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Araştırma Makalesi / Research Article

INFLUENCE OF SUBSTRATE TEMPERATURE ON STRUCTURAL AND ELECTRICAL PROPERTIES OF ZnO FILMS

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Abstract: Zinc oxide (ZnO) films have been deposited by spray pyrolysis technique at different substrate temperatures. The effects of substrate temperature on the structural and electrical properties of ZnO films produced by this technique have been investigated. X-ray diffraction spectra of the films have shown that the films are polycrystalline and hexagonal wurtzite in structure. From these spectra, grain size and texture coefficient (TC) are calculated. The conductivity of ZnO films was determined from current-voltage characteristics measured at room temperature and in dark. The ohmic conduction mechanism was observed to take place in all the films.
***Key words*:** Grain size, spray pyrolysis technique, x-ray diffraction spectra, ZnO film.

Taban Sıcaklığının ZnO Filmlerinin Yapısal ve Elektriksel Özelliklerine Etkisi

Özet: Çinko oksit (ZnO) filmleri püskürtme yöntemi kullanılarak farklı taban sıcaklıklarında üretilmiştir. Üretilen bu filmlerin yapısal ve elektriksel özelliklerine taban sıcaklığının etkisi incelenmiştir. Filmlerin x-ışınları kırınım desenlerinden polikristal ve hekzagonal yapıda oldukları görülmüştür. Buradan tanecik boyutu ve yapılanma katsayısı (TC) hesaplanmıştır. ZnO filmlerinin iletkenlikleri karanlıkta ve oda sıcaklığında alınan akım-voltaj ölçümlerinden belirlenmiştir. Bütün filmlerin ohmik iletim mekanizmasına sahip olduğu gözlenmiştir.
***Anahtar kelimeler*:** Tanecik boyutu, püskürtme yöntemi, x-ışını kırınım desenleri, ZnO film.

Introduction

Due to their optical and electrical properties zinc oxide (ZnO) films have been widely studied and have received considerably attention in recent years. ZnO has also gained much attention due to the many advantages over other oxide thin films such as In_2O_3, $CdSnO_4$ or SnO_2. These advantages include non-toxicity, good electrical, optical and piezoelectric behaviors, stability in hydrogen plasma atmosphere and low price. Moreover, ZnO films have many interesting potential applications such as transparent electrode, piezoelectric device, and gas sensor and it can be used as windows layer in heterojunction solar cells (Natsume and Sakata, 2000; Nunes et al., 2001; Paraguay et al., 1999). Pure zinc oxide is an intrinsic semiconductor with high electrical resistivity and a direct band gap of about 3.2eV.

In the past decades, many techniques have been employed in the deposition of ZnO films such as metal organic chemical vapour deposition (MOCVD) (Wang et al., 2005), magnetron sputtering (Bachari et al., 1999; Li et al., 2003; Minami et al., 1990), pulsed laser deposition (PLD) (Shan and Yu, 2004), sol gel (Kozuka et al., 1997) and spray pyrolysis (Krunks and Mellikov, 1995; Messaoudi et al., 1995; Nunes et al., 1999; Oktik et al., 1996; Sanchez-Juarez et al., 1998). Among these methods, the spray pyrolysis technique has the advantages of low cost, easy-to-use, safe, and can be implemented in a standard laboratory.

In this work, the influence of the substrate temperature on the structural and electrical properties of ZnO films deposited by spray pyrolysis are presented and discussed.

Experimental Details

Spray pyrolysis system was used to obtain ZnO films. The spray pyrolysis set up is shown in our previous paper (Ilican et al., 2005). The ZnO films were deposited onto glass substrates at temperatures 300, 325 and 350°C. 0.1M starting solution of zinc acetate $\left[Zn(CH_3CO_2)\cdot 2H_2O\right]$ diluted in methanol and de-ionized water (3:1) was used. The solution was sprayed onto glass substrates using a carrier gas N_2. The nozzle to substrate distance was 28cm and during deposition, solution flow rate was held constant at 4mlmin^{-1} and carrier gas pressure at 0.2kgcm^{-2}. The substrate temperature was measured using an Iron-Constantan thermocouple and the temperature was held within an accuracy of $\pm 5^{\circ}$C. The film thicknesses were estimated by weighing method.

The structural analysis of the films was performed with a RIGAKU RINT 2000 Series X-Ray Automatic Diffractometer with CuK_{α} (λ=1.5405Å) radiation and scanning angle 2θ was varied in the range between 20° and 60°.

For the dc electrical measurements two gold electrodes were deposited on the film by vacuum deposition using Leybold Heraus 300 Univex system. HP 4140B pA/dc power supply was used for dc characteristics of the films. The I-V measurements were carried out in dark and at room temperature.

The conductivity type of the films was measured by the hot-probe method.

Results and Discussion

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. Besides, all the films fit a hexagonal (wurtzite) structure. The substrate temperature plays a significant role in determining the structure of the ZnO films.

As shown in Figure 1, the preferred orientation changed with a temperature increase (Krunks and Mellikov, 1995, Oktik et al., 1996; Riad et al., 2001; Tiburcio-Silver et al., 1998; Van Heerden and Swanepoel, 1997). The preferred orientation of the ZnO films was evaluated by the texture coefficient (TC), calculated from the equation (Barret and Massalski, 1980)

$$\mathrm{TC(hkl)} = \frac{\mathrm{I(hkl)/I_0(hkl)}}{\frac{1}{N}\sum_N \mathrm{I(hkl)/I_0(hkl)}} \quad (1)$$

Where TC is the texture coefficient of the (h k l) plane, I the measured or normalized intensity, I_0 the corresponding standard intensity given in ASTM data, and N the number of reflections. The preferred orientation of a film will be (h k l) plane for the higher value of TC. The TC are calculated from Equation (1), for the reflections (100), (002), (101), (102) and (110) of the hexagonal ZnO at the examined substrate temperature range. From the TC's in Figure 2 it appears that at the substrate temperature ranged from 300 to 350°C the preferential (002) orientation is enhanced while the (101) orientation suppressed.

The average crystalline size of the ZnO film was estimated from X-ray diffraction using Scherrer formula (Cullity, 1978).

$$D = \frac{K\lambda}{\beta\cos\theta} \quad (2)$$

Where β is the full-width of the half-maximum (FWHM) of the peak corrected for instrumental broadening, λ is the wavelength of the X-ray, θ is the Bragg diffraction angle and K is Scherrer's constant.

The values found for the grain size at three different substrate temperatures are in the range 35-58nm which agrees with the values reported in the literature (Bachari et al., 1999; Natsume and Sakata, 2000; Ohya et al., 1994; Tran et al., 1999). Grain size was derived from the XRD data revealing that the grain size increases with the substrate temperature (Figure 3). This behavior has also been observed by A. Sanchez-Juarez et al (Sanchez-Juarez et al., 1998).

The electrical conductivity of ZnO films was measured from the I-V characteristics. The I-V measurements are carried out at room temperature and in dark. The I-V characteristics of ZnO films deposited at three different substrate temperatures are shown in log-log plot of I-V in Figure 4. For all the films studied, the ohmic conduction was observed to be the dominant mechanism. All the films exhibited n-type conductivity which was determined by the hot-probe method.

The dependence of conductivity on substrate temperature is shown in Figure 5. It can be observed that for the films deposited at three different substrate temperatures the conductivity improves as substrate temperature increasing. It is well known that the n-type conductivity in ZnO is due to the oxygen vacancy and interstitial zinc atoms, both act as donors. Hence, these can give rise to a high carrier concentration as substrate temperature increases. On the other hand, the enhancement in conductivity with increasing substrate temperature may also be attributed to the increase in grain sizes.

Conclusion

The ZnO thin films have been deposited by spray pyrolysis technique onto glass substrate at different substrate temperatures. The structural and electrical properties of ZnO films prepared by spray pyrolysis technique depend strongly on the substrate temperature. The orientation of ZnO films was changed with substrate temperatures increasing. The films deposited at 300°C substrate temperature do not exhibit the (002) preferred orientation; however 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. The conductivity of the ZnO film estimated from the I-V characteristic at room temperature was observed to increase as substrate temperature increasing. The increase in the conductivity can be attributed to the increase in the grain size and the high carrier concentration because of the interstitial zinc atom and oxygen vacancy which act as donor.

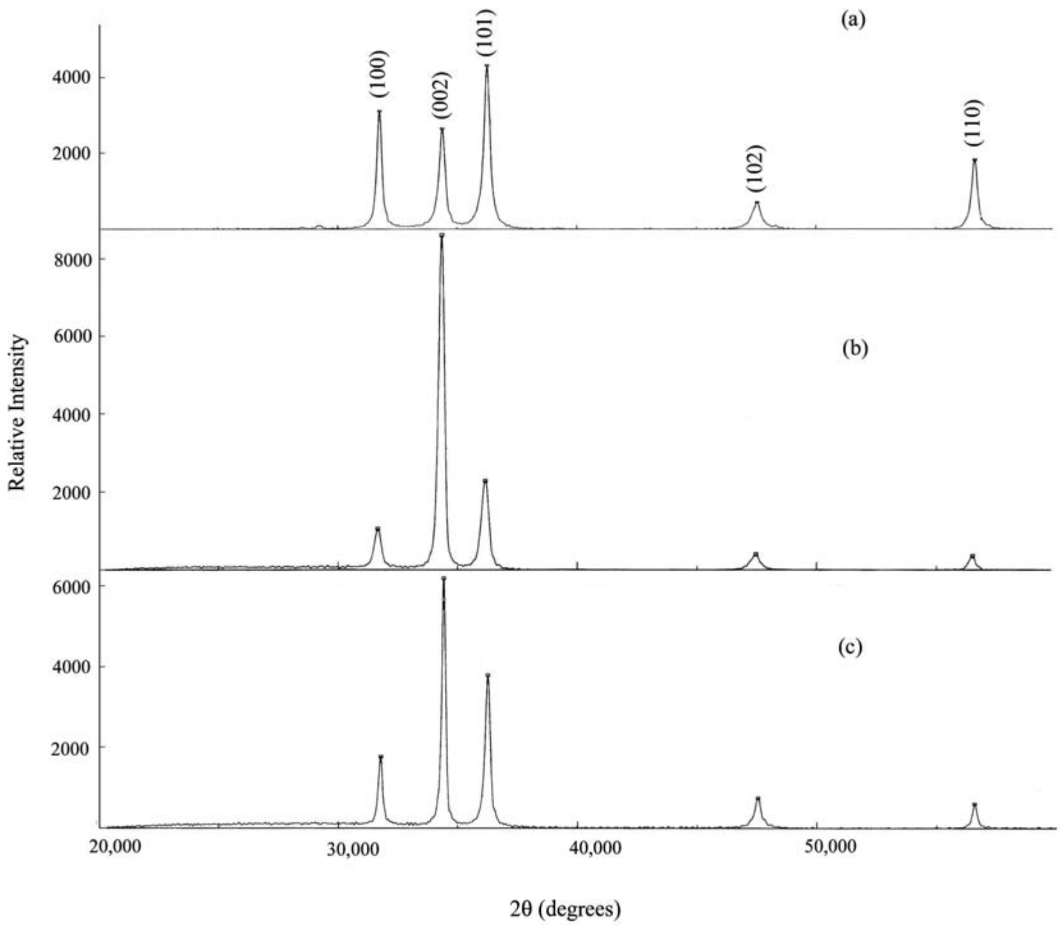

Figure 1. X-ray diffraction patterns of ZnO films at (a) 300°C (b) 325°C and (c) 350°C substrate temperature.

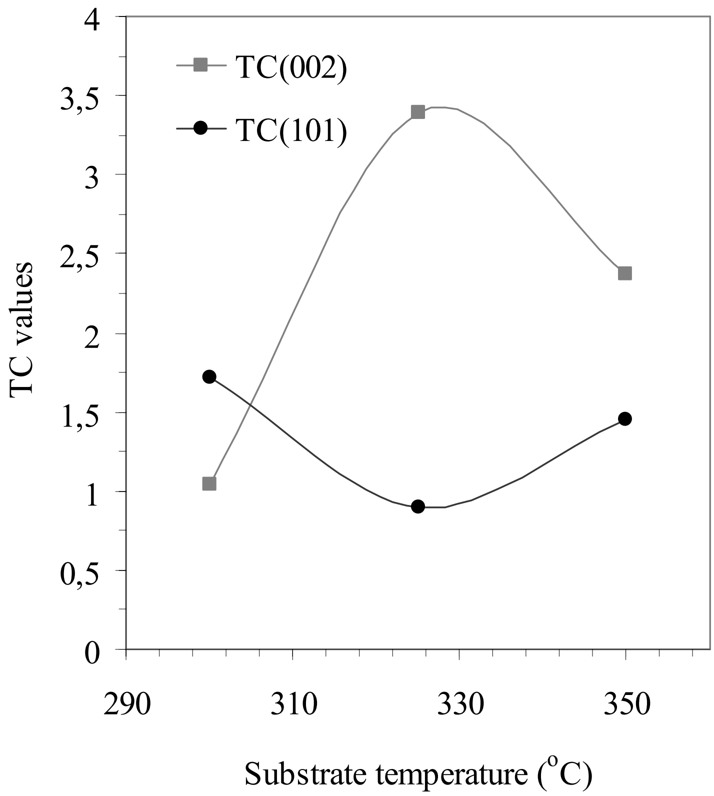

Figure 2. Variation of the TC values with the substrate temperature.

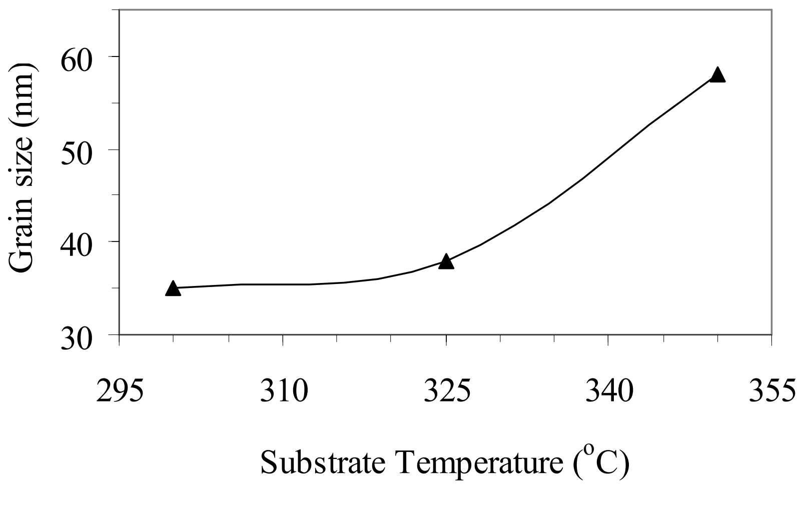

Figure 3. Dependence of the grain size on the substrate temperature.

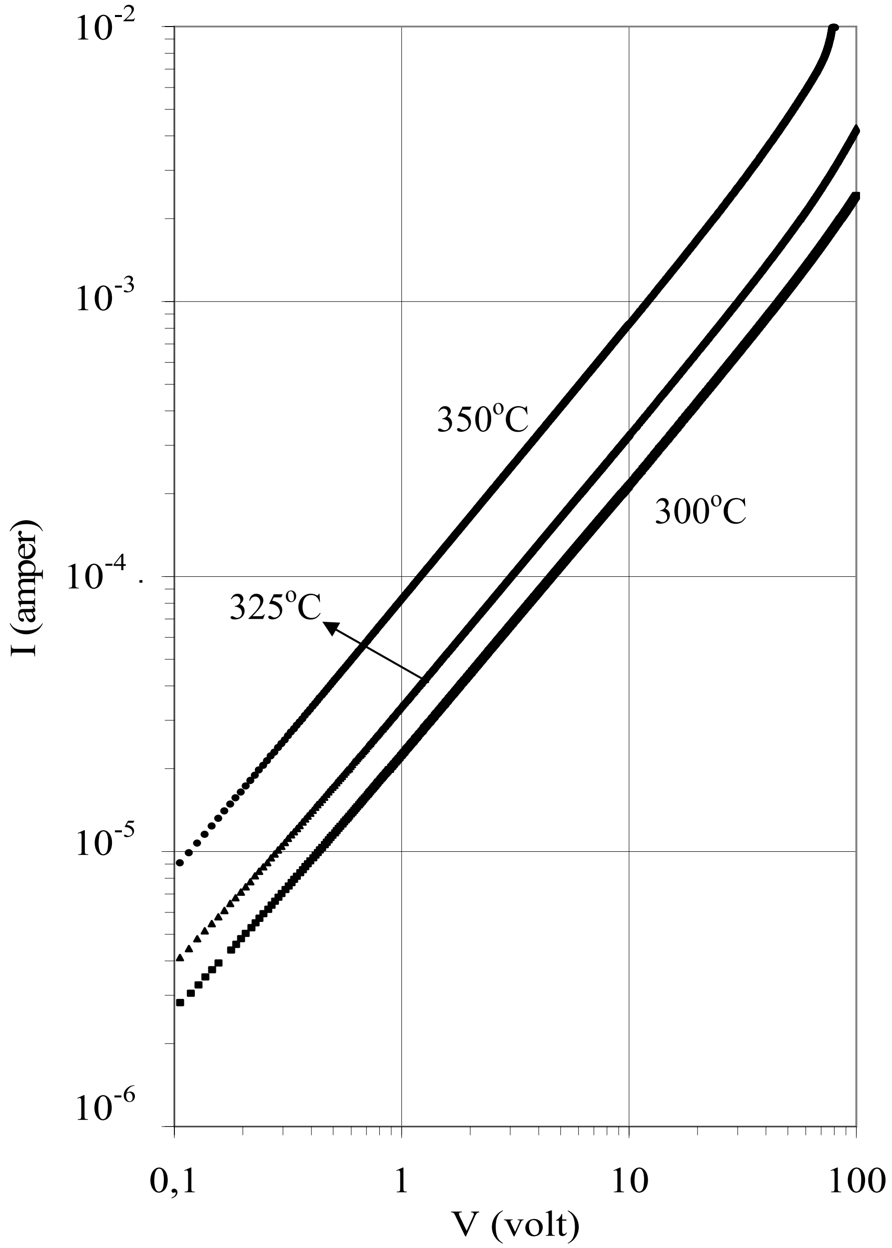

Figure 4. I-V characteristics of ZnO films at room temperature.

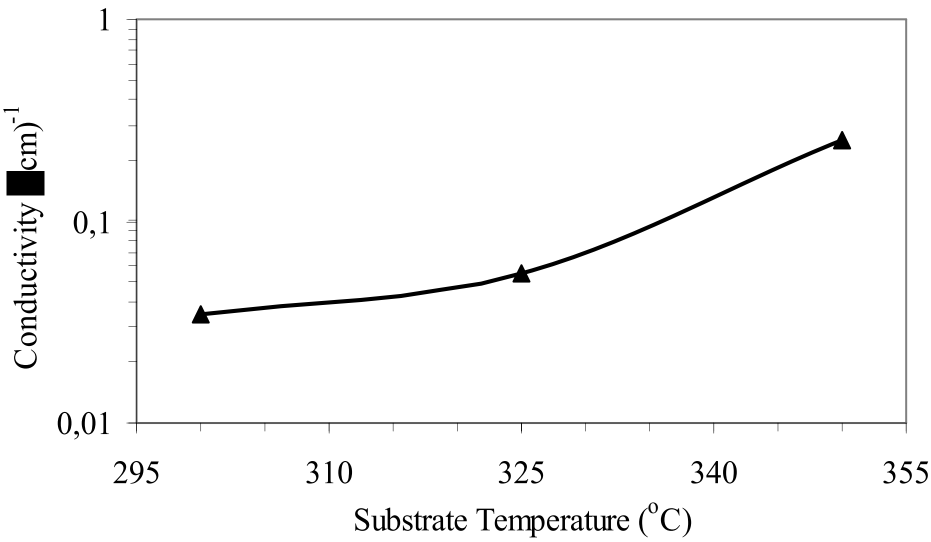

Figure 5. Dependence of the conductivity on the substrate temperature.

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