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Surface textured molybdenum doped zinc oxide thin films prepared for thin film solar cells using pulsed direct current magnetron sputtering

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ABSTRACT

In this study, we examined the effect of etching on the electrical properties, transmittance, and scattering of visible light in molybdenum doped zinc oxide, ZnO:Mo (MZO) thin films prepared by pulsed direct current magnetron sputtering. We used two different etching solutions – KOH and HCl – to alter the surface texture of the MZO thin film so that it could trap light. The experimental results showed that an MZO film with a minimum resistivity of about 8.9×10^{-4} Ω cm and visible light transitivity of greater than 80% can be obtained without heating at a Mo content of 1.77 wt.%, sputtering power of 100 W, working pressure of 0.4 Pa, pulsed frequency of 10 kHz, and film thickness of 500 nm. To consider the effect of resistivity and optical diffuse transmittance, we performed etching of an 800 nm thick MZO thin film with 0.5 wt.% HCl for 3–6 s at 300 K. Consequently, we obtained a resistivity of $1.74–2.75\times10^{-3}$ Ω cm, total transmittance at visible light of 67%–73%, diffuse transmittance at visible light of 25.1%–28.4%, haze value of 0.34–0.42, and thin film surface crater diameters of 220–350 nm.

1. Introduction

In_2O_3, SnO_2, and ZnO are the main materials used for transparent conducting oxide (TCO) thin films. They have very good optoelectronic properties and are widely used in all types of optoelectronic devices, such as flat panel displays, light-emitting diodes, and solar cells [1–4]. To use TCO thin films as front electrodes in solar cells, we need low resistivity, high transmittance, and better light trapping structural characteristics to enhance the light path in solar cells and increase light absorption [5–7]. ZnO-based TCO thin films are less expensive, non-toxic and have a simple production process [8,9]. They have a very high development potential and may not be easily affected by the hydrogen plasma process [10]; therefore, they have been widely studied. Based on the electron configurations of Mo and Zn, the difference between the valence electrons of Mo^{6+} and Zn^{2+} is 4; therefore, a very small amount of Mo doping can reach enough free carriers and reduce the ion scattering effect [11]. In addition, Mo has high thermal stability; when used to dope ZnO, the thermal stability may be increased. TCO thin films have great application potential. Investigations of MZO films are lacking in the literature. However, Xiu et al. [12] used RF magnetron sputtering to sputter MZO films onto a glass substrate. MZO film with a thickness of 400 nm showed a minimum resistivity of 9.2×10^{-4} Ω cm, and the visible light transmittance was greater than 84%. In addition, surface textured TCO has a light trapping structure. This light trapping structure can – through reflection, refraction, and scattering – divide the incident light into rays traveling at different angles to enhance the light path in solar cells and increase light absorption [13]. Moreover, the light scattering capability of the TCO front electrode depends on the dimensional features and surface morphology. The main objectives of this study are to use pulsed magnetron sputtering to deposit transparent, conductive MZO thin films on a glass substrate and to study the effect of etching on the electrical properties, transmittance, and scattering of visible light after the thin film is etched for application in thin film solar cells as the front electrode.

2. Experiments

In this study, the pulsed DC magnetron sputter method was used to prepare MZO thin films on 1737 glass substrates. To study the effect of the Mo content (1.28–2.92 wt.%) on the thin film conductivity, the position of the Mo metallic pieces on the ZnO target material was varied as a means to alter the doping content of Mo within ZnO. Meanwhile, the effect of altering the process parameters – including power (20–120 W), working pressure (0.4–1.33 Pa), pulsed frequency (10–50 kHz), film thickness (200–800 nm), and substrate temperature (300–473 K) – on the microstructure and optoelectronic characteristics of MZO films was studied. The thin films were analyzed with an α-step (Kosaka laboratory Ltd. ET3000) to measure the deposition rate and thickness. The chemical compositions were analyzed with an energy dispersive spectrometer (Hitachi S3000N). The chemical state of the thin film was analyzed by an X-ray

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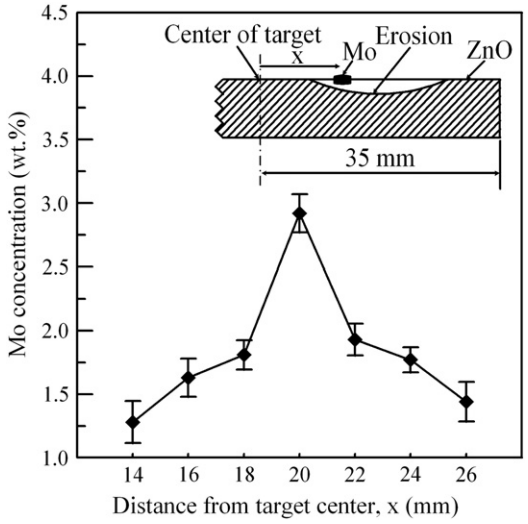

Fig. 1. Correspondence chart of Mo metallic piece location and Mo content at a power of 100 W, working pressure of 0.4 Pa, film thickness of 500 nm, frequency of 10 kHz, and pulse reverse time of 5 μs.

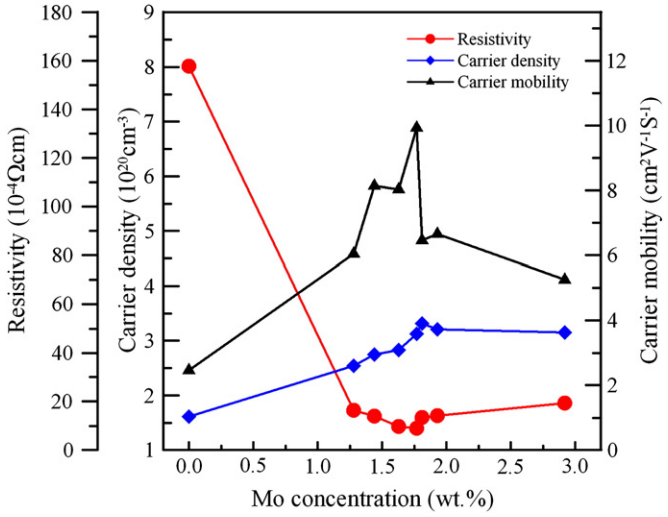

Fig. 3. High-resolution Mo 2p5/2 core level spectrum.

photoelectron spectroscope (XPS, PHI 5000, VersaProbe) with Al Kα(1486.6 eV, width 0.85 eV), the pressure in the XPS analysis chamber was 1×10^{-7} Pa. In order to avoid the alternation of bond due to pre-sputtering, the sample was analyzed the chemical state of each element directly. XPS survey spectra (0–1100 eV) on the initial surface and on the bulk of MZO films. The values of resistivity, carrier concentration, and mobility were obtained by Hall effect measurements (ECOPIA HMS-2000). The crystal structure was analyzed by X-ray diffraction (XRD, SHIMADZU XRD-6000) with Cu Kα radiation at an incident angle of 2°. In addition, the initial optical band gap energy can be obtained from the transmittance chart by extending the straight-line portion and extrapolating it on the horizontal axis. That is, it intersects with the wavelength; using Eq. (1), the value of the optical band gap E_g can be calculated. Here, h is the Planck constant, c is the optical velocity, and λ is the optical wavelength.

$$E_g = \frac{hc}{\lambda} \tag{1}$$

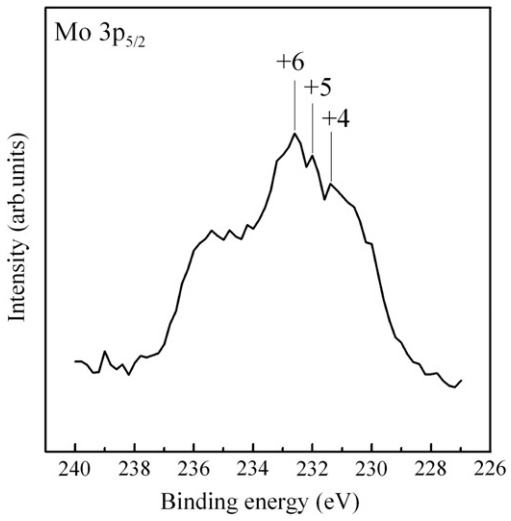

Fig. 2. Resistivity, carrier concentration, and Hall mobility of MZO films prepared at various Mo contents.

After the thin film was prepared, we selected the MZO thin film with the lowest resistivity and with average visible light transmittance greater than 80%; the wet etching method was then performed at room temperature (300 K). Etching solutions of 0.5 wt.% HCl were used to immerse the films for 3, 6, and 9 s; the specimens were dipped into 33 wt.% KOH etching solutions for 33, 66, and 100 s to obtain the optimal light trapping structure. A thermal field emission scanning electron microscope (JEOL TF-SEM JSM7000F) was then used at an operating voltage of 15 kV to further understand the surface morphology of the thin film. A changeable angle optical characteristic measurement system with an integrating sphere of 38 mm diameter (Hon Ming MFS-630) was used in the wavelength range of 250–900 nm to measure the total transmittance and specular transmittance. Using Eqs. (2) and (3), the diffuse transmittance spectrum and haze value of strength percentage of the scattered light were

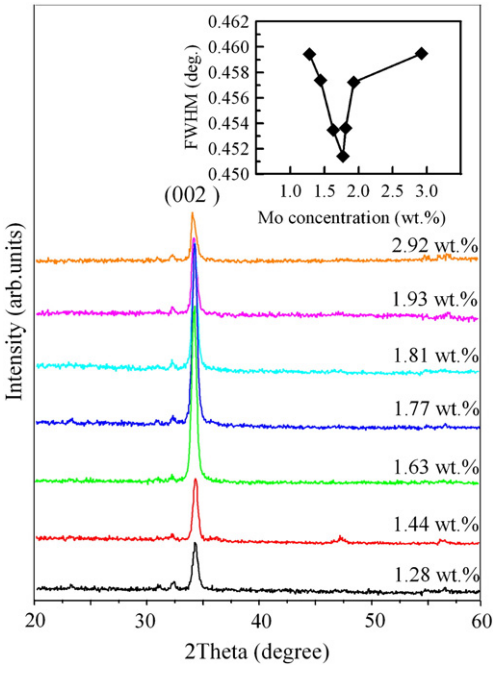

Fig. 4. XRD pattern and FWHM of MZO films prepared at various Mo contents.