The Effect of Non-Thermal Plasma on the Topographical and Optical Constants of Cd Doped ZnO Thin Films

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Abstract. Nanostructured ZnO and Cd doped ZnO were deposited employing spray pyrolysis technique. Atomic force microscope and double beam spectrophotometer were utilized to study the influence of non-thermal plasma on topographical and some optical constants. AFM results indicate that the average diameter was 43.4-68.81 nm before exposure and their values was slightly influenced by exposure to plasma to be 42.74-69.25 nm and all the result indicate the deposited films have a nanostructure. Surface roughness Ra and root mean square roughness Rrms were in the ambit of (2.09-5.3 nm), (2.43-6.12 nm) before exposure to plasma, while their values were in the ambit of (2.09-5.3 nm), (2.58-10.3 nm) after the influence of plasma. Optical constants such as absorbance was increased with the increment of Cd content, the same trend was noticed after exposure to non thermal plasma. High absorbance was seen near 400 nm. Whereas extinction coefficient, refractive index show a decrement with the increment of Cd content before and after exposure to plasma. Reflectance also offers the same trend of the above optical constants, a comparatively low reflectance is shown for the pure ZnO thin films before and after exposure. Finally, all the studied parameters were influenced by plasma exposure.

Keywords: non-thermal plasma, optical constants, reflectance profile, ZnO nanostructure.

1. Introduction

Metal oxides have gained great awareness in the last decade [1-15]. ZnO was interesting due to its good physical and chemical characterization, non-toxic compound, wide bandgap [16-20]. It is interned in many fabrication devices like solar cells [21], gas sensor[22], photocatalyst[23], photodetector[24], photoanode[25], lithium ion battery[26]. Various techniques were employed to fabricate ZnO films including, thermal evaporation[27], pulsed laser deposition [28], sol gel [29] SILAR[30], physical vapor deposition [31] and spray pyrolysis[32]. The physical characteristics of thin film could be tuned upon doping, whereas the literature on cd doped ZnO is scarce. Guzman-Embus et al. [33] studied the morphology
and optical properties of ZnO: Cd employing hydrothermal method showing a decrease in the crystalline order as Cd content increase. Kumar, and Srivastava [34] approved that photoresponsivity and photoluminescence were boost via Cd doping. Vinoth et al. [35] show that 20% of Cd content was enough to enhance gas sensitivity for methanol. Zhao et al. [36] try to enhance the response of by adding 2.5% as doping material in ZnO nanoparticle. Buyukbas-Ulusan et al.[37] fabricate a device employing Cd as dopant in ZnO, the result indicate that Cd was affected the performance of ZnO that the capacitance was increased upon Cd doping. In this work Spray Pyrolysis technique SPT was utilized to deposited ZnO: Cd thin film to study their morphology and optical constants before and after exposure to non-thermal plasma.

2. Experimental

ZnO and ZnO:Cd films were deposited employing SPT. A solution containing 0.1 M of (Zn(CH$_3$CO$_2$)$_2$·2H$_2$O) and 100 ml of deionized water was utilized to get the spraying solution. Cd(CH$_3$COO)·2H$_2$O of 0.1 M was dissolve in deionized water adding to the solution as a volumetric percentage of (2,4,6). Many experiments were done to obtain the optimum status that recached the following, base to spout to nozzle distance was 30 cm, base temperature was 400 °C, spray rate, spray time interval time between to sprayer were 5 ml/min, 10 S and 1.5 min respectively. Film thickness was evaluated via weighing method and was about 450± 50 nm. Absorbance spectra were recorded via Shimadzu spectrophotometer. XRD was employed to set film structure. AFM was employed to set films morphology. Non-thermal plasma device was utilized to study the effect of cold plasma, it operating voltage was 12.5 KV and exposure time =10 min( the experimental setup was discussed in detail in reference [38].

3. Results and Discussion

‘Figure 1’ offers the AFM images of the deposited film before and after exposure to non-thermal plasma. It can be clearly seen that images display violently congested columnar crystalline grains and homogenous, suffer from some aggregation and agglomeration. All the images prove that these films fell in the category of nano as nanostructured films. Their values were analyzed by granularity cumulation distribution report see ‘figure 2’. They were in the domain of (42.74- 68.81 nm) before exposure to plasma whilst their values were in the domain of (43.3-68.83 nm) after exposure to plasma. It seem that there is a slight increase in their value after exposed to plasma except the value of znO:6% Cd. These results are fit with the results obtained by Mishjil et al. [39] concerning the crystallite size after exposure. This could be attributed to the improvement in crystallinity after exposure, that means cold plasma act as healing to improve crystallinity. Surface roughness $R_a$ and root mean square roughness $R_{rms}$ were in the ambit of (2.09-5.3) nm, (2.43-6.12) nm before to plasma. While their values were in the ambit of (2.09-5.3) nm, (2.58-10.3) nm. It can be noticed that plasma exposure affects the $R_a$, $R_{rms}$ and offer increment in their values (see Table 1). This behavior is in good fit with Tilmatine et al. [40].
Before exposure to plasma for pure ZnO

After exposure to plasma for pure ZnO

Before exposure to plasma for pure ZnO:2% Cd

After exposure to plasma for pure ZnO:2% Cd
Before exposure to plasma for pure ZnO:4% Cd

After exposure to plasma for pure ZnO:4% Cd

Before exposure to plasma for pure ZnO:6% Cd

After exposure to plasma for pure ZnO:6% Cd

Figure 1. AFM images before and after exposure to plasma for all the doping percentages.
Figure 2. Granularity cumulation distribution (a-d) before exposure (e-h) after exposure to plasma.
Table 1 AFM parameters for the ZnO:Cd thin films.

| Sample          | G.S. before Plasma | G. S. after plasma | R_a before plasma | R_a after plasma | R_rms before plasma | R_rms after plasma |
|-----------------|--------------------|--------------------|-------------------|------------------|----------------------|--------------------|
| ZnO             | 42.74              | 43.4               | 2.09              | 2.23             | 2.43                 | 2.58               |
| ZnO :2% Cd      | 52.18              | 52.92              | 4.21              | 4.88             | 4.86                 | 6.51               |
| ZnO :4% Cd      | 60.24              | 60.87              | 4.66              | 5.34             | 5.38                 | 8.87               |
| ZnO :6% Cd      | 68.81              | 68.83              | 5.3               | 8.87             | 6.12                 | 10.3               |

Figure 3’ displays the absorbance (A) against wavelength, it can be clearly seen that A increases as the Cd content increase, the same behavior was noticed after exposure to plasma but their value after exposed to plasma was less than its value before the exposure. High absorbance was seen near 400 nm, this results agree well with Saleem et al. [41]. Besides their curves were spread after exposure in comparison with the curves before exposure.

The extinction coefficient (k) was obtained utilizing the formula [42]

\[ k = \frac{\alpha \lambda}{4\pi} \] (1)

Figure 4’ offer the relation of K with wavelength for all the specimen under study. It can be seen that by increasing wavelength, extinction coefficient values decrease, this can be deduced to normal semiconducting dispersion behavior of the material, this behavior were in fit with Kumar and Rao [43]. On the other hand \( k \) suffer an exponential decay till 440 nm and 420 nm for the curves before and after exposure to cold plasma respectively, then it seems that there is a semi-linear relation after these values for both before and after exposure to plasma. We can mention that \( k \) was affected by increasing their values after exposure to plasma.

Figure 5’ is a plot of reflectance as a function of wavelength for ZnO and ZnO: Cd (2, 3, 6 %). The film shows an average reflectance of 12.8% and 16.05% in the wavelength range of (400 - 900) nm for the deposited films before and after exposure to non-thermal plasma respectively. A relatively low reflectance can noticed for the pure ZnO thin films before and after exposure, which can be served as an anti-reflecting coating material [44].
Figure 3. Absorbance as a function of wavelength for the deposited films.
Figure 4. Extinction coefficient versus wavelength of the deposited films.
Figure 5. Reflectance versus wavelength of the deposited films.
The refractive index (n) is a remarkable coefficient for optical materials and their implementation. So it is essential to determine the complex n of the films. n of the films was obtained employing the following relation [45].

\[
R = \frac{(n-1)^2}{(n+1)^2}
\]

The variation of refractive index varies with wavelength for all the films is offer in 'Figure 6', which shows that The refractive index increase as Cd content increases, which may be related to an increase of the compactness of the films [46]. The decrease in refractive index after exposure to plasma is related to the increase in grain size. This behavior coincides with Wang et al. [47].

![Refractive index of the deposited thin films](image-url)
4. Conclusions

Zinc oxide and ZnO: Cd was prosperous utilizing SPT. AFM images indicate that the average diameter of all the prepared film fall in nano-area. The affect of non-thermal plasma was studied which confirmed that topography, absorbance, extinction coefficient, reflectance and refractive index are influenced by cold plasma.

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