Determination of the refractive index and the thickness of double side coated thin films

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The well-known Swanepoel's method to calculate the refractive index and the thickness of thin films based on their optical transmission, is only applicable to single facet coated substrates (SFCS), and does not return the correct values when applied to double facet coated substrates (DFCS). In this work, we present a novel model and an analytical method to characterize the thin film coated on both sides of a substrate. In order to confirm the validity of our novel method, we have fabricated two samples; a DFCS and a SFCS with identical thin films. The thin film on SFCS is analyzed using Swanepoel's method, and the thin films on DFCS are analyzed using our novel method. The refractive index and the thickness value calculated with these two different methods on two different substrates are in agreement with each other and also with the SEM measurements.

Keywords: Sol-gel, Thin films, Optical transmission, Refractive index, ZnO

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1. Introduction

When an electromagnetic wave enters from one medium into another with a different refractive index, part of the wave reflects and only a portion of the wave is transmitted to the next medium, all due to the electromagnetic boundary conditions originating from Maxwell's equations [1]. By measuring the amount of light that is transmitted through (or reflected from) a substrate with multiple coating layers, it is possible to calculate certain parameters such as the complex refractive index of the media, the thickness of a layer, etc. [2-4].

The analytic transmission function and a method to determine the refractive index and the thickness of the thin film on a single facet coated substrate (SFCS) as shown in Fig. 1a, is previously reported by Swanepoel [5,6] and others [7]. However, certain coating methods such as sol-gel dip coating, chemical bath deposition (CBD) or Langmuir-Blodgett method, results in a double facet coated substrate (DFCS) as shown in Fig. 1b.[8-10]. A DFCS has a different transmission function and Swanepoel's method should not be used to calculate the optical properties or the thickness of the thin film.

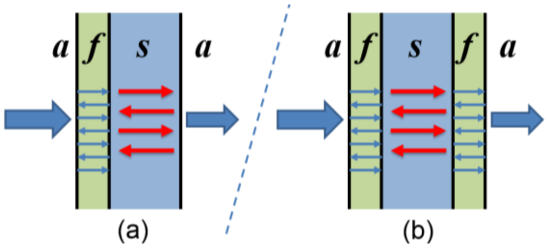


Fig. 1. (a) Transmission through a thin film coated single sided substrate, (b) Transmission through a dip coated double sided substrate (a:air, f:film, s:substrate)

In this paper, we introduce, for the first time to our knowledge, a theoretical model for the optical transmission of a double facet coated substrate and a novel method to determine the optical properties of the corresponding thin film. The proposed new theoretical method is also supported by the experimental results.

2. Optical transmission through a double facet coated substrate

The well-known Fresnel coefficients of reflection and transmission at normal incidence angle for an interface between medium *a* and medium *f* are given as follows:

$$r_{af} = \frac{\eta_a - \eta_f}{\eta_a + \eta_f} \tag{1a}$$

$$t_{af} = \frac{2\eta_a}{\eta_a + \eta_f} \tag{1b}$$

where η_a and η_f are the complex refractive indices of the corresponding media, defined as $\eta = n + ik$, with n being the refractive index, and k being the extinction coefficient. If there are multiple interfaces, then the transmitted light will reflect from the next interface with an additional phase shift, and this will result in an infinite summation for the total reflection and transmission. The resulting electric field reflection and transmission coefficients of a standard air/film/substrate system are given by:

$$r_{afs} = \frac{r_{af} r_{fs} \exp(i\theta)}{1 + r_{af} r_{fs} \exp(i\theta)} \quad (2)$$

$$t_{afs} = \frac{t_{af} t_{fs} \exp(i\theta / 2)}{1 + r_{af} r_{fs} \exp(i\theta)} \quad (3)$$

where $\theta = 4\pi\eta_s d / \lambda$, the phase shift at each roundtrip through the film of thickness d. The corresponding intensity reflectance and transmittance of such a configuration are:

$$R_{afs} = r_{afs} r_{afs}^{*} \quad (4)$$

$$T_{afs} = \frac{n_s}{n_a} t_{afs} t_{afs}^{*} . \quad (5)$$

These equations are also the basis of Swanepoel's formula after introducing the effect of finite substrate [12]. For a double side coated substrate, the effect of finite substrate needs to be modified, since the light interacts with the substrate/film/air interfaces before exiting the system. In short there will be three infinite summations that define the whole system, two infinite field summations for the multiple reflections inside the two thin films where the acquired phase is taken into account, and one infinite intensity summation for the multiple reflections between the two thin films where the phase is ignored due to large thickness of the substrate. In this work, we have derived, for the first time to our knowledge, the mathematical formula for the transmission through a double facet coated substrate as follows:

$$T_{system} = \frac{T_{afs} \cdot T_{sfa}}{1 - R_{sfa} \cdot R_{sfa}} \quad (6)$$

After tedious arithmetic simplifications (and assuming k_f is equal to zero), the transmission formula is calculated to be:

$$T_{system} = \frac{A \cdot x^2}{B - C \cdot x + D \cdot x^3 - E \cdot x^4}, \quad (7)$$

Where

$$A = 32 n^3 s, \quad (7a)$$

$$B = (n+1)^4 (n^2 + s^2), \quad (7b)$$

$$C = 2(n+1)^2 (n^2 - 1)(n^2 - s^2) Cos(\theta), \quad (7c)$$

$$D = 2(n-1)^2 (n^2 - 1)(n^2 - s^2) Cos(\theta), \quad (7d)$$

$$E = (n-1)^4 (n^2 + s^2), \quad (7e)$$

$$x = \exp(\alpha d), \quad (7f)$$

$$\theta = 4\pi n d / \lambda . \quad (7g)$$

In Equation 7, n and s are the refractive indices of the film and the substrate respectively following Swanepoel's widely used notation. d is the film thickness and α is the absorption coefficient of the film. In the lossless regime, where we assume α = 0, the transmission function simplifies to:

$$T_{system} = \frac{4n^2 s}{(n^2+1)(n^2+s^2) - (n^2-1)(n^2-s^2) Cos(\theta)} \quad (8)$$

Equation 8 has two unknowns (film's refractive index n, and the film thickness d, that is embedded inside the cosine term), and therefore it cannot be solved directly to obtain the values of n and d. The cosine term in this equation is responsible for the oscillation of the transmission value between the maximum (when the cosine is equal to +1) and the minimum (when the cosine is equal to -1) transmission values depending on the ratio between the film thickness and the wavelength of light. The functional form of maximum transmission ($T_{\max}$) and minimum transmission ($T_{\min}$) for a DFCS are found by replacing the cosine term with +1 and -1 respectively, and then it is straightforward to derive the following formula:

$$\left(\frac{1}{T_{\min}} - \frac{1}{T_{\max}} \right) = \frac{(n^2-1)(n^2-s^2)}{2n^2 s} . \quad (9)$$

Since equation 9 is independent of the film thickness, it has only one unknown, which is n. All other parameters of this equation can be determined by other means. $T_{\max}$ and $T_{\min}$ can be experimentally determined by extrapolating the maximum and minimum values of the transmission data, and the refractive index of the substrate (s) can be calculated from the optical transmission data through the uncoated substrate [5]. Once these maximum and minimum transmission functions are experimentally determined, then the refractive index of the thin film can be calculated as:

$$n = \sqrt{\frac{1}{2}\left(P + \sqrt{P^2 - 4s^2} \right)}, \quad (10)$$

where $P = 1 + s^2 + 2s\left(\frac{1}{T_{\min}} - \frac{1}{T_{\max}} \right)$.

This refractive index formula is equivalent to Swanepoel's method but corrected for a DFCS.

3. Experimental verification

In order to experimentally confirm the validity of our novel approach, a DFCS sample and a SFCS sample are fabricated by coating a soda lime glass substrate by ZnO thin films by sol-gel dip method. In this method, Zinc acetate dihydrate (ZnAc, $Zn(CH_3COO)_2.2H_2O$) was used as the precursor materials and methanol (ME, CH_3OH) and monoethanolamine (MEA, C_2H_7NO) were used as solvents and sol stabilizer. ZnAc is dissolved in ME with a concentration of 0.25M and MEA is added to solution as ZnAc:MEA ratio is kept at 1:1. The final solution mixed with a magnetic stirrer at room temperature until a transparent solution was obtained. The pH of the solutions was measured by standard pH meter. Viscosity of the solutions was controlled by adding ME.

For the success of thin films, it is essential to develop a scalable surface cleaning procedure to clean the soda lime glass used as substrate before deposition of the thin film. Soda lime glass is first washed with detergent, rinsed with distilled water, sonicated with 20% sulfuric acid / distilled water solution for five minutes and rinsed with distilled water again. Cleaned substrates are dried under nitrogen flow. It was found the cleaning treatment removed all of the contaminants successfully from the surface of soda lime glass substrate.

The cleaned glass substrates were dipped into the ZnO solutions and then pulled through the vertical furnace at 400 °C. The film thickness on the substrate was controlled by the withdrawal speed, the number of dipping and the dilution of the solution. Process was repeated 20 times in order to achieve a dense and uniform film for the desired thickness.

Once the coating process was completed, coated substrates are heated at 600°C for 30 minutes to form a crystal structure. After the coating was complete, the substrate was cut into two pieces; one piece was used as the DFCS sample, and the other piece was transformed into a SFCS sample by leaving the ZnO thin film on one facet and by removing the thin film from only one facet by etching it with 20% sulfuric acid / distilled water solution and cleaning with distilled water. The removal of the thin film is controlled under a microscope to examine the etching process and any unintended residues. As a result, one DFCS and one SFCS sample are obtained both having a thin film of the same type and thickness as shown in Figure 1.

The optical transmission measurements are performed with Shimadzu UVmini 1240 UV/Vis/NIR spectrophotometer. XRD scans were recorded using a Rigaku diffractometer with Cu K_α radiation. Microstructure properties of prepared samples were observed using a scanning electron microscope (JEOL, JSM-5910LV).

The optical transmission spectra of the DFCS and SFCS samples are shown in Fig. 2.

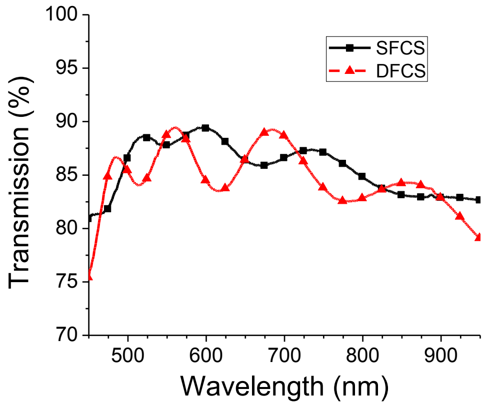


Fig. 2. Optical transmission spectra through a single facet coated and a double facet coated substrate.

By applying the Swanepoel's method to the transmission spectrum of the SFCS sample, the refractive index of the thin film is calculated (shown in Fig.3a) as reference. Later, the Swanepoel's method is unjustly applied to the transmission spectrum of the DFCS, and the resulting refractive index is shown in Fig.3b. As expected, Swanepoel's method does not return the correct refractive index when applied to a DFCS. To confirm the validity of our novel method, equation 10 was applied to the transmission spectrum of the DFCS, and the resulting refractive index is graphed in Fig.3c, which is in agreement with the reference value calculated by the Swanepoel's method applied to SFCS.

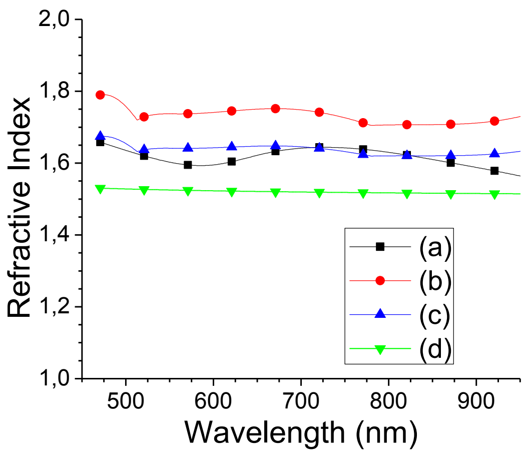


Fig. 3. (a), n calculated from SFCS data using Swanepoel's method, (b): n calculated from DFCS data using Swanepoel's method, (c): n calculated from DFCS data using our novel method, (d) refractive index of the substrate

4. Calculating the film thickness

The thickness of the thin film is responsible for the acquired phase shift between multiple reflections, which leads to wavelength dependent interference. This interference shows itself in the cosine term of the transmission formula as discussed earlier. It is easy to show that the acquired phase difference between two wavelengths (λ_a and λ_b) that correspond to a transmission maxima or minima is 2π. As a result the thickness of the thin film, d, can be calculated as follows:

$$d = \frac{\lambda_a \lambda_b}{2\left(n(\lambda_a)\lambda_b - n(\lambda_b)\lambda_a\right)}. \tag{11}$$

Using the Swanepoel's method on the SFCS transmission data, the thickness of the thin film is calculated to be ~977 nm. Using our novel method on the DFCS transmission data, the thickness of each film is calculated to be ~962 nm which is only 1.5% off from the Swanepoel's result. However, if one uses the Swanepoel's method on the DFCS data, the thickness of each film is found to be ~910 nm, which is approximately 7% off from the reference value.

In order to verify our calculated thickness values, the thin films are observed using a scanning electron microscope. The cross-sectional SEM measurements revealed the thickness of the thin film as approximately ~956 nm, which is in a very good agreement with the predicted value by our novel method. The cross-sectional SEM micrograph of the ZnO thin film deposited on the glass substrate is shown in Fig. 4. The film thickness of 956 nm is determined from the clear image contrast. Textured smooth, crack-free and pinhole -free ZnO (002) thin film could be grown on glass substrates by using the sol–gel dip-coating process. Fig. 5a shows the SEM surface morphology of ZnO thin film. The film depicts homogeneous surface with uniformly distributed grains. Energy Dispersive Spectroscopy (EDS) spectrum of ZnO is seen in Fig. 5b. Zn and O peaks are clearly seen. Fig. 6 shows the X-ray $\theta/2\theta$ scan of the 5-dip coated ZnO thin film on glass substrate. The scan shows that there is only one peak at 33.06° which is the (002) reflection of ZnO thin films. It is highly c-axis oriented with significant intensity.

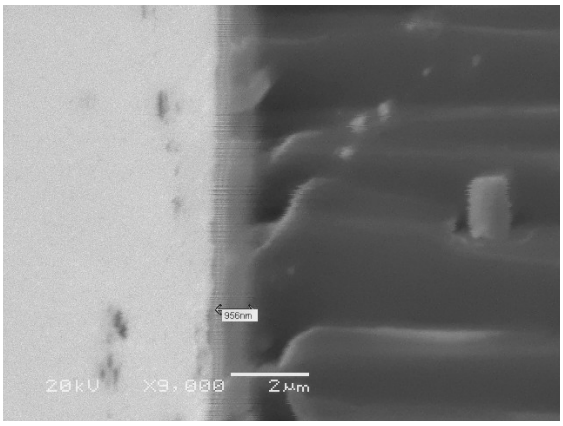
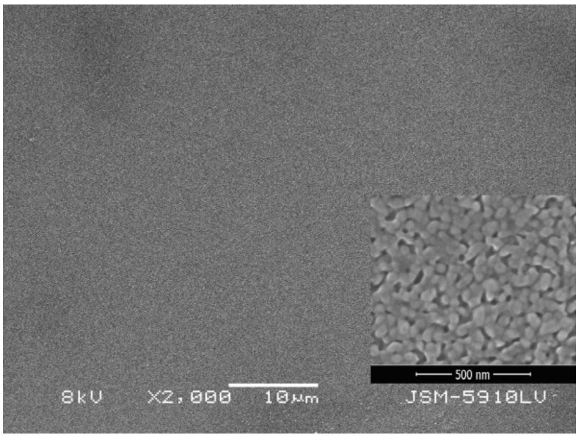
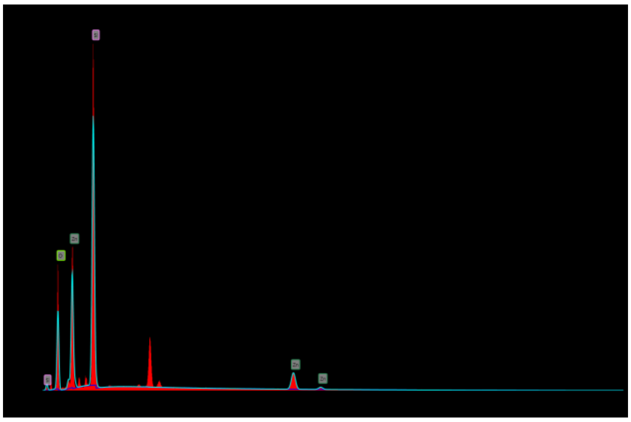


Fig. 4. SEM micrographs of a longitudinal cross-section of ZnO film deposited on glass substrate.



a)



b)

Fig. 5a) the SEM surface morphology and b) EDS spectrum of ZnO thin film

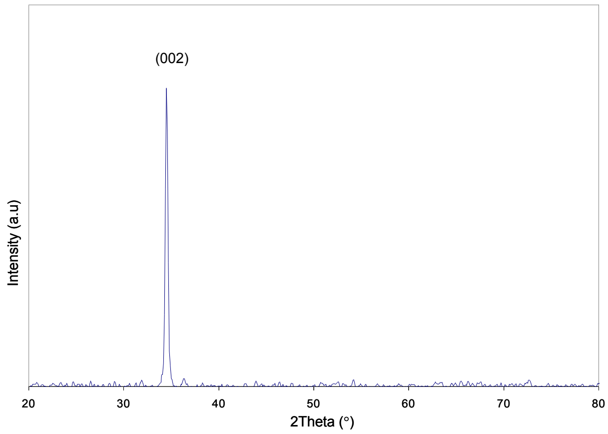


Fig. 6. XRD patterns of the ZnO film.

5. Conclusion

We have proposed and experimentally verified a novel method to obtain the refractive index and the thickness of thin films, which are coated on both sides of a substrate. This novel method is based on optical transmittance of the coated substrates, and can be thought of as a modified Swanepoel's method that is applicable to double facet coated substrates.

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