Structural, optical and wettability properties of zirconium oxide thin films deposited at various helium partial pressure

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Abstract. The aim of the present work is to deposit zirconium oxide thin films by reactive magnetron sputtering on glass substrates. The influence of helium partial pressure on structural, optical and wettability properties are investigated. The structural properties were investigated using X-Ray Diffraction, which shows that the films deposited has (111) peak of Zirconium Oxide. The intensity of the peak increased with the increase in helium partial pressure. UV-Vis-NIR spectrophotometer was used to study the optical properties of the films; the deposited films were transparent and had excellent transmittance of 95%. Surface roughness measured was in the range of 20.9nm to 21.8nm, the roughness of the deposited films decreased with increase in helium partial pressure. The wettability property measured using contact angle goniometer had a maximum contact angle of 94.10, which proves that the deposited film has hydrophobic property when measured using water.

KEY WORDS: Zirconium Oxide; Hydrophobicity; Sputtering; Transmittance; Roughness

1. Introduction

Metal oxides belong to the group of materials that have picked up consideration because to their extraordinary and fascinating optical properties in recent years. Thin films that are coloured and are resistant to corrosion and scratch are attracting more and more research work [1]. From an optical perspective, zirconium oxide has a high transparency, wide band gap and high refractive index. Due to these great optical properties, zirconium oxide has been generally utilized as a part of different optical applications, including broadband interference filters, high reflectivity mirrors and low-loss waveguides [2,3]. Optical, mechanical and structural properties of ZrO2, is influenced by various parameters and deposition technique. Various structure of deposited films like amorphous, cubic, monoclinic, tetragonal and orthorombic were observed for various deposition techniques including Vacuum Arc Deposition (VAD), Sol–gel, Sputtering, Chemical Vapour Deposition (CVD) and Electron Beam Physical Vapour Deposition (EB-PVD) [4]. The most frequently utilized deposition technique is Magnetron sputtering, because of the prevalence in giving a uniform film on an enormous substrate [5].
2. Experimental Details

Reactive Magnetron Sputtering was used to sputter deposit Zirconium (Zr) metallic target (99.99% pure) on corning glass substrates. The distance between target and substrate was consistent (50 mm) during deposition. The cleaning of the substrates were done by rinsing the substrates in ultrasonic baths of acetone and methanol. For depositing thin films, helium was used as inert gas and oxygen was used as reactive gas and the flow of gas was controlled by Mass Flow Controller. The partial pressure of helium was varied from 45.50% to 57% and that of reactive gas was kept steady at 15sccm. The deposition time for all the coatings were 60 minutes and the sputtering pressure was kept constant at 2.5Pa. The parameters for deposition is given in table 1 below:

| Table 1: Parameters for depositing zirconium oxide thin films |
|---------------------------------------------------------------|
| Target | Zr (99.999%) |
| Substrate | Corning glass |
| Target-substrate distance | 50 mm |
| Vacuum pressure | 6 x 10⁻⁴ Pa |
| Working Pressure | 2.5Pa |
| Gas Ratio (He:O₂ in sccm) | 12.5:15, 15:15, 17.5:15, 20:15 |
| Sample names | Z12.5, Z15, Z17.5, Z20 |
| Rf Power | 225W |
| Substrate temperature | 550°C |

Bruker D2 phaser, advance diffractometer with Cu-Kα radiation having wavelength 1.54Å was used to study the structural properties of the deposited thin films. UV–Vis–NIR spectrophotometer (Shimadzu 3600) was used to study optical transmittance and the wettability studies was carried out using Contact angle measurement system (Rame Hart 290).

3. Results and Discussion

The deposited zirconium oxide films were analysed by XRD to observe the structural properties obtained at different helium partial pressure. Figure 1. shows the X-Ray Diffraction patterns for zirconium oxide films deposited at various helium partial pressure.
Figure 1. X-Ray Diffraction patterns for zirconium oxide thin films deposited at various helium partial pressure

The deposited films of zirconium oxide showed (111) peak of ZrO$_2$ phase (JCPDS card No. 89-9066). When the partial pressure of helium was 45.50% a low intensity peak of (111) ZrO$_2$ was observed. As the helium partial pressure increased from 50% to 57% the intensity of the peak also increased. Maximum intensity of the peak (111) for ZrO$_2$ was observed at 57% partial pressure. Goedicke et al. (2000) deposited thin films using reactive pulsed magnetron sputtering and studied the variation of argon flow rate on structural properties and concluded that sputtering pressure had a significant influence on the films coated. XRD results showed only single strong and relatively broad diffraction peak of (111) which is of monoclinic phase of ZrO$_2$. Also tried to get rough estimation of grain size of (111) reflex of monoclinic phase using full width and half maximum [6].

Kuhaili and Durrani observed that zirconium oxide films deposited were amorphous which attributed to high heat which formed ZrO$_2$, it obstructs the re-arrangement of oxygen–metal bonds at low temperatures and that results in formation of a crystalline phase. The predominance of the monoclinic phase can be perceived based on the thermodynamics of crystal growth. Mostly, the crystal plane that has the lowest Gibbs free energy will grow preferentially [6].

The crystalline size was assessed by FWHM (full width at half maximum) of the XRD peaks using Scherrer’s method [2]. The results showed that as the intensity of the partial pressure of helium increased the average crystalline size also increased. The average crystalline size of the thin films changed from ~1 to ~2nm as intensity of the helium partial pressure increased.
Figure 2. Spectral transmission curve of zirconium oxide thin films deposited at various helium partial pressure

The spectral transmission curve of zirconium oxide thin films is showed in Figure 2. The average transmittance of the deposited films are in the range of 85-95%, which means that the deposited films were transparent. It can be observed from the graph that the transmittance for films deposited at 45.50% helium partial pressure had a maximum transmittance of 95%, which reduced to 90% as the helium partial pressure increased to 57%.

Zhao et al. (2014) deposited zirconium oxide thin films and observed the four group of oxygen compositions using spectral transmission curves. It was noticed from the analysis that as the oxygen flow rate increased to 4.5sccm the transmittance of the films improved. At 4.5sccm flow rate average transmittance observed was 89.16% and the curves did not had any critical variation in the range of 340~400 nm. High OMR ratio was responsible for the full combination of zirconic and oxygenic atoms, prompting a reduced film layer with strengthening crystallization density [5]. The zirconium oxide films synthesized at higher oxygen ratio values displayed higher transmittance [7]. So the optical properties observed in this research are similar to as observed in literature.

The wettability property and roughness of the films synthesized is shown in Figure 3. It was noticed from the results that contact angle increased with decrease in helium partial pressure. The zirconium oxide films coated at 45.50% partial pressure had a maximum contact angle of 94.1° when measured with water, which showed that the films deposited as varying partial pressure had a hydrophobic property. It is seen from the graph that the lowest contact angle value of 67.5° was found at 57.0% partial pressure. Also from the analysis it was confirmed that the surface energies of the deposited samples decreased as the contact angle increased.

Surface roughness measured is also aligned to the results of contact angle measurement. The roughness of the films deposited decreased from 21.8nm for 45.50% partial pressure to 20.90nm for
57.0% partial pressure. Patel et al. (2016) studied the effect of varying nitrogen gas flow on zirconium nitride films and found that the films deposited had a hydrophobic property when measured with water and the results showed that the surface energy increases with decrease in contact angle [8].

Rawal et al. (2011) observed that surface structure is important to achieve the hydrophobic property. Besides the surface roughness, the structure formed on the surface is equally important to decide the wettability of the films [9]. When the films are hydrophilic, the surface energies are higher when compared to films, which are hydrophobic [10, 11, 12]. Hence, the results achieved by our research are in agreement with the literatures.

4. Conclusion

Zirconium oxide thin films were deposited using variation in helium partial pressure and the deposited films showed a high intensity (111) peak of ZrO2 and as the partial pressure of helium decreased from 57.0% to 45.50% the intensity of the peak also decreased. The average crystalline size of the films were in the range ~1 to ~2nm and as the intensity of the helium partial pressure increased the crystalline size also increased. The maximum transmittance observed was 95% for the least partial pressure of helium and the average transmittance decreased to 90% as the partial pressure increased to 57.0%, which proves that the deposited films are transparent. The contact angle measurement for 45.50% helium partial pressure had a maximum contact angle of 94.1° when measured with water and the roughness was 21.8nm which reduced to 20.9nm which was validated with result of contact angle which also reduced to 67.0° for 57.0% helium partial pressure.
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6. References

[1] S. K. Rawal, A. Kumar, V. Chawla, R. Jayaganthan, and R. Chandra, “Structural, optical and hydrophobic properties of sputter deposited zirconium oxynitride films,” Mater. Sci. Eng. B, vol. 172, no. 3, pp. 259–266, 2010. doi:10.1016/j.mseb.2010.05.027.

[2] Al-Kuhaili and Durrani Effect of annealing on pulsed laser deposited zirconium oxide thin films. Journal of Alloys and Compounds, 509(39), 9536–9541, 2011. doi:10.1016/j.jallcom.2011.07.062.

[3] S. Zhao, F. Ma, K.W. Xu, H.F. Liang, J. Alloys Compd. 453 (2008) 453.

[4] O. Goldberg, E. Goldenberg, V. N. Zhitomirsky, S. R. Cohen, and R. L. Boxman, Surface & Coatings Technology Zirconium vacuum arc operation in a mixture of Ar and O 2 gases: Ar effect on the arcing characteristics, deposition rate and coating properties. Surf Coat Technol. 2012;206(21):4417-4424. doi:10.1016/j.surfcoat.2012.04.082.

[5] X. Zhao, J. Jin, J. Cheng, J. Lee, and K. Wu, “NU SC,” Thin Solid Films, 2014. doi:10.1016/j.tsf.2014.05.060.

[6] K. Goedicke, U. Liebig, O. Zywitzki, and H. Sahm, “Influence of process parameters on the structure and the properties of ZrO 2 coatings deposited by reactive pulsed magnetron sputtering Z PMS .,” pp. 37–42, 2000.

[7] D. Pamu, K. Sudheendran, M. G. Krishna, K. C. J. Raja, and A. K. Bhatnagar, “Ambient temperature stabilization of crystalline zirconia thin fi lms deposited by direct current magnetron sputtering,” Thin Solid Films, vol. 517, no. 5, pp. 1581–1585, 2009. doi:10.1016/j.tsf.2008.09.074.

[8] N. P. Patel, K. V. Chauhan, J. M. Kapopara, N. N. Jariwala & S. K. Rawal, Characterization of sputtered zirconium nitride films deposited at various argon: nitrogen ratio 10.1088/1757-899X/149/1/012015

[9] S. K. Rawal, A. K. Chawla, V. Chawla, R. Jayaganthan, and R. Chandra, “Characterization of bi-phased Zr2ON2-ZrO2coatings deposited by RF magnetron sputtering,” Thin Solid Films, vol. 520, no. 5, pp. 1589–1596, 2011.

[10] S. K. Rawal, A. K. Chawla, R. Jayaganthan, and R. Chandra, “Structural, Wettability and Optical Investigation of Titanium Oxynitride Coatings: Effect of Various Sputtering Parameters,” J. Mater. Sci. Technol., vol. 28, no. 6, pp. 512–523, 2012.

[11] S. K. Rawal and R. Chandra, “Wettability and Optical Studies of Films Prepared from Power Variation of Co-sputtered Cr and Zr Targets by Sputtering,” Procedia Technol., vol. 14, pp. 304–311, 2014.

[12] H. V Patel, H. N. Patel, P. A. Soni, H. D. Parmar, P. Nicky, and K. V Chauhan, “Characterization of sputtered zirconium nitride thin films deposited at various RF power and sputtering pressure” vol. 020093, no. October, 2019. doi:10.1063/1.5130303