

Properties of Ti-doped Al_2O_3 thin films deposited by simultaneous RF and DC magnetron sputtering



Su-Shia Lin*, Yu-Lun Gao, Shao-Yin Hu, Sheng-You Fan, Yung-Shiang Tsai

Department of Applied Materials and Optoelectronic Engineering, National Chi Nan University, Puli, Nantou Hsien 54561, Taiwan, ROC

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ABSTRACT

The Ti-doped Al_2O_3 ($\text{Al}_2\text{O}_3:\text{Ti}$) films were prepared by simultaneous RF magnetron sputtering of Al_2O_3 and DC magnetron sputtering of Ti. The advantage of this method is that the Ti content could be independently controlled. Decreasing the DC power or increasing the ratio of O_2 to Ar pressure made the $\text{Al}_2\text{O}_3:\text{Ti}$ film be more stoichiometric. By decreasing the DC power or increasing the ratio of O_2 to Ar pressure, the hydrophilic $\text{Al}_2\text{O}_3:\text{Ti}$ film exhibited lower surface roughness, higher average visible transmission, higher linear refractive index and lower stress-optical coefficient.

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1. Introduction

Alumina is a technologically important oxide because of its high hardness and melting point, wear resistance, chemical stability and optical transparency. Measuring and understanding self diffusion in alumina has been a matter of interest for nearly half a century because sintering, grain growth, creep and all types of solid state reactions are strongly controlled by atomic diffusion [1–3]. For theoretical modeling and control of these phenomena reliable diffusion data of both constituents (oxygen and aluminum) are required. Over the last 50 years many investigations have been carried out concerning oxygen diffusion in alumina [3]. To avoid difficulties which could arise from impurities in the samples, single $\alpha\text{-Al}_2\text{O}_3$ crystals intentionally doped with Ti were used [2,3]. Transition metal (chromium and titanium)-doped $\alpha\text{-Al}_2\text{O}_3$ crystals have attracted attention for many years not only as beautiful gemstones, but also due to their application as high power laser media [4]. As a tunable laser medium, high quality titanium-doped sapphire crystals are required to have uniform distribution of dopants.

Different applications and environments demand different kinds of properties of the thin films. During recent years, there has been a growing interest in the study of doped films because of their very stable optical properties [5,6]. Among the physical vapor deposition (PVD) techniques, magnetron sputtering provides more

advantages in controlling the microstructure and composition of the films [7]. The characteristics of prepared films are affected by the preparation conditions such as working pressure, substrate temperature, types of substrates, and the thickness of the films [8,9]. In this study, Ti-doped Al_2O_3 ($\text{Al}_2\text{O}_3:\text{Ti}$) films were prepared by simultaneous RF magnetron sputtering of Al_2O_3 and DC magnetron sputtering of Ti. The influence of DC power and the ratio of O_2 to Ar pressure on the $\text{Al}_2\text{O}_3:\text{Ti}$ films with respect to the hydrophilicity and optical properties was investigated.

2. Experimental procedures

The $\text{Al}_2\text{O}_3:\text{Ti}$ films were deposited on glass (Eagle 2000) by simultaneous RF magnetron sputtering of Al_2O_3 and DC magnetron sputtering of Ti. The dimension of the glass substrates was $24\text{ mm} \times 24\text{ mm} \times 1.1\text{ mm}$. Before deposition, the substrates were ultrasonically cleaned in alcohol, rinsed in deionized water and dried in nitrogen. Two circular targets were used (5 cm diameter, 5 mm thickness); the first was sintered stoichiometric Al_2O_3 (99.99% purity), and the other was metallic Ti (99.999% purity).

A turbo-molecular pump, backed by a rotary pump, was used to achieve a base pressure of $1.3 \times 10^{-4}\text{ Pa}$ before introducing a pure Ar or a mixed Ar– O_2 atmosphere. The pressure was measured using an ion gauge (M-13, ULVAC, Japan). An RF power (13.56 MHz, RGN-1302, ULVAC, Japan) of 50 W was supplied to the Al_2O_3 target, and a DC power (DCS0052B, ULVAC, Japan) of 5–9 W was applied to the Ti target. The targets were first sputtered for 10 min at $4.8 \times 10^{-1}\text{ Pa}$ in an Ar atmosphere for cleaning purpose.

* Corresponding author. Tel.: +886 49 2910960x4771; fax: +886 49 2912238.
E-mail address: sushia@ncnu.edu.tw (S.-S. Lin).

For the deposition of the films, the sputtering was with a target-to-substrate distance of 15 cm and the substrates were not heated. The chamber was back-filled with a pure Ar or a mixed Ar–O₂ atmosphere at a working pressure of 1.5 Pa. Two separate mass flow controllers (SEC-E40, HORIBA, Japan) were used to monitor the gas flow rates of argon and oxygen. The gas flow rates of argon and oxygen were 21–23 sccm and 0–10 sccm, respectively. No external bias voltage was applied to the substrate, and the rotating speed of the substrate was 20 rpm for depositing Al₂O₃:Ti films with thickness of 100 nm.

Film thickness was measured using a surface profiler (Alpha-Step 500, TENCOR, Santa Clara, CA). Elemental compositions were investigated by X-ray photoemission spectroscopy (XPS; PHI 5000 VersaProbe, Japan). Surface morphologies and surface roughness were examined by atomic force microscopy (AFM; Agilent 5500, Santa Clara, CA). The surfaces of films were observed by field emission gun scanning electron microscopy (FEG-SEM; JEOL JSM-6330F, Japan). The optical transmission spectra of films in the ultraviolet–visible–near infrared (UV–VIS–NIR) region were obtained using a spectrophotometer (HP 8452A diode array spectrophotometer, Hewlett Packard, Palo Alto, CA). Linear refractive indices of samples were recorded using a spectrometer (MP100-ST, Fremont, CA). Young's moduli of samples were measured using the Nano Indenter XP System (MTS Systems Corporation, MN, USA). The water contact angles on samples were measured by a contact angle meter (Model 100SB, Sindatek, Taiwan).

Moiré deflectometry is a powerful tool for measuring the nonlinear refractive indices of materials. The main advantages of the Moiré deflectometry technique are its extreme experimental simplicity, lower cost and lower sensitivity to external disturbances than other interferometric methods. In this study, this method was applied to measure the nonlinear refractive indices of Al₂O₃:Ti films on glass substrates under illumination with a 5-mW He–Ne laser ($\lambda = 632.8$ nm).

Fig. 1 shows the Moiré deflectometry experimental set-up that is used to measure the nonlinear refractive indices of Al₂O₃:Ti films on glass substrates. Lens L₁ focused a 5-mW He–Ne laser beam (wavelength of 632.8 nm), which was re-collimated by lens L₂. The focal lengths of lenses L₁, L₂ and L₃ were 100, 200 and 200 mm, respectively. Two similar Ranchi gratings, G₁ and G₂ with a pitch of 0.1 mm were used to construct the Moiré fringe patterns. The distance between the planes of G₁ and G₂ was set to 64 mm, which is one of the Talbot distances of the used gratings. The Talbot distances satisfy $z_t = tp^2/\lambda$ where p is the periodicity of the grating; λ is the wavelength of light, and t is an integer. In this work, the Moiré fringes were clearly formed at a Talbot distance of $z_{t=4} \approx 64$ mm. The Moiré fringe patterns were projected onto a computerized CCD camera by lens L₃, which was placed at the back of the second grating.

3. Results and discussion

Table 1 shows the elemental composition of Al₂O₃:Ti films under different sputtering conditions analyzed by XPS. The Ti content

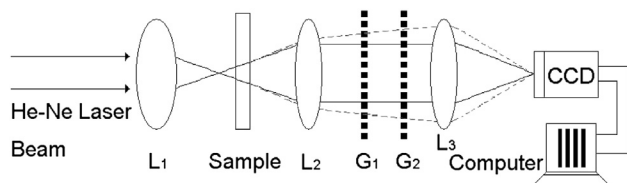


Fig. 1. The experimental set-up for measuring nonlinear refractive index by the Moiré deflectometry technique.

Table 1

Elemental composition of Al₂O₃:Ti films under different sputtering conditions analyzed by XPS.

RF power (W)	DC power (W)	O ₂ /Ar	O content (at.%)	Al content (at.%)	Ti content (at.%)	O/(Al + Ti)
50	5	0	59.5	37.9	2.6	1.47
50	6	0	58.9	37.9	3.2	1.43
50	7	0	58.5	37.8	3.7	1.41
50	8	0	57.8	37.9	4.3	1.37
50	9	0	57.3	37.9	4.8	1.34
50	9	0.09	57.7	37.5	4.8	1.36
50	9	0.16	58.2	37.0	4.8	1.39
50	9	0.22	58.5	36.7	4.8	1.41
50	9	0.27	59.1	36.1	4.8	1.44
50	9	0.32	59.4	35.8	4.8	1.46

of the sputtered film increased with the DC power to the Ti target. The O/(Al + Ti) atomic ratio was increased by decreasing DC power or increasing the ratio of O₂ to Ar pressure. It suggested that the deposited films became more stoichiometric when DC power decreased or the ratio of O₂ to Ar pressure increased.

The bonding conditions of titanium on the surfaces of Al₂O₃:Ti films were investigated by XPS spectra. Fig. 2 shows Ti 2p photoelectron peaks in the XPS spectra of Al₂O₃:Ti films deposited under different conditions. The DC power and the ratio of O₂ to Ar pressure are: (a) 5 W, 0; (b) 9 W, 0 and (c) 9 W, 0.32. The Ti 2p spectra consist of Ti 2p_{3/2} and Ti 2p_{1/2} peaks. In Fig. 2(a)–(c), the binding energy corresponding to the Ti 2p_{3/2} state in the measured samples were 458.5 ± 0.06 eV, 458.5 ± 0.02 eV, and 458.5 ± 0.02 eV, respectively. All are shifted by 5 eV as compared with metallic titanium (453.5 eV). The binding energy shift of this value indicates that the films contain titanium at the highest oxidation state Ti⁴⁺ [10]. The highest and the lowest energy components have been assigned to Ti⁴⁺ and Ti⁰, respectively, while the intermediate component has the energy shift relative to TiO₂ that falls in between that of Ti³⁺ and Ti²⁺ [11]. According to Fig. 2(a)–(c), no energy shift relative to TiO₂ could be observed. It suggested that the contribution of oxidation states of Ti was probably only owing to Ti⁴⁺ for Al₂O₃:Ti films in this study.

Fig. 3 shows the morphologies of Al₂O₃:Ti films deposited under different conditions. The DC power and the ratio of O₂ to Ar pressure are: (a) 5 W, 0; (b) 9 W, 0 and (c) 9 W, 0.32. By increasing the DC power, the root-mean-square (RMS) roughness increased. The roughness values were very close to the morphologies of growing films [12]. By comparing Fig. 3(b) with Fig. 3(c), the Al₂O₃:Ti film exhibited lower roughness as the ratio of O₂ to Ar pressure increased to 0.32. Because the probability of collisions of particles increased by mixing oxygen atmosphere, the collisions of these particles with the growing film could smooth the thin film by surface diffusion mechanism and enhanced surface atom mobility [13].

Fig. 4 shows the scanning electron micrograph of Al₂O₃:Ti films deposited under different conditions. The DC power and the ratio of O₂ to Ar pressure are: (a) 5 W, 0; (b) 9 W, 0 and (c) 9 W, 0.32. It could be observed that the Al₂O₃:Ti film developed a denser structure by decreasing DC power or increasing oxygen pressure.

Fig. 5 shows the average visible transmission of Al₂O₃:Ti films deposited under different conditions. The DC power and the ratio of O₂ to Ar pressure are: (a) 5–9 W, 0 and (b) 9 W, 0–0.32. The average visible transmission exceeded 94% for all films. However, the average visible transmission increased when the DC power decreased or the ratio of O₂ to Ar pressure increased. Comparing Fig. 5 with Table 1, the Al₂O₃:Ti film with a higher O content showed higher average visible transmission. It indicated that an O content could improve the average visible transmission of Al₂O₃:Ti film.

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