



Effect of Substrate Temperature and Deposition Power on the Surface Morphology and Optical Properties of ZnO:Mg Thin Films Deposited by DC Magnetron Sputtering

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Abstract

Magnesium doped zinc oxide (ZnO:Mg) thin films were deposited on soda lime glass slides by DC magnetron sputtering method. Atomic force microscope (AFM), and UV/VIS spectrophotometer were used to investigate the effect of sputtering power and substrate temperature on the surface morphology and optical properties of ZnO:Mg thin films. AFM images revealed that sputtering power and deposition temperature have significant influence on surface morphology of the ZnO:Mg thin films. For all sputtering powers and substrate temperatures investigated, ZnO:Mg films had peak transmittance above 85%. Samples deposited at 110 W sputtering power and 450 °C substrate temperature showed the best peak transmittance of > 90% at 560 nm (visible range). Optical band gap of ZnO:Mg films was in the range of 3.44– 3.69 eV depending on the substrate temperature. The results indicated the potential of the films for transparent conductor applications.

Key words: ZnO:Mg, Transparent conducting oxides, Band gap energy, Optical properties, morphology properties

Introduction

High optical transmittance is usually associated with dielectrics which are inherently poor conductors, while high electrical conductivity is usually associated with metallic materials which are usually opaque (Chopra et al. 1983). Transparent conductive oxides (TCOs) are materials with unique combination of very high optical transmittance, especially in the visible part of the solar spectrum, with high electrical conductivity (Granqvist 2007). TCOs are mainly applicable in opto-electrical devices including thin film solar cells, panel displays, liquid crystal displays, and heat mirrors (Chopra et al. 1983, Major and Chopra 1988,

Ellmer 2001, Maloda and Malisa 2020, Rwenyagila et al. 2021). Several materials are in use as candidates for TCO layer in devices. These include Fluorine doped Tin Oxide (SnO₂:F), Cadmium Oxide (CdO), Zinc Oxide (ZnO), Indium Tin Oxide (ITO) etc. ITO is a widely used TCO, however, it has several limitations, particularly toxicity and scarcity (Minami 2008). Zinc oxide (ZnO) thin films on the other hand have several advantages over other TCOs, mostly due to its chemical and mechanical stability, high abundance, nontoxic in nature and good transparency (Wenas et al. 1991, Ellmer 2001, Samwel et al. 2015).

ZnO belongs to II–IV group in a periodic table with the band gap of 3.37 eV at room temperature (Suchea et al. 2007). ZnO thin films have low conductivity and low optical transmittance in the visible range (Pawar et al. 2005). One of the possibilities to improve electrical conductivity and optical transmittance is by adding foreign elements such as B, Al, and Ga (Pholds et al. 2013, Samwel et al. 2015, Maloda and Malisa 2020). It should be noted that there exist other ways of improving ZnO properties such as fabrication of ZnO/metal/ZnO multilayer films (Rwenyagila et al. 2014). Studies have shown that it is possible to add Mg in ZnO lattice without any structural deformation due to fairly comparable radii between Mg^{2+} (0.57×10^{-10} nm) and Zn^{2+} (0.60×10^{-10} nm). ZnO doped with magnesium has its band gap enlarged compared to undoped ZnO, causing the optical absorption edge to shift to lower wavelength, and consequently increasing overall transmittance of the films. The increased transmittance may make ZnO:Mg thin film a suitable candidate material for optoelectronics (Pawar et al. 2005, Yusuf et al. 2014, Maloda and Malisa 2020).

Several factors influence physical properties of DC magnetron sputtered ZnO:Mg thin films, the most important being the deposition parameters and target composition. It was reported that, using metallic targets, one for zinc and the other for the dopant in preparing sputtered alloys of ZnO give rise to high quality films (Suchea et al. 2007). Moreover, high quality doped ZnO thin films with good physical properties can also be obtained by preparing the films from alloy targets (Samwel et al. 2015). This paper explores the effect of deposition parameters (deposition power and substrate temperature) on the surface morphology and optical properties of DC sputtered ZnO:Mg thin films.

Materials and Methods

ZnO:Mg thin films were deposited on soda lime glass substrates by DC magnetron sputtering in an argon atmosphere using Balzers BAE 250 coating unit. The sputtering

target was ZnO:Mg alloy with 95:5 wt% and 99.99% purity. The base and working pressures for film deposition were 1×10^{-5} mbar and 6×10^{-3} mbar, respectively. The films were deposited at different substrate temperatures of 300 °C, 350 °C, 400 °C and 450 °C; and sputtering powers of 80 W, 90 W, 100 W and 110 W. The optical transmission of the films was determined by UV–VIS spectrophotometer in the 300 nm to 800 nm wavelength range. The band gap of ZnO:Mg thin films was obtained through extrapolation of $(\alpha h\nu)^2$ versus $h\nu$ (photon energy) plots assuming direct band gap following Equation 1 (Sawa et al. 2018).

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \quad (1)$$

Where α is the absorption coefficient, $h\nu$ is the photons quantum energy constant, A is a constant and E_g is the band gap energy. The absorption coefficient α was determined from transmittance T measurements and film thickness t as per Equation 2 (Maloda and Malisa 2020).

$$\alpha = \frac{1}{t} \ln \frac{1}{T} \quad (2)$$

Surface morphology of the ZnO:Mg thin films was determined using Atomic Force Microscopy (Digital Instruments IIIa) in tapping mode, using RTESP7, 125 μ m pyramidal silicon tips with a resonant frequency of about 300 kHz.

Results and Discussions

The AFM images of ZnO:Mg thin films indicate that sputtering power has a significant influence in morphology of ZnO:Mg thin films. Figure 1 shows AFM micrographs for films deposited at room temperature with varying sputtering powers of 80 W to 110 W. The figure shows somewhat rough morphology with heterogeneous nano sized particles with estimated mean grain size of 1470 nm², 1484 nm², 1779 nm² and 2000 nm² for the sputtering powers of 80 W, 90 W, 100 W and 110 W, respectively (Figure 2). Moreover, the AFM cross section profiles (Inserts in Figures 1a–d) show maximum cross section (grain) height of 11.60 nm, 12.43 nm, 30.2 nm and 34 nm for films deposited with sputtering power of 80 W, 90 W, 100 W and

110 W, respectively. The data show an improvement in film grains growth with increasing sputtering power. Films prepared at 100 W and 110 W sputtering powers have relatively more homogeneous surface morphology with relatively larger and clearly defined grains. High sputtering power leads to high kinetic energy and flux of sputtered atoms on the substrate, resulting into enhanced surface diffusion of ad atoms and hence increased growth of grains (Petrov et

al. 2003). However, even at high sputtering powers, the film structure for samples prepared at room temperature was of low quality in terms of grains homogeneity. The inhomogeneous growth of the films is due to low mobility and diffusion rate possessed by the condensed atoms at room temperature. This trend was also reported for aluminum doped zinc oxide thin film (AZO) (Ghorannevis et al. 2015).

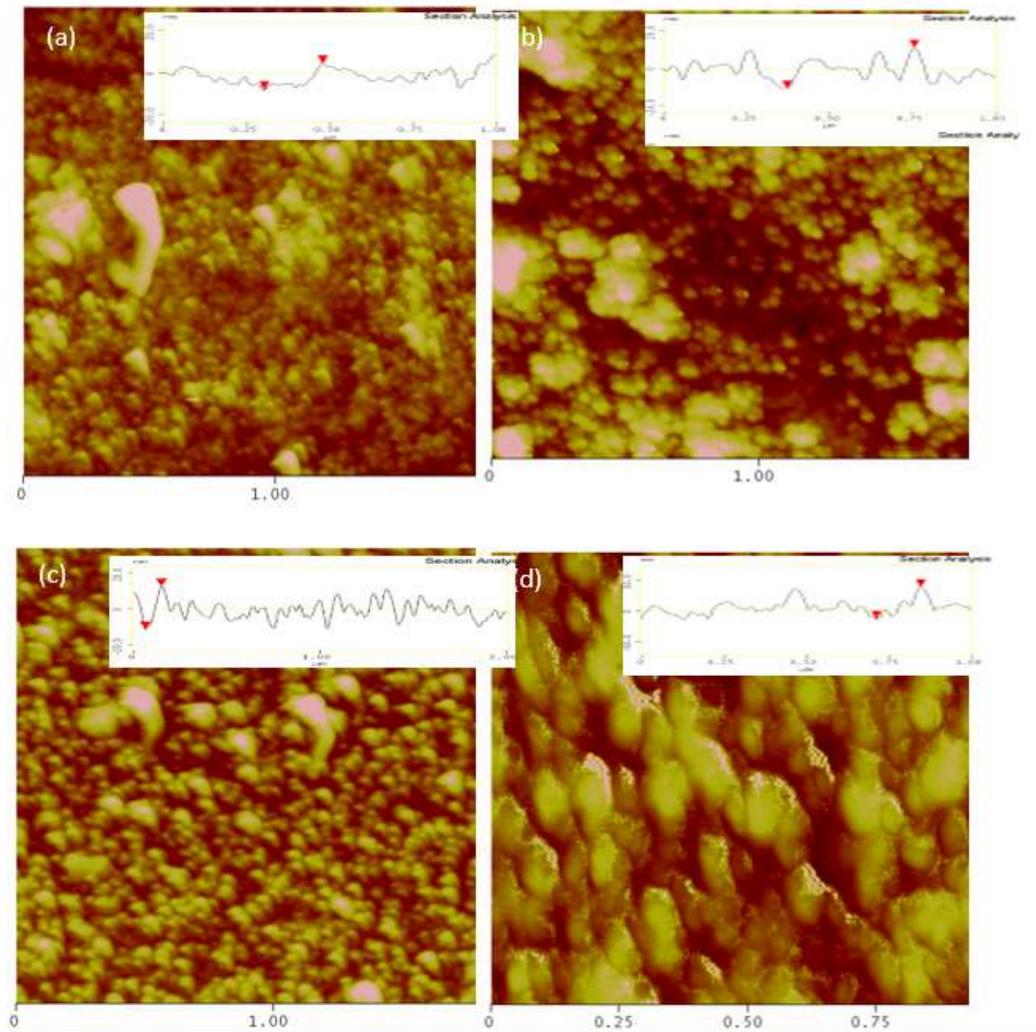


Figure 1 AFM images of magnesium doped ZnO thin films deposited at (a) 80 W (b) 90 W (c) 100 W and (d) 110 W sputtering powers. The inserts are cross-section profiles of the films.

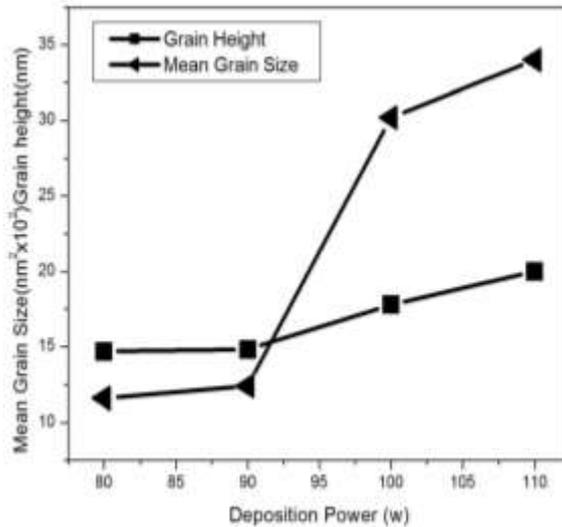


Figure 2: Variation of mean grain size and grain height of ZnO:Mg films with deposition power.

Figures 3 a - d, show surface morphology AFM images of ZnO:Mg thin films deposited at different substrate temperatures. The images show film grains and morphology evolution as the substrate temperature is increased from 300 °C to 450 °C. Samples deposited at 300 °C have inhomogeneous grains in terms of size and distribution and roughness is of very small scale as revealed in Figure 3a. The estimated mean grain size is 957 nm² and maximum cross section (grain) height is 9 nm. The grains evolution is evident when the substrate temperature reaches 350 °C and 400 °C where the grains seems to have agglomerated, more defined and larger (Figures 3 b and c). Analysis from

Figures 3 b and c, revealed that the film mean grain size and maximum cross section height are 1154 nm² and 19 nm; and 1979 nm² and 24 nm for films sputtered at substrate temperatures of 350 °C and 400 °C, respectively (Figure 4). Large, smooth and compact columnar grains with mean size of 6006 nm² and maximum cross section height of 64 nm were observed in the films deposited at substrate temperature of 450 °C (Figure 3d). This indicates that, the deposited atoms had enough thermal energy for enhanced ad atoms mobility and re-crystallization (Kumar et al. 2006, Liang et al. 2019).

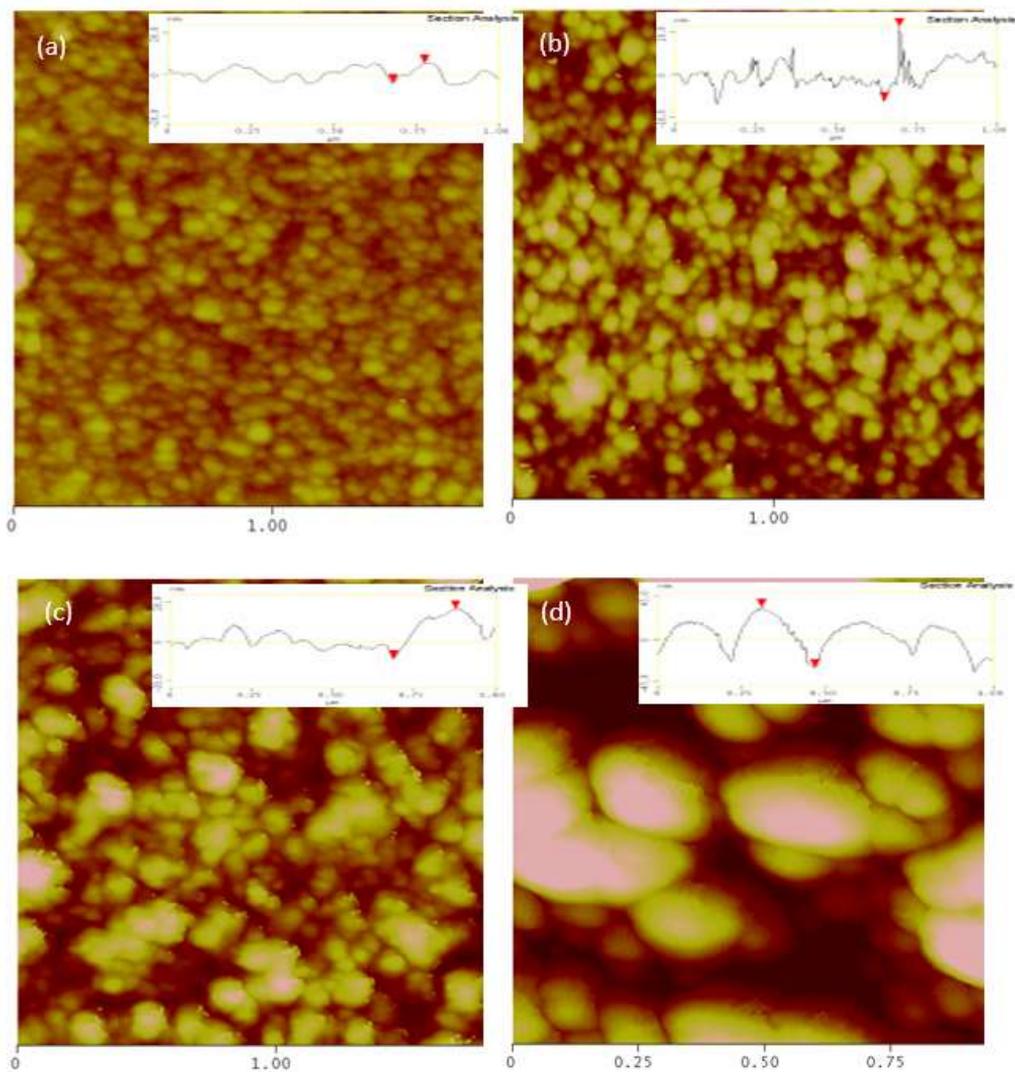


Figure 3. AFM images of ZnO:Mg thin films deposited at substrate temperatures of (a) 300 °C (b) 350 °C (c) 400 °C and (d) 450 °C. The inserts are cross-section profiles of the films.

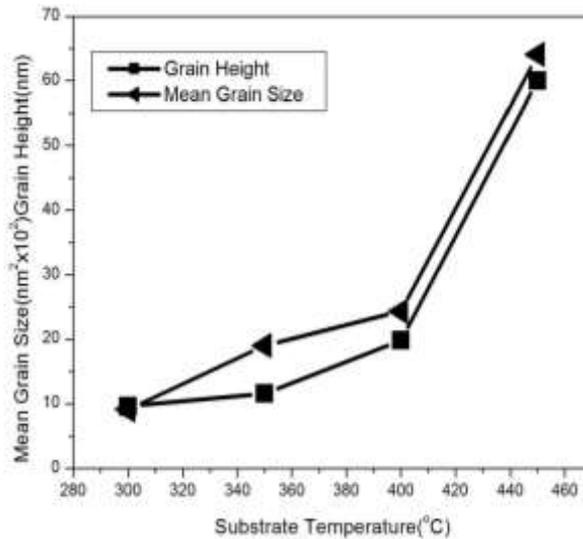


Figure 4: Variation of mean grain size and grain height of ZnO:Mg films with substrate temperature.

The transmittance spectra of ZnO:Mg thin films deposited at various sputtering powers are shown in Figure 5. The transmittance in the visible range for all films is above 80% except for films deposited at 80 W sputtering power that has a deep in the visible range at about 78%. The observed deep could be a result of poor crystallinity of the films due to slow growth rate (Lee et al. 2006). The transmittance falls sharply in the UV region for all films owing to the onset of

fundamental absorption. Films deposited at 90 W, 100 W and 110 W were observed to show improved transmittance compared to those deposited at 80 W. The improvement is attributed to reduced optical scattering as a result of reduced films roughness and improved microstructure as demonstrated by the AFM data. This observation was also reported by other authors (Selmi et al. 2010, El hamali et al. 2016).

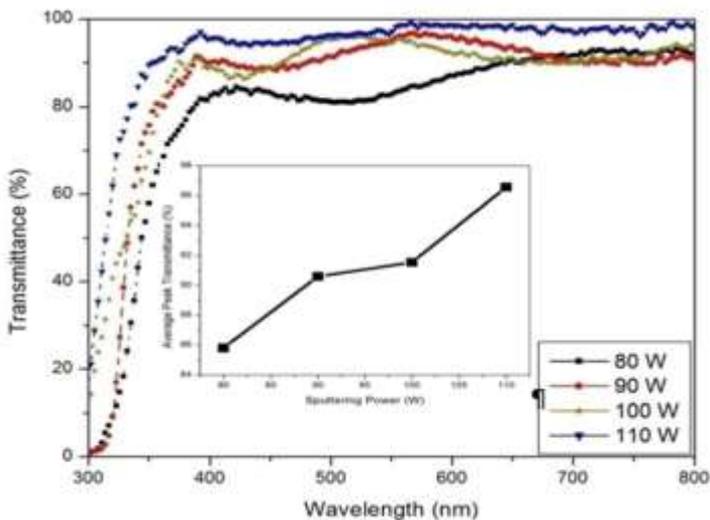


Figure 5: The influence of sputtering power on the spectral transmittance of ZnO:Mg films. The insert shows average peak transmittance as a function of sputtering power.

The transmittance spectra of ZnO:Mg thin films as a function of substrate temperature is shown in Figure 6. The figure shows interference effects in the spectra for wavelengths, $\lambda > 400$ nm. The effect is more pronounced as the deposition temperature increases from 300 °C to 450 °C indicating smoothness and low scattering loss of the films surface (Xie et al. 2012). The average

peak transmittance of the films increased with deposition temperature from ~ 81% for samples deposited at 300 °C to ~ 88% for samples deposited at 450 °C (Figure 6 insert). The results show that deposition substrate temperature enhances optical transparency of the films. Similar results were reported by Devi et al. (2015).

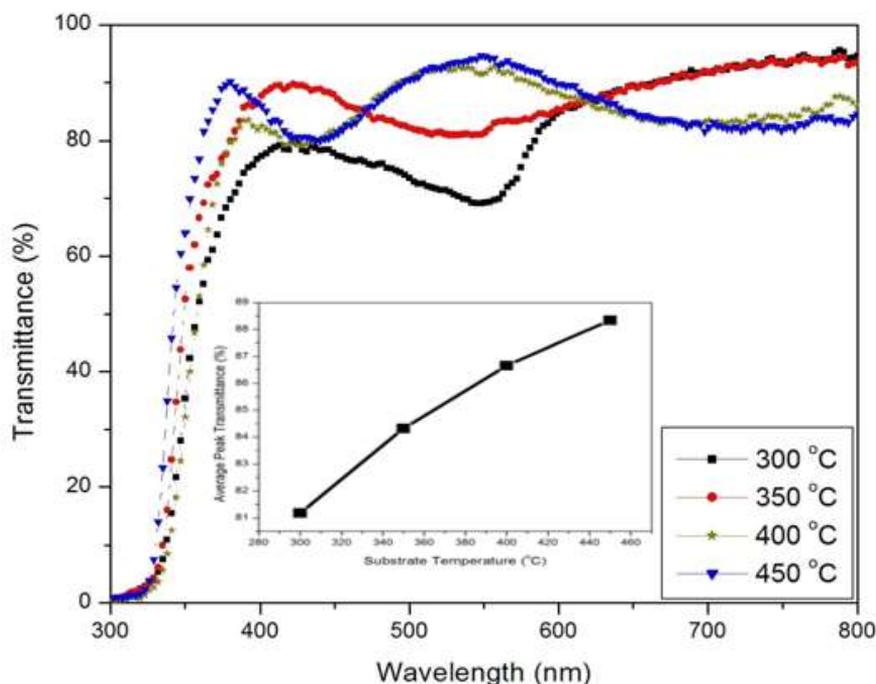


Figure 6: The influence of substrate temperature on the optical transparency of ZnO:Mg films. The insert shows average peak transmittance as a function of sputtering temperature.

Figure 6 further shows a significant blue shift in the fundamental absorption edge most likely owing to reduction in defects (Singh et al. 2007) as was observed from AFM data. The estimated band gap energy values increased with increase in deposition temperature from 3.44 eV for samples deposited at 300 °C to 3.69 eV for samples deposited at 400 °C (Figure 7). Upon further increase in substrate temperature to 450 °C, the band gap energy decreases slightly to 3.63 eV. Similar results were reported by

Devi et al. (2015). The band gap values obtained are larger than that for bulk ZnO (Suchea et al. 2007), indicating usefulness of Mg doping and high temperature deposition on improvement of ZnO based thin films as transparent conducting oxide material. The ZnO:Mg thin films optical data from this study, combined with reported high conductivity data for the films (Lekoui et al. 2023) makes the material potential for TCO applications.

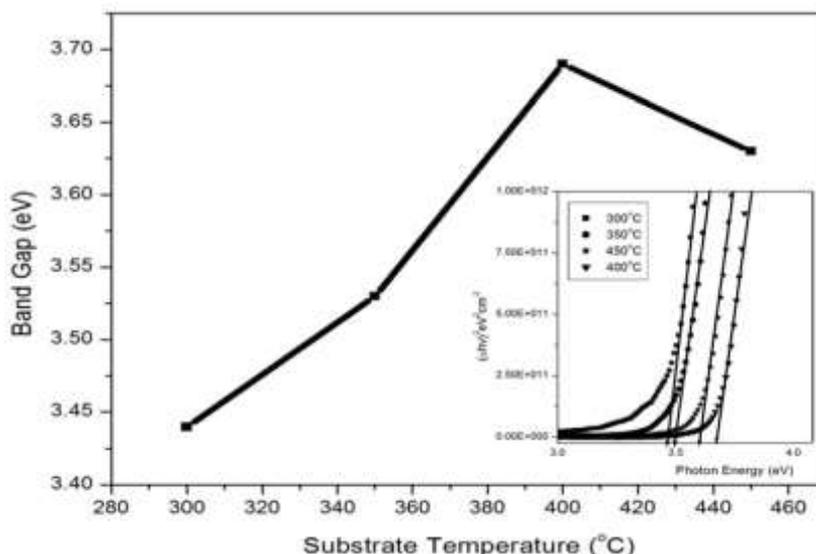


Figure 7: The energy band gap graph of ZnO:Mg thin films deposited at different substrate temperatures. The insert is the plot of $(\alpha hv)^2$ vs. $h\nu$ plots for ZnO:Mg thin.

Conclusions

Magnesium doped zinc oxide (ZnO:Mg) thin films were successfully prepared by DC magnetron sputtering. Clear evolution of film structure with increasing sputtering power was observed. Films deposited at 110 W showed relatively more homogeneous surface morphology and larger grains compared to those deposited at lower powers. Improvement in optical transmittance was observed for films deposited at higher powers. Substrate temperature had more pronounced effect on the surface morphology of the films. Grain size increased from 957 nm² to 6006 nm² as substrate temperature was increased from 300 °C to 450 °C. At 450 °C, the grains were smooth and compact indicating complete film crystallization. The average optical transmittance and band gap energy of the films increased from 81% to 88% and 3.44 eV to 3.63 eV, respectively as the substrate temperature was increased from 300 °C to 450 °C. These results show that sputtering power and substrate temperature have great influence on the structure and optical properties of ZnO:Mg thin films.

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