grown on the Corning glass substrate with annealing temperature at 500, 550 and 600°C.

For further reach about the optical energy gap (E_g) of all ZnO films, the Tauc plot method [5] is executed to obtain the E_g , the relationship between transmittance (T) and absorption coefficient (α) is shown as equation (1).

$$\alpha = (1/d) \ln(1/T), \quad (1)$$

where d is the thickness of the ZnO films. And then, the equation of the relationship between the α and the E_g of the ZnO nanocrystalline films is shown as equation (2).

$$(\alpha h\nu)^2 = A(h\nu - E_g), \quad (2)$$

where A is a constant and $h\nu$ is the photon energy. The relationship is used to find the E_g of all samples. Tauc plots of the ZnO nanocrystalline films are shown as Fig. 2.

Drived from using extrapolation method in the Tauc plots of Fig. 2, the E_g slightly increase form $E_g=3.2626\text{eV}$ for $Ta=500^\circ\text{C}$, $E_g=3.2723\text{eV}$ for $Ta=550^\circ\text{C}$, to $E_g=3.2765\text{eV}$ for

$Ta=600^\circ\text{C}$, which was resulted from the enhancement of grain crystallization induced by increasing annealing temperature.

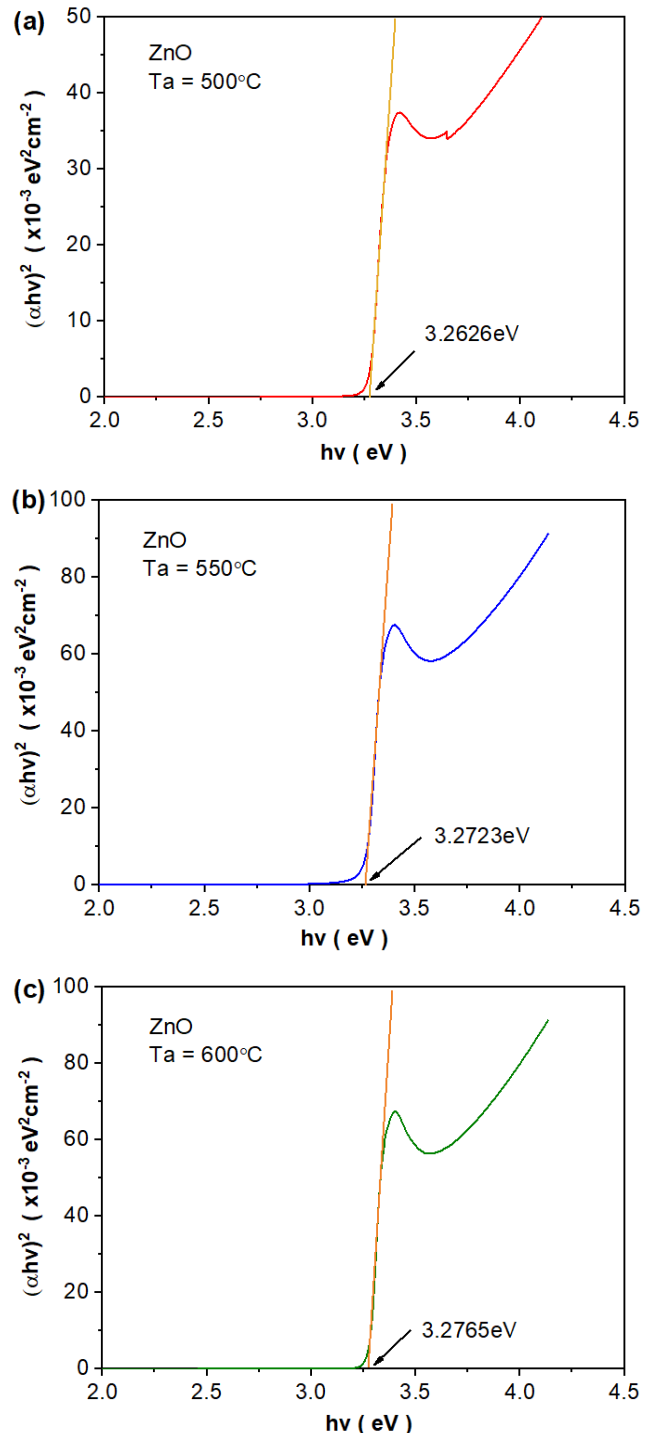


Figure 2. The Tauc plots of the ZnO nanocrystalline films grown on the Corning glass substrate with annealing temperature at (a) 500°C, (b) 550°C and (c) 600°C.

Fig. 3 shows the I-V curves of the ZnO nanocrystalline films grown on the glass substrate with annealing temperature at 500°C, 550°C and 600°C, respectively. The I-V curves were measured in the dark (dark-current, noted as I_{dark}) and under UV illumination (photo-current, noted as $I_{\text{UV-photo}}$), respectively, for the exploration of the UV photodetection observation as shown in the Fig. 3.

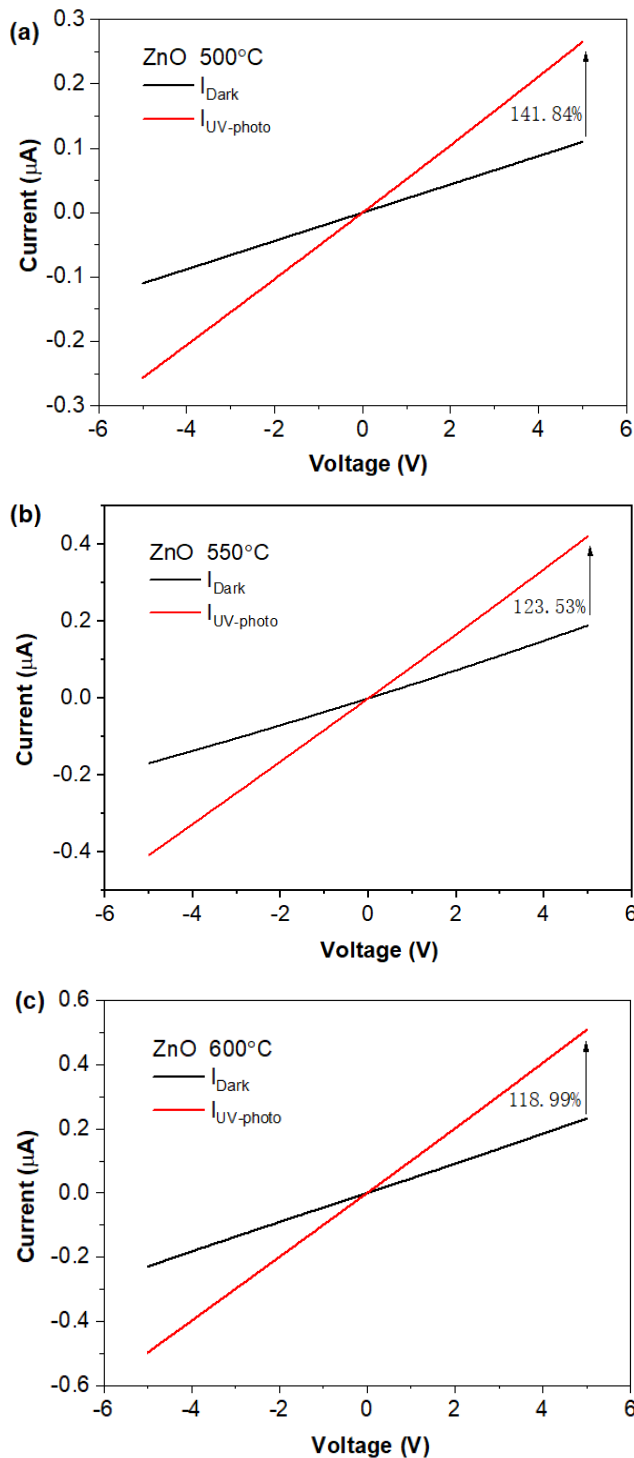


Fig. 3 The I-V curves with applied voltage from -5V to 5V of the ZnO nanocrystalline films grown on the glass substrates separately with annealing temperature at (a) 500°C, (b) 550°C and (c) 600°C.

As listed in TABLE 1, the I_{dark} measured at 5V of the ZnO nanocrystalline films increases from 0.1097, 0.1885, to 0.5085 μA with the increase of the annealing temperature from 500°C, 550°C to 600°C, respectively. Meanwhile, the $I_{\text{UV-photo}}$ measured at 5V also increases from 0.2652, 0.4214, to 0.5085 μA for the annealing temperature from 500°C, 550°C to 600°C, respectively, due to the increase of grain size and the corresponding increase of UV light induced electron-hole pairs. Besides, an obvious increase of current under UV illumination than that of in the dark is observed.

The I_{dark} and $I_{\text{UV-photo}}$ current values along with UV photo-induced current variation ratio (I%) of the ZnO nanocrystalline films in Table 1. The I% is defined as $(I_{\text{dark}} - I_{\text{UV-photo}}) / I_{\text{dark}}$ at 5V bias voltage to evaluate the UV photodetection property characteristic. Due to the obviously increase of I_{dark} than that of $I_{\text{UV-photo}}$ with the increase of the annealing temperature, the I% decreases from 141.84%, 123.53%, to 118.99% with the annealing temperature 500°C, 550°C to 600°C, respectively. As a result, we obtain a decreased UV photo induced I% with the increase of annealing temperature. However, the high UV photo induced I% of all samples show the well possibility for UV photodetection application.

TABLE 1. The I_{dark} , $I_{\text{UV-photo}}$ and I% measured at +5V bias voltage of the ZnO nanocrystalline films.

Annealing Temperature (°C)	$I_{\text{UV-photo}}$ (μA)	I_{dark} (μA)	I%
500	0.2652	0.1097	141.84%
550	0.4214	0.1885	123.53%
600	0.8539	0.5085	118.99%

4. CONCLUSIONS

The annealing effect on the optical properties of the ZnO nanocrystalline films and corresponding application on the UV photodetection properties are investigated in this study. Observed from transmittance measurements, slightly increase of transmittance ratio and optical bandgap show the enhancement of crystallization with increase of coating thickness. From the I-V curve measurements, the UV photo-induced I% decreases from 141.84%, 123.53%, to 118.99% with the annealing temperature increases from 500°C, 550°C to 600°C, respectively. However, high UV photo induced I% of all samples the well possibility for future UV photodetection application.

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