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Optical and structural properties of sputter deposited ZnO thin films in relevance to post-annealing and substrate temperatures

A.A. Ahmad [a,*], A.M. Alsaad [a,b], B.A. Albiss [a], M-Ali Al-Akhras [a], H.M. El-Nasser [c], I.A. Qattan [d]

[a] Department of Physical Sciences, Jordan University of Science & Technology, P.O. Box 3030, Irbid 22110, Jordan
[b] Department of Physics, University of Nebraska-Omaha, P.O. Box 886105, NE 68182, USA
[c] Department of Physics, Al al-Bayt University, P.O Box 130040, Mafraq, Jordan
[d] Department of Applied Mathematics and Sciences, Khalifa University of Science, Technology and Research, P.O. Box 127788, Abu Dhabi, United Arab Emirates

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ABSTRACT

The optical properties of zinc oxide (ZnO) thin films were investigated in relevance to the post-annealing temperatures and compared to results obtained against the substrate temperatures. The films were d.c. sputter deposited on (100) silicon substrates. The films were treated with post-annealing under atmospheric pressure at various temperatures (300, 500 and 700 °C) for a one hour period. The optical properties were investigated using Variable Angle Spectroscopic Ellipsometry in the range between 250 and 1240 nm. The index of refraction n and the extinction coefficient k were investigated through modeling the experimental ellipsometric ψ and Δ angles using Sellmeier's second-ordered formulation for n and Cauchy-like dispersion for the k. The optical band gap energies were approximated by Tauc plot formulation. The index of refraction is fitted to Wemple/DiDomenico's effective single oscillator model to the estimate oscillator energy, dispersion energy, wavelength, average strength, moments of the optical spectra and the static index of refraction. The absorption coefficient, Urbach's binding energy, excitonic interactions and optical band gap energy were estimated through the complex transition behavior. The films' X-ray diffraction patterns reveal that our ZnO thin films have preferred (002) orientation microstructure. The SEM and EDAX analyses reveals the surface microstructure and the chemical composition. The samples deposited at various substrate temperatures contain uncompensated Zn atoms while Zn atoms have been almost removed by post-annealing treatment. Our results indicate that samples treated at the 500 °C post-annealing temperature have the best quality of microstructure and optical band gap.

1. Introduction

Zinc oxide is an n-type conductive and transparent wide band gap material that has attracted the attention of researchers due to its large potential applications in optical and optoelectronic devices. It has been fabricated commercially for a short wavelength light-emitting material applications due to its room temperature large direct band gap (3.37 eV) and large exciton binding energy (60 meV) [1–3]. Because ZnO-based thin films have shown large efficient excitonic emission at elevated substrate and post-annealing temperatures, they possess a great potential for optoelectronic device applications [3]. Several other applications make ZnO-based materials of great interest, such as, optical waveguides, gas sensors, surface acoustic wave devices, transparent conductive electrode and biomedical applications [4–6]. Since the physical properties of the thin films are crucially affected by the method of deposition and the parameters employed in each method, it would be very interesting to investigate the influence of the substrate and the post-annealing temperatures on the physical properties of the films during and after the sputtering process, respectively. In addition, other parameters in the post-annealing treatment such as, gases, atmospheric and time periods are of crucial impact on the physical properties [7–9]. We previously investigated the effect of varying the d.c. power on the structural and optical properties of the films at fixed substrate temperature (200 °C) [10]. We found that a d.c. power of 250 W is the best value for the d.c. power for producing good quality ZnO thin films [10]. In another related work [11], we investigated the effect of varying the substrate temperature, while fixing the applied d.c. power at 200 W, on the optical and structural properties of ZnO thin films and found that the best properties were obtained using 200 W d.c. power and 300 °C substrate temperature. In this work, the effect of post-annealing temperature on both; the structural and optical properties of ZnO thin films are presented while keeping the substrate temperature at 300 °C and the d.c. power at 200 W, respectively. The optical properties of ZnO thin films were compared with those investigated by varying the substrate temperature. Details of the experimental methods and analyses were presented in our previous works [10,11], and only brief description of the experimental techniques and

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* Corresponding author.
E-mail addresses: sema_just@yahoo.com, sema@just.edu.jo (A.A. Ahmad).

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mathematical modeling is provided in the current work when necessary. Although ZnO thin films have been produced by a variety of methods, not much work in the literature has been presented on ZnO films that have been prepared by d.c. sputtering using zinc target rather than using zinc oxide target and oxygen reactive gas including the various combinations of our experimental parameters. Also not much effort has been given to study their optical properties via the Wemple/DiDomenico analysis using light–material interactions. Since Sellmeier's first order model is limited and purely mathematical representation in producing the refractive index for transparent material in the visible region, Wemple/DiDomenico employs one effective-single oscillator model including its physical quantities.

2. Experimental details

2.1. Film preparation

Zinc oxide thin films were prepared through unbalanced magnetron d.c. sputtering process using zinc target (99.99% purity from Aldrich Co. Inc.). The substrates used are silicon wafers with (100) orientation. A combination of argon inert gas and oxygen reactive gas were used with 7.5/15 cm^3/s flow rates and 6.6/1.4 mTorr partial pressures, respectively. The films were optimized for their best quality by either varying the power while fixing the substrate temperature or by varying the substrate temperature while fixing the power [10,11]. The samples were reproduced at fixed d.c. power of 200 W and substrate temperature of 300 °C. Four pieces of silicon substrates were kept at the substrate holder during the same deposition process for a thirty minute run. The film thickness was measured by a mechanical stylus and found to be around 685 nm. The deposition rate was found to be around 22.83 nm/min. One sample was kept as-deposited without post-annealing treatment for reference analysis. The three other samples were treated separately with post-annealing at atmospheric pressure for 1 h at 300, 500 and 700 °C, respectively. The films were fabricated in the Center for Microelectronics and Optical Materials Research (CMOMR) at the University of Nebraska — Lincoln, Nebraska, USA.

2.2. Spectroscopic ellipsometry

Spectroscopic scans were performed on the samples using Variable Angle Spectroscopic Ellipsometry (VASE) system (J. A. Woollam Co., Inc., Lincoln, NE, USA) in an ex-situ acquisition mode [10,11]. The spectroscopic scans were performed for three different angles of incidence $\theta = 65°, 70°$ and $75°$, respectively. The light incident wavelength ranges between 250 and 1240 nm ($\approx$1 and 5 eV). The ellipsometric angles (ψ and Δ) were measured by the automated rotating analyzer ellipsometer in steps of 2 nm wavelengths. The measured values for both ψ and Δ were evaluated over thirty automated measured values for each pair of angles. The angles (ψ and Δ) were measured experimentally based on the ellipsometric equation given by [11]:

$$\rho = \frac{R_P}{R_S} = \tan\psi e^{i\Delta}, \tag{1}$$

where R_p and R_s are the complex coefficients of reflectance for the light polarized parallel (p) and (s) perpendicular to the plane of incidence, respectively, and ρ is their ratio.

3. Results and discussion

3.1. Spectroscopic ellipsometry and sample modeling

Although detailed mathematical modeling analysis and literature review used for ZnO characterization are provided in our previous works, a brief description for evaluating the optical constants for the ZnO thin films is presented in the current work [10,11]. The spectroscopic ellipsometry characterization technique is used to evaluate the optical constants including n and k. The spectroscopic ellipsometry is known to be an indirect and non-destructive characterization technique for the optical properties of materials, including bulk and thin films. Since our real samples are made of silicon substrates and bare ZnO films, structural models representing the samples were built through the powerful analytical software (Windows based variable angle spectroscopic ellipsometry WVASE 32®, J. A. Woollam Co., Inc., Lincoln, NE, USA provided with the ellipsometer). Each sample was represented by a structural model representing the ZnO film on the Si substrate. The ZnO film was represented by surface roughness containing 50% of void on top of the ZnO film material and an interface layer containing both Si and ZnO materials. The roughness and interface layers were modeled individually by the Bruggman effective medium approximation (BEMA) [10]. Including the interface layer in the model did not improve the fitting quality, so it was excluded from the fitting process. However, the roughness layer was allowed to vary as a fitting parameter while the void fraction was kept at 50% with ZnO material. The optical constants obtained by D. Aspnes and A. Studna [12] were used to represent the Si(100) substrate. However, the wavelength-dependent index of refraction $n(\lambda)$ and extinction coefficient $k(\lambda)$ for the ZnO layer were represented by parametric mathematical formulas including the film thickness. The film thickness estimated by the mechanical stylus was used as a starting value for fitting the real film thickness. The film thickness and the parameters in the mathematical formulas for $n(\lambda)$ and $k(\lambda)$ were allowed to vary to better match the experimental and generated ψ and Δ values using the equations for polarized light–material interactions [12]. The minimum mean square error (MSE) based on the Levenberg–Marquardt weighted error algorithm and the least 90% confidence correlation matrix was used to obtain the physical optical constants for the films [13–16]. This approach is considered to be the normal fitting analysis in the VASE analysis technique. It is not expected that all the values of ψ and Δ fit each other exactly by the normal fitting process. Therefore, a second stage of fitting the values of $n(\lambda)$ and $k(\lambda)$ is performed in order to force the generated ψ and Δ values to better match the measured ψ and Δ values at each λ over the whole range of the spectrum. In this stage of the analysis, the film thickness and the mathematical model parameters (in $n(\lambda)$ and $k(\lambda)$) were kept fixed at their best normal fit values. This approach is called; point-by-point fitting analysis. The new values for $n(\lambda)$ and $k(\lambda)$, at the best point-by-point fit, represent indirectly the optical constants for the real ZnO film. From $n(\lambda)$ and $k(\lambda)$ curves, one can extract various optical properties such as the absorption coefficient, optical band gap, Urbach's binding energy, excitonic transition, and simple effective oscillator characteristics.

The data analysis method used in our previous works has been implemented in this study. Similar mathematical modeling formulas for the index of refraction $n(\lambda)$ and the extinction coefficient $k(\lambda)$ have been used to calculate the optical properties of the ZnO films as related to the post-annealing temperatures rather than the substrate temperatures or the applied d.c. powers [10,11]. The parametric index of refraction $n(\lambda)$ for the ZnO film layer in the structural model which represents the sample was formulated using the second ordered Sellmeier's formula given by [10,11]:

$$n^2(\lambda) = A_n + \frac{B_n\lambda^2}{\lambda^2 - C_n^2} + \frac{D_n\lambda^2}{\lambda^2 - E_n^2}, \tag{2}$$

where A_n, B_n, C_n, D_n and E_n are fitting parameters. On the other hand, the extinction coefficient $k(\lambda)$ for the ZnO layer was represented by Cauchy-like dispersion formula with first order wavelength dependence as:

$$k(\lambda) = F_k\lambda e^{-G_k\left(\frac{1}{H_k} - \frac{1}{\lambda}\right)}, \tag{3}$$

where F_k, G_k and H_k are the fitting parameters.