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Preparation of Ti-doped ZnO transparent conductive thin films by PLD method

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Ti-doped ZnO thin films were prepared on a soda-lime glass substrate without any post heat treatment by a pulsed laser deposition (PLD) method. Processing parameters such as deposition substrate temperature, the amount of Ti-doping and oxygen flow rate were investigated. It was found that the Ti-doped ZnO thin films exhibited a strongly preferred orientation along a C-axis (002) plane and their structural, electrical and optical properties depended strongly on these parameters. Transparent conducting ZnO oxide thin films with 1 mol% Ti content formed under the conditions of a substrate temperature of 100°C in an oxygen flow rate of 10 sccm showed an electrical resistivity of $3.3 \times 10^{-2} \Omega$ cm, a mean optical transmittance of 92.3% with a thickness of 480 nm.

Key words: Pulsed laser deposition (PLD), ZnO, Transparent conducing oxide (TCO).

Introduction

Zinc oxide (ZnO) ceramic is one of II-VI semiconductors with a hexagonal wurzite structure, a wide band gap of ~3.3 eV and high optical transmittance in the visible range. It also exhibits high dielectric characteristics due to its high C-axis preferred orientation and therefore ZnO has been used for many industrial applications such as varistors, transparent conducting electrodes, surface acoustic wave (SAW) filters, UV lighting emitting diodes (LEDs), emitter and laser applications, and gas sensors etc [1].

Recently, metal oxide doped ZnO thin films have been widely studied as transparent conducting oxide (TCO) materials [2] because ZnO, unlike conventionally used ITO (Indium Tin Oxide), is inexpensive, nontoxic and chemically stable under the hydrogen plasma process that is normally used for the production of solar cells [3]. However, although ZnO thin film has a high transmittance in the visible range and low electrical conductivity, the sheet resistance of pure ZnO thin film, which is in a non-stoichiometric state, increases due to either chemisorption and desorption of oxygen ion or heat treatments in a vacuum [4].

Therefore, a great deal of effort has been devoted to improving the characteristics of ZnO thin films such as high transmittance in the visible range or creating stable electrical conductivity by doping with various metallic elements [4, 7]. It was reported that ZnO films doped with 3d-transition metallic elements exhibited unique electrical, magnetic and magneto-optical properties [8, 9]. It is thought that some 3d transition metals could donate an extra free electron to the oxide system when used as dopants [10].

ZnO thin films have been fabricated using diverse deposition techniques such as chemical vapor deposition (CVD) [3, 11], a sol-gel method [7], pulsed laser deposition (PLD) [4, 5, 10], magnetron sputtering [6] and a spray pyrolysis method [12]. Among these deposition methods, the PLD method results in a high deposition rate, producing a thin film which is quite close to the composition of the target materials which crystallizes film at a lower substrate temperature because of the high kinetic energy (> 1 eV) of atoms and ionized species produced by the laser in the PLD method [13]. This study is aimed at property enhancement of ZnO thin films by studying the effect of titanium doping on the structural, electrical, and optical properties of the films on soda lime glass substrates using PLD.

Experimental Procedure

A KrF eximer laser (Lambda physics LPX 305, wavelength: 248 nm, and pulse duration: 30 ns) was used for the deposition of Ti-doped ZnO films on soda lime glass substrates. The laser was operated at a repetition rate of 10 Hz with an energy density of 200 mJ/cm². The distance from target-to-substrate was 4.8 cm. The substrate was heated by a halogen lamp and its temperature was measured by a thermocouple. Pure ZnO (99.99%) and TiO₂ (99.99%) powders were used for preparing the target material and the level of Ti-doping of the ZnO target was varied to have 1, 2, 3, and 5 mol%. The mixed powder of ZnO and TiO₂ was

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ball-milled for 6 hours and calcined for 4 hours at 800°C. The prepared powders were sintered using a SPS (spark plasma sintering, Sumimoto coal Mining, S-515S, Japan) method typically at 950°C for 20 minutes [14]. The sintered target was typically 25 mm in diameter and 4 mm in thickness. The soda lime glass substrate was cut into 1 cm \times 1 cm pices, cleaned in an ultrasonic bath with acetone, ethanol and distilled water for 10 minutes and dried with nitrogen gas.

The deposition chamber was initially evacuated to 3.0×10^{-6} torr (4.0 × 10⁻⁴ MPa) and a substrate was heated from room temperature to 500°C. After deposition, the substrate was cooled to room temperature without post heat treatment at the same working pressure. During deposition, oxygen background gas was introduced into the chamber to the desired working pressure of 100 mtorr $(1.33 \times 10^{-5} \text{ MPa})$, and the oxygen flow rate was controlled using a pressure/flow controller (FC260E). In order to prevent the formation of pits an the particular area and maintain a highly uniform film, the target was rotated at a speed of 15 rpm. The aims was to establish the optimum deposition conditions for a high quality film as a function of oxygen flow rate, substrate temperature and level of Tidoping.

Film thickness and sheet resistance (R_s) were measured using a stylus profilometer (Tencor Alpah-Step 250, USA) and a 4-point probe, respectively. By assuming that the thickness of film was uniform, the film resistivity (ρ) was determined using a simple relation [3], $\rho = R_s \cdot t$, where t is the film thickness. Optical transmittance was measured by a UV-VIS-IR spectrometer (Perkin-Elmer Lambda 25, USA) in the visible range from 400 nm to 800 nm. The crystal structure and preferred orientation were determined using X-ray diffraction (XRD, Rigaku, D/max-2C, Japan) and scanning electron microscopy (SEM, JEOL JSM-5900LV, Japan).

Results and Discussion

The X-ray diffraction peaks of the deposited films as a function of Ti-doping content are shown in Fig. 1. All films were deposited at 100°C, at a working pressure of 100 mtorr (1.33×10^{-5} Mpa) and with an oxygen flow rate of 10 sccm. The deposited films exhibited a strong preferred (002) plane orientation but the crystalline peaks become wider with increasing Ti-doping content, indicating an increment of crystal disorder. The excess Ti element over the solubility limit decreases the grain size in the ZnO films and therefore increases the electrical resistivity, because of grain boundary scattering and ionized impurity scattering [5]. Therefore, the optimum doping level was thought to be 1 mol%; which value is well-matched with a consideration of the electrical properties of the film.

Figure 2 shows the X-ray diffraction patterns of the 1



Fig. 1. X-ray diffraction patterns for Ti-doped ZnO thin films as a function of Ti content. (substrate temperature; 100°C, and oxygen flow rate; 10 sccm)



Fig. 2. X-ray diffraction patterns for 1 mol% Ti-doped ZnO thin films as a function of substrate temperature. (10 sccm)

mol% Ti-doped ZnO thin films as a function of substrate temperature. The peak intensities of the film formed at room temperature were weak but the intensity of the (002) peak was increased strongly with increasing the substrate temperature. This indicates the film was in an amorphous state at room temperature and then preferentially oriented to the (002) plane by increasing the substrate temperature. The crystallinity of the film increased with an increase of the substrate temperature but its other properties were degraded, so the optimum substrate deposition temperature was determined to be 100°C. Dense Ti-doped ZnO thin films were observed in all samples (Fig. 3).

The electrical properties of the Ti-doped ZnO thin films were found to be strongly dependant on the process parameters such as composition, substrate temperature and oxygen flow rate. Figure 4 shows the vari-



Fig. 3. FE-SEM cross-sectional images of 1 mol% Ti-doped ZnO thin films deposited at (a) room temperature, (b) 100°C, (c) 200°C and (d) 500°C. (10 sccm)



Fig. 4. Dependence of resistivity vs. Ti content of ZnO thin films. (100°C, 10 sccm)

ation of electrical resistivity as a function of Ti-doping content. These films were deposited at a substrate temperature of 100°C under a working pressure of 100 mTorr (1.33×10^{-5} Mpa), and oxygen flow rate of 10 sccm. The resistivity of the undoped film was 4.3×10^{-1} Ω cm but one of 1 mol% Ti-doped ZnO film decreased to 3.3×10^{-2} Ω cm. This decrease in resistivity is thought to be due to excess free electrons as a result of substitutional incorporation of Ti⁴⁺ ions into Zn²⁺ ion sites, or incorporation of Ti⁴⁺ ions at interstitial positions from the Ti-doping.



Fig. 5. Dependence of resistivity vs. substrate temperature for 1 mol% Ti-doped ZnO thin films. (10 sccm)

However, the resistivity of the film decreased by 1 mol% Ti-doping to a minimum value and then gradually increased on increasing the Ti-doping content. This is attributed to an excess of Ti-doped content above the solubility limit which may have formed second phase cluster of TiO₂, which would act as carrier traps rather than as electron donors and would induce crystal disorder, which would cause phonon scattering and ionized impurity scattering [3, 4]. As confirmed from the XRD results in Fig. 1, the films showed a strong C-axis, (002) and (004) plane preferred orientation, but the (002) peak lost its sharpness withan increase in Ti-doping content. Therefore, crystal disordering due to the excess Ti-doping content above 1 mol% increased its resistivity as shown in Fig. 4.

According to the variation of resistivity as a function of the deposition substrate temperature (Fig. 5), the resistivity of films decreased from 4.2 Ω cm (at room temperature) to $3.8 \times 10^{-2} \Omega$ cm (at 100°C). This decrease is attributed to the diffusion of Ti atoms into Zn²⁺ cation sites rather than into interstitial sites or grain boundaries. When Ti⁴⁺ is substituted into a Zn²⁺ site, the Ti atoms act as an electron donor in the Ti-doped ZnO film and the free electron content is increased, and as a result diffusion of Ti atoms this increased with increasing substrate temperature and therefore the resistivity is decreased by the excess free electrons [15].

This explanation may be confirmed by reference to Fig. 2 that is the resistivity decreased due to a reduction of grain boundary scattering resulting from an increase in grain size with crystallization of the film increasing as a function of an increase in the substrate temperature [16]. However, the resistivity increased again above 100°C, due to the microstructural variation of the soda lime glass substrate resulting from the contamination of the film by the alkali ion, sodium, which diffused from the soda lime glass substrate when the substrate temperature increased [17]. The number of alkali ions which diffuse into the grain boundaries of the film is increased bt a rise in the substrate temperature and therefore the depletion layer at the grain boundaries is increased.

Figure 6 shows the variation of electrical properties with oxygen flow rate. The resistivity of films, after reaching a minimum value of 1.6×10^{-2} Ω cm at 5 sccm, gradually increased with an increase in the oxygen flow rate. This increment is thought to be due to a decrease in the amount of oxygen vacancies in the films as the oxygen flow rate increases. The decrease



Fig. 6. Dependence of resistivity of 1 mol% Ti-doped ZnO thin films as a function of oxygen flow rate. (100°C)

in oxygen vacancy concentration induces an increment of resistivity because of the decreased free electron content, since one oxygen vacancy creates two free electrons.

From Fig. 7, the variation of the mean transmittance as a function of substrate temperature in the visible range from 400 nm to 700 nm is shown. The mean transmittance gradually increased with substrate temperature from room temperature up to 200°C, where it is reached a maximum value of 93.2%, and subsequently decreased as the substrate temperature increased further [18]. The maximum optical transmittance of the film results from high crystallinity but the subsequent decrease of optical transmittance is due to the weakness of the crystallinity and interaction between the film and the glass substrate.

Figure 8 demonstrates the variation of mean optical transmittance with oxygen flow rate. The film exhibits a low optical transmittance at a low oxygen flow rate of 5 sccm but its optical transmittance slightly



Fig. 7. Optical mean transmittance of 1 mol% Ti-doped ZnO films as a function of substrate temperature. (10 sccm)



Fig. 8. Optical mean transmittance of 1 mol% Ti-doped ZnO films as a function of deposition oxygen flow rate. (100°C)

increases by increasing the oxygen flow rate. This tendency is also related to the development of crystallinity in ZnO films [19].

Summary

Ti-doped ZnO transparent conductive thin films were fabricated by a PLD method on soda lime glass substrates, and their electrical, optical and structural properties were investigated as a function of Ti-doping content (1~5 mol%), substrate deposition temperature (RT~500°C) and oxygen flow rate (5~100 sccm). The 1mol% Ti-doped ZnO thin film exhibited the lowest resistivity. The resistivity increment above 1 mol% Ti content seems to be attributed to Ti clusters forming a depletion layer and crystal disorder. The resistivity of 1 mol% Ti-doped ZnO thin film was $1.6 \times 10^{-2} \,\Omega cm$ with the lowest value at 5 sccm oxygen flow rate, but the optical transmittance shows a relatively low value of 86.9%. This low resistivity at a lower oxygen flow rate results from an increment in the number of oxygen vacancies at the higher oxygen flow rate. The optimun conditions for forming 1 mol% Ti-doped ZnO thin films was a substrate temperature of 100°C, an oxygen flow rate of 10 sccm, which gave a typical thickness of 480 nm, an electrical resistivity of $3.3 \times 10^{-2} \Omega$ cm and a mean transmittance of 92.3% in the visible range.

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