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Preparation, microstructure and photoelectrical properties of Tantalum-doped zinc oxide transparent conducting films

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ABSTRACT

Transparent and conducting Tantalum-doped zinc oxides thin films have been prepared for the first time by RF magnetron sputtering method on glass and silicon substrates at room temperature. The doped contents are 0 wt.%, 2 wt.%, 5 wt.%, 7 wt.% and 10 wt.%. The test result shows that Ta element in the film is in the state of Ta^{5+}. The ratio of O/Zn is 84.73% for ZnO:Ta film doped with 5 wt.% Ta_2O_5, which indicates the films is in a state of oxygen deficiency. As the content of Ta increases, the crystallite size has been estimated to be in the range of 9.4–13.5 nm. AFM studies indicate the maximum average particle size 94.46 nm and the minimum surface roughness 4.480 nm can be obtained for the ZnO:Ta films with the Ta_2O_5 content of 5 wt.%. These structural changes are accompanied by significant variations of electrical property and optical property. The resistivity of this film first decreases and then increases with the increase of the Ta_2O_5 content. The optical property analysis shows that the average transmittance in the visible range is above 85% for all the films. The optical band gap value of the film initially increases and then shows a decrease with the increase of the Ta_2O_5 content. The ZnO:Ta films containing 5 wt.% Ta_2O_5 presents the maximum optical band gap 3.38 eV. These findings shows that the highest figure of merit obtained is $2.20 \times 10^{-4}\ \Omega^{-1}$ for the as-grown ZnO:Ta films doped with 5 wt.% Ta_2O_5.

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1. Introduction

The technology of photovoltaic conversion and display has been developed to a new level in the past few decades, giving a push to the field of transparent conducting oxide. Transparent conducting oxide films have been widely applied as transparent electrodes for light-emitting diodes and solar cells [1,2]. The materials of TCO are the oxidate of Zn, Sn, In, and Cd. As an important wide band gap (3.37 eV) semiconductor with a large exciton binding energy (60 meV), ZnO has triggered great interest due to its great performance and potential applications in electro-optical, ferroelectric, pyroelectric and piezoelectric [3,4]. Compared with other materials of TCO, ZnO based transparent conducting film has the advantages of lower cost, non-poisonous, environmental friendly, relatively lower deposition temperature and the ability of keeping steady under the hydrogen plasma. Usually, undoped ZnO has higher electrical resistivity, while doping Al, Ga, Ta, etc., can reduce the resistivity.

Ta has good chemical stability, relatively higher refractive index and lower absorption rate in the visible spectral region and high dielectric constant [5]. The doped Ta^{5+} can give more electrons than Zn^{2+} that compared with ITO it will decrease the impurity level.

In this study, the series of different mass fractions of ZnO:Ta films were prepared by RF magnetron sputtering. The chemical composition, structure, surface, topography, electrical and optical property were investigated using X-ray photoelectron spectrometer (XPS), X-ray diffractometer (XRD), Atomic Force Microscopy (AFM), ultraviolet–visible spectroscope (UV–Vis) and four-point probe instrument.

2. Experimental

The substrates of glass and silicon slices were firstly cleaned by ultrasonic in acetone for 10 min, in deionized water for 10 min, then in ethyl alcohol for 10 min. After drying, they were placed into the ultra high vacuum magnetron sputtering apparatus (JGP560I). The target materials were ceramics of different mass fraction of Ta_2O_5 (0 wt.%, 2 wt.%, 5 wt.%, 7 wt.% and 10 wt.%) and ZnO(99%) sinter forging. Sputter for 30 min. The sputtering conditions are in Table 1.

The microstructures of ZnO:Ta were tested by XRD (MAC, M18XHF) employing CuKα radiation. The thickness of the films was characterized by surface profiler (XP-1). The surface morphology of ZnO:Ta films was tested by AFM (AJ-III). XPS (Thermo, ESCALAB250) was employed to analyze the surface composition of the samples. The absorption spectra of samples were recorded by an UV–Vis spectrophotometer (Shimadzu, UV-2550) within the wavelength range of 200–900 nm. And the electrical resistivity of the films was characterized by four-point probe instrument (SZ-82).

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Table 1
Experimental conditions for RF sputtering ZnO:Ta films.

Parameter	Data
Background vacuum degree (Pa)	9.0×10^{-4}
Flow of Ar (SCCM)	30
Sputtering pressure (Pa)	0.7
Voltage (V)	450
Sputtering current (A)	0.18
Target-substrate distance (mm)	60
Substrate temperature (K)	≈293
Sputtering time (min)	30

3. Results and discussion

3.1. Composition analysis

Fig. 1 is the XPS survey spectrum of ZnO:Ta film doped with 5 wt.% Ta_2O_5. It shows that surface layer of the films contains C, O, Zn and Ta.

Fig. 2 is the binding energy of Zn $2p_{3/2}$ on the face of the film. From the figure, the peak locates on 1021.85 eV, just according with the bulks of ZnO (1021.75 eV), which shows that the form of Zn in the film is Zn^{2+}, not elemental Zn [6,7].

Fig. 3 is the Photoelectron spectroscopy of O 1s. The map can be exploded to three peaks of 530.31 eV (O_I), 530.97 eV (O_{II}) and 532.17 eV (O_{III}). O_I stands for the O^{2-} in the hexagonal wurtzite, while O_{II} correspond to the O^{2-} of anoxic area in the ZnO. O_{III} stands for the absorbed Oxygenium, which exist in $-CO_3$, H_2O, –OH and O_2. To calculate the proportion of O/Zn, the O_I and O_{II} are effective. Chen [8] discovered that in the Al-doped ZnO films the O 1s also has three different chemical states.

In Fig. 4 photoelectron spectroscopy of Ta 4f, the characteristic peaks is on 26.24 eV and 28.04 eV, which stand for Ta $4f_{7/2}$ and Ta $4f_{5/2}$. Obviously, the valence state of Ta is more approaching to the Ta^{5+} in Ta_2O_5 (26.3 eV) than the zero valence Ta (21.7 eV) [9,10]. So the form of Ta in the films is Ta^{5+}.

The percentage of each component in the film can be calculated by the formula [11]:

$$x\% = \frac{\frac{A_x}{S_x}}{\sum_{i=1}^{N} \frac{A_i}{S_i}}$$

The result is in Table 2. The O/Zn is 84.73%, less than the ideal stoichiometric ratio of ZnO, explaining that the film is oxygen-poor. Then, the proportion of Ta/(Zn + Ta) is 3.29%, higher than the calculation percentage 1.9% of 5 wt.% Ta_2O_5 target. The reason is the different saturated vapor pressure of ZnO and Ta_2O_5, which the higher one of ZnO leads to the desorption of Zn on the surface of the film.

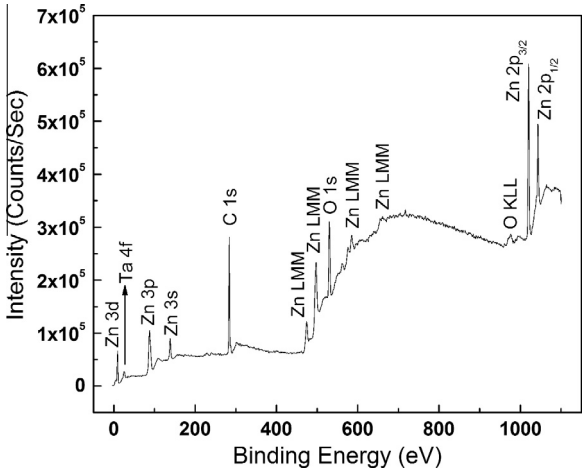

Fig. 1. XPS survey spectrum of ZnO:Ta film doped with 5 wt.% Ta_2O_5.

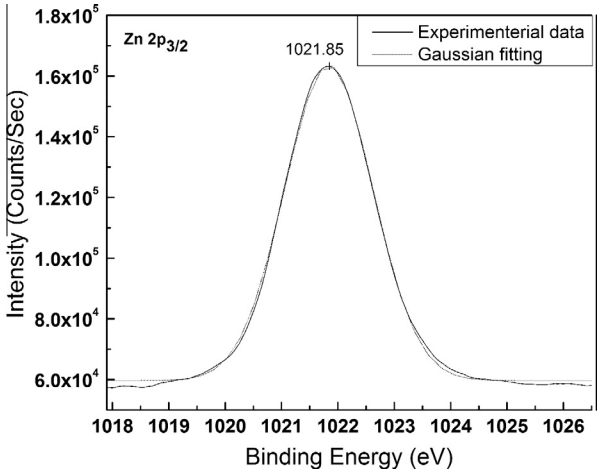

Fig. 2. Photoelectron spectroscopy of Zn 2p3/2 for ZnO:Ta films doped with 5 wt.% Ta_2O_5.

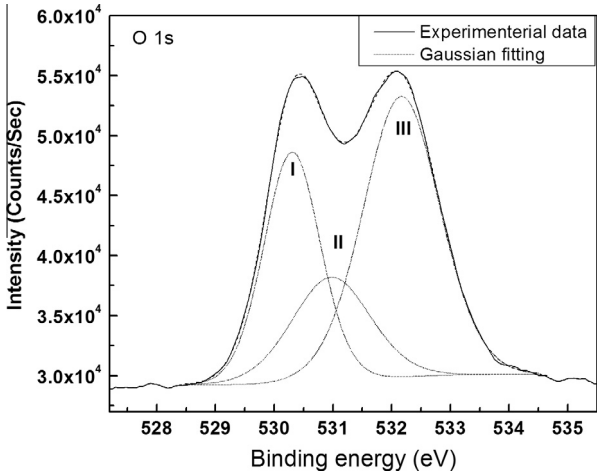

Fig. 3. Photoelectron spectroscopy of O 1s for ZnO:Ta films doped with 5 wt.% Ta_2O_5.

3.2. Microstructure analysis

Fig. 5 shows the XRD patterns of the ZnO:Ta film for different Ta_2O_5 content. The diffraction peaks are consistent with standard spectrum diagram of ZnO. For the undoped ZnO film, the highest diffraction peak is on the $2\theta = 34.18$, which represents the crystal face of (002). Besides, there are relatively lower peaks of (100), (101) and (102). While doped, all of these films only have peaks of (002) and (103) on the diffraction pattern. It illustrates that there is no new phase producing in the film, which another way of saying is the doping of Ta did not change the structure of hexagonal wurtzite. The Ta just replaced the position of Zn in the crystal lattice.

The crystal quality of the films can be evaluated by the diffraction half peak width (FWHM) and crystal particle size. Fig. 6 is FWHM and crystallite size of ZnO:Ta film with different Ta_2O_5 content. The figure shows that as the proportion of the impurities increased from 0 wt.% to 5 wt.%, the intensity of (002) diffraction

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