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Synthesis and Characterization of DC Magnetron Sputtered ZnO Thin Films Under High Working Pressures

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Abstract

ZnO thin films were deposited on glass substrates using direct current (dc) magnetron sputtering under high working pressures. A pure zinc target was used, and sputtering was carried out in an oxygen atmosphere. The working pressure was varied between 50-800 mTorr. XRD characterization showed that for a window of working pressures between 300-500 mTorr, the deposited films were polycrystalline, with strong preferential orientation of grains along the c-axis. The film deposited at 400 mTorr had the highest (002) peak with the largest estimated grain size. Outside this window, the crystallinity and c-orientation of grains is lost. The microstructure of the films was investigated by Atomic Force microscopy (AFM). Optical transparency of the films was about 85%. The films produced were highly resistive, which might provide new alternatives for the synthesis of ZnO thin films aimed for SAW devices.

Keywords: magnetron sputtering, working pressure, grain size

1. Introduction

Zinc oxide (ZnO) is a II–IV semiconductor with a direct wide band gap of 3.2 eV at room temperature. It is also a well-known piezoelectric material with wurtzite hexagonal structure. Thin films of this oxide have been receiving much attention for a long time due to their many attractive applications in varistors, transparent electronics, gas-sensing

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devices...etc. One of the very successful applications of ZnO is when implemented in Thin-Film Surface Acoustic Wave (SAW) devices. Thin-Film SAW devices need a thin film material that is piezoelectric [1,2], which is a natural property of ZnO because of its anisotropic wurtzite structure. The piezoelectric effect can be increased by increasing the electrical resistivity of the film, and by having an oriented crystalline structure [1]. The hexagonal wurtzite structure leads to an anisotropy of the surface free energy which can result in films growing with a preferential orientation of the grains even on amorphous substrates [3]. Highly oriented ZnO thin films have been reported in the literature for decades, having the crystallographic c-axis oriented parallel to the substrate normal.

Because of its wide bandgap, zinc oxide should have an intrinsic resistivity exceeding 10^{20} Ω.cm [2]. However, native defects (most probably oxygen vacancies and/or zinc interstitials [4]) do not allow such a high resistivity. Defects concentrations and the structural quality of the film are important factors in this regard. Pure ZnO thin films, with resistivities ranging between 10^{-4} -10^{13} Ω.cm have been reported [5,6,7].

The synthesis of ZnO thin films is one of the easiest, and many techniques have been used for the fabrication of ZnO thin films. ZnO thin films, with high orientation of grains along the c-axis, have been synthesized by DC magnetron sputtering [1-3,7,8]. ZnO thin films obtained by this technique are usually resistive [8], and can be made with high texture under low working pressures with the substrate being heated [1,8]. Deposition by DC magnetron sputtering is carried out usually at 10^{-2}-10^{-3} Torr in order to allow a larger mean free path for the sputtered atoms to reach the substrate [8]. Working at higher working pressures is reported to lead to amorphous thin films [3]. Up to best of our knowledge, DC magnetron sputtering deposition of ZnO thin films at high pressures in the order of 0.1-1 torr has not been investigated in the literature. In this work, we report on the successful synthesis of highly crystalline ZnO thin films by DC magnetron sputtering technique under high working pressures of pure oxygen (50-800 mTorr), and without substrate heating.

2. Experimental

ZnO thin films were deposited by DC reactive magnetron sputtering on ordinary optical microscope glass slides that were cut into a size of $1'' \times 1/2''$. The slides were cleaned with acetone and alcohol before thin film deposition. A disc of pure (99.999 %) metallic zinc of 50 mm diameter was used as a target. The sputtering chamber was pumped down to about 1×10^{-3} Pa. Then, high purity oxygen was introduced. Before deposition, the zinc target was pre-sputtered for about 5 minutes with a shutter covering the substrate. Sputtering deposition was performed with a direct current power of about 40-50 W. The sputtering time was about 30 minutes.

The structure of the thin films was studied by using a Shimadzu XRD-6000 X-ray diffractometer using a Cu anode (K_α, $\lambda = 1.5418$Å). The microstructure and surface morphology was studied by Atomic Force Microscopy using NanoMan AFM system (Nanoscope IV, Veeco) in tapping mode. The optical transmittance of the films was measured between 200 nm and 800 nm using a JASCO V-570 Spectrophotometer. Resistivity measurements were carried out by a Hall effect system (EGK, model: HEM-2000) using Van der Pauw Method.

3. Results and Discussion

Figure 1 shows the XRD spectra of the ZnO films grown at different working pressures. It can be noticed that highly crystalline ZnO thin films with strong orientation along the c-axis (reflected by the strong 002 peak at 34.4 ^{o}) could be obtained only within the 'window' between 300-500 mTorr. It should be pointed out that all other conditions (power, time, …etc) were the same for all the films; only the working pressure was varied. Films grown outside this pressure window had very poor crystallinity.

It can also be noticed from the XRD spectra in figure 1 that the preferential orientation along the c-axis was observable only in films grown at the working pressures between 300-500 mTorr. Outside this pressure window, the texture was absent. At 800 mTorr, the peaks themselves disappeared indicating that the film was amorphous.

The working pressure at which the sputtering takes place has an important impact on the growth process of thin films. At high working pressures, the sputtered atoms reach the substrate with reduced kinetic energies. High kinetic energies are needed for the rearrangement of atoms on the substrate which leads to an improved crystallinity. Therefore, thin films grown at high working pressures are usually amorphous [3]. Our results confirms that samples produced at pressures as high as 200 mTorr (and without substrate heating) are of poor crystallinity, but we report also on the reproduction of crystallinity again at pressures higher than that. This can be explained by a systematic flow of the ZnO molecules coming toward the substrate at very high pressures, rather than random movements and collisions. Falling on the substrate in a systematic and ordered way reduces the need for energy to arrange the ZnO molecules in their crystalline order. At some optimum working pressure which turns out to be 400 mTorr in our case), the systematic flow of ZnO molecules is best to make the crystalline structure.

The (002) peak position in the XRD spectra of the grown films showed a systematic increase with increasing working pressure. Figure 2 shows the position of the (002) peak (2θ) versus working pressure. This increase in 2θ implies a decrease in the lattice spacing between the (002) planes. The (002) peak of the bulk ZnO lies at 34.4^{o}. For our films, it increased from 34.3^{o} to about 34.6^{o} with increasing the working pressure from 50 mTorr to 600 mTorr, which might be due to an increasing uniform stress along the c-axis.

The vertical grain size can be estimated from the XRD diffraction peak by using Sherrer formula:

$$\text{grain size} \approx \frac{\lambda}{\text{FWHM}\cos\theta}$$

where FWHM is the Full Width at Half the Maximum of the XRD peak after subtracting the instrumental broadening. The (002) peak was used to estimate the vertical grain size, since it is the most intense, and it appeared in all the samples. Figure 3 shows the change in FWHM of the (002) peak and estimated vertical grain size, as a function of the working pressure. The film prepared at 400 mTorr had the minimum peak width, and the vertical grain size estimated from Sherrer formula is ~ 90 nm.

Figure 4 shows a 2-D AFM image for the sample prepared at 400 mTorr. The image shows the development of a dense film structure. The absence of clear pores and defects in the film can also be noticed. The lateral grain size is almost uniform over the surface and it is about ~ 80 nm. The shape of grains is almost spherical as can be noticed from figure 4, which supports the similarity between the vertical grain size estimated by XRD and lateral grain size measured by AFM.

The resistivity of the ZnO films was relatively high. Generally, the resistivity of the films decreased with increasing the working pressure. Figure 5 shows the resistivity versus the working pressure. The interpretation of the decrease of the resistivity is not straightforward as the films' structural properties such as the grain size and density of point defects (atomic defects) affect the mobility and the charge carrier concentration.

The optical band gap of the grown films did not change very much with increasing the working pressure as the transmittance data of the films revealed. Figure 6 shows the optical transmittance of the films. All the films were highly transparent in the visible region, with a transmittance of about 85%. The optical band gap was estimated from the transmittance data. The extrapolation of the plot of $(\alpha E)^2$ vs. E cuts the energy axis at the value of the band gap. Figure 7 shows the graph of $(\alpha E)^2$ versus E for some of the films. The optical band gap did not change very much for all the films; it was between 3.28-3.29 eV.

Figure 8 shows the thicknesses of the films versus working pressure. The thickness decreased from about 1 μm at 50 mTorr to 300 nm at 800 mTorr. This result is consistent with the fact that at low pressures the sputtered atoms have a larger mean free path because of fewer collisions with the plasma ions and atoms, hence more sputtered atoms reaching the substrate. The films thicknesses were estimated from the transmittance spectra using the formula:

$$d = \frac{1}{2n}\left(\frac{\lambda_1 \lambda_2}{\lambda_1 - \lambda_2}\right)$$

where d is the thickness of the film, n is the refractive index, λ_1 and λ_2 are the wavelengths of two adjacent peaks in the transmittance spectra.

4. Conclusion

The effect of high working pressures on the growth of ZnO thin films using dc magnetron sputtering was investigated. XRD characterization showed that for a window of working pressures between 300-500 mTorr, the deposited films are polycrystalline, with strong preferential orientation of grains along the c-axis. The film deposited at 400 mTorr had the highest (002) peak, with a grain size of about ~80-90 nm. Outside this window, the crystallinity and c-orientation of grains is lost. The films produced were highly transparent and highly resistive.

Acknowledgement

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Figures

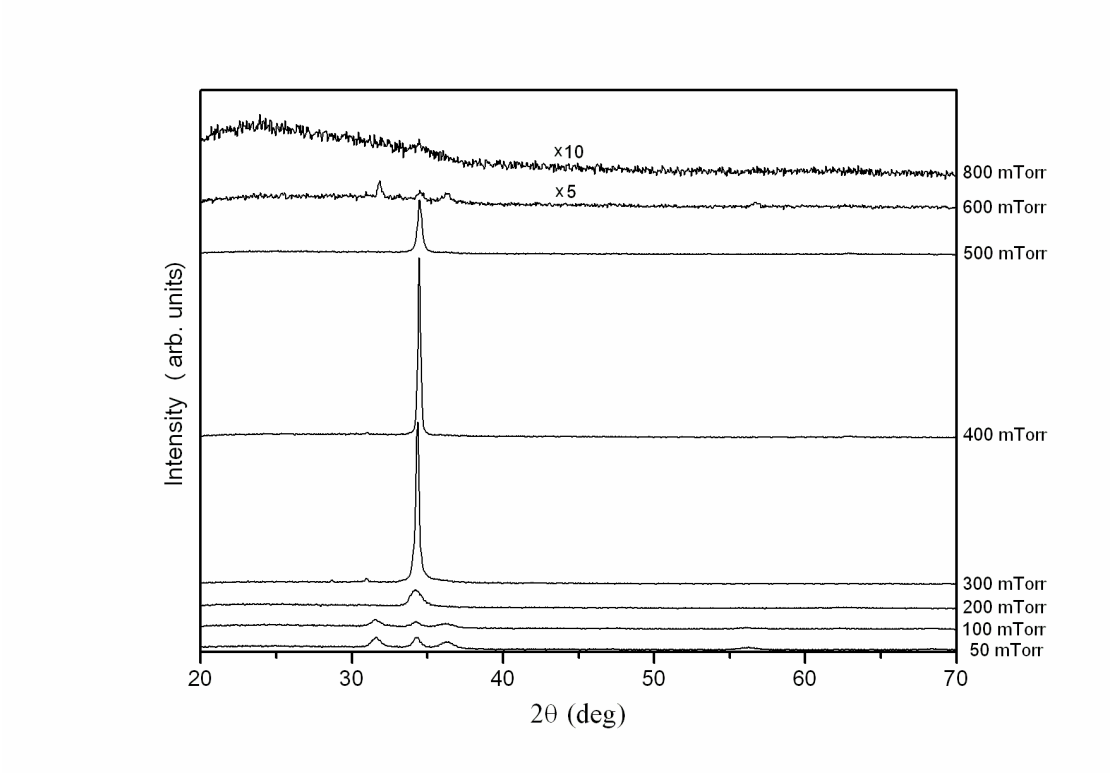

Figure 1: XRD patterns of ZnO thin films deposited at different working pressures of oxygen.

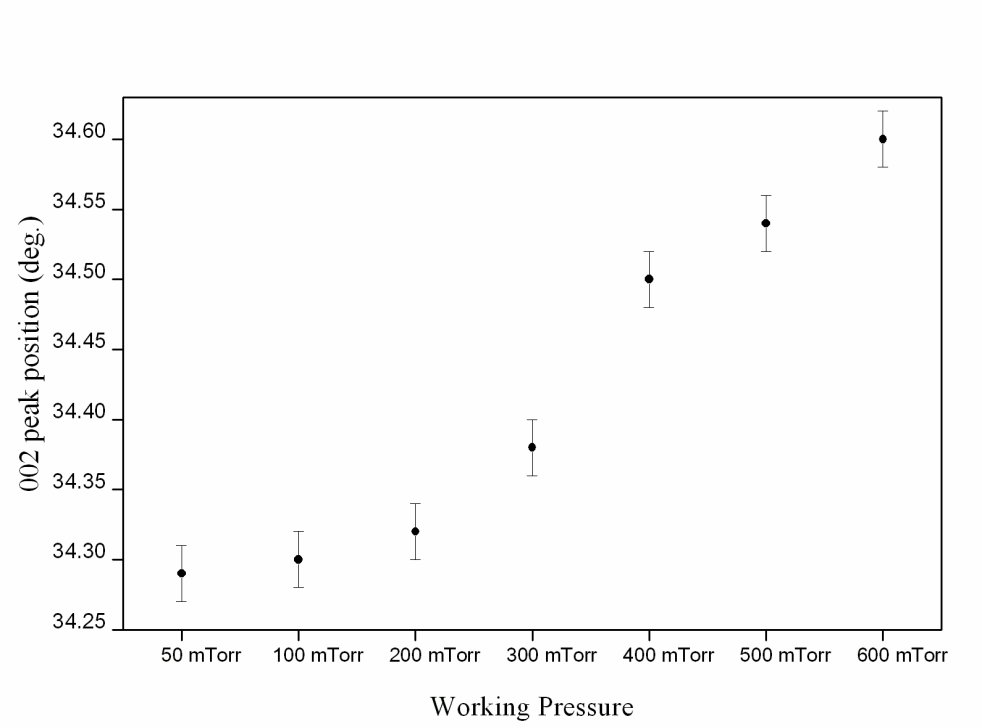

Figure 2: (002) XRD peak positions for ZnO thin films deposited at different working pressures.

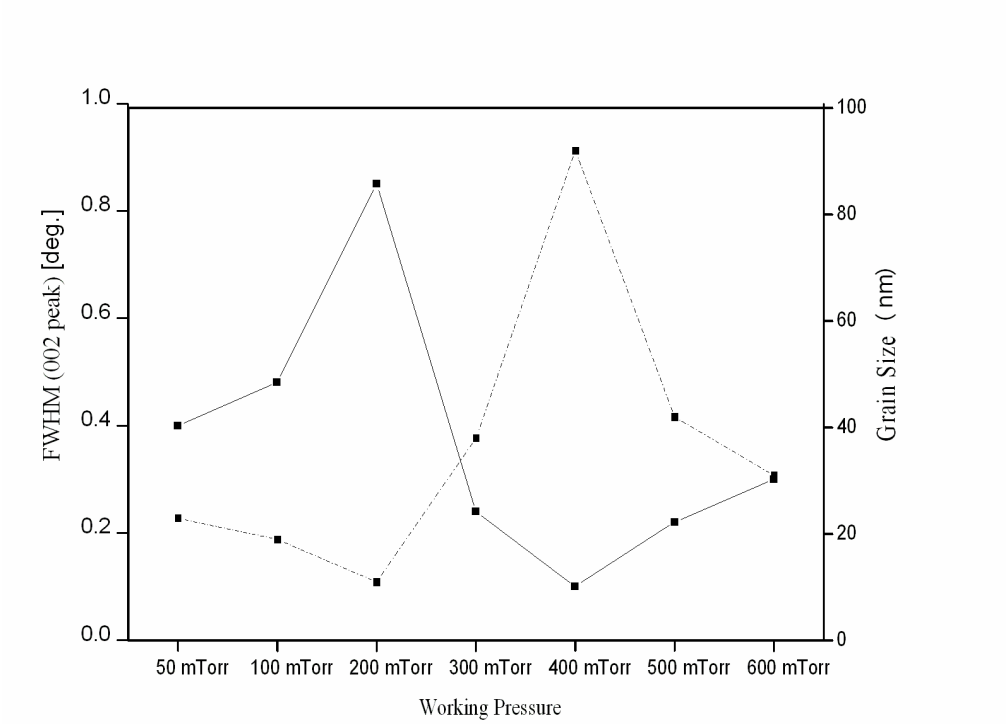

Figure 3: Variation of FWHM of the (002) peak and the grain size with the working pressure. (Solid Line – FWHM, Dot-Dot Line – Grain Size).

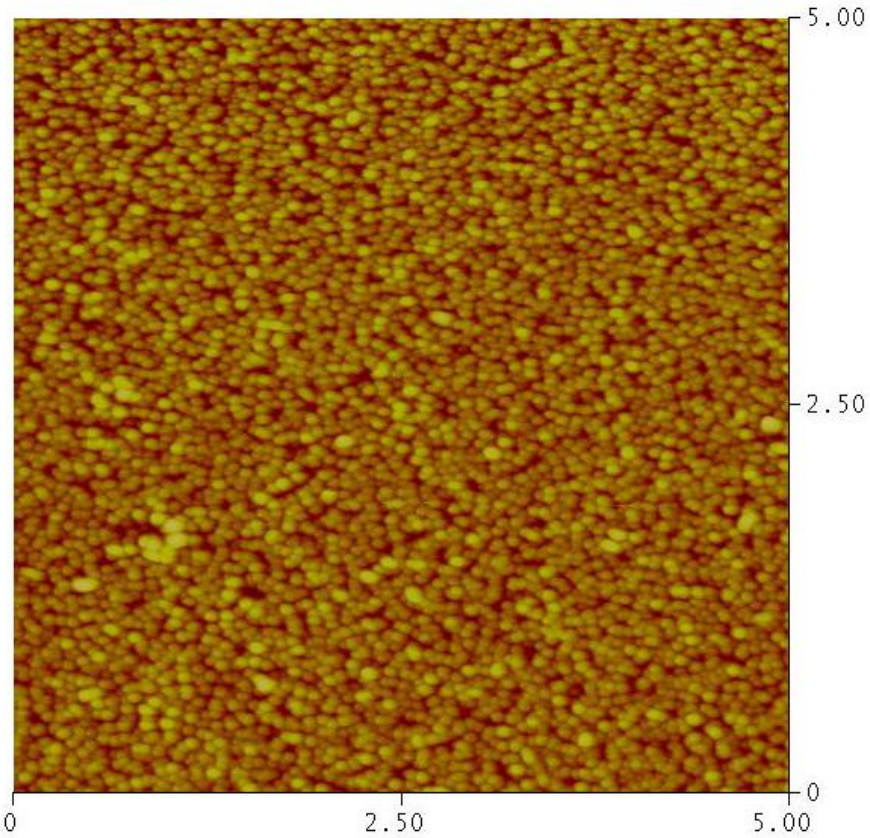

Figure 4: A 5×5 μm^2 AFM image of the ZnO thin film prepared at working pressure of 400 mTorr, and with the substrate not heated.

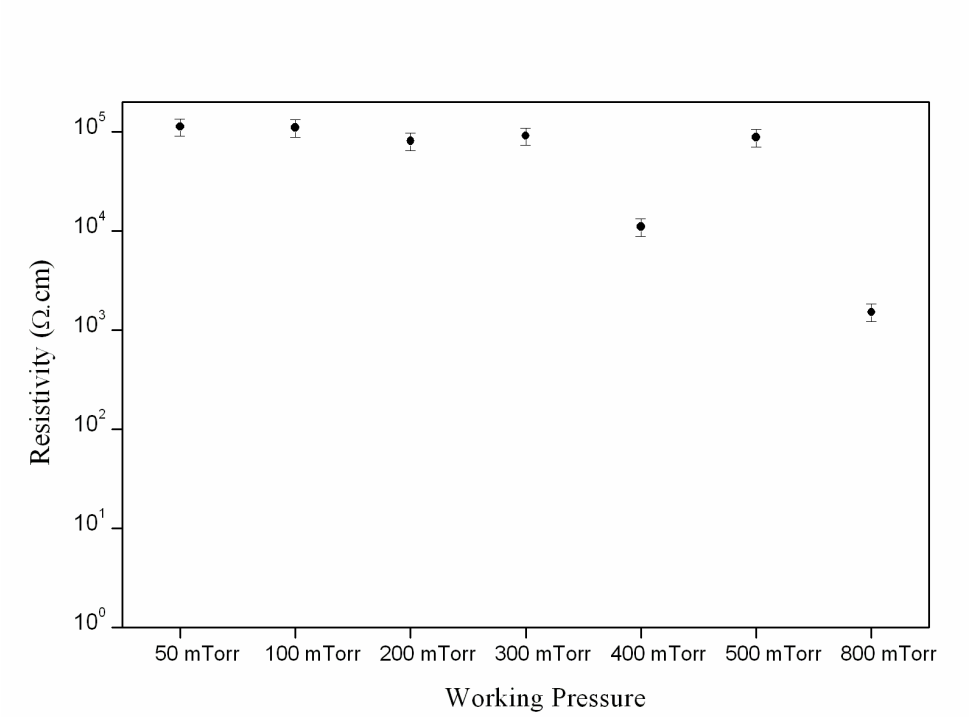

Figure 5: Electrical resistivities of ZnO thin films prepared at different working pressures.

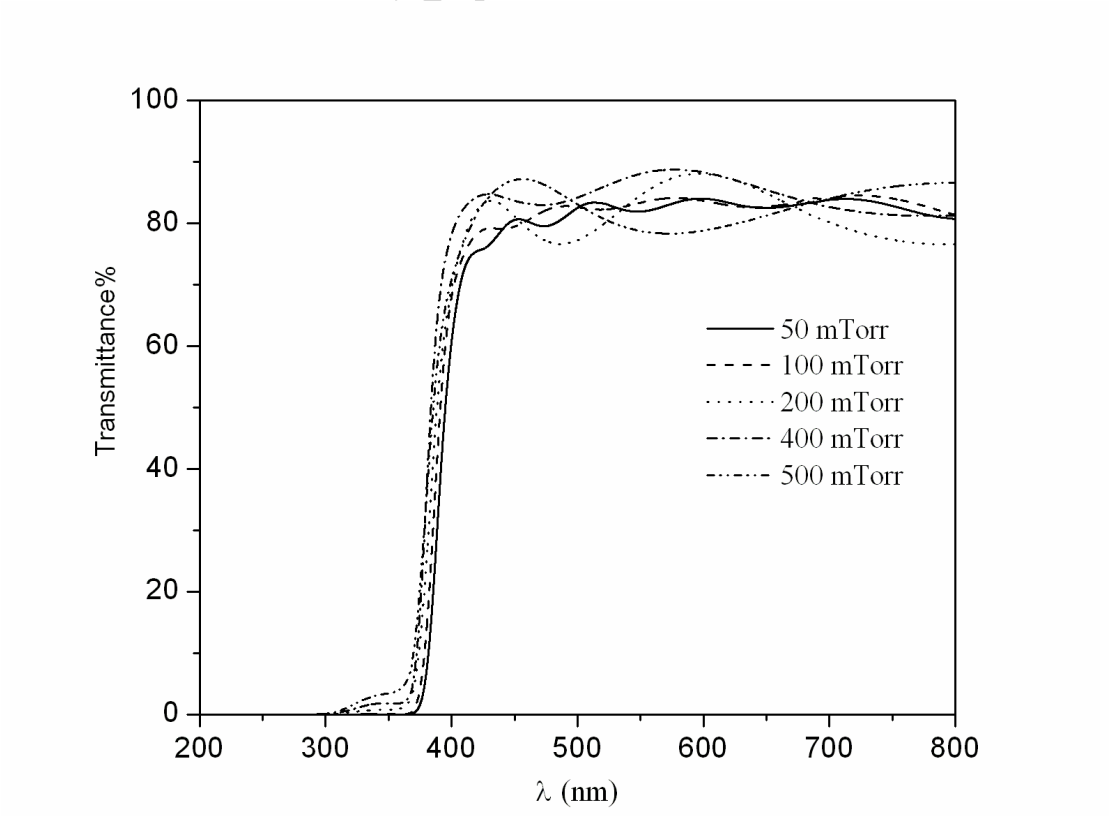

Figure 6: Optical transmittance spectra of ZnO thin films prepared at different working pressures.

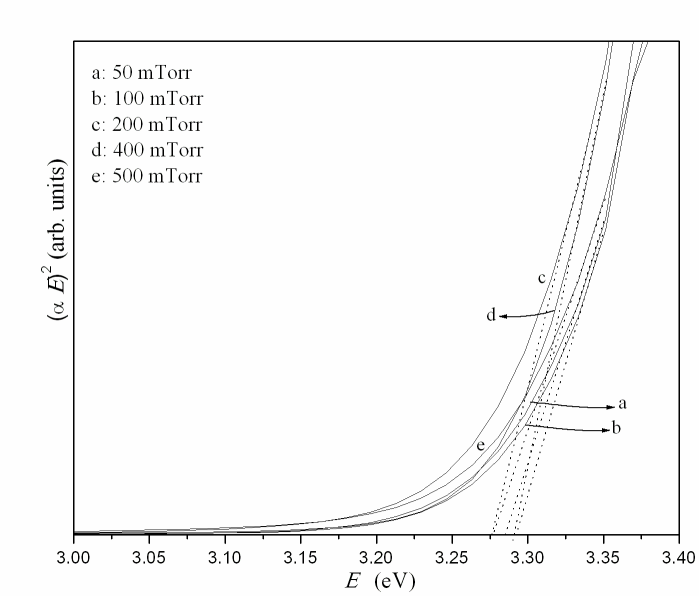

Figure 7: $(\alpha E)^2$ versus E graph for the determination of optical band gaps of ZnO thin films prepared at different working pressures.

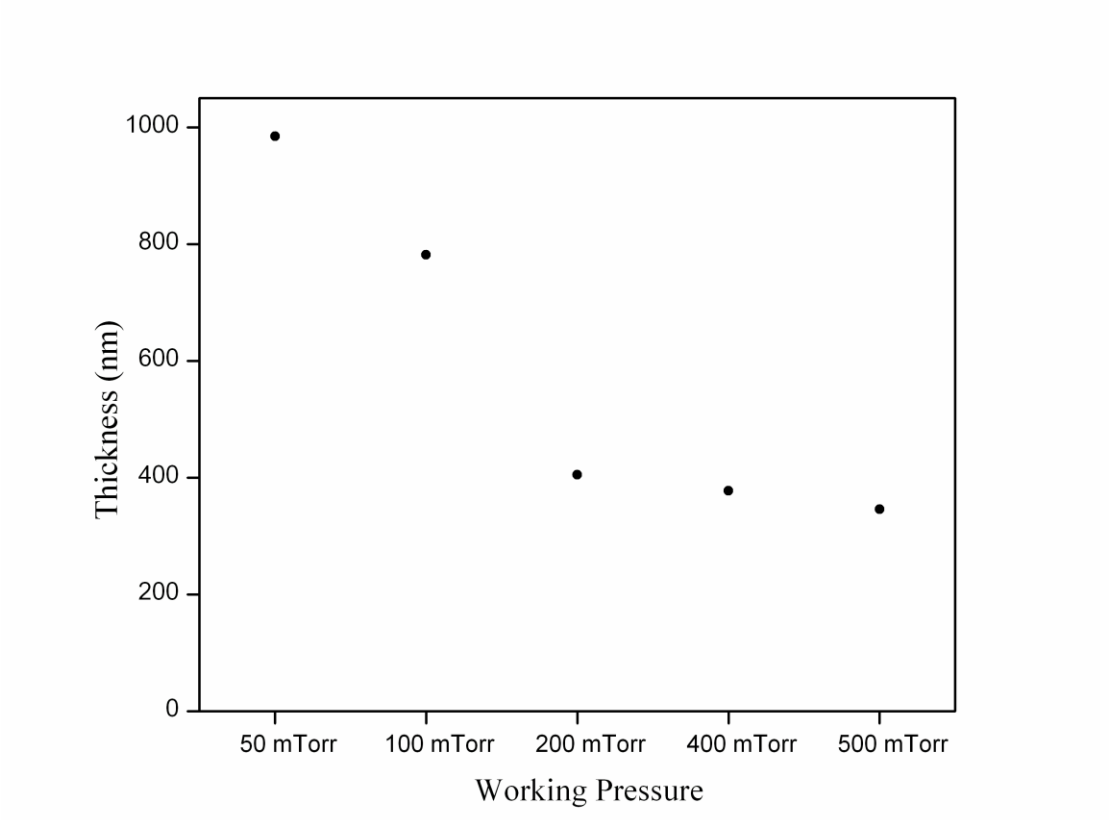

Figure 8: Thicknesses of ZnO thin films prepared at different working pressures.