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Influence of annealing on the physical properties of filtered vacuum arc deposited tin oxide thin films

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Abstract

Tin oxide (SnO_2) thin films were deposited on UV fused silica (UVFS) substrates using filtered vacuum arc deposition (FVAD). During deposition, the substrates were at room temperature (RT). As-deposited films were annealed at 400 and 600 °C in Ar for 30 min. The film structure, composition, and surface morphology were determined as function of the annealing temperature using X-ray diffraction (XRD), atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS). The XRD patterns of the SnO_2 thin films deposited on substrates at RT indicated that the films were amorphous, however, after the annealing the film structure became polycrystalline. The grain size of the annealed films, obtained from the XRD analysis, increased with the annealing temperature, and it was in the range 8–34 nm. The AFM analysis of the surface revealed an increase in the film surface average grain size from 15 nm to 46 nm, and the surface roughness from 0.2 to 1.8 nm, as function of the annealing temperature. The average optical transmission of the films in the visible spectrum was >80%, and increased by the annealing ~10%. The films' optical constants in the 250–989 nm wavelength range were determined by variable angle spectroscopic ellipsometry (VASE). The refractive indexes of as-deposited and annealed films were in the range 1.83–2.23 and 1.85–2.3, respectively. The extinction coefficients, $k(\lambda)$, of as-deposited and annealed films were in the range same range ~0–0.5. The optical energy band gap (E_g), as determined by the dependence of the absorption coefficient on the photon energy at short wavelengths, increased with the annealing temperature from 3.90 to 4.35 eV. The lowest electrical resistivity of the as-deposited tin oxide films was $7.8 \times 10^{-3}\ \Omega$ cm, however, film annealing resulted in highly resistive films.

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1. Introduction

There have been some extensive studies of electrically conducting, optically transparent, and good IR reflectors wide band gap undoped and doped semiconductor, as they are often used in thin film electronics and optoelectronic devices [1–3]. These films have been used in solar cells, light emitting diodes, flat panel displays, and other optoelectronic devices such as architectural windows and in gas sensors. Undoped tin oxide (SnO_2), which is a wide band gap n-type semiconductor (~3.6 eV) [4], belongs to the important family of oxide materials that combine low electrical resistance with high optical transparency in the visible range of the electromagnetic spectrum [3]. SnO_2 films have some practical advantages over transparent and conducting oxide

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(TCO) films that contain In or Cd, as they are less expensive and non-toxic. Doped or undoped SnO_2 thin films were prepared by spray pyrolysis [5], reactive electron beam evaporation [6], rf magnetron sputtering [7,8], chemical vapour deposition (CVD) [9], reactive ion assisted deposition [10] and filtered vacuum arc deposition (FVAD) [11–17].

The main advantage of the filtered vacuum arc deposition method is its very high deposition rate (up to ~10 nm/s), producing thin films characterized by high adhesion and high density [18]. In addition, SnO_2 thin films could be deposited with FVAD system on low temperature substrates, such as polymers that could not sustain temperatures above 80 °C [16]. The dependence of the structure, composition, and electrical properties of room temperature FVA deposited SnO_2 thin films on the oxygen background pressure (0.42–1.06 Pa), and film thickness (100–800 nm) were reported by Ben-Shalom et al. [11], Kaplan et al. [12], Alterkop et al. [14] and Parkansky et al. [15]. All deposited films were amorphous, with the lowest electrical resistivity of $3–5 \times 10^{-4}\ \Omega$ cm, obtained by rapid thermal annealing (RTA) [11,12]. The atomic concentration ratio O:Sn of the films reported by Ben-Shalom et al. [11] and Kaplan et al. [12] was close to the stoichiometric value (2.02:1).

The O:Sn atomic concentration ratio reported by Alterkop et al. [14] was found to be affected by a short term annealing, up to 10 min, at 300 °C in air, and was in the range 1.45–2.00, indicating a large deviation from stoichiometry. The O:Sn ratio on the film surface decreased relative to its value before annealing and reached a minimum after annealing for 7 min. After annealing in air for 10 min, the O:Sn ratio increased relative to the minimum value but was lower than the ratio before annealing. The O:Sn ratio in the bulk decreased monotonically for annealing times longer than 1 min [14]. Alterkop et al. [14] also showed that the resistivity was correlated with the variation in the O:Sn ratio. Annealing with applied electric field at 300 °C affected the resistivity, where the lowest resistivity ($6 \times 10^{-4}\ \Omega$ cm) was obtained by applying a transverse electric field ~100 V/cm [15].

However, the effects of annealing in inertial atmosphere, at temperatures above 300 °C, and for duration longer than 10 min on the composition, structure, morphology, and electrical resistivity of FVA deposited SnO_2 thin films were not reported before. In addition, no detailed study was made using spectroscopic ellipsometry of the optical properties of these films before and after annealing, detailing the dependence of the optical constants (n, k), and the optical energy band gap (E_g) on the annealing process.

The objective of the present work is to expand the study of the effects of post deposition annealing on the structure, composition, morphology, and the optical and electrical properties of FVAD SnO_2 thin films. Annealing in Ar was decided on to avoid the effects of oxidation that are possible during the annealing in air. The film structure, surface morphology, and composition were determined by XRD, AFM and XPS diagnostics. The optical characterization of the films was carried out using spectrophotometry and ex situ variable angle spectroscopic ellipsometry (VASE). The electrical resistivity of the samples was determined with four-point probe method.

2. Film preparation and characterization

A cathode made of a tin was used to deposit SnO_2 films by FVAD. The deposition system comprised of a vacuum arc plasma source, and a magnetic quarter-torus macroparticle filter. The deposition system was previously described by Ben-Shalom et al. [11] and Kaplan et al. [13], however, in the present work the substrates were placed 15 cm further away from the macroparticle filter exit. The arc current was 150 A, and the deposition pressure was 0.67 and 0.93 Pa. Film deposition time was 120 or 180 s, on $50 \times 50 \times 1$ mm commercially polished UVFS substrates. The deposition was performed with substrates at RT and the films were annealed in argon (Ar) at 400 and 600 °C. The annealing temperature was monitored and controlled during the annealing, and was constant ±2 °C. The annealing in Ar lasted 50 min in total: 5 min heating time, 30 min annealing time, and 15 min cooling time.

XRD patterns were recorded using a symmetric Bragg geometry 'Scintag' powder diffractometer equipped with Cu K_α radiation source, and a liquid-nitrogen-cooled Ge solid-state detector. The film grain size was determined by the Scherrer equation [19] from the widths of first Bragg reflections, corrected for instrumental broadening. In addition, the lattice parameters a and c for the tetragonal structure were calculated using:

$$d_{hkl} = \frac{1}{\sqrt{\frac{h^2+k^2}{a^2} + \frac{l^2}{c^2}}}, \tag{1}$$

where h, k, and l are the integer indexes of the lattice planes, and a and c are the lattice constants [20].

The surface morphology (grain size and surface roughness) was investigated with an atomic force microscope (Park Scientific Instruments model M5 with Proscan image-processing software), using the non-contact AFM mode with UL20B cantilevers and conical tips of 10 nm radius and 12° angle. The elemental composition of the films on the surface and in the bulk was determined using a PHI scanning 5600 AES/XPS multi-technique system and Ar ion sputtering.

Optical transmission in the wavelength range of 250–1100 nm relative to air of all films was determined using a UV–VIS–NIR double beam spectrophotometer (JASCO V-530). A variable angle spectroscopic ellipsometer (J.A. Woollam M-2000) with rotating analyzer was used to record the ellipsometric parameters Psi (Ψ) and Delta (Δ), obtaining the ratio of the complex Fresnel reflection coefficients, r_p and r_s (p – in the plane of incidence, and s – perpendicular to the plane of incidence) polarization in terms of the ellipsometric parameters according to:

$$\rho = \frac{r_p}{r_s} = \tan\psi \exp(i\Delta). \tag{2}$$