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Structural, optical, and morphological properties of laser ablated ZnO doped Ta_2O_5 films

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ABSTRACT

ZnO doped tantalum oxide films (doping concentration 0, 1, 3 and 5 wt.%) have been prepared by pulsed laser deposition technique in reactive oxygen atmosphere and the films are annealed at temperatures 973 and 1173 K. The films are characterized using grazing incidence X-ray diffraction (GIXRD), micro-Raman and Fourier transform infrared (FTIR) spectroscopy, atomic force microscopy (AFM) and UV–visible spectroscopy. XRD analysis shows that the ZnO doped films annealed at 973 K are crystalline in nature, whereas, the annealed counterpart of pure Ta_2O_5 is amorphous. On annealing at 1173 K, the undoped film shows good crystallinity, whereas, the ZnO doped film presents a decline in crystallinity compared to that of the films annealed at 973 K. The lattice constants, particle size and biaxial strains of the films are calculated from the XRD data. FTIR and micro-Raman measurements confirm the presence of Ta–O, Ta–O–Ta and O–Ta–O bands in the films. Ta_2O_5 nanorings of diameter around 700 nm have been observed in the AFM micrographs of 3 and 5 wt.% ZnO doped Ta_2O_5 films. Optical parameters like transmittance, reflectance, band gap energy, refractive index, and extinction coefficient of the films are calculated and are found to vary with ZnO doping.

1. Introduction

Ta_2O_5 is an interesting material with very high dielectric constant ($\varepsilon_r \approx 25$), high refractive index ($n \approx 2.2$ @ $\lambda = 633$ nm), wide band gap ($E_g = 4.2$ eV) and transparent nature in a wide wavelength range from 300 nm to 2 μm [1,2]. It is widely used for applications like optical waveguides, interference filters, anti-reflection coatings, electroluminescent devices [3,4], corrosion barrier coatings, solid state oxygen sensors and thin film catalysts [5,6]. It has gained the attention as a memory dielectric mainly due to the excellent step coverage characteristics and high dielectric constant combined with relatively low leakage currents enabling high values of charge storage [7]. In the chemical point of view, Ta_2O_5 is an interesting material, as the complexity of its crystal structure allows it to accomodate many different dopant ions in significant concentrations with only minor changes in crystal structure [8]. TA_2O_5 possess excellent chemical and thermal stability and promise good compatibility with standard microelectronic processing operations [9].

Ta_2O_5 films can be deposited by a number of techniques such as chemical vapour deposition [10], sol–gel synthesis [11], sputtering [12], electron beam evaporation [13], pulsed laser deposition (PLD) [14–19], etc. The versatility of PLD lies in the fact that many experimental parameters like laser fluence, wavelength, pulse duration and repetition rate, preparation conditions, including target-to-substrate distance, substrate temperature, back ground gas and pressure etc., can be altered, which then have a strong influence on the film properties. Moreover in this method, since the energy source is located outside the chamber, the use of ultrahigh vacuum (UHV) as well as ambient gas is possible [20].

In the present investigation, ZnO doped (0,1, 3 and 5 wt.%) Ta_2O_5 thin films are deposited on quartz substrates using pulsed laser deposition technique and annealed in air at temperatures 973 and 1173 K for 1 h. It is well known that the annealing temperature not only improves the crystal quality of thin films, but also leads to the reaction between the film and the dopant as well as the substrate, especially at high annealing temperatures [21]. The suppression in crystallization in Ta_2O_5 films by doping with ZnO are explained using GIXRD, FTIR, micro-Raman and AFM studies.

2. Experiment

High purity Ta_2O_5 powder (99.99% pure, Sigma–Aldrich) is mixed with (0, 1, 3 and 5 wt.%) ZnO powder (99.99% pure, Sigma–Aldrich) with polyvinyl alcohol (PVA), which acts as a binding agent. The mixed powder is grounded well using agate mortar and pressed into pellets of diameter 11 mm and thickness 5 mm

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using a KBr press under a pressure of 1.5 tonnes. The pellets are heated to temperature of 873 K with a temperature rise of 4 K/min for removing the binding agent. The pellets are then sintered at a temperature of 1273 K for 10 h and the sintered pellets are used as targets for laser ablation. The deposition of the films is performed inside a stainless steel vacuum chamber with a *Q*-switched Nd: YAG laser (Quanta–Ray INDI–series, Spectra Physics), using frequency doubled wavelength of 532 nm with a maximum energy 250 mJ (pulse width – 7 ns and repetition frequency – 10 Hz). Before irradiation, the vacuum chamber was evacuated down to a base pressure $\sim 10^{-6}$ mbar. The target is fixed at an angle of 45° to the direction of the laser beam. The deposition of the films is done at room temperature (300 K) on quartz substrates kept at a distance of 6.5 cm (on-axis) from the target using laser energy 55 mJ under an oxygen ambience (partial pressure 0.002 mbar) for duration of 15 min. The target is rotated with a constant speed ~33 rpm during ablation to avoid pitting of target at any given spot and to obtain uniform thin films. The films are annealed at temperatures 973 and 1173 K. The as-deposited Ta_2O_5 films doped with ZnO (0, 1, 3 and 5 wt.%) are designated as TO, 1ZTO, 3ZTO and 5ZTO, respectively. The corresponding films annealed at 973 K are designated as TO973, 1ZTO973, 3ZTO973 and 5ZTO973, respectively, and that annealed at 1173 K are designated as TO1173, 1ZTO1173, 3ZTO1173 and 5ZTO1173, respectively. The thickness of the films is calculated using a Stylus Profilometer.

The crystalline structure of the films is investigated by Grazing Incidence X-Ray diffraction (GIXRD) using Siemens D5000 diffractometer with Cu-Kα radiation at wavelength $\lambda = 1.5406$ Å. The angle of incidence of X-rays is fixed to be 0.5° for all the GIXRD measurements. Micro-Raman spectra of films are recorded using Labram-HR 800 spectrometer equipped with an excitation radiation of wavelength $\lambda = 488$ nm from an argon-ion laser. Spectra are acquired by an 1800 greeds/mm grating, a super-notch filter having a cut-off at 50 cm^{-1} and a Peltier cooled CCD camera, allowing a spectral resolution of about 1 cm^{-1}. Laser radiation of power 5 mW was focused on to a spot of 2 mm size during Raman measurements for all the samples. FTIR spectra of the films are recorded in the 650–1200 cm^{-1} wave number region using FTIR-Thermo-Nicolet Avatar 370 spectrophotometer using pure quartz plate as the reference to obtain the subtracted spectra of the deposited films. The surface morphology and surface roughness of the films are studied using atomic force microscopy (AFM) in the contact mode (Digital Instruments Nanoscope E) equipped with Si_3N_4 100 μ cantilever having a force constant of 0.58 N/m and radius of the tip ~20 nm. The optical transmission, absorption and reflection spectra of the films are recorded using UV-VIS-NIR spectrophotometer (JASCO V-550) in the spectral range of 190–900 nm.

3. Results and discussion

3.1. X-ray diffraction studies

XRD analysis shows that all the as-deposited films are amorphous in nature (figure not shown). The undoped films annealed at 973 K (TO973) is amorphous; whereas, the film annealed at 1173 K (TO1173) is polycrystalline in nature. Fig. 1(a) shows the GIXRD patterns of the ZnO doped Ta_2O_5 films annealed at 973 K. As evident from the patterns, film 1ZTO973 shows polycrystalline nature showing the characteristic peaks of orthorhombic β-Ta_2O_5 phase (JCPDS data card no. 89-2843) with preferred orientation of crystal growth along (0 0 1) plane. The XRD pattern of 3ZTO973 shows a decline in crystallinity with the appearance of a single weak peak of lesser intensity along (0 0 1) direction. However, the XRD patterns of 5ZTO973 show better crystalline nature with the same crystalline phase as in 1ZTO973. Fig. 1(b) shows the GIXRD spectrum of the JCPDS card no. 89-2843 used for indexing the peaks observed in the films.

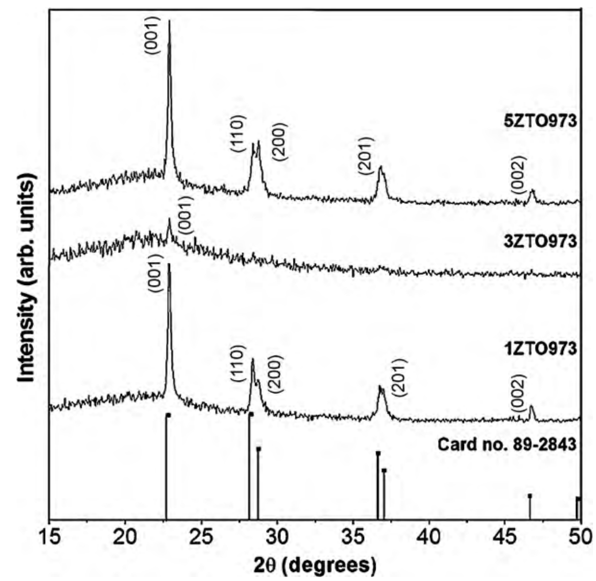

Fig. 1. GIXRD patterns of ZnO doped Ta_2O_5 films annealed at 973 K and standard card no. 89-2843.

Fig. 2 shows the GIXRD patterns of the films annealed at 1173 K. The XRD patterns of TO1173 film show a polycrystalline nature with the presence of orthorhombic β-Ta_2O_5 (O) phase (JCPDS data card no. 89-2843) with preferential orientation along (0 0 1) plane. It is interesting to note that for the film 1ZTO1173, there is a drastic decline in crystallinity with the appearance of only a single less intense peak corresponding to (0 6 1) plane of the cubic Ta_2O phase (JCPDS data card no. 34-0977). In 3ZTO1173 film, a slight improvement in crystallinity can be seen, with appearance of orthorhombic β-Ta_2O_5 (O) phase (JCPDS data card no. 89-2843), but with only lesser number of peaks. The XRD pattern of the film 5ZTO1173 also present orthorhombic β-Ta_2O_5 (O) phase (JCPDS data card no. 89-2843) with improved crystallinity compared to 3ZTO1173 film, but the intensity and sharpness of the peaks are less compared to the film T01173. The GIXRD results of the standard card (card 89-2843) have also been given in Fig. 1 for comparison.

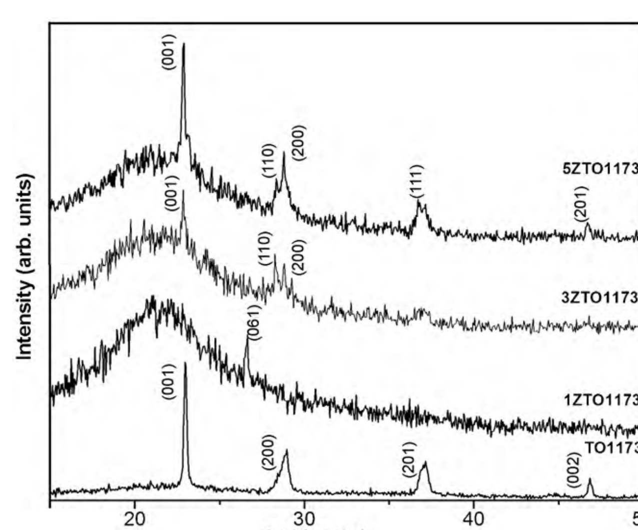

Fig. 2. GIXRD patterns of undoped and ZnO doped Ta_2O_5 films annealed at 1173 K.