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Effect of Annealing Temperature on the Structural and Optical Properties of Nanocrystalline ZnO Thin Films Prepared by Sol-gel Method

(Kesan Suhu Sepuhлиндap Terhadap Struktur dan Sifat Optik Filem Nipis ZnO Nanohablur

Disediakan dengan Kaedah Sol-gel)

N.B. IBRAHIM*, S.M. AL-SHOMAR & S.H. AHMAD

ABSTRACT

Undoped zinc oxide (ZnO) thin films were prepared by a sol-gel method. The effect of annealing temperature from 500 to 700°C on the structural and optical properties of the films was studied. The films nanostructure characterized by the X-ray diffraction method showed that the films were single phase ZnO with wurtzite structure. The surface morphology studied using the field emission scanning electron microscope showed that the thickness of the films increased with the increment of annealing temperature. The grain size of the films increased with the increment of the annealing temperature. The film surface roughness measured using the atomic force microscope showed that the surface roughness of the film decreased (from 2.3 to 1.02 nm), when the annealing temperature increased from 500 to 600°C then it increased to 3.06 nm at 700°C. The optical properties were studied by the UV-Vis spectrophotometer. The results showed that the films had high transmittance (above 80%) in the visible range and the exciton absorption occurred at a wavelength of 379 nm. The energy gap decreased with the increment of annealing temperature.

Keywords: Annealing; optical; sol-gel; XRD; ZnO films

ABSTRAK

Filem nipis ZnO tak terdop telah disediakan dengan kaedah sol-gel. Kesan suhu sepuhлиндap daripada 500 to 700°C terhadap struktur dan sifat optik filem telah dikaji. Nanostruktur filem yang dicirikan dengan kaedah pembelauan sinar-X menunjukkan bahawa filem adalah ZnO sefasa dengan struktur wurtzite. Morfologi permukaan yang telah dikaji dengan mikroskop elektron imbasan pancaran medan menunjukkan bahawa ketebalan filem bertambah dengan pertambahan suhu sepuhлиндap. Saiz butiran filem meningkat dengan pertambahan suhu sepuhлиндap. Kekasaran permukaan filem telah diukur dengan mikroskop daya atom menunjukkan bahawa kekasaran permukaan filem berkurangan (daripada 2.3 ke 1.02 nm) apabila suhu sepuhлиндap bertambah daripada 500 ke 600°C kemudian meningkat ke 3.06 nm pada 700°C. Sifat optik telah dikaji dengan spektrofotometer UV-Vis. Hasil menunjukkan bahawa filem mempunyai transmisi yang tinggi (lebih 80%) dalam julat nampak dan penyerapan eksiton berlaku pada panjang gelombang 379 nm. Jurang tenaga berkurangan dengan penambahan suhu sepuhлиндap.

Kata kunci: Filem ZnO; optik; sepuhлиндap; sol-gel; XRD

INTRODUCTION

ZnO is an important wide band-gap optoelectronic material because it has high chemical and thermal stability at room temperature (27°C) and a large exciton binding energy of 60 meV. These characteristics made ZnO thin film a good excitonic emitter, thus a good candidate for ultraviolet emission applications (Mandalapu et al. 2008; Zhu et al. 2009). ZnO thin films usually show high transmittance in the visible range and possess excellent n-type conductivity when doped with Al, Ga and In, thus they can be used as transparent electrodes (Oh et al. 2006) and window layers of solar cells (Hagiwara et al. 2001).

Many thin film preparation techniques have been used to prepare ZnO thin films such as spray pyrolysis, sputtering, electrodeposition, sol-gel method (Ivanova et al. 2010) and pulsed laser deposition (Zhao et al. 2006).

Zhao et al. (2006) have reported that ZnO films prepared at different substrate temperatures by pulsed laser deposition have nanocrystalline structures with grain sizes in the range of 30–45 nm. Cho et al. (1999) have reported that ZnO emission synthesized by thermal oxidation of metallic Zn at 1000°C, shows only UV emission.

A sol-gel method has many advantages such as a low cost method because no expensive apparatus is required, able to produce film with uniform thickness and simplicity of working principle (Zhang et al. 2007).

Znaidi et al. (2012) have reported on the investigation of pure and Al doped ZnO thin films prepared by the sol-gel method for optical wave guiding applications. The films show a very strong (0 0 2) preferential orientation and display well guided modes meaning that the coupling and confinement of the light in the films are efficient (Znaidi et

al. 2012). Therefore, the sol-gel method was proved to be well adapted to the elaboration of thin films for photonic applications.

Annealing process is one of the most important factors that can strongly affect the properties of ZnO thin films. Nunes et al. (2001) have reported on the comparison of optical, structural and electrical properties of pure ZnO films and ZnO doped with indium and aluminum prepared by spray pyrolysis. They studied the effect of annealing temperature and atmosphere (air/forming gas) on these properties. The film electrical resistivity decreases with the increment of annealing temperature. Ivanova et al. (2010) have studied the effect of annealing temperature on ZnO films prepared by a sol-gel method, the sol stabilizer used was triethanoamine (TEA), however the surface morphology of the films have not been reported. In this research, the effects of annealing process on the structural, surface morphology and optical properties of ZnO thin films prepared by a sol-gel method were investigated.

EXPERIMENT

Zinc acetate dehydrate, 2-methoxy ethanol and monoethanolamine (MEA) were used as starting material, solvent and stabilizer, respectively. Zinc acetate dehydrate was first dissolved in a mixture of 2-methoxy ethanol and MEA solution at room temperature (27°C). The molar ratio of MEA to zinc acetate was maintained at 1.0 and the concentration of zinc acetate was 0.35. The solution was stirred at 65°C for 3 h to yield a clear and homogeneous solution. The precursor solution was aged for 1 day at room temperature. The quartz substrate was cleaned with acetone, ethanol and distilled water. Film deposition was carried out in air at room temperature. The spin coating time was 40 s: The first spin-speed of the coater was 500 rpm to ensure good distribution of the sol and full coverage of the surface of the substrate, the second spin-speed was 3000 rpm. Then the film was dried in a furnace at 350°C for 10 min at a heating rate of 5°C/min. The preheat-treatment temperature of 350°C is sufficient for the complete evaporation of organics compound and crystallization of

the films (Raoufi & Raoufi 2009). Finally, the films were annealed at 500, 600 and 700°C in the air for 1 h.

An X-ray diffractometer (Bruker AXS D8) with CuK α radiation ($\lambda=1.5406\text{\AA}$) was used to characterize the film structure. An atomic force microscope (NTEGRA Prima) was used to study the film-surface morphology. The film thickness and grain size were measured using a Field Emission Scanning Electron Microscopy (FESEM). The optical transmission spectra of ZnO films were measured using a UV-Vis -NIR spectrophotometer (Perkin Elmer Lambda 900).

RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction patterns of the as-prepared and annealed ZnO films. It is clear from the figure that the as-prepared film is amorphous and the films started to crystallize at 500°C. All of the films have wurtzite structures and are preferentially oriented along the c-axis. The film preparation conditions influence the growth orientation of ZnO thin films. Some researchers have reported that MEA which was used as the sol stabilizer is favorable for the formation of a highly c-axis oriented film (Ohyama et al. 1997; Wang et al. 2007).

The major peaks observe at 2θ are 31.8°, 34.4°, 36.3°, 47.5° and 56.6° which correspond to the (100), (002), (101), (102) and (110) plane reflections of hexagonal ZnO with $a = 3.25\text{\AA}$ and $c = 5.21\text{\AA}$ (Phan & Chung 2011). The peaks in the XRD spectra do not appear clearly for as-prepared film and only appeared when the annealing temperature was increased, indicating that the crystallization process occurred at 500°C.

Table 1 shows the summary of the films average grain sizes and thickness measured using a field emission scanning electron microscope (FESEM). The grain size of ZnO films increases with the increment of annealing temperatures. This is due to the small grains coalesced together to produce larger grains. Ivanova et al. (2010) also reported the grain size of their sol-gel ZnO films increased as the annealing temperature increased. The films were prepared on Si substrates and the sol stabilizer was triethanolamine (TEA).

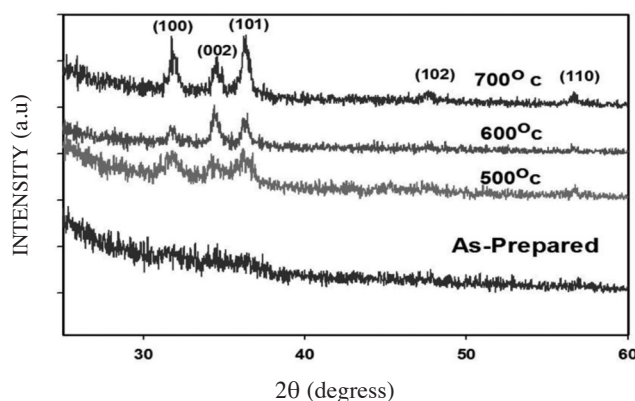


FIGURE 1. XRD patterns of as-prepared ZnO film and ZnO films annealed at different temperatures

TABLE 1. The average grain size and thickness of ZnO samples

Annealing temperatures (°C)	Average Grain size (nm)	Thickness (nm)
As-prepared	-	50
500	21	95
600	34	170
700	45	147

The film thickness increases with annealing temperatures then it decreases when the annealing temperatures reached at 700°C due to the solvent evaporation and the densification of the film. In this study the crystalline quality of ZnO thin films is generally improved with the increment of the film thickness. Similar results have also been reported by Xua et al. (2011) who have studied the effect of thickness on the structure of ZnO film prepared by the sol-gel method.

Figure 2 shows the AFM two-dimensional surface images of the as-prepared and annealed films. It is obvious that the surfaces of these films are very smooth. The roughness is 0.115, 2.304, 1.02, 3.06 for the as prepared and films annealed at 500, 600 and 700°C respectively. The surface roughness of the films decreases while the annealing temperature increases from 500 to 600°C then it increases to 3.06 nm at 700°C. The rapid increment of the surface roughness is due to the major grain growth. The process of grains coalescence causes major grain growth resulting in increasing porosity and surface roughness (Fang et al. 2005).

According to the above discussion, it can be concluded that the annealing temperature can strongly affect the structural properties of ZnO films and suitable annealing temperature is around 500°C leading to the improvement of ZnO crystallinity, such as high C-axis orientation and smooth surface.

The optical transmittance spectra of zinc oxide films annealed at different temperatures is shown in Figure 3. All films have high transmittance (above 80%) in the visible range. The transmittance of ZnO thin films in the visible range is gradually improved with the increment of the annealing temperatures. This improvement is due to the change of the film thickness with the annealing temperatures. From the above results, it can be known that ZnO thin films prepared by a sol-gel method have high transmittance in the visible range, which can be used as transparent window materials in many optoelectronic devices (Lee et al. 2000). Figure 4 shows the UV-Vis absorption spectra of the films annealed at different temperatures. The exciton absorption is at 379 nm similar as reported by Raoufi and Raoufi (2009).

The optical band gap was determined by the following relation (Serpone et al. 1995):

$$(ah\nu)^2 = A(h\nu - E_g), \quad (1)$$

where A is a constant depending on the electron-hole mobility having a value between 10^5 and 10^6 , α the absorption coefficient and $h\nu$ is the photon energy.

Assuming the absorption coefficient, α corresponding to the direct band gap energy of the wurtzite structure in

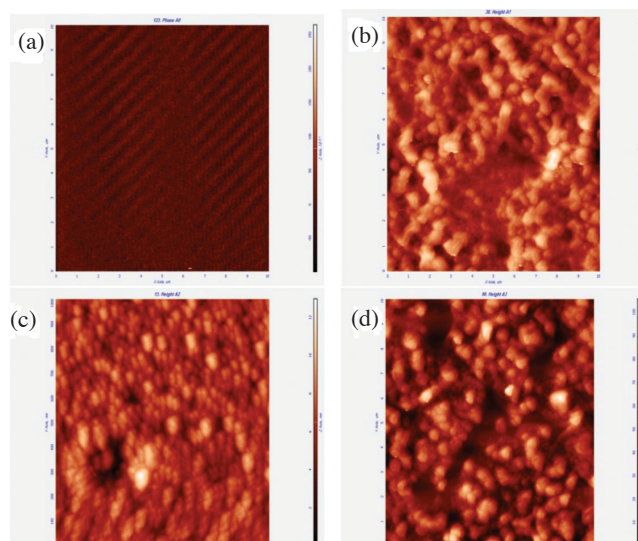


FIGURE 2. The AFM surface morphology images of the samples a) as-prepared, annealed at b) 500°C, c) 600°C and d) 700°C

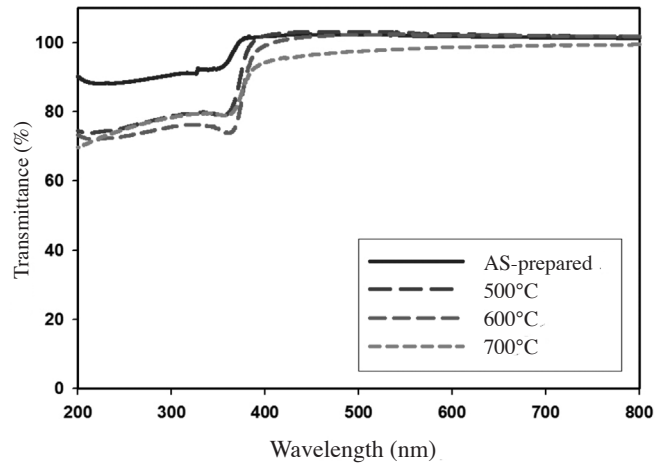


FIGURE 3. Transmittance spectra of the samples at different annealing temperatures

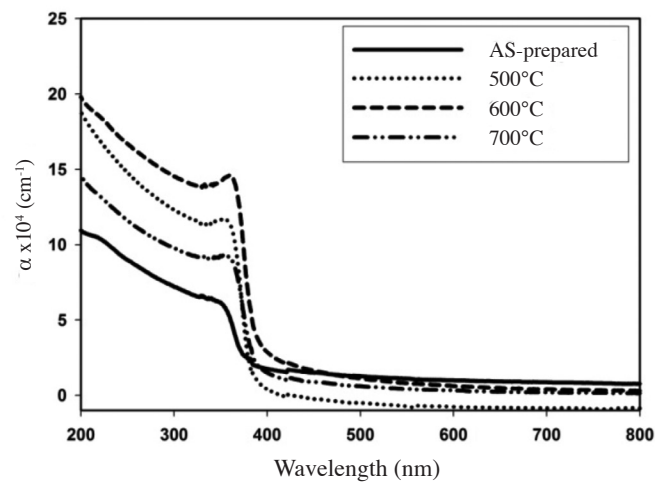


FIGURE 4. Absorbance spectra of ZnO thin films annealed at different temperatures

the fundamental region, better linearity was observed from $(ah\nu)^2$ versus $(h\nu)$ plot which was used to determine the band energy (El Zawawi & Abd. Alla 1999). The band gap of ZnO thin films decreases from 3.27 to 3.24 eV as the annealing temperature increases from 500 to 700°C (Figure 5). Zhao et al. (2005) have estimated the band gap of pulsed laser deposition ZnO films prepared at different substrate temperatures and oxygen pressures, is in the range of 3.25–3.27 eV.

CONCLUSION

In this work, the structural and optical properties of ZnO thin films prepared by a sol-gel method with various annealing temperatures has been investigated. The microstructure study showed that the as-prepared films were amorphous and after the annealing process the ZnO thin films were highly c-axis oriented. The AFM results

showed that the surface of the ZnO thin films was very smooth. The grain size and film thickness increased with the increment of annealing temperatures. The ZnO thin films have high transmittance in the visible range which is gradually improving with the annealing temperatures and the exciton absorption was at 379 nm. The optical band gap of ZnO thin films decreased as the annealing temperature increased. These results suggest that the nanocrystalline thin films prepared by a sol-gel method have good c-axis orientation and optical properties. These films are suitable for opto-electronic applications.

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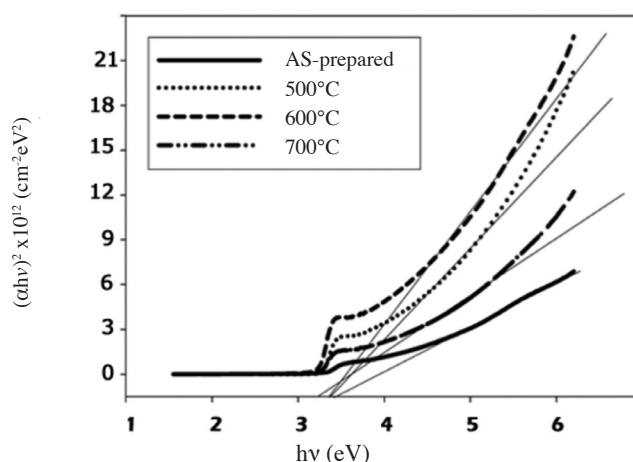


FIGURE 5. $(\alpha hv)^2$ vs. $h\nu$ curves of the ZnO thin films annealed at different temperatures

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- N.B. Ibrahim* & S.H. Ahmad
School of Applied Physics
Faculty of Science and Technology
Universiti Kebangsaan Malaysia
43600 UKM Bangi, Selangor
Malaysia

S.M. Al-Shomar
Physics Department, Faculty of Science
Hail University
Kingdom of Saudi Arabia

*Corresponding author; email: baayah@ukm.my

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