Thickness Effect on the Nanostructural and Optical Properties of ZnO Nanocrystalline Films

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Abstract - The ZnO nanocrystalline films deposited by sol-gel spin-coating method have been grown on the glass substrates for the nanostructural and optical properties observation and for the UV photodetection investigation. Four different thickness with 4, 6, 8, and 10 ZnO layers deposited by sol-gel spin-coating method, respectively. The FE-SEM images show that the thickness and grain size increases with the increase of layer thickness. The x-ray diffraction (XRD) patterns show well (002) crystallized phase for all films. Besides, the transmittance spectra of all ZnO nanocrystalline films show the same ultraviolet emission indicating the similar crystallite state with an slightly increase of optical bandgap form Eg=3.2655 eV for 4 layers, Eg=3.2781 eV for 6 layers, Eg=3.2753 eV for 8 layers, to Eg=3.2831 eV for 10 layers with the increase of film thickness. Finally, the I-V curves are measured in the dark and under UV illumination separately. The results show an obvious increase of current variation ratio that increases apparently from 4698.65%, 5218.81%, 13490.81%, to 24182.47% for 4, 6, 8, and, 10 layers samples, respectively, defined as $(I_{photo}-I_{dark})/I_{dark}$ ***with increasing ZnO layer thickness resulting in an apparent enhancement of ultraviolet photodetection characteristics which may be resulted from the increase of grain crystallization.***

Keywords: zinc oxide; nanocrystalline; film; grain; UV photodetection characteristics.

I. INTRODUCTION

Solid-state photodetectors fabricated by compound semiconductors other than group IV elements such as silicon opens new possibilities for commercial applications [1-2]. Compared with Si-based devices, ultraviolet (UV) photodetectors with wide bandgap compound semiconductors are especially attractive due to solar-blind ultraviolet detection property [3]. The compound semiconductor ZnO with a wide bandgap of 3.37 eV, high thermal stability, low-cost synthesis processes and compatibility with Si- based microelectronics makes itself become one of the most promising photonic materials for UV photodetection [4]. Recent researches further denoted that synthesis, characterization, and novel applications of the ZnO nanostructures have been intensive subjects due to their remarkable electrical, optical, and chemical properties [5]. Numerous researches have been reported on the ZnO-based UV detectors with nano-scale thin films for the improvement of photonic characteristics. In this study on UV detection devices, the sol-gel spin-coating method is utilized to fabricate the ZnO thin films and four different thickness of the ZnO nanocrystalline films are designed to grow on the glass substrates for the investigation of the nanostructural and optical properties. Besides, the application of the the ZnO nanocrystalline films for UV photodetection is also discussed.

II. EXPERIMENTAL

The ZnO nanocrystalline films were deposited on the glass substrate by sol-gel method. The source solutions were prepared by zinc acetate dehydrate $Zn(C_2H_3O_2)_2{\cdot}2H_2O$, 2-methoxyethanol $C_3H_8O_2$, and 2-aminoethanol (ethanolamine) C_2H_7NO. Zinc acetate dehydrate and yttrium acetate tetrahydrate were firstly dissolved in 2-methoxyethanol in stoichiometric proportions. The concentration of metal ions was kept at 0.5 M. Then, 2-methoxyethanol was added into the solutions to form stable precursor solutions. After stirring at 150^{o}C for 1 h on a hotplate, transparent solutions were obtained. The ZnO thin films deposited on glass substrate were prepared by spin coating technique. The precursor sols were dropped on the glass substrate and spun at 2500 rpm for 30 sec. After the spin coated process, the samples were heated on the hot plate at 300°C and this setup was repeated for 4, 6, 8, and, 10 times to fabricate four ZnO nanocrystalline film samples with 4, 6, 8, and, 10 layers thickness. After that, the samples annealed by high temperature quartz tube furnace at 600°C in air for 5 hours with a heating rate of 1^{o}C/min.

The surface morphologies and cross-section images of the nanocrystalline films were observed to observe the film thickness and grain crystallization by a field emission scanning electron microscope (FE-SEM, JEOL JSM-6700F) at 3.0 kV. The crystal structure of both ZnO nanocrystalline films was determined by the *x*-ray diffraction (XRD) patterns using a Rigaku D/max 2200 x-ray diffractometer with Cu-Kα radiation. The XRD data were recorded in the 2θ range from 20° to 60° with a step width of 0.01° and a scan speed of 0.5°/min. Then, transmittance spectrometer was used to measure the optical properties of all ZnO nanocrystalline films. Finally, the current-voltage (I-V) curves of all ZnO nanocrystalline films with the bias voltage from -5 V to 5 V were performed in the dark and under UV illumination

using the two-point probe I-V curve method with a Keithley 2400 source meter.

III. RESULTS AND DISCUSSION

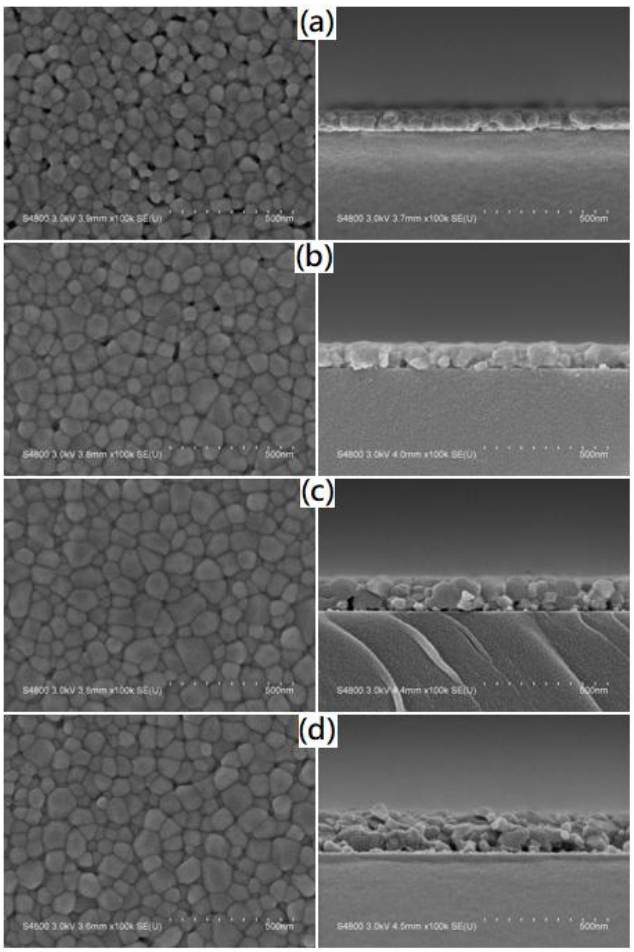

Fig. 1 FE-SEM top view and cross section images of the ZnO nanocrystalline films grown on the glass substrate with (a) 4, (b) 6, (c), and (d) 10 layers.

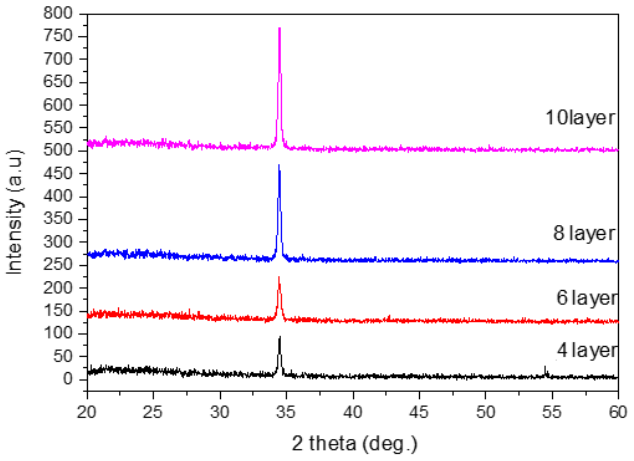

Fig. 1 XRD patterns of the ZnO nanocrystalline films grown on the glass substrate with (a) 4, (b) 6, (c), and (d) 10 layers.

Fig. 1 shows the FE-SEM top view and cross section images of all ZnO nanocrystalline films 4, 6, 8, and, 10 layers thickness grown on the glass substrates, respectively. The thickness of the films increases from 86, 108, 112 to 173 nm with increasing the layers from 4, 6, 8 to 10 coating layers. By the comparison of top-view images, the slightly increase grain size indicates the increase of layers will enhance the grain crystallization of ZnO nanocrystalline films.

Fig. 2 shows the XRD patterns of all ZnO nanocrystalline films 4, 6, 8, and, 10 layers thickness grown on the glass substrates, respectively. As the XRD patterns shown, all ZnO nanocrystalline films are found to have the same wurtzite hexagonal structure with space group P63/mc. Th results indicates the well ZnO crystallization quality is obtained for all films.

The transmittance spectra from 300 to 800 nm of the ZnO nanocrystalline films grown on the glass substrate with 4, 6, 8, and 10 layers were measured as shown in Fig. 3, respectively. The transmittance is above 80% within 400-800 nm light wave range. For further reach about the energy E*g*, the equation $\alpha=(1/d)\ln(1/T)$ exhibits the relationship between transmittance T and absorption coefficient α, where d is the ZnO film thickness [6]. Equation $\alpha h\upsilon=A(h\upsilon-Eg)^{1/2}$ exhibits the relationship between the absorption coefficient α and optical band gap E*g* of the ZnO nanocrystalline films, where A is a constant thus and $h\upsilon$ is the photon energy [7].

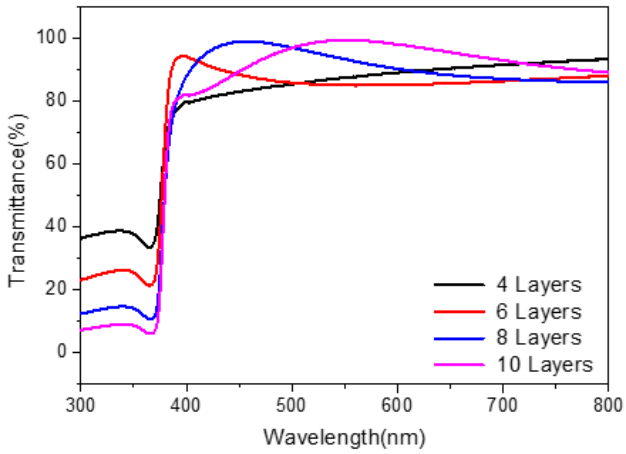

Fig. 3 The transmittance spectra from 300 to 800 nm of the ZnO nanocrystalline films grown on the glass substrate with (a) 4, (b) 6, (c), and (d) 10 layers.

The relationship is used to find the optical band gap of all samples. The optical band gap E*g* of all ZnO nanocrystalline films increases progressively with the increase of film thickness form E*g*=3.2655 eV for 4 layers, E*g*=3.2781 eV for 6 layers, Eg=3.2753 eV for 8 layers, to E*g*=3.2831 eV for 10 layers. The slightly increase of E*g* is consistent with the results observed from the FE-SEM images which shows the slightly increase of grain size resulted in the increase of layers will enhance the grain crystallization of ZnO nanocrystalline films.

Fig. 4 shows the I-V curves of the ZnO nanocrystalline films grown on the glass substrate with 4, 6, 8, and 10

layers grown on the glass substrates, 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_{photo}), respectively, for the exploration of the UV photodetection application.

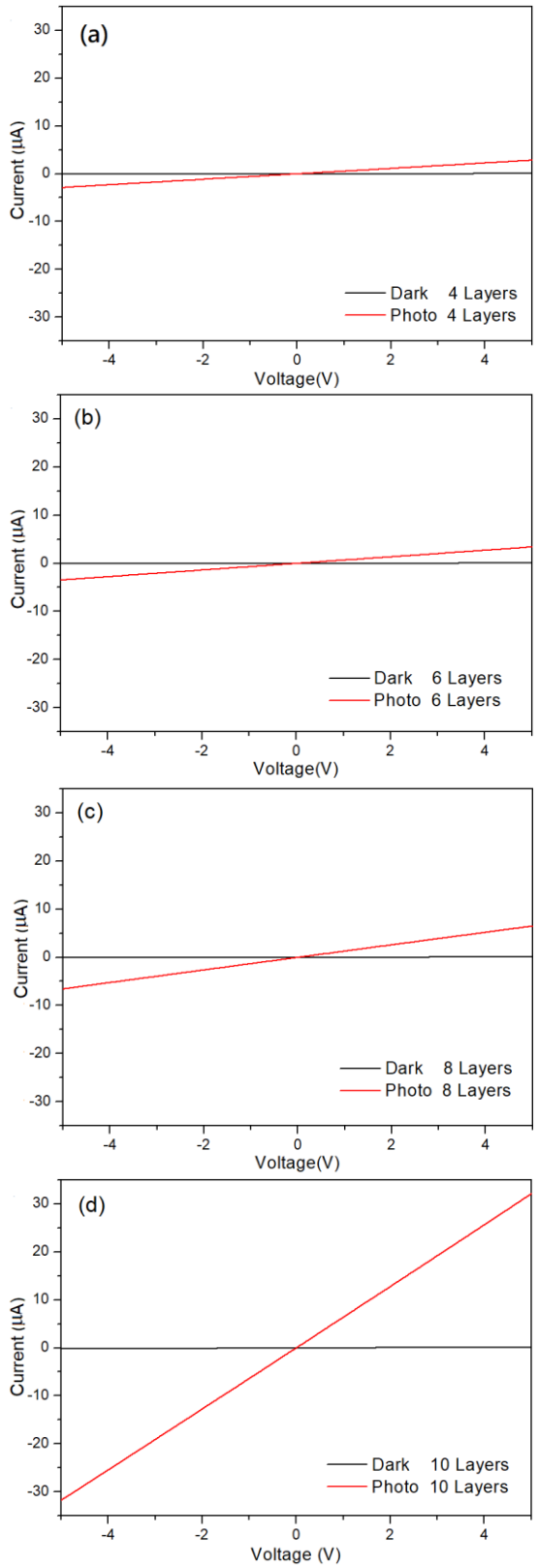

Fig. 4 I-V curves in the dark and under UV illumination of the ZnO nanocrystalline films grown on the glass substrate with (a) 4, (b) 6, (c), and (d) 10 layers.

As listed in TABLE 1, the I_{dark} obviously increases from 0.0596, 0.0643, 0.0479, to 0.1324 μA with the increase of ZnO layer thickness for 4, 6, 8, and, 10 layers samples, respectively. Moreover, the I_{photo} increases obviously from 2.86, 3.42, 6.51, to 32.15 μA for 4, 6, 8, and, 10 layers samples, respectively. due to the increase of grain size and the corresponding increase of UV light induced electron-hole pairs. Meanwhile, an obvious increase of current under UV illumination than that of in the dark is observed. The I_{dark} and I_{photo} current values measured at 5V along with UV photo-induced current variation ratio (R) of the ZnO nanocrystalline films in Table 1. The UV photo-induced current variation ratio is defined as $(I_{dark}-I_{photo})/I_{dark}$ at 5V bias voltage to evaluate the UV photodetection characteristic. Due to the obviously increase of of I_{photo} than that of I_{dark} with the increase of the ZnO layers thickness, the R increases apparently from 4698.65%, 5218.81%, 13490.81%, to 24182.47% for 4, 6, 8, and, 10 layers samples, respectively. As a result, we obtain an obviously increased UV photo-induced current variation ratio (R) with increasing seed layers thickness which illustrates the possibility for photodetection application.

TABLE 1. Dark and photo current values measured at 5V along with current variation ratio of the ZnO nanocrystalline films.

layers	I_{dark} (μA)	I_{photo} (μA)	R (%)
4	0.0596	2.86	4698.65%
6	0.0643	3.42	5218.81%
8	0.0479	6.51	13490.81%
10	0.1324	32.15	24182.47%

IV. CONCLUSION

The influence of layer thickness on the nanostructural, optical and electrical properties of the ZnO nanocrystalline films and corresponding application on the UV photodetection are investigated in this study. The thickness of the ZnO nanocrystalline thin films increases with 4, 6, 8, and 10 sol-gel spin-coating layer as shown in the FE-SEM images. All XRD patterns of the ZnO nanocrystalline films reveal the same hexagonal wurtzite structure. Slightly increase of transmittance and optical bandgap show the enhancement of crystallization with increase of coating thickness. From the I-V measured results, the UV photo-induced current variation ratio increase apparently from from 4698.65%, 5218.81%, 13490.81%, to 24182.47% for 4, 6, 8, and, 10 layers samples, respectively, respectively, which shows the well possibility for UV photodetection application.

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