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Effect of process conditions on the optoelectronic characteristics of ZnO:Mo thin films prepared by pulsed direct current magnetron sputtering

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ABSTRACT

The purpose of this study is to use pulsed magnetron sputtering to deposit transparent conductive ZnO:Mo (MZO) film on a Corning 1737 glass substrate. Various process parameters, including power, work pressure, pulsed frequency, film thickness, and substrate temperature, were analyzed for their effects on the microstructure and optoelectronic characteristics of MZO thin film. Experimental results show that MZO film with a low resistivity of approximately 8.9×10^{-4} Ω cm and a visible light transitivity of greater than 80% can be obtained using a Mo content of 1.77 wt.%, sputtering power of 100 W, work pressure of 0.4 Pa, pulsed frequency of 10 kHz, and film thickness of 500 nm without heating. The value of optical band gap of MZO increased upon increasing the crystallinity of the MZO thin film, and the range of the optical band gap of MZO thin film is from 3.30 to 3.35 eV.

1. Introduction

In_2O_3, SnO_2, and ZnO are the primary components of transparent conducting oxide thin (TCO) films. They have very good optoelectronic properties, and are widely used in all kinds of optoelectronic devices, including flat panel displays, light-emitting diodes, and solar cells [1–4]. Using TCO film as the front electrode in solar cells requires low resistivity, high transmittance, and better light trapping structure characteristics to enhance the light path in solar cells and increase light absorption [5–7]. Though very costly, ZnO-based TCO thin films are non-toxic and easy to fabricate [8,9]. These films have exhibited a high development potential as they are not easily affected by hydrogen plasma processing [10], and have been widely studied. Based on the electron configurations of Mo and Zn, the valence electron difference between Mo^{6+} and Zn^{2+} is 4. Therefore, only a tiny amount of Mo doping can produce enough free carriers to reduce the ion scattering effect [11]. In addition, Mo has high thermal stability that is enhanced even further when it is doped with ZnO. As a result, ZnO-based TCO thin films have a great potential in numerous applications. Investigations on ZnO:Mo (MZO) film are very scarce in the literature. However, Xiu et al. [12] used radio frequency (RF) magnetron sputtering to sputter MZO film onto a glass substrate. The lowest possible resistivity of MZO film with a thickness of 400 nm is 9.2×10^{-4} Ω cm, and its visible light transmittance exceeds 84%.

The pulsed direct current (DC) magnetron sputtering process is one of the best methods for the preparation of Mo:ZnO films because it has a lot of advantages such as low substrate temperature, good surface roughness, and low cost. Furthermore, it has a higher deposition rate of defect-free ceramic films than the conventional RF magnetron sputtering process and it can particularly alleviate the occurrence of arc events at the oxide targets involved in the continuous DC sputtering process [13,14]. However, it has a disadvantage such as surface damage [12]. The main objective of our research is to prepare MZO thin film on a glass substrate by pulsed magnetron sputtering. This paper also investigates the effect of various process parameters on the microstructure and optoelectronic characteristics of MZO thin films.

2. Experimental details

This study reports the preparation of MZO thin film on a Corning 1737 glass substrate using pulsed DC magnetron sputtering. The position of Mo metallic pieces on the ZnO target material was varied to alter the doping content of Mo within ZnO. This study also examines the effect of process parameters on the microstructure and optoelectronic characteristic of MZO film by adjusting process parameters, including power (20–120 W), work pressure (0.4–1.33 Pa), pulsed frequency (10–50 kHz), film thickness (200–800 nm) and substrate temperature (300–473 K). The deposition rate and thickness of thin films were measured using an alpha-step profilometer (Kosaka laboratory Ltd. ET3000). Chemical compositions were analyzed by an energy dispersive spectrometer (Hitachi S3000N). The chemical state of the thin film was analyzed by an X-ray photoelectron spectroscope (XPS, PHI 5000, VersaProbe) with Al Kα (1486.6 eV, width 0.85 eV), and the pressure in the XPS analysis chamber was 1×10^{-7} Pa. In order to avoid the alteration of the bond

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due to pre-sputtering, the sample was without cleaning. XPS surveys spectra (0–1100 eV) on the initial surface and on the bulk of MZO films. Film resistivity, carrier concentration, and mobility were measured by Hall effect measurements (ECOPIA HMS-2000). Crystalline analysis was conducted using an X-ray diffraction (XRD, CuKα, λ = 1.54052 Å). The optical band gap energy was initially obtained from the transmittance chart by extending the straight line part and extrapolating it on the horizontal axis. That is, the straight line intersects with the wavelength. The value of the optical band gap, E_g, can be calculated from Eq. (1). Here, h is the Planck constant, c is the optical velocity, and λ is the optical wavelength.

$$E_g = \frac{hc}{\lambda}. \quad (1)$$

3. Results and discussion

Fig. 1 shows the electrical properties resulting from various Mo contents on MZO thin film at a power of 100 W, work pressure of 0.4 Pa, film thickness of 500 nm, frequency of 10 kHz, pulse reverse time of 5 μs, and duty cycle of 95%. As Fig. 1 shows, when the Mo content reached 1.28 wt.%, the resistivity began to decrease continuously, and the carrier concentration and carrier mobility increased. When the Mo content was 1.77 wt.%, it had the lowest resistivity of 8.9×10^{-4} Ω cm. As the Mo content increased, the carrier concentration and carrier mobility decreased and the resistivity increased. Fig. 2 shows the electrical properties of MZO thin film under various powers and a Mo content of 1.77 wt.%, work pressure of 0.4 Pa, film thickness of 500 nm, frequency of 10 kHz, pulse reverse time of 5 μs, and duty cycle of 95%. This figure shows that at 100 W, the lowest resistivity obtained was 8.9×10^{-4} Ω cm. However, when the sputtering power exceeded 100 W, the resistivity increased. Jung et al. [13] used DC magnetron sputtering to deposit indium tin oxide (ITO) thin film and Fortunato et al. [14] used RF magnetron sputtering to deposit ZnO:Al (AZO) film. These studies show that the resistivity decreases when the sputtering power increases, which is similar to part of the results in the current study; the reason can be analyzing the XRD results. Fig. 3 shows the XRD results, and Fig. 2 shows the full width at half maximum (FWHM). When the power is 100 W, Fig. 3 shows a sharp (002) XRD peak; this indicates a better film crystallinity. At a lower or higher deposition power, the film crystallinity became loose; meanwhile, the collision from higher energy plasma spaces destroyed the structure, leading to the possible deterioration of the microstructure of the thin film. Malinovska et al. [15] used RF magnetron sputtering to deposit AZO film, showing that when the power is too high, the plasma spaces bombard the film surface with relatively large energy. This, in turn, leads to the generation of defects on the film surface and a deterioration in film crystallinity. Lin et al. [16] prepared ZnO thin film by RF magnetron sputtering, showing that increasing the sputtering power caused a narrowing XRD peak in the ZnO thin film. This finding matches the experimental result of this experiment. Figs. 4 and 2 depict samples prepared under the same process parameters. These figures show the effects of various sputtering powers on the transmittance and optical band gap of MZO thin film. Fig. 4(a) shows slightly different thin film transmittances at various sputtering powers, but they all reached an average transmittance of over 80% in the visible light region. Fig. 4(b) shows that as the sputtering power reached 100 W, the maximum optical band gap obtained was 3.34 eV. A comparison with the XRD results in Fig. 3 reveals a close relationship between E_g and thin film crystallinity.

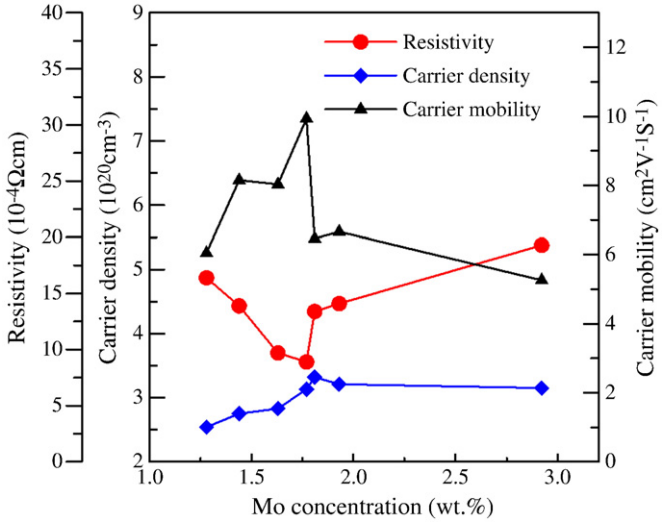

Fig. 1. Resistivity, carrier concentration, and Hall mobility of MZO films were prepared under various Mo contents.

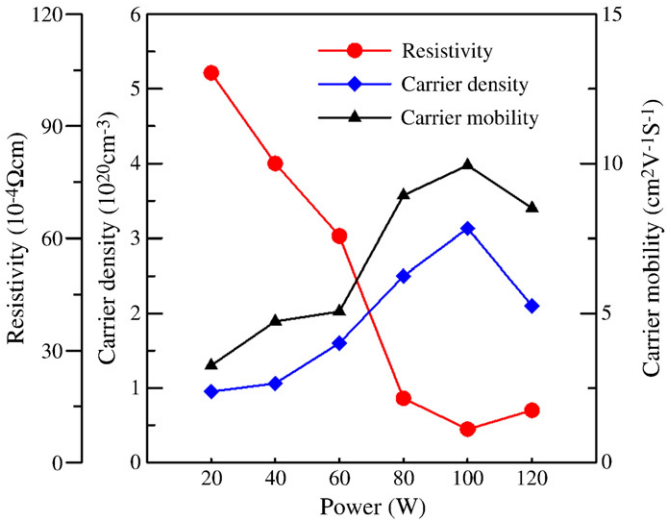

Fig. 2. Resistivity, carrier concentration, and Hall mobility of MZO films were prepared under various powers.

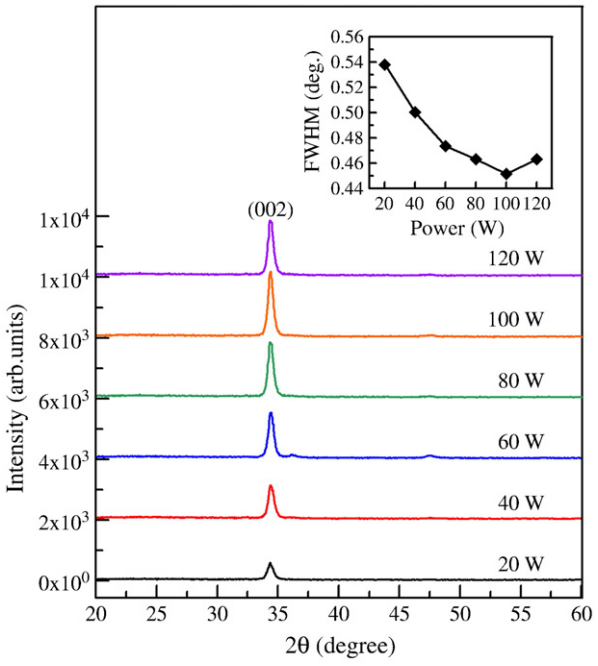

Fig. 3. XRD patterns and FWHM of MZO films were prepared under various powers.