Study on the ZrO_2 Thin Films with Spectroscopic Ellipsometry

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Keywords: ZrO_2 thin film; spectroscopic ellipsometry; optical properties

Abstract: In order to get the optical properties of ZrO_2 thin film, two samples deposited on K9 glass which produced by optical automatic vacuum coating machine were measured and analyzed with spectroscopic ellipsometry. For sample 1, both Cauchy model and Tauc-Lorentz model can be well described the properties of thin film. For sample 2, by dividing the film into three layers, got the smallest mean square error, and the thickness was closest to the calculated value of TFCalc film design software. Meanwhile, got the refractive index curve in the spectrum range from 380nm to 2250nm. The results has certain reference value to the preparation and design of ZrO_2 multilayer films.

1. Introduction

ZrO_2 has excellent mechanical, thermal, electrical and optical properties [1-4]. It has high-melting-point (2608 °C), high dielectric constant and refractive index, high transparency in both visible and near-infrared regions, good mechanical properties and chemical inertness, high laser-induced damage threshold. And the excellent optical properties has widely used as a high refractive index material at multilayer film design. There are many methods for preparing thin films [5], such as electron beam evaporation, magnetron sputtering, ion-beam aid deposition and sol-gel method, etc. But different preparation methods and processes conditions will create a difference in the characteristics of the thin films. It is very important to obtain the thickness and optical constants (refractive index “n”, extinction coefficient “k”, etc) of thin film at the multilayer design. The optical constants of thin films were usually measured by spectrophotometry, spectroscopic ellipsometry (SE), waveguide method, etc. SE has the advantages of high precision, high sensitivity, non-destructive to samples and non-harsh to the environment, etc. It can obtain the layer’s structure of thin films, now become an important mean to measure the thickness and optical constants of ultra-thin films and multi-layer films. LIANG Li-ping [6] used swanepoel extreme envelope method combined with wempel-didomenico dispersion formula (simplified Sellmeier) to obtain the optical constants of ZrO_2 thin films which prepared by sol-gel method. WANG Shan [7] used a variety of measurement methods to get the characteristics of ZrO_2 thin films prepared by sol-gel, and used SE to obtain the thickness and refractive index of the films. ZrO_2 thin films prepared by electron beam evaporation at room temperature were monoclinic phase [8]. However, there were few studies on the selection of the model for measuring ZrO_2 thin films and the stratification measurement of thin films with SE.

2. Theory

According to the theory of SE, when polarized light hit the thin film sample at an angle, it will interact with the sample and the polarization state of the light will change. Parameters (ψ,Δ) were introduced to describe the changes of polarized light, in which parameters were usually described by the following formula [9]

$$\rho = \frac{r_p}{r_s} = \tan\psi \cdot e^{i\Delta} \tag{1}$$

where r_p and r_s are the Fresnel reflection coefficient of p light and s light; ψ is the polarization

  DOI: 10.25236/mmmce.2019.053

angle; Δ is the phase difference of p light and s light. Generally, ψ ranges from 0 to $\pi/2$, and Δ ranges from 0 to 2π . Parameters can be directly obtained by the SE's own calculation software.

Using SE to get the parameters, but ultimately what we want is the thickness and the optical constants of the thin film. The relation between them can be expressed as

$$n^2(\omega)=k^2(\omega)+\sin^2(\theta)\left[1+\tan^2(\theta)\frac{\cos^2 2\psi-\sin^2 2\psi\sin^2 2\Delta}{(1+\sin 2\psi\cos\Delta)^2}\right] \tag{2}$$

$$k(\omega)=\frac{\sin^2\theta\tan^2\theta\sin(4\psi)\sin\Delta}{2n(\omega)(1+\sin 2\psi\cos\Delta)^2} \tag{3}$$

where θ is the angle of incidence. The parameters can obtain by fitting, then the optical constants of the film can be obtained by substituting parameters into equation (2) and (3).

In the common fitting models of SE, Cauchy model [10] was suiTable for low absorption materials. In this model the refractive index n and extinction coefficient k can be described by the following formula

$$n(\lambda)=n_0+10^6 n_1/\lambda^2+10^{12}n_2/\lambda^4 \tag{4}$$

$$k(\lambda)=k_0+10^6 k_1/\lambda^2+10^{12}k_2/\lambda^4 \tag{5}$$

where λ is the wavelength of the incident light. $n_0, n_1, n_2, k_0, k_1, k_2$ are the six fitting parameters. Very often, the series expansion was ended after the first two terms and the terms in λ^{-4} were not used.

Jellison and Modine first proposed Tauc-Lorentz model (TL) [11] (1996), which was applicable to the dispersion relationship between low-absorption dielectric materials and amorphous materials. The model can be expressed as

$$\varepsilon_1(E)=\varepsilon_1(\infty)+\frac{2}{\pi}P\int_{E_g}^{\infty}\frac{\tau\varepsilon_2(\tau)}{\tau^2-E^2}d\tau \tag{6}$$

$$\varepsilon_2(E)=\begin{cases}\dfrac{ACEE_0}{\left(E^2-E_0^{\ 2}\right)^2+C^2E^2}\dfrac{\left(E-E_g\right)^2}{E^2} & for\ E>E_g\\ 0 & for\ E\le E_g\end{cases} \tag{7}$$

Where P, $\varepsilon_1(\infty)$, E_0, E_g, A, C are the six fitting parameters. Various parameters of the thin films can calculated by the above parameters.

The main idea of fitting is to take the measured parameters as the target file, by selecting the appropriate model and setting the appropriate parameters in the model. If the mean square error (MSE) of the fitting is tiny, the set parameters and model are considered to be the real values of the tested material. Meanwhile, obtained the physical parameters such as the refractive index, extinction coefficient and thickness of the sample. The MSE can be described by the following formula

$$MSE=\sqrt{\frac{1}{2N-M}\sum_{i=1}^{N}\left[\left(\frac{\psi_i^{Mod}-\psi_i^{Exp}}{\sigma_{\psi,i}^{Exp}}\right)^2\left(\frac{\Delta_i^{Mod}-\Delta_i^{Exp}}{\sigma_{\psi,i}^{Exp}}\right)^2\right]} \tag{8}$$

where N,M,σ, ψ_i^{Mod}, Δ_i^{Mod}, ψ_i^{Exp}, Δ_i^{Exp} can be obtained from the measured and calculated values from model. The smaller the MSE, the better the fitting.

3. Experimental and Discussion

3.1 Sample preparation

Kwang-Chi OTFC-1300 optical control automatic vacuum coating machine was used in the experiment. Two single-layer ZrO_2 film samples named as sample 1 and sample 2 were deposited on the K9 glass substrate. The parameters of the instruments were set as follows: the monitoring wavelength of sample 1 was 850nm, and that of sample 2 was 700nm, the deposition rate was 0.5nm/s, average pressure was 2.0×10^{-2}Pa, temperature kept at 200° C, the ion accelerating voltage was 1000V, and the ion flow was 900mA, incident angle of SE was 70°, the spectrum range from 380nm to 2250nm.

3.2 Discussion

It is very critical to set the fitting initial values of film thickness, unreasonable initial values can lead to incorrect results. TFCalc film design software was used in this article to ascertain the initial values. By calculating, the thickness of sample 1 was 124.73nm, the thickness of sample 2 was 548.18nm. These data were used as the initial values.

The uneven surface of the substrate will generate a rough-layer on the surface during the process of growth. The layer is usually several nanometers which will affect the optical properties of thin film. Cauchy model is suiTable for ZrO_2 which is low absorption material. Bruggeman model [12] was introduced into ZrO_2 thin films to describe the effective medium approximation of surface rough-layer (a complex film of 50% air and 50% ZrO_2).

For sample 1, the initial thickness of thin film was set as 120nm, and the rough-layer was set as 3nm. Marked "K9/ Cauchy layer/ Rough-layer/ Air" as model I, the geometric model was shown in Fig.1(a). By fitting the parameters of $n_0, n_1, n_2, k_0, k_1, k_2$ in model I, the MSE was 0.749, the fitting curves of Ψ (psi) and Δ (delta) were shown in Fig.2. It was reasonable to introduce rough-layer, the MSE was relatively small and the dispersion model was well matched with the film characteristics.

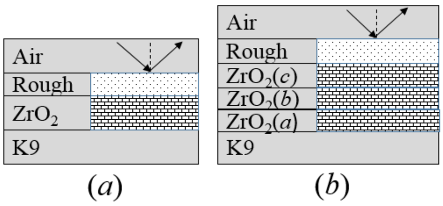

Fig.1 Two geometric models for ZrO_2 film

Marked "K9/ TL layer/ Rough-layer/ Air" as model II, the geometric model was shown in Fig.1(a). The initial thickness was set as 120nm, and rough-layer was set as 3nm. By fitting the parameters of P, ε_∞, E_0, E_g, A and C in this model, MSE can be obtained as 0.753. The fitting curves of Ψ and Δ were shown in Fig.2. Model II was well matched with the film properties.

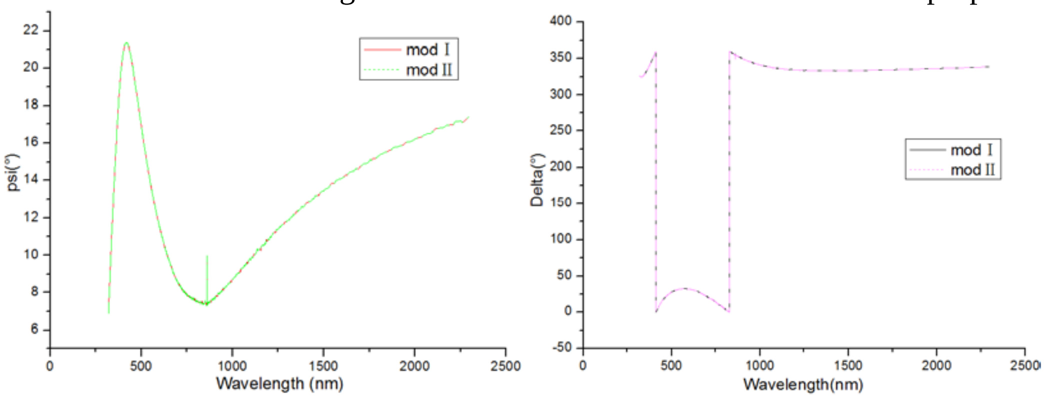

Fig.2 Fitting curve of Ψ and Δ about model I and II

The film thickness obtained by model I and model II were 124.90nm and 124.86nm. The wavelength of incident light was 532.0nm, the refractive index was 1.881 and 1.878. The refractive index was same as the refractive index in literature [13]. The fitting curves of the parameters with model I and model II were very similar. Also, the obtained thickness and optical constants were very similar, which were very close to the thickness calculated by TFCalc film design software.

For sample 2, Marked "K9/ Cauchy layer/ Rough-layer/ Air" as model III, the geometric model was shown in Fig.1(a). The initial thickness was set as 550nm, and the rough-layer was set as 5nm. The MSE obtained after fitting was 1.513, the fitting curves of Ψ was shown in Fig.3(a). As can be seen from the figure, the parameter Ψ fitting in the direction of long-wave was not particularly good. That's going to make the MSE a little bigger, the thickness and refractive index of the film obtained were shown in Table 1.

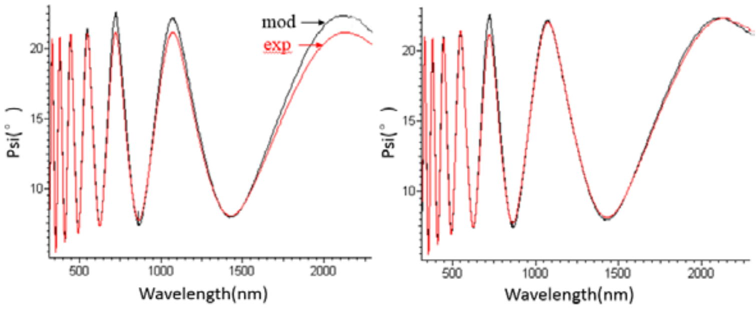

Fig.3 (a): Fitting curve of Ψ in model III; (b): Fitting curve of Ψ in model IV

Due to the stoichiometric deviation of the film composition in the preparation process, the prepared film was no longer uniform and dense in structure [14]. The film coating was non-uniform, limited, unsmooth interface. Considering the thickness of sample 2 was relatively thick that the single-layer film was divided into three uniform film layers, the geometric model was shown in Fig.1(b). The initial thickness of each layer was set as 185nm, and the rough-layer was set as 5nm. Marked "K9/ Cauchy layer(a)/ Cauchy layer(b)/ Cauchy layer(c)/ Rough-layer/ Air" as model IV, the MSE can be obtained as 1.132, the fitting curves of Ψ was shown in Fig. 3 (b). Meanwhile, the curve of refractive index n was shown in Fig.4

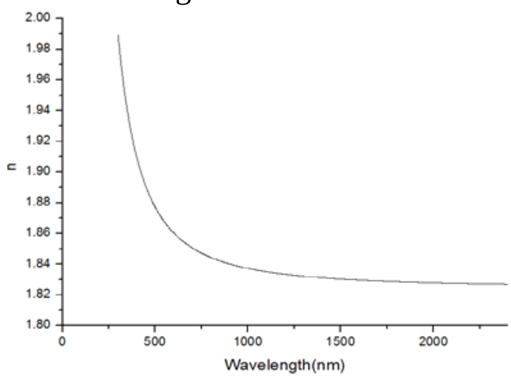

Fig.4 Refractive index curve of model IV

Comparing the curves in Fig.3, Model IV fits better than model III in the direction of long-wave. The thickness and refractive index of each layer obtained by model IV were shown in Table 1

Table 1 Fitting results of model III and IV

	Thin film (nm)	Rough-layer (nm)	Total thickness (nm)	Refractive index (incident light at 632.8nm)	MSE
Model III	541.36	5.83	547.19	1.8558	1.513
Model IV	(c) 189.85 (b) 180.13 (a) 172.58	5.71	548.27	1.8484 1.8529 1.8619	1.132

Comparing the results in Table 1, it can be seen that the MSE obtained by model IV was significantly reduced by 0.381. Considering the defects and heterogeneity of the thin film layers [15], the calculation difficulty was increased after dividing single-layer film into three layers, but more accurate results can be obtained. Therefore, the model “K9/ Cauchy layer(a)/ Cauchy layer(b)/ Cauchy layer(c)/ Rough-layer/ Air” can be better described the characteristics of sample 2.

4. Conclusion

This article measured and analyzed two single-layer ZrO_2 thin film samples with SE850. The parameter curves were obtained in the spectrum range from 380nm to 2250nm. Cauchy model and TL model can be well described the characteristics of sample 1; by dividing the film into three layers, got the smallest MSE. The reason may be the stress during the coating process of growth. This is the basis for further application of ZrO_2 as a high refractive index material in membrane system design.

Acknowledgement

Foundation Project: 1) Universities of Guangxi young and middle-aged teachers basic ability improvement project (NO: 2018KY0751); 2) University-level scientific research of Nanning University (NO: 2017XJ09).

References

[1] LEE J W, SCHLESINGER T E, STAMPER A K, et al. Characterization of yttria-stabilized zirconium oxide buffer layers for high-temperature superconductor thin films [J]. J Appl Phys, 1988, 64: 6502-6504.

[2] YAMASHITE T, CHEN G L. Sputtered ZrO_2 overcoat with superior corrosion protection and mechanical performance in thin film rigid disk application [J]. IEEE Trans on Magn, 1988; 24: 2629-2634.

[3] KAO A S. Comparison of zirconia thin film sputtered from material and compound targets by reactive ion-beam process [J]. J Vac Technol, 1991, 69(5): 3309-3315.

[4] YANG M M, REITH M, LIN C J. Process effects on radio frequency diode reactively sputtered zirconia film [J]. J Vac sci Technol, 1990, 8(6): 3925-3928.

[5] SHAO Shu-ying, FAN Zheng-xiu, FAN Rui-ying et al. Influence of deposition temperature on the properties of ZrO_2 films prepared by electron beam evaporation [J]. Chinese Journal of Lasers, 2004, 31 (6): 701-704.

[6] LIANG Li-ping, HAO Jian-ying, QIN Mei. Determination of the optical constants of sol-gel derived ZrO_2 films simply from the transmission spectra [J]. Journal of Physics, 2008, 57(12): 7906-7911.

[7] WANG Shan, SHEN Jun. Effect of preparation conditions on property of zirconia optical films [J]. Material Review, 2007, 21(1): 133-135.

[8] WU Shi-gang. Phase transition model analysis of ZrO_2 thin film deposited by electron-beam evaporation [J]. High Power Laser and Particle Beams, 2008, 20(10): 1724-1726.

[9] Liang Min-ji. Ellipsometry and Polarized Light [M]. Beijing, Science Press, 1986, 103-113.

[10] LI Wei, JIN Cheng-xu. Analytical approach and methods for ellipsometry on thin film [J]. Chinese Journal of Spectroscopy Laboratory, 2010, 27(1): 66-76.

[11] JELLISION G E JR, MODINE F A. Parameterization of the optical functions of amorphous materials in the interband region [J]. Appl.Phys.Lett, 1996, 69(3): 371-373.

[12] PAN Yong-qiang, WU Zhen-sen, HANG Ling-xia. Interface roughness of multilayer dielectric optical thin film [J]. Infrared and Laser Engineering, 2009, 38(3): 433-436.

[13] Yuan Jing-mei, Tang Zhao-sheng, Qi Hong-ji, et al. Analysis of optical property for several ultraviolet thin film materials [J]. Acta Optica Sinica, 2003, 23(8): 984-988.

[14] ZHANG Hui-ping, WANG Qing, ZHENG Xiao–jun. Measurement of optical film thickness and properties [D]. Nanjing, Nanjing University of Science and Technology, 2013.

[15] WANG Qing, SHEN Hua, WANG Wei. Ellipsometry by simulated annealing algorithm [J]. Aata Photonica Sinica, 2008, 37(2): 63-65.