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ARAŞTIRMA MAKALESİ /**RESEARCH ARTICLE**

STRUCTURAL AND OPTICAL PROPERTIES OF ZnO FILMS PREPARED BY SPRAY PYROLYSIS TECHNIQUE

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ABSTRACT

ZnO thin films have been produced by spray pyrolysis technique at different substrate temperatures, and the structural and optical properties of ZnO films produced by this technique have been investigated. X-ray diffraction pattern of the films have shown that the films are polycrystalline and hexagonal (wurtzite) in structure. It is observed that substrate temperature affects the grain size, which increases as the substrate temperature increases. The optical absorption spectra of the films produced have shown that the ZnO films have a direct band gap and the optical band gap is about 3.14 eV. No significant effect of substrate temperature was observed on optical band gap of ZnO.

Key word: Spray pyrolysis, X-ray diffraction spectra, Absorption spectra, Optical band gap.

PÜSKÜRTME TEKNİĞİ İLE ELDE EDİLEN ZnO FİLMLERİNİN YAPISAL VE OPTİK ÖZELLİKLERİ

ÖZ

ZnO filmleri püskürtme tekniği ile farklı taban sıcaklıklarında elde edilmiş ve elde edilen bu filmlerin yapısal ve optiksel özellikleri incelenmiştir. X-ışını kırınım desenleri, filmlerin hekzagonal ve polikristal yapıda olduklarını göstermiştir. Taban sıcaklığı arttıkça tanecik boyutunda artış olduğu gözlenmiştir. Absorpsiyon spektrumu ölçümlerinden ZnO filmlerinin direk bant geçişli olduğu ve yasak enerji aralıklarının yaklaşık olarak 3.14 eV olduğu belirlenmiştir. ZnO'in yasak enerji aralığına taban sıcaklığındaki artışın önemli bir etkisinin olmadığı gözlenmiştir.

Anahtar Kelimeler: Püskürtme, X-ışını kırınım desenleri, Absorpsiyon spektrumu, Yasak enerji aralığı.

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1. INTRODUCTION

Zinc oxide is a technologically important material. The electrical and optical properties of ZnO in the bulk form have been studied extensively (Major et al., 1983). Because ZnO films are n-type wide-gap semiconductors with optical transparency in the visible range, ZnO films have been targeted as a useful material for developments of electronic and optoelectronic devices such as: transparent conductors, solar cells windows, gas sensors, photodiodes, image sensors, surface acoustic wave devices and piezoelectric devices (Natsume and Sakata, 2000; Nunes et al., 2001; Paraguay et al., 1999).

ZnO thin films can be produced by various techniques such as sputtering, reactive evaporation, pulsed laser deposition, chemical vapor deposition, sol-gel process and spray pyrolysis (Natsume and Sakata, 2000; Paraguay et al., 1999; Messaoudi et al., 1995; Nunes et al., 1999). Films prepared by these techniques are generally polycrystalline in structure and their properties are extremely influenced by the deposition process. In addition, spray pyrolysis technique is particularly attractive because of its simplicity and low cost.

In the present work, structural and optical properties of ZnO thin films prepared by a spray pyrolysis technique onto glass substrates are investigated.

2. MATERIALS AND METHODS

2.1 Sample Preparation

The ZnO films were deposited onto glass substrates at temperatures 300, 325 and 350 $^{\circ}$C, using the spray pyrolysis technique. The solution used was 0.1 M zinc acetate diluted in methanol and de-ionized water (3:1). The solution was sprayed onto glass substrates using a carrier gas N_2. The nozzle to substrate distance was 28 cm and during deposition, solution flow rate was held constant at 4 $mlmin^{-1}$ and carrier gas pressure at 0.2 $kgcm^{-2}$. The substrate temperature was measured using an Iron-Constantan thermocouple and the temperature was held within an accuracy of ±5 $^{\circ}$C. The film thicknesses were estimated by weighing method.

2.2 Measurements

The structural analysis of the films was performed with a RIGAKU RINT 2000 Series X-Ray Automatic Diffractometer with CuK_{α} radiation.

Optical absorption measurements at room temperature were obtained in the range 200-900 nm, using a SHIMADZU UV-2101 PC UV-VIS Scanning Spectrophotometer.

3. RESULTS AND DISCUSSION

3.1 Structural Properties

The crystal structure and orientation of the ZnO thin films were investigated by x-ray diffraction pattern. Figure 1 shows the diffraction patterns of ZnO thin films prepared at three different substrate temperatures. This figure indicates that the films are of polycrystalline nature. X-ray diffraction spectra of all the films were taken at room temperature and found to show almost similar behavior. The peaks with the Miller indices given belong to the ZnO (JCPDS file reference number Card No: 361451) film in hexagonal form.

The substrate temperature plays an important role in determining the structure of the ZnO films. As shown in Figure 1, the orientation changed with a temperature increase. The film deposited at 300 $^{\circ}$C (Figure 1. (a)) is a polycrystalline, with a weak (101) preferred orientation. Secondary peaks present are (100), (002), (110) and (102). As the substrate temperature is increased to 325 $^{\circ}$C and 350 $^{\circ}$C (Figure 1. (b) and (c)) the crystallites undergo a reorientation, with (002) preferred orientation and a substantial decrease in the secondary peak intensities. This result is in agreement with those reported for ZnO thin films prepared by the same process (Van Heerden and Swanepoel, 1997; Krunks and Mellikov, 1995; Riad et al., 2001; Oktik et al., 1996; Tiburcio-Silver et al., 1998).

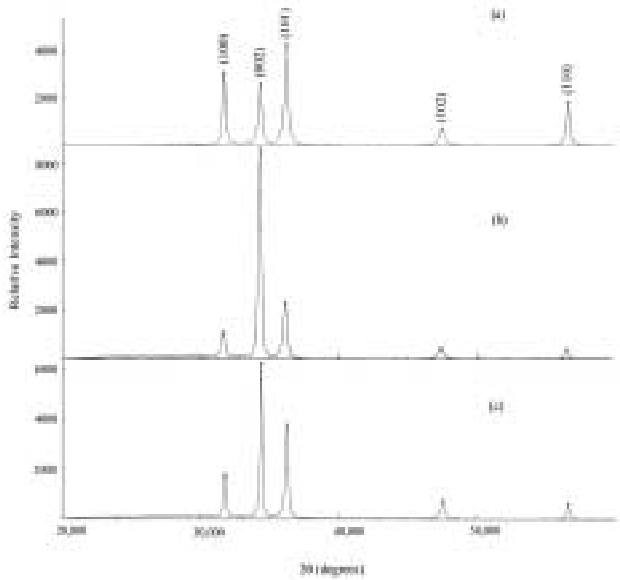

Figure 1. X-ray Diffraction Patterns of ZnO Films at (a) 300°C (b) 325°C and (c) 350°C Substrate Temperature.

The grain size of crystallites was calculated using a well-known Scherrer’s formula (Cullity, 2001):

$$D = \frac{0.9\lambda}{\beta \cos \theta} \qquad \textbf{(1)}$$

where D is the grain size of crystallite, λ(=1.5405 Å) the wavelength of X-rays used, β the broadening of diffraction line measured at half its maximum intensity in radians (FWHM) and θ is the angle of diffraction. The values found for the grain size at three different substrate temperatures are given in Table 1. In addition to this the values of β (FWHM) and 2 θ for different substrate temperatures are also given in this table. These values agree with the reported in the literature (Natsume and Sakata, 2000; Ohya et al., 1994; Bachari et al., 1999; Tran et al., 1999). Within the substrate temperature range used, the larger grains of about 58 nm have been obtained at 350 °C. This value is higher than grain size values estimated from XRD patterns of the films deposited at 300 °C and 325 °C. From these results, it can be concluded that the grain size has a tendency to increase with the increase of substrate temperature (Figure 2). The similar behavior has also been observed by A. Sanchez-Juarez et al.

Table 1. The values of grain size,β (FWHM) and 2θ for different substrate temperatures.

Substrate Temperature(°C)	2θ	(FWHM) β	D(nm)
300	36,24	0,239	35
325	34,34	0,217	38
350	34,42	0,144	58

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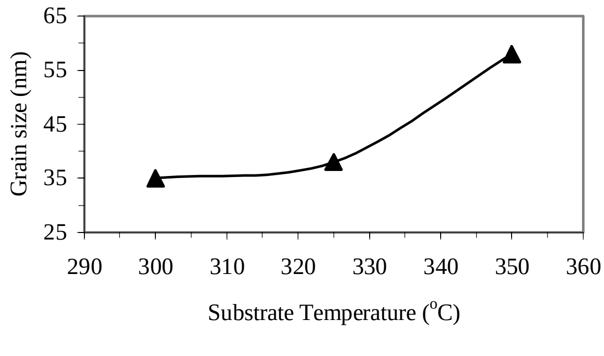

Figure 2. Dependence of The Grain Size on The Substrate Temperature

3.2 Optical Properties

The optical absorption data were used to determine the optical band gap of the semiconductor materials. The optical band gap (E_g) of the ZnO thin films was deduced from the photon energy dependence of the absorption coefficient. All the optical measurements were carried out at room temperature.

The optical absorption data were further used to determine whether the material has a direct or an indirect band gap. Figure 3, 4 and 5 show the plot of $(\alpha h\nu)^2$ versus hν for ZnO films produced at 300, 325 and 350 °C substrate temperature, respectively. The deduced E_g values are given as follows 3.11 eV at 300 °C and 3.14 eV at 325 °C and 350 °C. The optical band gap energies of the ZnO thin films prepared at different substrate temperature by spray pyrolysis technique are approximately same. Plots of $(\alpha h\nu)^2$ versus hν and $(\alpha h\nu)^{1/2}$ versus hν were analyzed for all the ZnO films. As seen in Figure 5 and 6, better linearity was observed in former case. Hence it is concluded that direct transitions dominate in ZnO thin films. From the plot, the optical band gap energy (E_g) was determined from the interception of the hν axis by extrapolating the linear portion of the graph. These energy gap values of ZnO films are in agreement with literature data (Messaoudi et al., 1995; Ambia et al., 1994; Major et al., 1986; Paraguay et al., 1999; Studenikin et al., 1998; Silver et al., 1994; Gould et al., 1994)

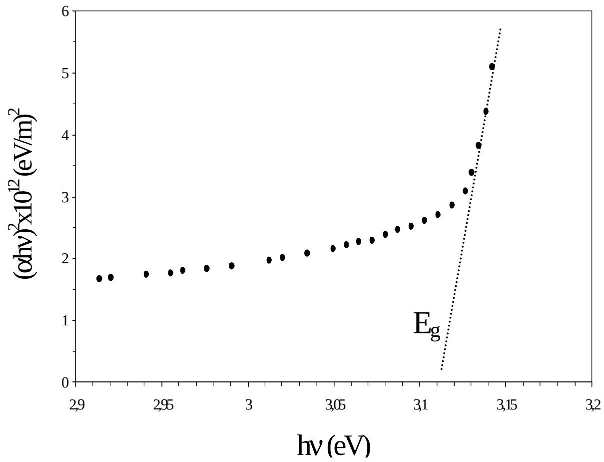

Figure 3. The Plot of $(\alpha h\nu)^2$ versus hν of ZnO Film Produced at 300 °C Substrate Temperature.

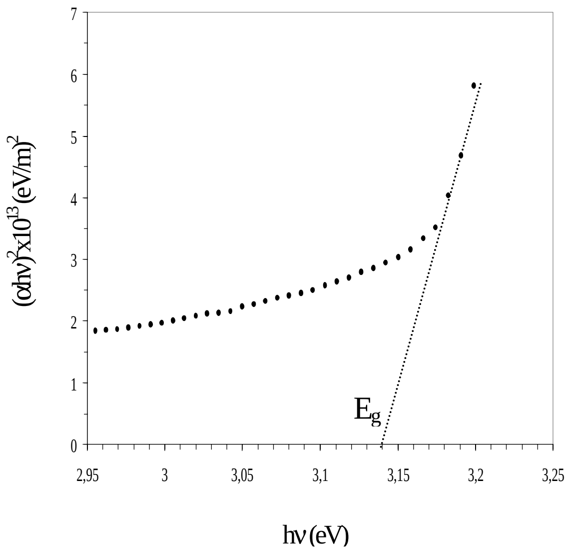

Figure 4. The Plot of $(\alpha h\nu)^2$ versus hν of ZnO Film Produced at 325 °C Substrate Temperatur.

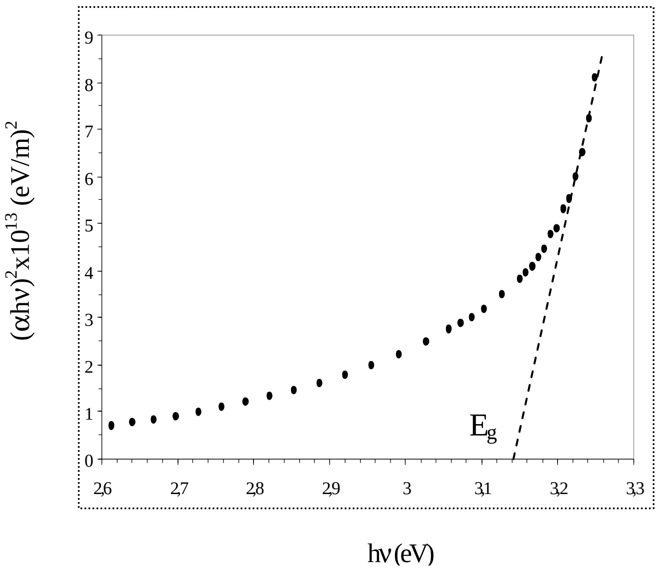

Figure 5. The Plot of $(\alpha h\nu)^2$ versus hν of ZnO Film.Produced at 350°C Substrate Temperature.

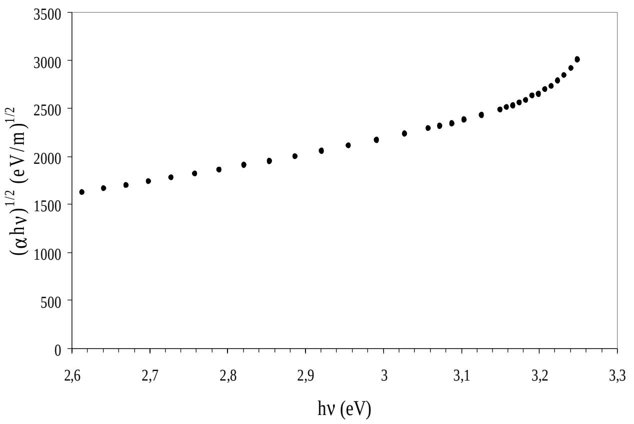

Figure 6. The Plot of $(\alpha h\nu)^{1/2}$ versus hν of ZnO Film Produced at 350°C Substrate Temperature.

4. CONCLUSION

The ZnO thin films have been deposited by spray pyrolysis technique onto glass substrates at different substrate temperatures. X-ray studies of ZnO films prepared by spray pyrolysis technique show that the films have polycrystalline nature and a hexagonal structure. From the XRD results of ZnO films deposited at different substrate temperatures it is seen that the substrate temperature plays an important role in determining the structure of the ZnO films. The films deposited at 300 °C substrate temperature exhibit the (101) preferred orientation, although a temperature increase bring about a reorientation and the (002) peak becomes enhanced. Furthermore, it was found that the grain sizes increase with the increment of the substrate temperature.

Optical absorption studies showed that the ZnO films have a direct band gap and their energy gap values are about 3.14 eV. The band gap values of the ZnO films deposited at different substrate temperatures are approximately same. So, no significant effect on E_g was observed in the case of the substrate temperature increasing.

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