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Preparation, Structural and Optical Characterization of ZnO / Ag Thin Film by CVD

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Zinc Oxide thin films doped with Ag have been synthesized by CVD technique. By increasing the dopant from 0 to 10 % Ag in ZnO thin films were found to lead to pronounced changes in their morphology. From optical properties the band gap energy of pure ZnO thin film was 3.25 eV, with the increasing of Ag doping from 1 to 10 % it is not affected. X-ray diffraction has shown that the maximum intensity peak corresponds to the (101) predominant orientation for ZnO and ZnO:Ag. SEM images show that more crystalline behavior by increasing the doping. EDXA analysis showed that the structure of ZnO film contains Zn and O elements and Ag, Cu, Si for doping at 10 % Ag.

Keywords: CVD, X-ray Diffraction, SEM.

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1. INTRODUCTION

Transparent conducting n-type semiconductor zinc oxide (ZnO) films have been extensively studied in recent year because they exhibit wide band gap [1, 2], optical transmission, electrical conduction and exciton binding energy of 60 meV [2] at room temperature. This exciton binding energy is much larger than the room temperature thermal energy (26 meV), suggesting that the electron-hole pairs are stable even at room temperature. It has crystalline structure of the wurtzite type and with lattice constants a = 3.24 ?, c = 5.19 ? [3]. ZnO thin film is a promising material in the applications of UV light devices, light emitting diodes (LEDs) and laser systems [4], and is used in antireflection coatings, transparent electrodes in solar cells, piezoelectric devices, gas sensors [5], etc. Several techniques were used to prepare ZnO thin films namely: thermal evaporation [6], spray pyrolysis [5-6], RF/DC magnetron sputtering [7], chemical vapour deposition (CVD) methods [5,8], Molecular beam epitaxy [9], pulsed-laser deposition (PLD) [10], chemical bath deposition technique [11], hydrothermal method [12] and sol–gel [13]. Doping is done to control the ZnO physical properties. Usually, n-type doping is obtained by Al, Ag, Ga or In. On the other hand, p-type doping is not easily obtained. However, it is difficult to achieve visible light absorption on a single ZnO material. The silver Ag have been mostly extensively investigated as the important candidate for wide band gap material to absorb light. Ag offer high performance absorption in visible light without any highly toxic elements. Many different methods have been used to prepare Ag–ZnO thin films , RF magnetron sputtering method [8], CVD [5], and so on. However, there are few report on the preparation of Ag–ZnO film on the glass substrate by CVD. It was an important method to synthesize films. The method is cost-effective, simple and can be carried out under low temperature. In this paper, the simple CVD method was used to obtain the ZnO/Ag thin film on the glass substrate. Effects of Ag doping on the optical and structural properties of ZnO films were investigated in detail.

2. EXPERIMENTAL

In order to prepare pure ZnO and doping films using chemical vapors deposition(CVD) techniques on glass substrates, the deposition material used were dissolved in water as follows: The solution (I) (10.8g) $Zn(CH_3COO)_{2.2}H_2O$ was mixed together with solution(II) (0.699g) AgNO3, the amount of Ag ranged from 0.08 to 7.7 mol% (i.e. 1–10 wt.%). Then with solution (III) (0.721g) PVP. The total amount of used water was 100 mL. The obtained solution (I+II+III) was placed in the heating unit. The pressurized air flow was also adjusted to the best flow rate which was found to be 2 L/min to produce the best samples. Various temperatures were tested when heating the deposition material and it was found that the temperature of (340-350□ C) is the appropriate temperature. The substrates were first cleaned in acetone, rinsed in deionized water and in absolute ethanol, and then placed in the deposition unit. While the temperatures were varied between (400-500°C) in order to ensure optimum film properties. After that prepared ZnO/Ag thin film with various Ag concentrations (1,5,10)% to investigate the influence of doping on the optical and structural properties.

The crystalline structure of the as-prepared ZnO/Ag films were characterized by X-ray diffraction (XRD) with a DX-2700 diffract meter using CuKα radiation (λ = 1.54178 nm). The diffraction angle was scanned from 20 to 80 at the scanning speed of 0:02±per second. The surface microstructure was obtained by scanning electron microscope (SEM) (JEUM-JSM-6756 F) operating at a voltage of 10 KeV. Optical properties were measured through spectrophotometer (ShimadzuUV-3150).

3. RESULTS AND DISCUSSION

3.1 X-ray diffraction

Figure 1 shows the XRD patterns of ZnO pure and

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ZnO/Ag thin films, which demonstrate that all the ZnO films are crystallized in hexagonal structure. In figure 1 the XRD pattern of ZnO and ZnO/Ag films recorded in the range of 20-80 °. X−ray diffraction measurements for pure ZnO films and doped showed multi crystalline with preferred direction of (101). All diffraction peaks (100), (002), (101), (102), (110), (103), (112) & (201) can be attributed to crystalline ZnO with the hexagonal structure. The data are in agreement with the Joint Committee on Powder Diffraction Standards (JCPDS) card for ZnO (JCPDS036-1451) [14]. At 1 % Ag doped, We observed that there is one peak with low intensity of orientation (111) which due to the silver, in addition to the other peaks due to ZnO films. But for the ZnO films doped with 5 % Ag appeared three new peaks (200) (220) and (311) which due to the silver and with increased of the intensity of (111) with comparing to the films at 1 % Ag. By increasing doping at 10 % Ag, the peak intensity of (111) is clearly increased with comparing to 1 % and 5 % Ag.

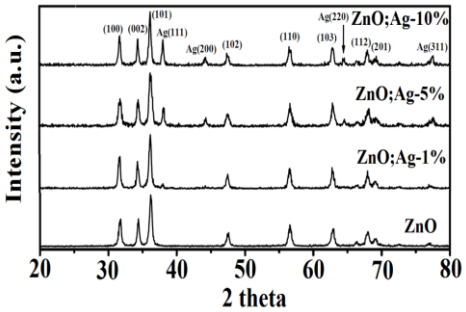

Fig. 1 – XRD pattern of ZnO: Ag with various concentrations (0, 1, 5, 10 % Ag) respectively

3.2 EDXA:

EDXA analysis for ZnO doped at 10 % Ag as shown in figure (3) which shows that the dominant composition of ZnO and the details of the relative analysis are depicted in table inside the figure. Fig. 3 shows two strong peaks corresponding to Zn which confirms the high purity of the ZnO thin films as well as two strong peaks corresponding to Si and O elements and presence peaks with low intensity due to Ag, Cu, O and Zn elements.

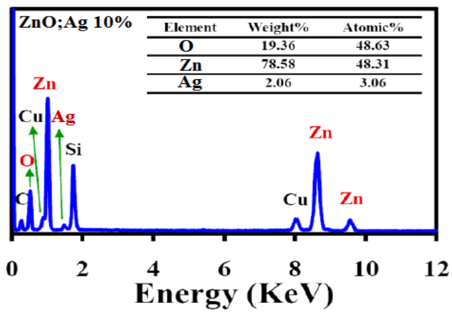

Fig. 2 – EDXA of ZnO doped at 10 % Ag

3.3 SEM

Scanning electron microscopy (SEM) was used for the study of surface morphological changes of pure and doped ZnO films prepared by CVD. Figs. (3 a-d) exhibit the SEM images of the films ZnO pure and ZnO doped at (1, 5, 10 %) Ag respectively. It can be seen that the grain size becomes larger by increasing of doping Ag.

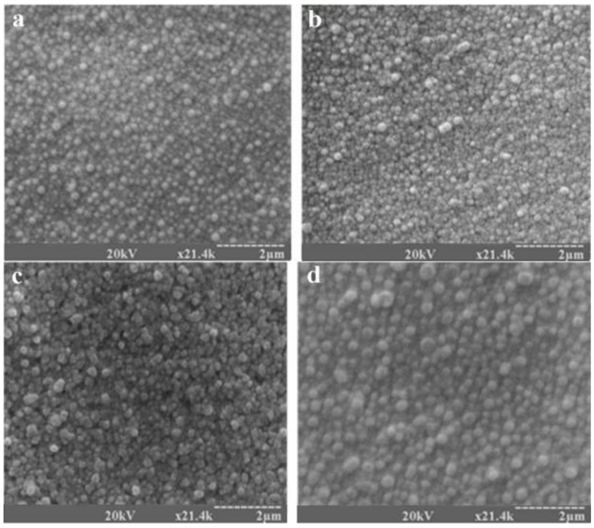

Fig. 3 – SEM of ZnO films a-pure b-1% c-5% d-10% Ag

3.4 Optical properties:

Figure 4 shows the optical transmittance spectra of ZnO/Ag thin films in the wavelength range between 350 to 1550 nm. The transparency properties of all thin films are nearly 80-90 % at a visible wavelength of (350-800 nm). It is observed that the transmittance has a tendency to increase with Ag doped.

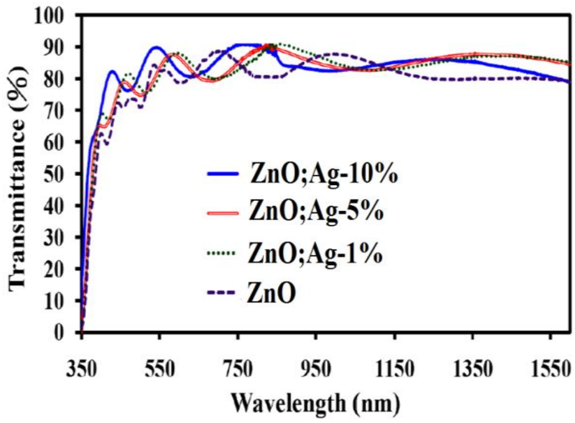

Fig. 4 – Optical transmittance spectra of ZnO pure and doped (1, 5, 10 %) Ag

The relation between absorption coefficient (α) and photon energy for direct transitions is given by [15].

$$\alpha h\nu = A(h\nu - E_g)/2 \qquad (3.1)$$

where, h is the Plank constant, ν is the frequency of the incident photon, A is a constant depending on the electron-hole mobility and E_g is the optical band gap energy.

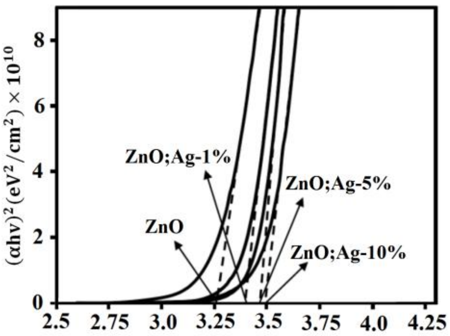

Fig. 5 – Plot of (αhν)2 vs. hν of ZnO pure& doped at (1, 5, 10 %) Ag

Fig. 5 shows the optical band gap energy versus Au doped and it also shows a blue shift in the thin film. By extrapolating the linear part of the curve that inter sects at the x axis, it will give the optical band gap energy value. For pure ZnO thin film, the band gap energy found to be 3.25 eV. With an increment in the Ag content as 1 %, the band gap nearly increased to 3.35 eV. This was followed by 3.45 and 3.5 eV for 5 and 10 % of Ag content, respectively as shown in fig. 5.

4. CONCLUSION

Zinc Oxide thin films doped with Ag using CVD technique (0 to 10 % Ag) . the dopping found to lead to pronounced changes in their morphology and the band gap energy of pure ZnO thin film was 3.25 eV, with the increasing of Ag doping it is not affected. X-ray diffraction has shown that the maximum intensity peak corresponds to the (101) predominant orientation for ZnO and ZnO:Ag. SEM images show that more crystalline behavior by increasing the doping.

REFERENCES

1. A.D. Pogrebnjak, N.Y. Jamil, A.K.M. Muhammed, *Metallofiz. Noveishie Tekhnol.* **33,** 235 (2011).
2. B. Lin, Zh. Fu, Yu. Jia, *Appl. Phys. Lett.* **79**, 943 (2001).
3. V. Srikant, D.R. Clarke, *J. Appl. Phys.* **81**, 6357 (1997).
4. T. Minami, H. Nato, S. Takata, *Thin Solid Films* **124**, 43 (1985).
5. A.D. Pogrebnjak, N.Y. Jamil, A.K.M. Muhammed, *Nanomater.: Appl. Prop.* **2**, 226 (2011).
6. K.L. Chopra, S. Major, D.K. Panday, *Thin Solid Films* **102**, 1 (1983)
7. A.D. Pogrebnjak, A.A. Muhammed, E.T. Karash, N.Y. Jamil, J. Partyka, *Przegląd Elektrotech.* **89***,* 315 (2013).
8. A.D. Pogrebnjak, A.K.M. Muhammed, *Visnyk KhNU* **962** No 15, 58 (2011).
9. J. Hupkes, B. Rech, O. Kluth, T. Repmann, B. Zwaygardt, J. Muller, R. Drese, M. Wuttig, *Sol. Energ. Mat. Sol. C.* **90**, 3054 (2006).
10. W.J. Jeong, S.K. Kim, G.C. Park, *Thin Solid Films* **506-507**, 180 (2006).
11. M. Suchea, S. Christoulakis, K. Moschovis, N. Katsarakis, G. Kiriakidis, *Thin Solid Films* **515**, 551 (2006).
12. W. Water, S.-Y. Chu, Y.-D. Juang, S.-J. Wu, *Mater. Lett.* **57**, 998 (2002).
13. F. Michelotti, A. Belardini, A. Rousseau, A. Ratsimihety, G. Schoer, J. Mueller, *Non-Cryst. Solids* **352**, 2339 (2006).
14. American Society for Testing and Material. *Powder Diffraction Files*; (Joint Committee on Powder Diffraction Standards: Swarthmore, PA, 1999, 3-888).
15. R. Azimirad, O. Akhavan, A.Z. Moshfegh, *J. Electrochem. Soc. E* **11-6**, 153 (2006).