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Physical properties of TiO_2-doped zinc oxide thin films: Influence of plasma treatment in H_2 and/or Ar gas ambient

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ABSTRACT

Transparent conducting TiO_2-doped zinc oxide (ZnO:Ti, TZO) thin films were prepared by radio-frequency magnetron sputtering and followed by plasma treatments with different $H_2/(H_2 + Ar)$ flow ratio (R_{H2}). The electrical, structural, and optical properties of the TZO thin films were investigated. Experimental results showed that resistivities of all the TZO thin films decreased after plasma treatment regardless of ambient gas, and the lowest resistivity was 1.13×10^{-3} Ω-cm (or 62% reduction) for $R_{H2} = 50\%$. All the TZO thin films exhibited a (002) preferred orientation along the c-axis, indicating a typical wurtzite structure. Surface roughness of the TZO films slightly increased from 1.58 nm to 1.63 −2.75 nm (RMS value) after plasma treatments. Average optical transmittance of the TZO films (containing glass substrates) in the visible region (400−700 nm) did not considerably change after plasma treatments and ranged from 82.7% to 84.3%. The largest figure of merit (FOM), 5.02×10^{-3} Ω^{-1}, was achieved for the plasma-treated film with $R_{H2} = 50\%$, and it increased by 237% as compared with that of the as-deposited film. These results indicate that the H_2 + Ar (1:1) plasma treatment is more effective than pure H_2 or Ar plasma treatment in improving opto-electronic properties of transparent conducting TZO thin films.

1. Introduction

Transparent conductive oxide (TCO) films have been extensively used in optoelectronic devices. Indium tin oxide (ITO) films are the commonly used transparent conductive oxide at present [1–3]. However, ITO films are unstable in high temperature environment and indium is rare and toxic; alternative materials for ITO films, therefore, are continually studied.

Impurity-doped zinc oxide (ZnO) films are promising substitutes to replace ITO films as transparent conducting films due to non-toxicity, abundance in nature, and chemical/thermal stability. The trivalent cation-doped ZnO films such as ZnO:Al [4–7], ZnO:Ga [8,9], and ZnO:In [9,10] present superior electrical conductivity and transparency over the visible spectrum and have been widely studied in past few years. The quadrivalent cation may provide two free electrons to contribute the conductivity in ZnO thin films. Titanium (Ti) is a quadrivalent cation and has a radius of 0.068 nm which is close to that of Zn (0.074 nm). Therefore, it is satisfactory as a donor in ZnO. The Ti content in the ZnO film is an important parameter because excess Ti may exist in interstitial site and act as the scattering center. Only a small amount of doped Ti^{4+} could contribute more electrons and avoid acting as scattering centers. A few researchers have studied the properties of TZO films [11–16]. For example, Chung et al. [12,13] investigated effects of Ti content, deposition pressure, and substrate temperature on TZO films prepared by radio-frequency (RF) magnetron sputtering. Our previous study [16] investigated influence of in situ hydrogen doping and substrate temperatures on physical properties of TZO thin films and achieved a low resistivity of 9.2×10^{-4} Ω-cm under the process conditions: the $H_2/(H_2/Ar)$ flow ratio of 7.5% and the substrate temperature of 373 K. Although these earlier literature indicated that the appropriate amount of Ti and H in TZO thin films and the optimal deposition parameters could enhance the opto-electronic characteristics of TZO thin films, many research efforts for further improvement on characteristics of various TCO thin films have been proposed continuously.

A few previous studies [17–24] make use of post-deposition treatments such as annealing and plasma treatment to enhance characteristics of TCO thin films. Fang et al. [17] studied the effects of vacuum annealing on the properties of the ZnO:Al (AZO) films

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and indicated that the annealing process led to improvement of (002) orientation, increased carrier concentration and band-gap of the AZO films. Oh et al. [18] described that the hydrogen annealing resulted in decreased resistivity and blue shift of absorption edge in transmission spectra of AZO films. Ohashi et al. [23] reported the influence of pulsed argon–hydrogen plasma on opto-electronic properties of ZnO films and concluded that hydrogen was actually a cause of shallow donors and hence increased carrier concentration of the films. We previously reported the effects of H_2 plasma treatment on the physical properties of AZO and TZO films with different substrate temperatures [6,24]. Those results motivated us to further study the characteristics of plasma treated TZO under different plasma conditions.

In this study, TZO films were prepared on glass substrates by using reactive RF magnetron sputtering and followed by plasma treatments under various H_2/Ar flow ratios. The plasma treatment was performed with a plasma-enhanced chemical vapour deposition (PECVD) system because it is convenient and practical for large-area applications such as flat-panel displays and thin-film solar cells. Effects of various plasma treatments on structural, electrical, and optical properties of TZO films were explored.

2. Experiments

Zinc oxide (99.999%) powder mixed with 1.5 mol% titanium oxide (99.999%) powder was mixed to form a TZO composition. After being dried and ground, these TZO powders were calcined at 1273 K and then ground again. Next, the powders were uniaxially pressed into a pellet of 5-mm thickness and 2-inch diameter using a steel die. After debinding, the TZO pellet was sintered at 1623 K for 3 h to form a ceramic target for sputtering. The TZO thin films were prepared on glass substrates (Corning 1737 glass) in an RF magnetron sputtering system. The TZO films with a thickness of about 330 nm were deposited at substrate temperature of 573 K with an RF power of 100 W. The base pressure was 6.67×10^{-4} Pa (6.67×10^{-6} mbar). The working pressure was maintained at 6.67×10^{-1} Pa (6.67×10^{-3} mbar) in Ar (99.995%) gas. The substrate holder spun at 40 revolutions per min. After deposition, the TZO films were treated by plasma under various H_2/Ar flow ratios at 573 K for 60 min by using a parallel-plate PECVD system.

The film thickness was determined by a spectroscopic ellipsometer (Nano-view, SE MF-1000). The structure of the TZO film was examined by X-ray diffraction (XRD) (PANalytical) analysis with Cu-Kα radiation ($\lambda = 1.54056$ Å, $\theta - 2\theta$ scan mode). The morphology of the TZO films was observed using a field emission scanning electron microscope (FE-SEM) (JEOL, JSM-6700) and an atomic force microscope (AFM) (Digital Instrument, NS4/D3100CL/Multimode). The resistivity, Hall mobility, and carrier concentration were measured using the Van der Pauw method (BIO-RAD, HL5500IU) at room temperature. The optical transmittance was measured by a UV/VIS/NIR spectrophotometer (Jasco V-570) in the 220–2500 nm wavelength range.

3. Results and discussion

The influence of RF power of the post-deposition plasma treatment on resistivity of TZO thin films was investigated and shown in Fig. 1. The plasma treatment time is 60 min. Results show the film resistivity decreased with increasing RF power up to 80 W, then increased for a further increase in RF power. It is considered that high RF power could increase the ion energy in plasma, which enhances hydrogen doping, surface cleaning, and annealing effect. However, a higher RF power than 80 W might result in high energetic ion bombardment leading to deteriorate the structure of the films. Thus, the following experiments were performed with a fixed

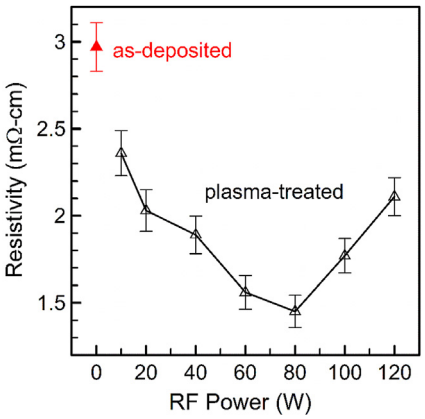

Fig. 1. Resistivity of TZO thin films as a function of RF power of the post-deposition plasma treatment.

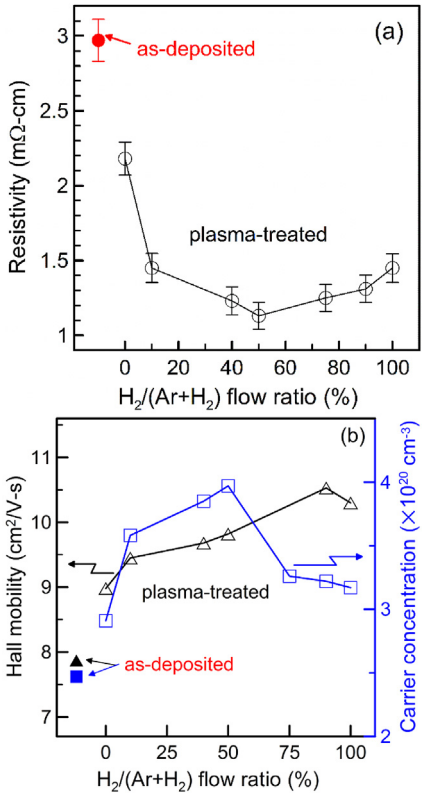

Fig. 2. Resistivity, Hall mobility, and carrier concentration for the as-deposited and various plasma treated TZO films.

RF power of 80 W during plasma treatments.

Fig. 2 shows the resistivity, Hall mobility, and carrier concentration of TZO thin films treated by plasma with various $H_2/(H_2+Ar)$ flow ratio (R_{H2}). The resistivity, Hall mobility, and carrier concentration of the as-deposited film were 2.97×10^{-3} Ω-cm, 7.84 cm^2/V-s, and 2.47×10^{20} cm^{-3}, respectively. After plasma treatment, the film resistivity remarkably decreased regardless of flow ratio compared to the as-deposited sample. The plasma treatment with $R_{H2} = 50\%$ achieved the lowest resistivity of 1.13×10^{-3} Ω-cm, a reduction of 62% as compared to the as-deposited films. We previously reported that in situ hydrogen doping and pure hydrogen plasma treatment effectively improved the conductivity of TZO thin films [16,24]. For the 573 K-deposited TZO thin films, the former

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