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Thermal treatment effect on the optical properties of ZrO_2 thin films deposited by thermionic vacuum arc

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ABSTRACT

This paper shows the ex situ thermal treatment effects of the ZrO_2 thin films obtained by TVA (thermionic vacuum arc) technique on the optical properties (e.g., transmittance, refractive index and band-gap energy) of ZrO_2 thin films. The crystal structure, surface and optical properties were investigated for ZrO_2 thin films deposited on glass substrates by thermionic vacuum arc (TVA) method. The thermal treatment effect on the optical properties of the thin films was determined. The XRD analysis showed that the deposited ZrO_2 thin films have baddeleyite (monoclinic) and zirconium (hexagonal) structures. The thicknesses and refractive index were determined by interferometric measurements. The thin films were thermal treated at different temperatures (350 °C, 450 °C and 550 °C), and the analysis showed that the optical properties of ZrO_2 deposited thin films were improved by thermal treatment at 450 °C.

1. Introduction

Zirconium oxide (ZrO_2) has several properties that make it a useful material. These properties include high density, hardness, electrical conductivity, wear resistance, high fracture toughness, low thermal conductivity, relatively high dielectric constant, and extreme chemical inertness [1–6]. ZrO_2 is an essential material in optics due to its excellent optical properties, such as a high refractive index, large optical band-gap, low optical loss and high transparency in the visible and near-infrared regions being used for high refractive mirrors, broadband interference filters, and active electro-optical devices [7–9]. Additionally, ZrO_2 is the most frequently used material for anti-reflection (AR) coatings in optical industries.

ZrO_2 thin films can be deposited by electron beam evaporation [10], sputtering [11,12], reactive sputtering [13–15], pulsed laser deposition, chemical vapor deposition, sol–gel processing [16–18], and ion beam deposition. The physical properties of the ZrO_2 thin films strongly depend on the deposition techniques and the ex situ thermal treatment process.

In this study, the microstructure and surface composition were determined before and after thermal treatment on the optical properties of ZrO_2 thin films. The thin films were thermally treated at 350, 450 and 550 °C for 60 min under atmospheric pressure.

ZrO_2 thin films were deposited on glass slides substrates by thermionic vacuum arc (TVA) for the anti-reflection (AR) properties. Glass slides are commercial product. These glass slides were cleaned by ethyl alcohol and ionized water in ultrasonic cleaner. A TVA classical electron gun is schematically shown in Fig. 1. TVA provides many advantages to deposited thin films than other techniques such as compactness, low roughness, nanostructures, homogeneities as compared to other deposition techniques. The use of TVA has several advantages over deposited thin films according to other methods for depositing thin films, such as pure thin film deposition, compactness, a low roughness, nanostructure formations, homogeneity, good adhesionproperties, a fast processing time (a few minutes), low-cost, and a high deposition rate [19–28]. TVA is an anodic plasma generator that works in high-vacuum conditions (10^{-5}–10^{-6} Torr) to generate the plasma in pure anode material. The deposition parameters of the TVA; filament current was 19.5 A, applied voltage was 2 kV, arc current is 200 mA.

All of the ZrO_2 thin films were produced under the same working conditions. X-ray diffraction (XRD) analysis was used to determine the crystal structure of the deposited thin films. Thermal and non-thermally treated films for 350, 450 and 550 °C were analyzed by UV–vis spectrometry and interferometry between 300 and 1100 nm to measure the transmittance, film thicknesses,

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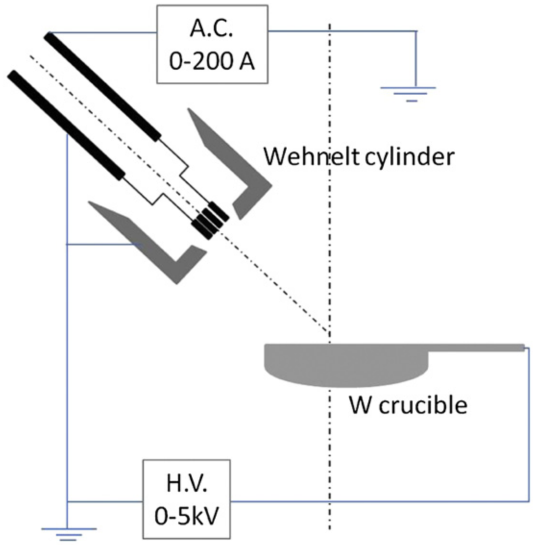

Fig. 1. Classical electron gun design of TVA.

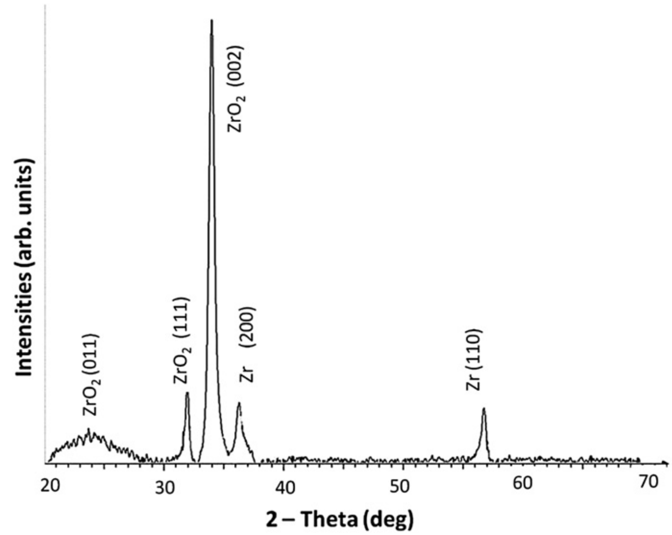

Fig. 3. XRD spectra of non-thermal treated ZrO_2 thin film.

refractive index and band-gap energies. The flow chart for experimental procedure is shown in Fig. 2.

Fig. 3 shows the x-ray diffraction (XRD) pattern of the ZrO_2 non-thermally treated thin film deposited on glass substrate. The deposited thin films contain two crystal structures: the monoclinic structure baddeleyite of ZrO_2 and the hexagonal structure of Zr. The as-deposited film shows the peaks corresponding to the monoclinic phase of ZrO_2. The main peaks are attributed to diffraction from the monoclinic phase of the deposited ZrO_2 thin films. As shown in Fig. 3, (011), (111) and (002) patterns are relative majority, so the deposited ZrO_2 thin films are in the (002) preferred orientation.

A JEOL-JSM 5600LV scanning electron microscope (SEM), equipped with an energy-dispersive X-ray (EDX) detector, was used to analyze the thin films. According to the SEM image at 11kX magnification, the deposited thin films are compact, exhibiting very rough surfaces. The percentage of Zr/O is very low approximately 7.74/34.90 because the thickness of the deposited thin films is 70 nm. The silicon (57.36%) and amount of the Oxygen impurities were derived substrates material were detected, and they likely originated from the substrates (glass slides) due to the very thin films. No other impurities were found in the deposited thin films.

The transmittance and absorbance spectra of the ZrO_2 thin films were determined by UV–vis spectrophotometers between 300 and 1100 nm. Fig. 4 shows the UV–vis transmittance spectra of ZrO_2 thin films measured at room temperature (RT) and at different thermal treatment temperatures. The thermal treated of the ZrO_2 thin films are more transparent at low absorption regions. The transmittance of thermal treated ZrO_2 thin films at 450 °C and at 550 °C showed a slight increase in the low absorption region relative to the non-thermal treated films. However, the ZrO_2 thin films thermal treated at 350 °C showed a slight decrease in the low absorption region relative compared with the non-thermal treated films. The maximum transmittance of the ZrO_2 thin films with a thermal treatment at 450 °C was 85% at 550 nm (Fig. 4), which represents an increase of approximately 10% relative to non-thermal treated ZrO_2 thin films. Fig. 5a shows the absorption spectra of ZrO_2 thin films. The absorption of the thermal treated ZrO_2 thin films at 450 °C and 550 °C showed a slight decrease in the low absorption region compared with non-thermal treated films. Nevertheless, the ZrO_2 thin films thermal treated at 350 °C had a low absorption region that was similar to non-thermal treated films. The minimum absorption was measured for ZrO_2 thin films with a thermal treated at 450 °C.

By increasing the thermal treatment temperature of the ZrO_2 thin films, the absorbance reached a minimum value. The variations

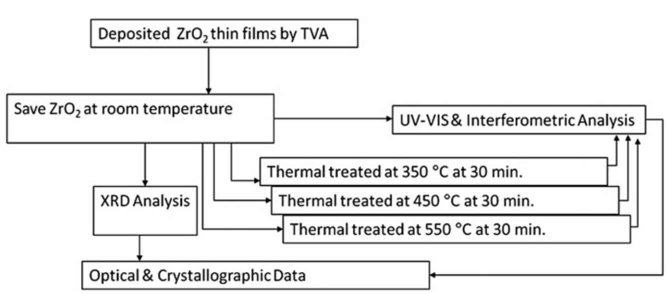

Fig. 2. Flowing chart of the prepared and analyzed ZrO_2 thin films.

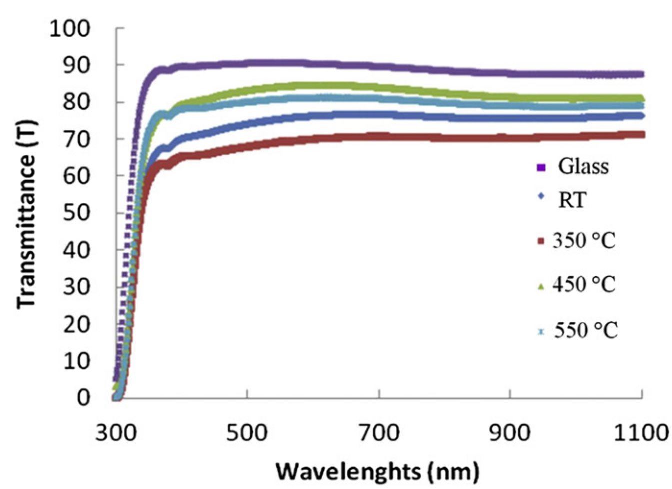

Fig. 4. Transmittance spectra of non-thermal treated and thermal treated ZrO_2 thin films.

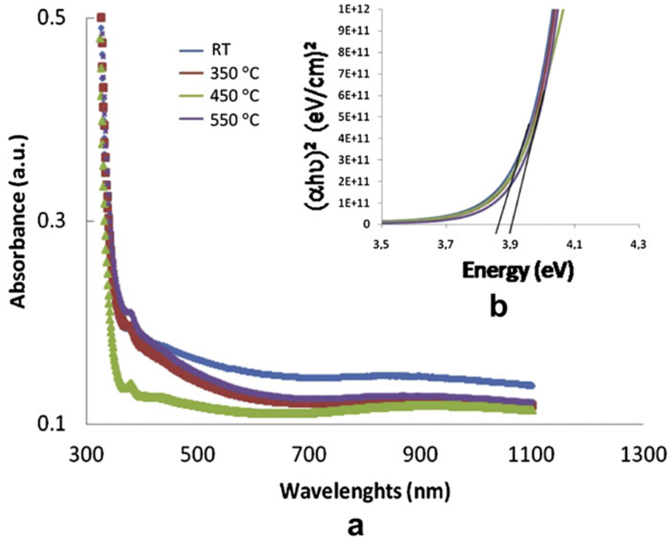

Fig. 5. Absorbance spectra and band-gap energies of non-thermal treated and thermal treated ZrO_2 thin films.

in the transmittance and absorbance of the deposited ZrO_2 thin films after thermal treated because of the removal of oxygen with increasing the temperatures [2].

The absorption coefficients (α) are calculated from the measured absorption (A) using Eq. (1) [3]:

$$\alpha = (2.303A/t), \tag{1}$$

where t is the thickness of the deposited ZrO_2 thin films. To determine the band-gap energies of the direct transitions (E_g), a Tauc method was used [4]. In this method, the following equations were used to calculate the band-gap energies, E_g.

$$(\alpha h\nu)^{1/2} = B(h\nu - E_g), \tag{2}$$

where α is the absorption coefficient and B is a constant. E_g can be determined from Tauc's law [4]. Fig. 5b shows the plot for the incident light, achieved with the results obtained after the calculus of $(\alpha h\nu)^2$ as a function of $h\nu$ for the incident light. The band-gap energies can be calculated by extrapolating the linear portion of the curve to the energy (hν) axis [2]. The band-gap energies of the deposited ZrO_2 thin films that were obtained by extrapolation of the curve ranged from 3.85 to 3.93 eV.

All of the band-gap energies of the obtained and thermal treated ZrO_2 thin films are nearly the same. However, the non-thermal treated films have the lowest energies. These values are small compared to previously reported values [2,4]. This difference could be a consequence of the deposition technology and method because they can change the packing density of thin films. The thermal treatment process can improve the packing density and the crystallinity [2].

The coating thicknesses were measured using an interferometer and the thickness measurement system Filmetrics F20. The average thickness of the thin films was found to be 70 nm.

The refractive indices of the ZrO_2 thin films were calculated by the following equation [29, 30]:

$$\frac{n^2-1}{2+n^2} = 1 - \sqrt{E_g/20} \tag{3}$$

The band gaps and calculated refractive index are 4; 3.96; 3.85 and 4.02 for 2.17; 2.18; 2.20 and 2.16, respectively.

ZrO_2 thin films were deposited using the thermionic vacuum arc (TVA) method. The optical properties of the deposited thin films were investigated to the show the effect of thermal treatment on optical properties such as transmittance, refractive index and band-gap. The transmittance of the ZrO_2 film increased with the thermal treatment temperature. The maximum transmittance was 85%, which corresponded to the films thermal treated at 450 °C. The band-gap energy is smaller after thermal treatment at 450 °C. The refractive index of its is higher than the thermal treated at 350 °C and 550 °C. We conclude that the optical properties necessary for ophthalmic usage were improved by thermal treatment the thin films at 450 °C.

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