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Influence of deposition rate on PL spectrum and surface morphology of ZnO nanolayers deposited on Si (100) substrate

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Abstract. **Zinc oxide (ZnO) thin films were deposited on Si (100) substrate through sputtering of zinc by DC magnetron, followed by thermal oxidation. Different deposition rates were used in coating films with 100 nm thickness (0·6–4·5 nm/s). Photoluminescence spectra of the produced samples were obtained and it was found that the violet emission peak intensity increases with deposition rate. Scanning electron microscopy (SEM) micrograph and atomic force microscopy (AFM) images for the zinc oxide films were obtained. Morphological changes due to various deposition rate are discussed in the light of changes observed in the ZnO crystals. Low coating rates produced smooth surface with small grains while higher deposition rates increased the surface roughness and larger grain size. AFM and SEM results are in good agreement and support the PL results.**

Keywords. **ZnO; Si substrate; deposition rate; AFM/SEM; PL.**

1. Introduction

Thin films of transparent conductive oxides (TCOs) play essential roles in a wide range of nano-electronic and opto-electronic applications such as sensors (Roy and Basu 2002; Wang *et al* 2006), solar cells (Karuppuchamy *et al* 2002), flat panel displays, piezoelectric (Gao and Wang 2005), surface acoustic wave (Wang *et al* 2008), etc. Recently, zinc oxide (ZnO) has attracted much attention within the scientific community as a potential material for future. ZnO is a II–VI compound semiconductor and an important semiconductor with excellent chemical and thermal stability. At room temperature, ZnO shows a wide band gap (3·37 eV) and large exciton binding energy (60 meV) (Ozgur *et al* 2005). ZnO is characterized by large bond strength and extreme stability of excitons indicated by stronger exciton binding energy which is larger than that of GaN (24 meV) (Hwang *et al* 2005; Liu *et al* 2005). The exciton stability makes ZnO a promising material for recognition of efficient exitonic lasing at room temperature (Samanta *et al* 2009). Lots of research results show that ZnO thin films and its nanostructures have high excitonic emission efficiency. So far, zinc oxide materials are still studied mainly in the form of thin films. Many researches indicate that the optical and electrical properties of ZnO thin films are directly connected with their crystallization quality. In our previous works, optical and structural properties of the ZnO thin films deposited on glass and $LiNbO_3$ substrates were investigated and low loss Zn:$LiNbO_3$ waveguide with very good crystal quality and surface morphology was successfully produced (Aghli-Moghadam *et al* 2009; Zendehnam *et al* 2010; Shirazi *et al* 2011). ZnO thin films have been prepared by many techniques such as pulsed laser deposition (PLD), electron beam evaporation, magnetron sputtering, chemical vapor deposition (CVD), molecular beam epitaxy (MBE) and sol–gel method (Czternastek 2004; Shamala *et al* 2004; Dikovska *et al* 2005; Zhong-Lin *et al* 2009; Kim *et al* 2010). In the present work, zinc oxide thin films have been produced by thermal oxidation of sputtered zinc films on the Si (100) substrate with 100 nm thickness. This deposition technique presents interesting advantages such as high deposition rate, low substrate temperature, good adhesion of thin films to Si substrate and finally, films' good packing density. It is well known that the physical characteristics of ZnO thin films depend on deposition rate, and to the best of our knowledge there is very little report on this subject; so the main goal of this study is investigation of deposition rate influence on photoluminescence spectra and the surface morphology of ZnO thin films.

2. Experimental

DC magnetron sputtering was employed to deposit thin layers of Zn on Si (100) substrate. Si (100), n type wafer was cut to required dimensions (1 × 1 cm) with 1 mm thickness and then used as substrate for deposition of Zn thin films. Before use, all Si substrates were ultrasonically cleaned by heated acetone and then by ethanol for 2 min. A vacuum system (Hind High Vacuum, H.H.V., 12"MSPT) with 10^{-6} mbar base pressure was employed, and a circular flat disc (3 mm thickness, and 125 mm diameter) of pure zinc (99·9%, MERCK) was fabricated and used as the sputtering target. For plasma formation, research grade pure argon (99·99%) was used and 2×10^{-2} mbar pressure was applied for Ar sputtering. Before sample preparation, discharge was carried out for about 5 min and the obtained plasma was checked

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using a spectrometer and observation through vacuum system part. The shutter was removed when line spectra belonging to Zn and Ar atoms and ions were observed, and no band spectrum due to contamination was detected. Substrate temperature was fixed (300 K) and measured by the use of an exact digital thermocouple. A conventional oven in open air with average humidity of 60% was used for thermal oxidation of Zn films and the samples oxidation took place at 400 °C temperatures. In this work, six samples with different deposition rates were coated. To change the coating rates of zinc (0·6–4·5 nm/s), the discharge current was varied from 200 to 1200 mA, and zinc thin films with 100 nm thickness were produced. Film thickness and the deposition rate were measured by the use of vibrating quartz crystal thickness monitor unit.

Photoluminescence (PL) spectra (Stellar Net EPP-200) were taken at room temperature under 355 nm xenon lamps as the excitation source. To investigate surface morphology of these ZnO thin films, the scanning electron microscopy (SEM) (Hitachi S-4160) and atomic force microscopy (AFM) (Park Scientific Instrument Auto Probe model CP) was also employed using force constant mode.

3. Results and discussion

In order to study the effects of zinc deposition rate on the PL spectra and surface morphology properties of the ZnO thin films, six samples with the following condition (which is presented in table 1) were prepared. These samples were produced under similar conditions (Ar pressure, substrate temperature, oxidation temperature and heating period).

Variation of Zn deposition rate against power is shown in figure 1; a linear relationship between the coating rate and electrical power is obtained.

Table 1. The produced samples with different deposition rates.

Samples	Current (mA)	Electrical power (W)	Deposition rate (nm/s)
E_1	200	86	0·6
E_2	400	184	1·2
E_3	600	288	1·95
E_4	800	408	2·75
E_5	1000	530	3·75
E_6	1200	672	4·5

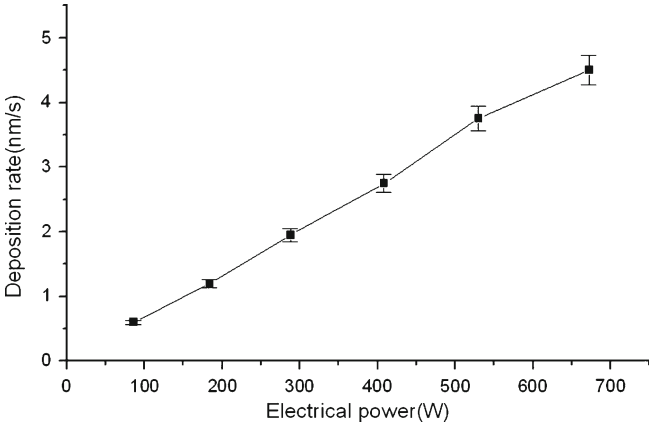

Figure 1. Variation of Zn deposition rate against electrical power.

3.1 *Photoluminescence properties*

Figure 2 shows PL spectra of ZnO thin films grown on Si (100) substrate at room temperature. Two main emission peaks are observed for all samples, the UV emission peak at 380 nm and a violet emission peak around 438 nm are obtained. The intensity of 438 nm (violet emission) increases with deposition rate while that of the UV emission peak almost remains the same. It is well known that the UV emission is attributed to free excitonic transition or the near-band-edge (NBE) emission and the violet emission is presumably resulted form a close relation with defects such as interstitial

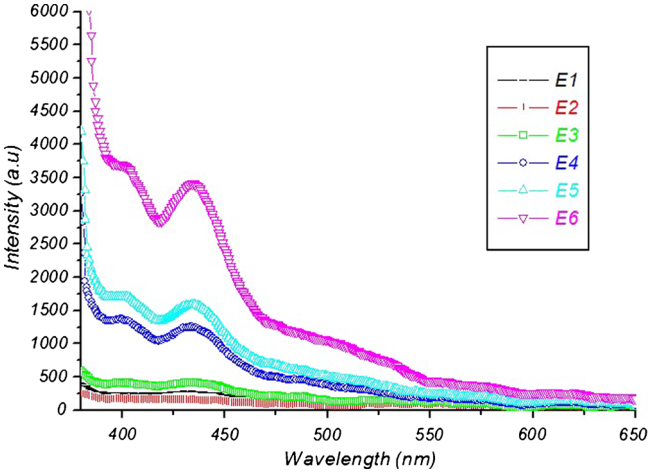

Figure 2. PL spectra of all samples at room temperature.

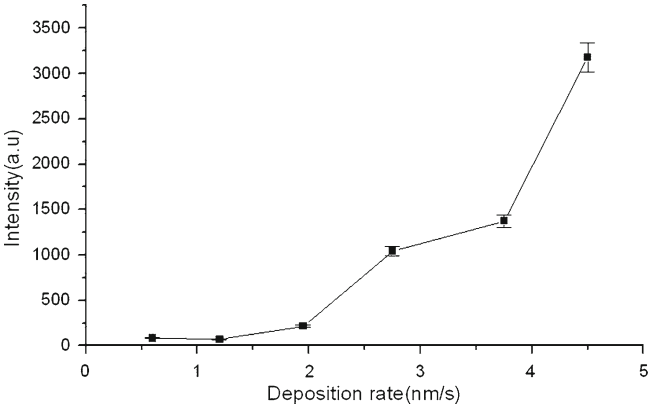

Figure 3. Variation of the violet emission intensity against deposition rate.

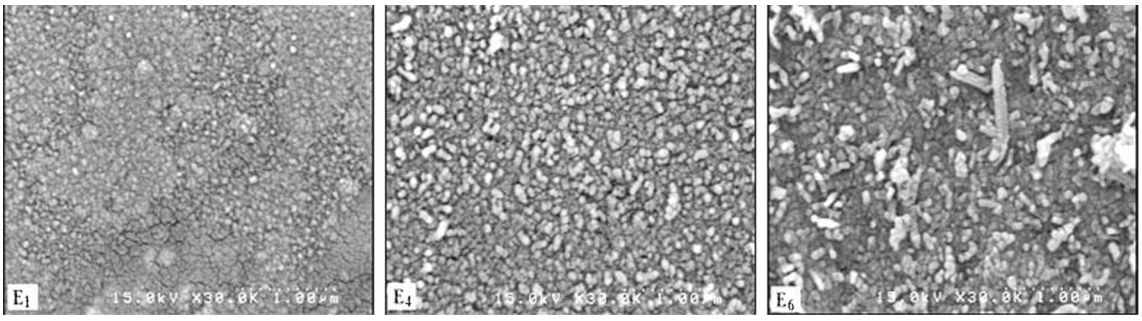

Figure 4. SEM images of E_1, E_4 and E_6 samples.

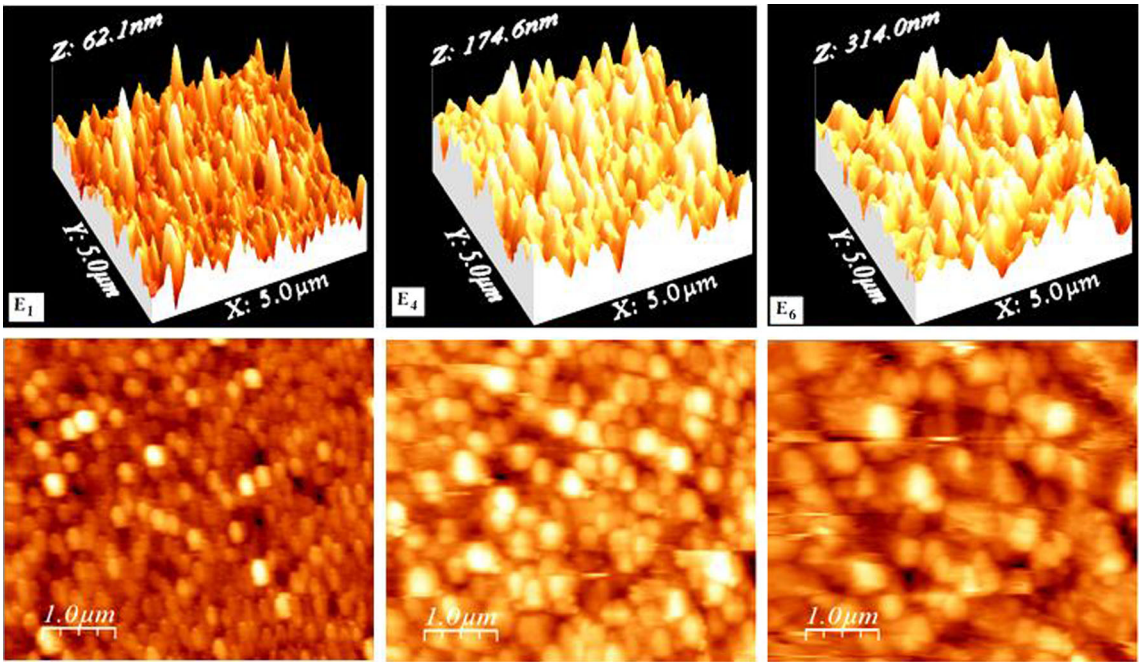

Figure 5. AFM images of E_1, E_4 and E_6 samples.

Zn atoms (Zn_i) and ions in the ZnO lattice. The obtained violet emission peak in PL spectra has been observed by other researchers especially when a Zn buffer layer was coated between ZnO film and Si substrate (Lee *et al* 2008). The high peak intensity of the UV emission is indicative of crystalline quality of the ZnO film. Meanwhile, the defect-related violet emission becomes stronger with increase of Zn deposition rate.

It is difficult to grow epitaxial ZnO films directly on Si substrate owing to amorphous SiO_2 formation and large lattice mismatch between ZnO and Si. Figure 3 shows variation of peak intensity of violet emission vs Zn deposition rate. Intensity remains roughly constant at low rates but increases sharply at high rates. So, these results indicate good crystal quality in the layers deposited with low coating rate. On the other hand, the samples coated with high rate are important for the production of PL lasers in violet region of spectrum with suitable intensity.

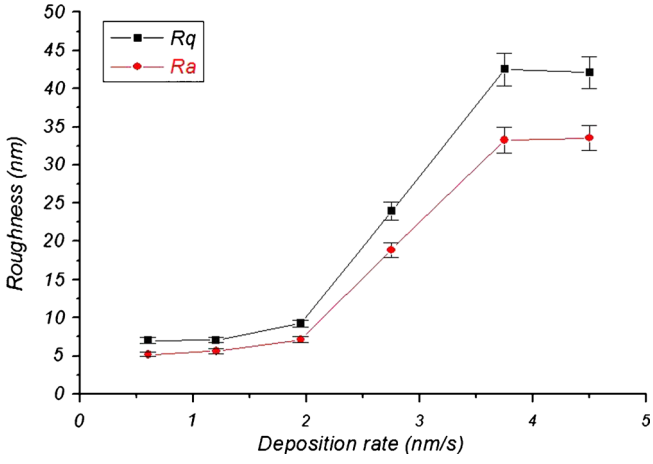

Figure 6. Surface roughness (R_a, R_q) vs deposition rate of zinc.

Table 2. Some commonly used roughness parameters.

Parameter name	Abbreviation	Formula
Roughness average	R_a	$R_a = \frac{1}{n}\sum_{i=1}^{n}\lvert Z_i - \overline{Z}\rvert$
Root-mean squared roughness	R_q or R_{rms}	$R_q = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(Z_i - \overline{Z})^2}$
Skewness	R_{sk}	$R_{sk} = \frac{1}{nR_q^3}\sum_{i=1}^{n}(Z_i - \overline{Z})^3$
Kurtosis	R_{ku}	$R_{ku} = \frac{1}{nR_q^4}\sum_{i=1}^{n}(Z_i - \overline{Z})^4$

Table 3. Skewness and kurtosis parameters.

Samples	Skewness (S_{sk})	Kurtosis (S_{ku})
E_1	0·99	5·66
E_2	0·58	3·87
E_3	0·26	3·23
E_4	0·16	3·12
E_5	0·11	3·27
E_6	0·15	3·10

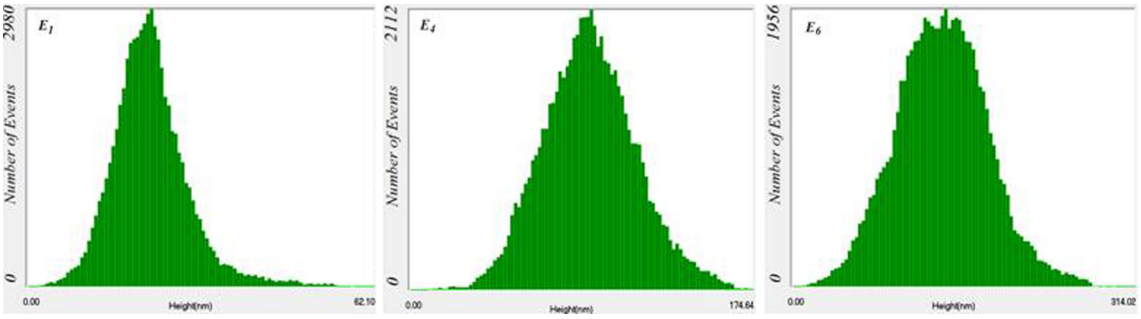

Figure 7. Height distribution histograms from AFM analysis.

3.2 *Surface morphology*

Figure 4 shows the micrographs of the surface morphology of ZnO thin films grown at different coating rates. For E_1 which deposited in low rate, the surface shows a smooth structure with small grain size particles. Rough surface and larger grain particles appear in E_4 and E_6. Samples coated with higher deposition rates prevent particles to grow perpendicular to the substrate surface and this causes the increase of particles diameter in ZnO film surfaces.

The surface roughness of ZnO thin films is an important parameter for various applications (optical, electrical and mechanical). In this line, the AFM images of all six samples of zinc oxide films were obtained.

Figure 5 shows two- and three-dimensional AFM images of ZnO thin films. The scanning area is 5×5 μm. The most commonly used roughness parameters are probably arithmetic roughness (R_a) and root-mean-squared (R_q or R_{rms}) roughness. Both of these values have a positive correlation. The values often give similar results, but R_q is always somewhat larger than R_a, and rather more sensitive to outlying points than R_a. The results illustrated in figure 5 show smooth and uniform surface for E_1 and rougher surface with large particle size for E_4 and E_6 which are consistent with the SEM results.

Variation of the surface roughness (root mean square (R_q) and average roughness (R_a)) was determined from these images. Figure 6 shows the behaviour of R_q and R_a against deposition rate. When low deposition rates are employed (< 2 nm/s), surface roughness would be low and remains nearly constant. But, when higher deposition rates are used, R_q, R_a would increase sharply. We think that large surface roughness at high coating rate increases incident light absorption and also the ZnO films defects cause high intensity for the violet emission peak obtained in the PL spectra.

There are some other commonly used statistical parameters for describing AFM images such as skewness (R_{sk}) and kurtosis (R_{ku}). These two parameters describe the distribution of the samples height data. The roughness parameters formulas are shown in table 2 (Daniel *et al* 2010).

The statistical analysis of AFM data was carried out using the height distribution histograms (figure 7). The height asymmetry is described by the statistical parameters, i.e. the surface skewness and kurtosis. Skewness is a measure of heights distribution asymmetry. Its positive value indicates above-average height and its negative values show below-average height. Kurtosis describes the 'peakedness' of height value distribution. A distribution with high kurtosis value would have a small number of extreme heights as opposed to many moderate height features. The values of skewness and kurtosis for the produced ZnO films are given in table 3. Film surface with positive skewness (larger than 0·2) and high kurtosis (larger than 3·0) values are favourable for tribological applications (e.g. low-friction bearings) (Eaton and West 2010).

4. Conclusions

The ZnO nano films were prepared on Si substrates with different Zn deposition rates by DC magnetron sputtering.

SEM, AFM and PL analysis have been carried out to characterize the films morphologies and photoluminescence properties. The increase of the deposition rate from 0·6 to 4·5 nm/s leads to larger grain sizes with more defects which show a violet emission peak at 438 nm in PL spectra. Also, it results in the increase of surface roughness. The AFM results reveal that higher deposition rates produce more surface roughness which is suitable for solar cell applications and thin film device fabrications. Higher rates produce rough surfaces and also higher intensity for violet emission peak (due to more defects) which is important in the production of violet PL lasers. The values of skewness and kurtosis for ZnO samples coated with low deposition rates (E_1, E_2, E_3) satisfied the required criteria for tribological applications.

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