Investigation of dip coated ZnO thin film: X-ray reflectivity and Fourier analysis

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Abstract: : In this study we fabricated Zinc Oxide thin film by sol-gel dip coating method on glass substrate. X-ray reflectivity (XRR) and its optimization have been used for characterization and extracting physical parameters of the film. Genetic Algorithm (GA) has been applied for this optimization process. Independent information was exploited from Fourier transform of Fresnel reflectivity normalized X-ray reflectivity. The Auto Correlation Function (Fourier transformation of X-ray reflectivity) yields thickness of each coated layer on substrate. This information is a starting point for constructing optimization process. Specular X-ray reflectivity optimization yields structural parameters such as thickness, roughness of surface and interface and electron density profile of the film. Acceptable agreement exists between results obtained from Fourier transformation and X-ray reflectivity fitting.

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1. Introduction

Sol-gel thin film technology is being applied for producing new novel devices and has been extensively explored for optical and electrical applications due to their very low cost and fast fabrication procedure (Banerjee, *et al.*, 2001, Morelhao, *et al.*, 2002). Application of these materials in solid state lasers, integrated circuits, light emitting devices, magnetic heads and tapes and coated window glass make them interesting in industry. Mechanical, magnetic, optical and electrical properties of these materials make use of them in industry. These aspects are related to their structural parameters such as thickness, roughness and electron density profile. Therefore research, development of applications, production and characterization of new thin films is essential effort (Dane, *et al.*, 1998, Zhu, *et al.*, 1998).

Fabrication of Zinc Oxide thin film can be accomplished with different techniques such as chemical vapor deposition (Nishino, *et al.*, 1997), sputtering (Hsu, *et al.*, 2008) and sol-gel process (Shao, *et al.*, 2006). Among these techniques sol-gel technique contests with the others due to its low cost and this technique is a process well suited to large scale production (Habibi, *et al.*, 2008).

There is a populous use of thin layered films with layer thickness in some nanometer range of thickness in modern technology and industry. Also manufacturing of high quality light emitting devices with longer operational lifetime needs smooth interface between hetero-junction structures. Controlling of structural parameters such as roughness at the surface and interface is essential in making high-performance devices, based on low-dimensional structures such as thin films and quantum wells. So analyzing the structure of the thin films is technologically very significant. Material characterization enables the improvement of new materials, structures and technologies. By developing instrumentation for improved measurement methods, there is an analogous need for the progress of techniques in order to operate these tools to their maximum benefits.

One of the most excellent techniques to study the structural and physical aspects of thin films is X-ray reflectivity (XRR). XRR is well established and nondestructive technique used for extraction density, thickness and roughness of surface and interface of thin film structures. In grazing incidence X-ray reflectivity (GIXR) technique, the X-ray beam is incident on the film at grazing angle and the interfered reflected beam is aggregated by X-ray detector. Presence of interfaces in the film causes interference process. The thickness of the layers causes interference periods and the amplitude of the interference oscillations depends on the both interfacial roughness and the electron density difference between the layers (Stoev, *et al.*, 1999).

A distinctive way to characterize the structural parameters of a film from its X-ray reflectivity is to construct a model that we expect logically qualifies its structure and from which we can simulate X-ray reflectivity. By calculating the differences between the experimental and simulated curves using a number of fitness functions, the model fitted by some optimization methods in order to minimize the difference between the two curves. This procedure is repeated until the difference between the two curves is arbitraged to be sufficiently small, at which point we believe that the model to be an accurate representation of the structure (Wormington, *et al.*, 1999).

A disadvantage of the X-ray reflectivity fitting for exploiting structural parameters of thin films is that more than one electron density profile may be used to generate a single reflectivity result. Therefore we require model independent information about the system to estimate a close model of the system for correct analysis of the data.

Fourier transformation process of the X-ray reflectivity is the quick method to obtain useful model independent information concerning to the real space structure. Use of the Fourier transformation of X-ray reflectivity (Auto Correlation Function - ACF) can prepare useful layer thickness measurements for constructing fitting procedure. The combined use of Fourier analysis and fitting procedures would make X-ray reflectivity data more practicable for realistic analysis of thin films.

Fitting algorithm, which minimizes the discrepancy between theory and experiment, is the main part of iteration process. Classical gradient based optimization procedures show acceptable performance but remain unreliable due to trapping in local extreme. In contrast genetic algorithms (GAs) combine the advantages of stochastic search with intelligent strategy of solution finding. G. R. Liu et al. (Liu, *et al.*, 2002) suggested computational method for material characterization of composites, by combining the advantages of least squares method and Genetic Algorithm in the inverse procedure. They applied displacement response as the structure action data for material characterization of composite plates. The material property can be found by minimizing error functions formulated using the measured displacement response. Application of GA in science and engineering has made this technique to be robust and effective (Dane, *et al.*, 1998).

Surface morphology and its acceptable characterization play an essential role in the study of thin films from different aspects. Generally each existing and future application of thin films needs specific optical, electrical, chemical and mechanical properties, which almost all strongly depend on the surface quality of the film. For this reason in this study Auto Correlation Function of Zinc Oxide thin film, obtained by calculating the Fourier transformation of the ratio of reflectivity data and Fresnel reflectivity, was applied for extracting layer thicknesses of Zinc Oxide thin film. This thickness information of the film is the starting point for constructing fitting procedure between the experimental and theoretical X-ray reflectivity. Genetic Algorithm was applied for optimization of the fitness function between logarithmic experimental and theoretical X-ray reflectivity. Structural parameters such as roughness of surface and interface, layer thickness and electron density profile were extracted by fitting procedure.

2. Material and Methods

2.1. Sample preparation

A Zinc Oxide thin film was fabricated by sol-gel dip coating method (Habibi. M.H, *et al.*, 2008). ZnO thin film preparation by dip coating was carried out at room temperature onto the substrate with a controlled withdrawal speed of 1 cm min−1. For each layer, the film was preheated at 275 ºC for 10 min and annealed at 350 ºC for an hour. The deposition was repeated five times to obtain five-layered film of Zinc Oxide. X-ray reflectivity measurement was performed using Bede GXR1 reflectometer at Durham University, Physics Department. The specular reflectivity curve was recorded with θ-2θ scan.

2.2. X-ray reflectivity

X-ray reflectivity is a method used to characterize the surface structure of materials irrespective of their crystalline perfection. Hence this technique can be applied to crystalline, polycrystalline and amorphous materials. Application of this technique for thin films provides information about thickness, roughness and electron density in the film.

By impinging X-ray beam (I_0) with a grazing incident angle on the film, a reflectivity is specified as

$$\left| r_{12} \right|^2 = \frac{I}{I_0}$$

Here I_0 and I are incident and reflected X-ray intensities.

The recursive formula for reflectivity is (Parratt, 1954)

$$r_{i,i+1} = \left[\frac{r_{i+1,i+2} + F_{i,i+1}}{r_{i+1,i+2} \times F_{i,i+1} + 1} \right] \times a_i^{\ 4}$$

Where

$$F_{i,i+1} = \left[\frac{g_i - g_{i+1}}{g_i + g_{i+1}} \right] \times \exp(-8\pi g_i g_{i+1} \sigma_{i+1}^{\ 2} / \lambda^2),$$

$$a_i = \exp(-i\pi g_i d_i / \lambda)$$

$$g_i = \sqrt{n_i^{\ 2} - \cos(\theta)^2} = \sqrt{(1 - \delta_i + i\beta_i)^2 - \cos\theta^2}$$

where θ , λ , d_j and σ_j are incident angle, X-ray wavelength, Jth layer thickness and surface roughness respectively.

The recursive equation was first obtained by Parrat for X-ray reflectivity simulation (Parratt, 1954). The roughness term was introduced in the framework of the Distorted Wave Born Approximation (DWBA)

(Tidswell, *et al.*, 1990). This expression indicates that the reflectivity profile will have series of minimum and maximum giving interface fringes, called Kiessig fringes, and the successive maxima in q-space ($q = \frac{4\pi}{\lambda}\sin\theta$) is inversely related to the thickness of the film.

For exploiting structural parameters of film GA optimization was performed in order to minimize the fitness function. The selection of a suitable fitness function is crucial for data-fitting procedure independent of the optimization method used. A number of fitness functions can be assumed, but in the case where a measured and a calculated curve are compared, a fitness function consisting of the Root Mean Squared Error (RMSE) of measured and the calculated data has been observed to work well in practice (Wormington, et al., 1999). We used the mean-squared error of the log transformed data as a fitness function

$$E = \frac{1}{N-1}\sum_{j=1}^{N}\left[LogI_{\exp,j} - LogI_{cal,j}\right]^2$$

where N is number of data points.

Before starting optimization, the thickness of the film was extracted by ACF of normalized X-ray reflectivity. For fitting the program with the experimental data, the Zinc Oxide thin film is considered to be made of a number of slabs of same thickness with varying electron density. Electron density in each slab and roughness of each interface are other fitting parameters.

2.3. Fourier transformation

The use of classical Maxwell equations for Fresnel reflectivity in terms of the scattering wave vector q yields (Tidswell, et al., 1990)

$$R_F(\theta) = \left|\frac{q - \sqrt{q^2 - q_c^2 + \frac{2i}{\mu}}}{q + \sqrt{q^2 - q_c^2 + \frac{2i}{\mu}}}\right|^2$$

where $q_c (= \frac{4\pi}{\lambda}\sin\theta_c)$, is the critical wave vector in air and is independent of wavelength.

If scattering wave vector is greater than the critical value q_c , then we can represent X-ray reflectivity as a Fourier transform of the derivative of the electron density profile ($\rho'(z) = \frac{d\rho(z)}{dz}$) (Banerjee, *et al.*, 2004).

$$R(q) = R_F(q)\left|\frac{1}{\rho_\infty}\int_{-\infty}^{\infty}\rho'(z)\exp(iqz)dz\right|^2$$

Here ρ_∞ is the substrate electron density and $R_F(q)$ is the Fresnel reflectivity of substrate. By taking Fourier transform of the fraction of reflectivity data and Fresnel reflectivity of substrate we can extract Auto Correlation Function of the derivative of the density profile.

$$ACF[\rho'(z)] = \int_{-\infty}^{\infty}\rho'(t)\rho'(t-z)dt = const\int_{-\infty}^{\infty}\frac{R(q)}{R_F(q)}\exp(-iqz)dz$$

The position of peaks in Auto Correlation Function corresponds to the distances between regions where electron density changing rapidly, or between interfaces.

Topography explanation of thin films by optical Fourier Transformation was investigated by J. Jaglarz (Jaglarz, 2008) .In his work, the major problems about the scattering of light by real surfaces and films are presented in view of results achieved with the bidirectional reflection distribution function (BRDF) method and optical profilometry (OP). The BRDF and OP studies permit one to get information about surface topography. The surface power spectral density (PSD) function for rough film has been found from the optical data. This function has been evaluated from the Fourier transform (FT) of the surface profiles. The utility of BRDF and OP methods in characterization of real surfaces was confirmed when analyzing the optical data obtained for metallic TiN thin films. J. Borowski te al. (Borowski, *et al.*, 2001) analyzed the effect of the Fourier transform of the incident beam on the measured diffracted intensity in X-ray diffraction. Their theory is a more precise physical picture of X-ray diffraction in the case of a narrow incident beam than the typically supposed spherical-wave theory. Their suggested method may be applied for direct calculations of the correlation function for electromagnetic fields and studies of the coherence degree of X-ray radiation.

3. Results

Fig. 1(a) indicates the measured X-ray reflectivity, normalized to Fresnel reflectivity, of Zinc Oxide thin film. Fig. 1(b) represents Auto Correlation Function computed from the Fourier transform of $\frac{R(q)}{R_F(q)}$. The peaks of Auto Correlation Function (ACF) represent the interfaces between different layers of the film. As can be seen from this figure, the first layer of Zinc Oxide has 90, 2nd 74, 3rd 68, 4th 78 and 5th layer 80 Å Thicknesses and the total thickness of the film is 390 Å. Since this calculation was done independent of the fitting procedure, extracted information is unambiguous and model independent. Also existence of the broad peaks in the ACF suggests that there are inter diffusions between film layers. C. Renard et al. (Renard, *et al.*, 2006) investigated The existence of a highly disturbed thin layer on top of the GaInAs by applying a model-independent Fourier transform procedure, applied to the high-resolution X-ray diffractometry profile. This procedure gave two thicknesses, one corresponding to the thickness from thin-layer to the sample surface and the other one corresponding to the thickness from thin-layer to the substrate surface. These calculated layer thicknesses must be compared with equivalent parameters derived from electron density profile perpendicular to the surface that extracted from fitting the X-ray reflectivity by genetic algorithm. Information that extracted from ACF is appropriate keyword for constructing 40-layer model for fitting and derivation physical parameters of the film.

The thicknesses of individual layer in addition to multi-layers of SrZrO3 thin films were extracted with reflectometry measurements by K. Galicka-Fau et al. (Galicka-Fau, *et al.*, 2008). They applied the model independent Fourier-inversion method to reflectivity curve to determine the individual thin thicknesses and multi-layers of a stack formed in the SrZrO3/Si films. Fourier-inversion technique applied to XRR profiles corresponds to a one-dimensional Patterson analysis of the interface positions and gives the Auto-Correlation Function (ACF) of the electronic density derivative, leading to distances between interfaces.

Fig. 2.a exhibits measured experimental X-ray reflectivity and best fit of theoretical reflectivity of Zinc Oxide thin film. The circles represent the experimental data and solid line represents recursive formalism based data after fitting process. This 40 layer model also applied for extracting electron density profile (EDP) perpendicular to the film surface form the XRR data fitting. This electron density profile is shown in fig. 2(b). We have considered 40 boxes each of 10 Å sizes for extracting electron density profile of X-ray reflectivity data.

One observable feature in the fit is that the electron density gradually increases from surface and decreases near interface. Three extra boxes added for extracting electron density of substrate. This electron density for silicon substrate was determined to be 0.77 e/ Å^3. The peaks in EDPs are imputed to transition layers formed at interfaces during annealing process, which have been reported by others (An, *et al.*, 1994). From oscillatory behavior of electron density with thickness one can deduce that with each application of new layer during spin coating, the whole film was not reconstructed and softened but they have inter diffusions. Oscillation of electron density profile corresponding to fit was also obtained by others (Morelhao, *et al.*, 2002) in sol-gel derived systems.

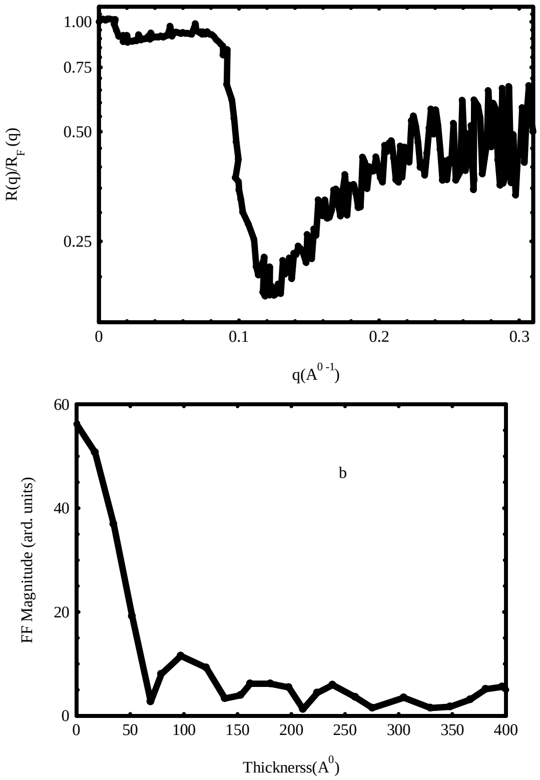

Figure 1. (a) Fresnel reflectivity normalized XRR scans (b) Fourier transformation

The electron density profile shows position of interfaces of 5 layers of the film. The peak in the electron density around a depth of 90Å could be due to interface between first and second layers in the film. In the EDP profile, we observe a jump down of the electron density beyond 390 Å and it approaches to a constant value of 0.77e/Å^3 which is the value of substrate electron density. The fitting was carried out using an average electron density 0.96e/Å^3 for the film. The total film thickness obtained from electron density profile after optimization process has good agreement with amount that obtained from Auto Correlation Function of X-ray reflectivity. The prominent oscillations in the electron density profile may be explained in terms of repulsive interactions between layers of the film.

The thickness of layers of chemisorbed hydrocarbon monolayer films coated on silicon substrate were extracted by fitting the data to reflectivity calculated from models of surface electron density and by calculating Patterson function directly from the data (Tidswell, et al., 1990). The surface and interface roughness and thickness of Mo/Si multilayer was calculated by considering additional interlayer of Mo-Si in addition to a pure layer of Mo and Si due to roughness phenomenon

(Modi, *et al.*, 2003). Recently G. Krishna Mohana Rao et al, by using neural networks and genetic algorithm optimization, have optimized surface roughness of die sinking electric discharge machining by considering the simultaneous effect of various input parameters (Krishna, 2009). C. L. Tien et al. (Tien, *et al.*, 2009) presented the measurement of surface roughness of optical thin films based on fast Fourier transform (FFT) associated with a Gaussian filter. With the aim of progress the accuracy, they normalized the fringe pattern to remove the background variation before using the FFT. The roughness profile was filtered by the Gaussian filter after the phase change was converted to surface height distribution. The root-mean-square value of surface roughness of optical thin films was extracted by their proposed method.

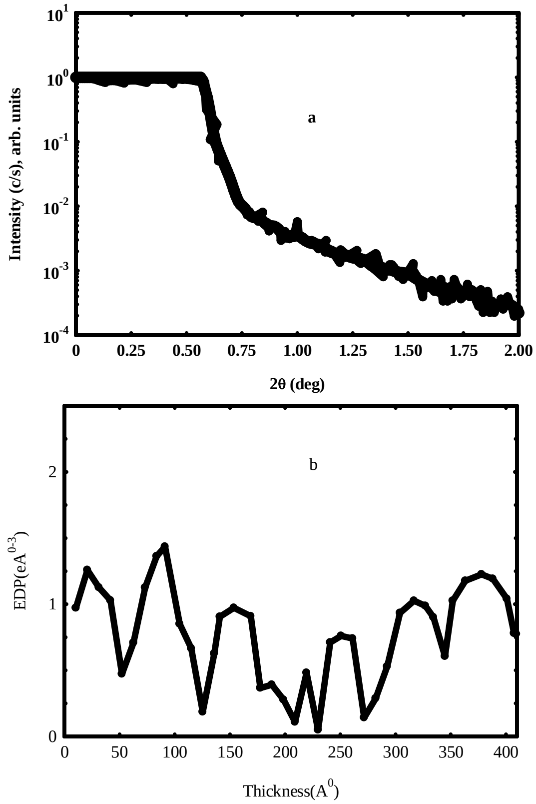

Figure 2. (a) XRR scans (circles) and calculated reflectivity after fitting (solid line) for Zinc Oxide thin film (b) corresponding electron density with thickness.

Table 1 summarizes results of parameters calculation of Zinc Oxide thin film by autocorrelation function method and X-ray reflectivity fitting. As can be seen from this table, layer thicknesses extracted from both methods have acceptable agreement. Also surface and interface roughness and mean electron density of layers only can be extracted from X-ray reflectivity fitting.

Table 1: Comparison of results from XRR and ACF

	XRR fitting			ACF
	Thickness(Å)	Roughness(Å)	Mean ED	Thickness(Å)
First	87±5	8.1±1	1.04±0.02	90±5
2nd layer	72±5	7.2±1	0.9±0.02	74±5
3rd layer	70±5	6.9±1	0.6±0.02	68±5
4th layer	74±5	7.4±1	0.72±0.02	78±5
5th layer	78±5	6.5±1	1.2±0.02	80±5
Substrate	∞	7.2±1	0.77±0.02	∞

4. Discussions

We have shown that one can fit the reflectivity profile using recursive formalism by considering a number of layers and extracting EDP from the fit parameters. As an independent calculation, the information about film thickness can be extracted directly from Auto Correlation Function of X-ray reflectivity normalized to the Fresnel reflectivity. The theoretical model that used in this study exhibits excellent agreement with experimental XRR pattern and give accurate information of thickness, roughness of surface and interface and EDP of each layer of the film. Frequency analysis of X-ray reflectivity data is feasible and significant when some careful analysis is need without depending on special model. We used Fourier transformation of X-ray reflectivity as independent process for extracting thickness of layers in the film. Combination of modern fitting procedures such as genetic algorithm with frequency analysis methods will make X-ray reflectivity more reliable in realistic analysis.

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