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Annealing temperature effect on the optical properties of thermally oxidized nano-crystalline ZrO_2 thin films grown on glass substrates

M.M. Larijani [a,*], E. Hasani [b], S. Safa [c]

[a] Radiation Application Research School, Nuclear Science and Technology Research Institute, P.O. Box 31485-498, Karaj, Iran
[b] Department of Physics, Islamic Azad University, Karaj Branch, P.O. Box 31485-313, Karaj, Iran
[c] Young Researchers Club, South Tehran Branch, Islamic Azad University, Tehran, Iran

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ABSTRACT

Optical properties of zirconium oxide films on glass substrates deposited by thermal oxidation method have been studied at different temperatures. Optical characteristics of films such as refractive index, extinction coefficient, average thickness and optical dielectric constants were calculated using Swanepoel's method. X-ray diffraction analysis (XRD) and atomic force microscopy were performed to investigate the film structure and morphology. It was found out that the optical properties of zirconium oxide films are affected by oxidation temperature which are due to changes of film microstructure and surface roughness.

1. Introduction

Because of their unique properties such as high refractive index, high band gap and transparency, zirconium oxides (ZrO_2) thin film have got extensive applications in engineering of optical materials such as reflective mirrors, interference filters, and optical-electrical devices; moreover, because of their physical properties such as suitable thermal stability and high optical dielectric constants, they can be a good alternative to SiO_2 in semiconductors technology [1,2]. They have also remarkable mechanical properties such as high corrosion and wear resistance, and a high threshold of resistance to incident laser flux [3]. ZrO_2 thin films have been synthesized on different substrates through using different methods such as sputtering [4–6], wet chemical methods [7,8], chemical vapor deposition [9], electron beam evaporation [10], and pulsed laser deposition [11]. One of the simple methods to produce films of controllable stoichiometry and thickness is the thermally oxidation of Zr films deposited on the samples [2,12,13].

Knowing that optical properties of synthesized films correlate with their microstructure and stoichiometry [1] and also, considering the significance of their optical property determination in optoelectronic industries, we have investigated the effect of the oxidation temperature on the structural and optical properties of the zirconium oxide films. Optical properties and thicknesses of different as-prepared films were determined employing transmittance spectrophotometry by Swanepoel's method [14].

2. Experimental

Zirconium oxide films were deposited on substrates using thermal oxidation of planar magnetron sputtered Zr films as it was reported in detail elsewhere [12]. In summary, the substrate temperature was raised up to 573 K with the use of plasma effect during zirconium deposition. The cathode voltage and discharge current were fixed to 300 V and 200 mA, respectively. The deposition conditions are presented in Table 1. The deposited samples were then placed into a quartz reactor for post-oxidation process. Thermal oxidation was performed within a resistance furnace in oxygen atmosphere with a flow rate of 200 sccm for 2 h at different temperatures ranging from 523 to 823 K.

Crystallinity of the films was studied with a Philips PW1800 X-ray diffractometer (XRD) using monochromatized Cu-Kα radiation. The scanning step size and the counting time at each step were set as 0.02 and 10 s, respectively. To determine the thicknesses and optical constants of ZrO_2 films deposited on the glass substrates, the transmittance spectrometry technique (Cary Varian 500) was utilized in the range of 200–750 nm. The surface roughness and morphology were determined with the help of height atomic force microscopy (AFM) images of different films collected with the use of a Park Scientific, model Autoprobe CP operated in non-contact mode.

* Corresponding author. Tel.: +98 261 4411101; fax: +98 261 4411106.
E-mail address: mmojtahedfr@yahoo.com (M.M. Larijani).

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Table 1
Deposition conditions of zirconium film.

Base pressure (Pa)	1.4×10^{-3}
Working pressure (Pa)	0.3
Substrate to target distance (m)	0.045
Substrate ion current (mA)	200
Plasma voltage (V)	300
Deposition time (s)	300

Table 2
Variation of surface roughness of different films.

Oxidation temperature (K)	523	773	823
R_A (°A)	9.57	6.25	5.78
RMS (°A)	12.9	7.99	7.89

3. Results and discussion

Fig. 1 illustrates XRD patterns of the films on the glass substrates oxidized in the temperature range of 523–823 K. The measurement at lower temperatures did not yield useful information because of insufficient scattering of zirconium oxide phase. Some remarkable peaks of monoclinic and tetragonal ZrO_2 have been formed in the temperature range of 773–823 K. A detailed discussion of XRD results is reported in Ref. [12].

Smoothness of the film oxidized at temperature 823 K on the glass substrate was deduced from the AFM micrograph shown in Fig. 2.

The average and RMS roughness values of the samples summarized in Table 2 show that higher oxidation temperatures can make smooth of surface by enhancing the adatoms and grain boundary mobility on the surface [12].

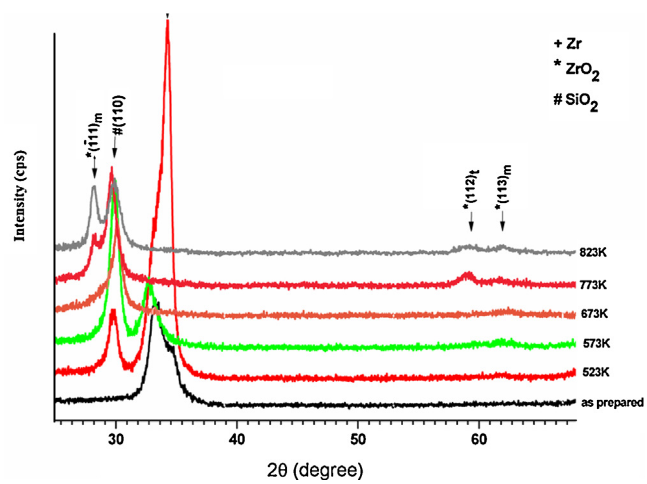

Fig. 1. XRD pattern of Zr films treated in various temperatures.

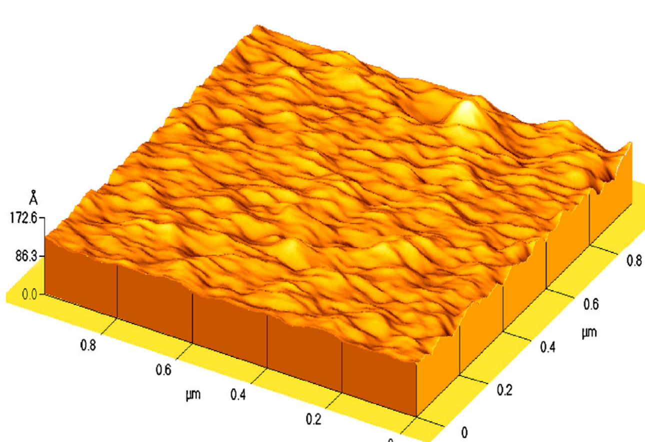

Fig. 2. AFM micrograph of Zr film oxidized at 823 K.

Transmittance and reflectance spectra of ZrO_2 films prepared at different oxidation temperatures in the range of UV–vis have been shown in Fig. 3.

Transmittance of deposited thin films increases as the oxidation temperature increases and attains the amount of 80% at 823 K. The increase in transparency at elevated temperatures in despite of the increase in zirconium oxide film thickness is due to stoichiometry of the films which approaches that of the transparent ZrO_2 phase at higher temperatures as reported in Ref. [13]. As can be seen, the reflectivity of ZrO_2 films will decrease by increasing the annealing temperature in UV–vis wavelength range. To explain this, it must be addressed that optical reflectivity is depends on the energy band structure and charge carriers density of studied samples. Therefore, by increasing the annealing temperature, thin films were going to find semiconducting characteristics with restricted electrons in the conduction band and as a result, a very low reflectance.

The interference fringes in Fig. 2 are formed through the spontaneous interference coming from continuous reflections of the light between the two surfaces of the thin films; i.e., between air/film and film/substrate interfaces. The formed maximums and minimums are connected with the real part of the complex refractive index ($\bar{n} = n - ik$) [15] where n and k are respectively the refractive

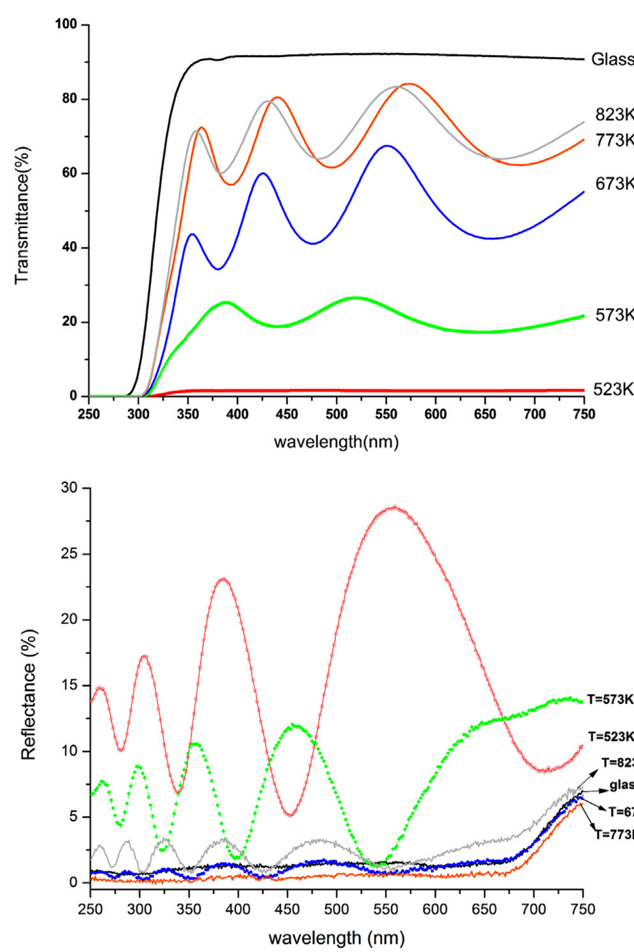

Fig. 3. Transmittance and reflectance spectra of annealed samples.