Mechanical Properties of ZnO:Mo Transparent Conducting Oxide Thin Film Prepared by Sputtering

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In this study, molybdenum doped zinc oxide (ZnO:Mo, MZO) transparent conductive films were prepared by using pulsed DC magnetron sputtering on glass substrates. The mechanical properties of MZO films under various film preparation parameters were investigated. Experimental results show that the amount of Mo doping with 1.81 wt % has the highest elastic modulus and hardness. The hardness of MZO film increased in conjunction with the deposition power, film thickness, and substrate temperature. The elastic modulus of MZO film increased in conjunction only with the deposition power and film thickness. The elastic modulus or hardness of MZO film is a function of the tilt angle of the crystal deposited. The values of the elastic modulus of the MZO films are in the range 110 ∼ 130 GPa.

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I. INTRODUCTION

Although In$_2$O$_3$ and SnO$_2$ transparent conductive film is widely used in industry, due to high temperature processes resulting in a decrease of the conductivity; it is not stable in performance, resulting in a decrease of the conductivity; therefore replacement materials have attracted increasing attention. ZnO-based transparent conducting oxide (TCO) thin films are less expensive, non-toxic, and have a simple production process [1–3]. They have a very high development potential and are not easily affected by the hydrogen plasma process [4]; therefore, they 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 [5]. In addition, Mo has a high thermal stability, that is enhanced even further when it is doped into ZnO. As a result, ZnO-based TCO thin films have great potential in numerous applications. Currently, the MZO films have been widely studied [6–9]. However, investigations of the mechanical properties for MZO films are lacking in the literature. 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 the preparation conditions on the mechanical properties of ZnO-based TCO thin films.

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II. EXPERIMENTAL

The MZO films were prepared by using pulsed DC magnetron sputtering on Corning 1737 glass substrates, through the placement on the ZnO target of various Mo metals, which were doped with various Mo contents. The MZO thin films were prepared by using pulsed DC magnetron sputtering, and were modulated by a number of process parameters, including power, film thickness, and substrate temperature, to analyze the MZO thin film microstructure and mechanical properties. The chemical compositions were analyzed with an energy dispersive spectrometer (Hitachi S3000N). The thin films were analyzed with an α-step (Kosaka laboratory Ltd. ET3000) to measure the deposition rate and thickness. The crystal structure was analyzed by X-ray diffraction (XRD, SHIMADZU XRD-6000) with Cu Kα radiation at an incident angle of 2°. A thermal field emission scanning electron microscope (JEOL TF-SEM JSM7000F) was then used at an operating voltage of 3 kV to further understand the surface morphology of the thin film. A nanoindentation was used to determine the hardness and elastic modulus of the MZO thin films. During the test, the diamond Berkovich-type indenter was used with a tip radius of 100 nm and edge angle of 130.6°. The maximum loading was 1 mN, and the load and unload times were set to 30 seconds (loading rate of 0.33 mN/s). The indentation depth of the film thickness was controlled to less than one-tenth of the thickness of the MZO thin film.

III. RESULTS AND DISCUSSION

Fig. 1 illustrates the hardness and the elastic modulus of the MZO film under various Mo content. Doping was 1.81", if the Mo doping is fixed how can the “hardness and elastic modulus” be “higher” and “increased with the doping level”, but perhaps the problem only starts with “the higher hardness and elastic modulus” (that phrase might be ok—but only if it is followed by something suitable); “higher” always implies a comparison, let me ask “higher than what?” the sentence does not say. Mo doping of 1.81 wt % resulted in the highest hardness and elastic modulus, which increased proportionally with the doping level, was highest. He Mo atoms are replaced by Zn atoms.” A system with less slip on the basal planes, when the Mo atoms are replaced by Zn atoms.” Because polycrystalline ZnO film is a hexagonal close-packed structure, an increase of the Mo content might result in a system with less slip on the basal planes, when the Mo atoms are replaced by Zn atoms. The atomic radius of Mo (0.145 nm) is greater than the atomic radius of Zn (0.135 nm), therefore the Mo atoms will have a compressive strain, and the replacement of the Mo atoms around the dislocation will result in the lowering of the overall strain energy, and thus enhance the mechanical properties. However, the amount of Mo doped in the lattice structure formed trap will continue to increase, resulting in lattice distortion and, consequently, a decrease of the mechanical properties. Fig. 2 shows the XRD patterns and full width at half maximum (FWHM) results from MZO films deposited with various Mo content. With the increase of the Mo content to 1.81 wt %, the MZO film average grain size of the grain growth increased from 16.6 nm to 17.4 nm. Veprek [10] proposed that an improved intensity is achieved when
the grain size is in the range of $10 \sim 20$ nm., which is due to the deformation mechanism problem; the intended meaning is not clear. in which the large grain is converted to the smaller grain under the grain boundary sliding mechanism. Fig. 3 shows the SEM cross-sectional images under various Mo contents of the MZO films. Fig. 3(c) demonstrates that the tilt angle $\theta$ enhances the overall structure of the intensity; a vanishing tilt angle angle $\theta$ of the structure enables the probe pressure to be easily directed, and exposes the flaws of the columnar structure of the interface, which lead to a lower structural strength. If the structure has a tilt angle $\theta$, it is more difficult to interface the probe directly onto the defect, however it can increase the structural strength.

**FIG. 1:** The hardness and elastic modulus of MZO film as a function of Mo content.

Figures 4 and 5 illustrate the load-depth curve and hardness and elastic modulus under various deposition power of the MZO film deposited, respectively. As illustrated in Fig. 5, when the deposition power was increased to 100 W, the elastic modulus of the MZO thin film increased slightly; however, the film hardness markedly increased when the deposition power was increased from 80 to 100 W. Bachari [11] indicated that this phenomenon may be attributed to Zn and O at various deposition rates, because Zn has a higher sputtering rate than O when the deposition power is increased. The increase in the energy of the incident atom is caused by the re-sputtering effect of the rate increase, which results in a lower crystallinity and increased roughness. Spaces caused by high-energy sputtering may change the surface structure resulting in a slight improvement in hardness. Fig. 6 shows the SEM cross-sectional images of the MZO films under various deposition
FIG. 2: XRD patterns of MZO films prepared with various Mo content.

As shown in Fig. 6 (c), when the deposition power was increased to 100 W, the agglomerated grain size increased and the grain shape of the MZO film gradually became angulated. When the deposition power was low, the MZO films grew in several directions, leading to the smooth aggregation of granules, as illustrated in Figs. 6 (a) and (b). Under this condition, we observed that the growth of the MZO films occurred in the non-preferred orientation, which is consistent with the results of the XRD analysis from reference [6]. The increase of the MZO film deposition power led to the grain agglomerates becoming gradually angulated, which helps to increase the deposition power of the film for a particular preferred orientation of growth, and is also consistent with the XRD patterns from reference [6].

Fig. 7 shows the hardness and elastic modulus of MZO film under various film thick-
FIG. 3: The SEM cross-sectional images of MZO films with various Mo content: (a) 1.33 wt %, (b) 1.57 wt %, (c) 1.81 wt %, (d) 2.03 wt %, (e) 2.56 wt %.

FIG. 4: The load-depth curve of MZO films prepared with various deposition power.
FIG. 5: The hardness and elastic modulus of MZO film as a function of deposition power.

FIG. 6: The SEM cross-sectional images of MZO films with various deposition power: (a) 60 W, (b) 80 W, (c) 100 W, (d) 120 W.
FIG. 7: The hardness and elastic modulus of MZO film as a function of film thickness.

FIG. 8: The hardness and elastic modulus of MZO film as a function of substrate temperature.
Fig. 9: The SEM cross-sectional images of MZO films with various substrate temperatures: (a) 300 K, (b) 373 K, (c) 473 K.

nesses. As illustrated in Fig. 7, the hardness and elastic modulus of MZO film both increase with increasing thickness. An increase in film thickness generally reduces the number of lattice defects, resulting in a more complete structure with increased crystallinity and grain size. According to previous studies [12, 13], when the film thickness is thin the nucleation of islands does not complete the connection between the islands, and a higher density of pinhole defects occur in the film. When the thickness is higher, the nucleation of the low defect density films gradually decreases.

Fig. 8 shows the hardness and elastic modulus of MZO film under various substrate temperatures. As illustrated in Fig. 10, the film hardness increased when the substrate temperature increased from 300 K to 473 K. This may also be due to the crystallinity of the film. Fig. 9 shows the SEM cross-section of the MZO films at various substrate temperatures. The columnar structure was observed when the substrate temperature was high, the surface is in a semi-dissolved state, and the film revealed a tighter cross-section.

IV. CONCLUSIONS

In this study, MZO films were prepared by using pulsed DC magnetron sputtering on glass substrates. The mechanical properties of MZO film under various film preparation parameters were investigated, which resulted in the following conclusions. The amount of Mo doping 1.81 wt % had the highest elastic modulus and hardness. The hardness of MZO film increased in conjunction with the deposition power, film thickness, and substrate temperature. The elastic modulus of MZO film increased in conjunction only with the deposition power and film thickness. The elastic modulus and hardness of MZO film is a function of the tilt angle of the deposition here, but my dictionary says that “crystalline” is an adjective. crystallinity deposited. The values of the elastic moduli of the MZO films are 110 ~ 130 GPa.

References