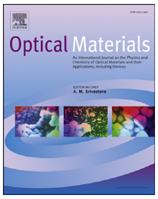
Optical Materials 75 (2018) 135–141

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat



Physical mechanism of refractive index inhomogeneity of hafnium oxide thin film prepared by ion beam sputtering technique

Huasong Liu [a, b, *], Lishuan Wang [a, b], Shida Li [a], Yugang Jiang [a], Dandan Liu [a], Xiao Yang [a], Yiqin Ji [a, b, **], Feng Zhang [a], Deying Chen [b]

[a] Tianjin Key Laboratory of Optical Thin Film, Tianjin Jinhang Technical Physics Institute, HIWING Technology Academy of CASIC, Tianjin, 300308, China
[b] National Key Laboratory of Science and Technology on Tunable Laser, Institute of Opto-electronics, Harbin Institute of Technology, Harbin, 150080, China

ARTICLE INFO

Article history:
Received 8 August 2017
Received in revised form
4 October 2017
Accepted 4 October 2017

PACS:
78.20.-e
81.40.Tv
78.66.-w
42.70.-a

Keywords:
HfO_2 thin film
Refractive index
Inhomogeneity
Grain size
Correlation

ABSTRACT

The HfO_2 thin films prepared by ion beam sputtering are thinned after heat treatment. The optical constants of the thin films were obtained by inversion of the ellipsometric parameters. The crystal structure of the films was characterized by X-ray diffractometer. The results show that the correlation coefficient between the refractive index and the grain size is more than 90%. The refractive index increases with the increase of the grain size. The physical mechanism of the refractive index inhomogeneity in the film thickness direction is crystallization of thin films.

1. Introduction

In recent years, with the development of high performance optical multilayer components, the theory and control technique of refractive index inhomogeneity of thin films have been widely investigated, and become one of the hotspots in the field of high performance thin film for laser optics [1–6]. HfO_2 thin film has high refractive index, excellent thermodynamic properties and high laser damage threshold, which is widely used in the field of high laser damage threshold film from short wavelength to near infrared [7–10].

HfO_2 thin films are mainly deposited by electron beam evaporation [11], plasma assisted deposition [12], ion beam sputter deposition [13], magnetron sputtering [14], atomic layer deposition [15], and sol-gel [16,17]. The refractive index inhomogeneity of the HfO_2 thin films prepared by electron beam evaporation have been reported. The spectral properties of the multilayers seriously deviated from the design objectives caused by the refractive index inhomogeneity limits the development of the high-performance and high-damage threshold films [4–6]. Compared with low refractive index materials (SiO_2, Al_2O_3), the HfO_2 thin films prepared by ion beam sputtering have the advantages of low scattering, low absorption and high density. It has been widely used in the field of high laser damage threshold thin films. Ion beam sputtering deposition technique has become one of the mainstream technologies for the preparation of HfO_2 thin films [18,19]. The refractive index, extinction coefficient, stress, crystal structure and band structure of HfO_2 thin films have been reported. But there are no report on the mechanism of refractive index inhomogeneity.

---

* Corresponding author. Tianjin Key Laboratory of Optical Thin Film, Tianjin Jinhang Technical Physics Institute, HIWING Technology Academy of CASIC, Tianjin, 300308, China.
** Corresponding author. Tianjin Key Laboratory of Optical Thin Film, Tianjin Jinhang Technical Physics Institute, HIWING Technology Academy of CASIC, Tianjin, 300308, China.
E-mail address: liuhuasong@hotmail.com (H. Liu).

https://doi.org/10.1016/j.optmat.2017.10.007
0925-3467/

In this paper, the HfO_2 thin film growth process is proposed in the reverse direction. The optical and crystalline properties of HfO_2 thin films by ion beam sputtering technique were investigated by ellipsometer and X-ray diffractometer, respectively. It is proved that the microstructure of HfO_2 film tends to crystallize in the growth process, which is the physical mechanism of the refractive index inhomogeneity of HfO_2 film.

2. Characterization of refractive index inhomogeneity

The physical model of the HfO_2 film is shown in Fig. 1, and the schematic diagram of the inhomogeneity of the refractive index in the longitudinal direction of the thin film is shown in Fig. 2, which shows a schematic diagram of the arbitrary refractive index inhomogeneity. Borgogno et al. [7] reported the refractive index inhomogeneity of five kinds of thin films: Y_2O_3, TiO_2, MgF_2, HfO_2 and SiO_2. The refractive index inhomogeneity of HfO_2 thin film is positive, which means the refractive index of the thin film outer surface (near air side) is higher than the inner surface of the film (near substrate side).

In the transparent spectral region, the optical constants dispersion of the HfO_2 thin film is usually represented by the Cauchy dispersion physical model:

$$\bar{n}(\lambda) = A + B/\lambda^2 + C/\lambda^4 \tag{1}$$

where λ is wavelength (um), and A, B, and C are constant terms, where B and C characterize the dispersion properties of the refractive index. Taking into account the refractive index inhomogeneity shown in Fig. 2, the inhomogeneity change equation of the refractive index is expressed by the following equation [20]:

$$n(\lambda, d) = \bar{n}(\lambda)\left[V\left(x^T - \frac{1}{T+1}\right)\right] \tag{2}$$

where $\bar{n}(\lambda)$ is average refractive index of the film, and x is any position in the thin film from the substrate direction of any position, and T is the refractive index gradient equation of the coefficient, and V is from the substrate to the air refractive index gradient.

According to the multi-beam interference theory of film-substrate system, the refractive index of the substrate, the incident medium and the thin film, and the physical thickness of the thin film uniquely determine its spectral characteristics. In calculating the spectral characteristics of the thin film, the continuous gradient of the thin film is subdivided in a matrix, and the continuous film is equivalent to a discrete N layers thin film [20]. In this paper, the ellipsometric parameters ψ_i^{exp} and Δ_i^{exp} of the film-substrate system were obtained using ellipsometer of J.A.Woollam, and the coefficients of equations (1) and (2) were obtained by numerical inversion. The functions to evaluate the inversion performance were as follows:

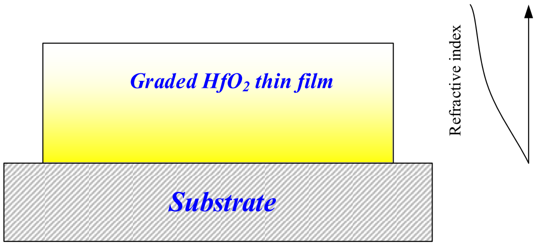


Fig. 1. The physical model of the film-substrate system.

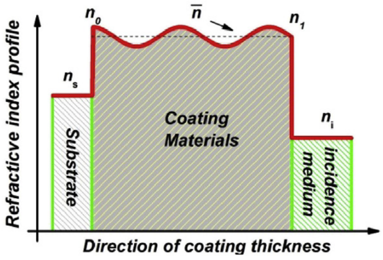


Fig. 2. The inhomogeneity of refractive index.

$$MSE = \left\{\frac{1}{2N-M}\sum_{i=1}^{N}\left[\left(\frac{\Psi_i^{\mathrm{mod}} - \Psi_i^{\mathrm{exp}}}{\sigma_{\Psi,i}^{\mathrm{exp}}}\right)^2 + \left(\frac{\Delta_i^{\mathrm{mod}} - \Delta_i^{\mathrm{exp}}}{\sigma_{\Delta,i}^{\mathrm{exp}}}\right)^2\right]\right\}^{\frac{1}{2}} \tag{3}$$

where MSE is the mean square deviation of the measured value and the calculated value from theoretical model, and N is the number of measurement wavelengths, and M is the number of variables, and ψ_i^{exp} and Δ_i^{exp} are measured values at the ith wavelength, and ψ_i^{mod} and Δ_i^{mod} are calculated value from theoretical model at the ith wavelength, and $\sigma_{\psi,i}^{exp}$ and $\sigma_{\Delta,i}^{exp}$ are the measurement error of the i-th wavelength, respectively. It can be seen from equation (3) that as MSE is weighted, the noise of the data is ignored, and MSE is used to evaluation the degree of agreement of theory calculated value and measured value.

3. Experimental methods

3.1. Sample preparation

HfO_2 thin films were prepared by ion beam sputtering on single crystalline silicon wafers ($\Phi 40 \times 0.32$ mm) and single-sided polished fused silica($\Phi 40 \times 1$ mm), which surface roughness of the substrate was better than 0.3 nm. The preparation parameters of the HfO_2 thin films were as follows: the ion source was a radio-frequency ion source with a diameter of 16 cm (ion beam viltage was 1250V and ion beam current was 500 mA), and the target was a high purity metal Hafnium target (purity≥99.9%), and the substrate temperature was room temperature, and the oxygen gas flow rate was 30sccm. Before deposition, vacuum chamber pressure was pumped as low as 1.0×10^{-3}Pa.

In the first group of samples, HfO_2 films on silicon substrates are labeled Si-3, Si-5, Si-6 and Si-7, and HfO_2 films on the fused silica substrates are labeled S-3, S-5, S-6 and S-7. In the second group of samples, the HfO_2 thin films on the silicon substrate were labeled Si-1, Si-2, Si-4 and Si-8, and the HfO_2 films on the fused silica substrates were labeled S-1, S-2, S-4 and S-8. In addition, the second group of samples in the atmosphere of heat treatment 300 °C, keep the temperature 16 h, take the way of natural cooling temperature to room temperature.

The chemical polishing was used to decrease the thickness of the film which was helpful to reproduce the refractive index distribution in the film thickness direction. Chemical solution was prepared by using hydrogen fluoride ammonia(NH_4HF_2, 13 g), glycerol (20 ml), eutralization solution ($NaHCO_3$, 10 g), ethylene glycol (10 ml) and deionized water (1100 ml, the water temperature maintained at about 80 °C). In order to ensure the uniformity of the etching of the film sample, the samples were placed vertically on a Teflon tray. The trays were placed in a beaker and sonicated in an ultrasonic cleaner. HfO_2 thin films of different physical thicknesses were obtained by controlling different etching times. All the thin