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ZnO Filmlerinin Optik, Elektrik ve Yüzey Özellikleri Üzerine Tavlama İşleminin Etkileri

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Anahtar Kelimeler
Gövde
Isı değiştiricisi
Basınç düşümü
Enerji.

Özet: ZnO filmleri 300±5 °C sıcaklıktaki cam tabanlar üzerine ultrasonik kimyasal püskürtme tekniği kullanılarak hazırlanmıştır. Depolanan filmler çeşitli sıcaklıklarda (350, 450, 550 °C) 2 saat süre ile tavlanmıştır. Tavlanmış ve tavlanmamış ZnO filmlerinin elektrik, optik ve yüzey özellikleri incelenmiştir. Tüm filmlerin optik geçirgenlik ve absorbans spektrumları UV-VIS Spektrofotometre ve optik bant aralıkları da optik metot kullanılarak belirlenmiştir. Ayrıca, ZnO'in görünür emisyon pikleri ve nokta kusurları da fotolüminesans spektrumu kullanılarak belirlenmiştir. Kalınlık, kırılma indisi ve sönüm katsayısı değerleri spektroskopik elipsometre tekniği ile elde edilmiştir. Elektrik ve yüzey özellikleri sırasıyla dört uç tekniği ve atomik kuvvet mikroskobu ile incelenmiştir. Elde edilen sonuçlara göre ZnO filmlerinin optik, elektrik ve yüzey özellikleri üzerine tavlama sıcaklığının etkisi araştırılmıştır.

Effect of Annealing Process on Optical, Electrical and Surface Properties of ZnO films

Keywords
ZnO films
Photoluminescence
Spectroscopic Ellipsometry
Four Point Technique
Atomic Force Microscopy

Abstract: ZnO films were prepared on glass at 300±5 °C substrate temperature by ultrasonic spray pyrolysis. The deposited films were annealed at various temperatures (350, 450, 550 °C) for 2 hours. Annealed and unannealed of ZnO films were characterized by studying their optical, electrical and surface properties. The optical transmittance and absorbance spectra of all films were examined by UV-VIS Spectrophotometer and the optical band gap was found using optic method. Besides, visible emission peaks and native point defects of ZnO films were determinate using photoluminescence spectra. Thickness, refractive index and extinction coefficient values were obtained with spectroscopic ellipsometry technique. The electrical and surface properties of the films were characterized four point technique and atomic force microscopy, respectively. According to result, the effects of annealing temperature on the optical, electrical and surface properties of the ZnO films are discussed.

1.Giriş

ZnO is one of the most important members of Transparent Conductive Oxide (TCO) materials (Rozati, 2006; Rozati vd., 2004; Martins vd., 2004; Ellmer vd., 2008). ZnO is a wide band gap non-stoichiometric n-type semiconductor with a low resistivity and high transmittance in the visible region in thin film form. ZnO is a very interesting material for many different applications in both microelectronic and optoelectronic devices. Also, ZnO is a well-known semiconducting material with many practical applications such as a transparent conductive contact (Chopra vd., 1983),
thin film gas sensor (Dayan vd., 1998; Mitra vd., 1998), varistor (Chen vd., 1997), luminescent material (Studenikin vd., 1998), surface electro-acoustic wave device (Gorla vd., 1999) ,UV laser (Tang vd., 1998; Reynolds vd. 1996), and others (Brown vd., 1976). ZnO films are easy to prepare; several techniques are well described in the literature such as sol–gel (Kang vd., 1997), spray pyrolysis (Ayouchi vd., 2003; Kaid vd., 2007), thermal evaporation (Ma Jin vd., 1996; Aida vd., 2006), pulse laser deposition (Jin vd., 2001) and r.f. (Mahmood vd.,

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2007), etc. Among these, spray pyrolysis is one of the most widely used methods. Spray pyrolysis has been developed as a powerful tool to prepare various kinds of films such as metal oxides, superconducting materials, and nanophase materials. In comparison with other chemical deposition techniques, spray pyrolysis has several advantages such as high purity, excellent control of chemical uniformity, and stoichiometry in multi-component system. Other advantages of the spray pyrolysis method are that it can be adapted easily for production of large-area films, and to get varying band gap materials during the deposition process. In this work, ZnO films were deposited by spray pyrolysis on glass substrates. The influence of annealing temperature on the electrical, optical and surface properties of ZnO films was investigated.

2. Experimental

In the spray pyrolysis technique, the precursor of the material to be deposited is in solution and sprayed onto a heated substrate using air as carrier gas. The apparatus we used for our sprayed process is diagrammed in Fig. 1. ZnO films were deposited onto the glass substrates at 300±5 °C substrate temperature. A total of 0.05 M solution of zinc acetate dehydrate [$Zn(CH_3COO)_2.2H_2O$] diluted in deionized water was used for all the films and a few drops of acetic acid were added to improve the clarity of solution. The nozzle was at a distance of 30 cm from the substrate during deposition. The solution flow rate was held constant at 5 ml/min. Air was used as the carrier gas, at the pressure of 1 bar. After deposition parts of the films were annealed in air atmosphere at 350, 450 and 550 °C for 2 hours and slowly cooled down to room temperature. The samples have been named as Z0(unannealed, as-deposited at 300 °C), Z1 (annealed at 350 °C) and Z2 (annealed at 450 °C), Z3 (annealed at 550 °C).

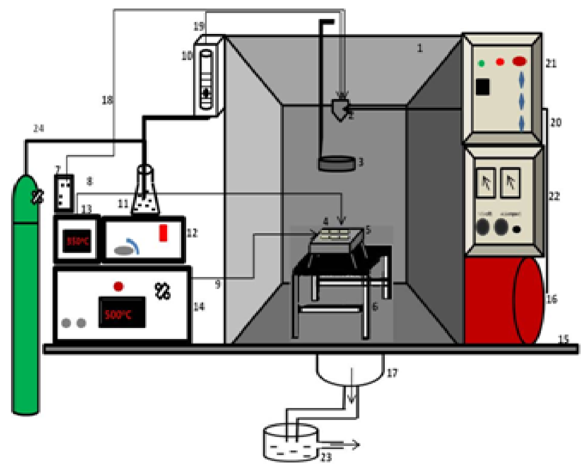


Figure 1. Spray pyrolysis set up (1) Spraying chamber, (2) Ultrasonic atomizer, (3) Moving pan (4) Glass substrates (5) Bronze block (5000-6000 Watt), (6) Moving base, (7) Oscillator, (8) 1. termocouple, (9) 2. termocouple, (10) Flowmeter, (11) Spraying solution, (12) Heater-magnetic mixer, (13) Temperature indicator, (14) Electrical heater, (15) Table, (16) Air gas, (17) Fan, (18) Cable of oscillator, (19) Spraying hose, (20) Air hose, (21) ac ampermeter (22) ac voltmeter, (23) water-filled container (24) Air tube

The optical measurements of the ZnO films were carried out at room temperature using Schimadzu UV-2550 UV-VIS Spectrophotometer in the wavelength range 300 to 900 nm. The thicknesses, refractive index and extinction coefficient of the film was measured using SC 620 Spectroscopic Ellipsometry (SE).

Photoluminescence (PL) spectra were measured at room temperature using PERKIN-ELMER.LS-55 by a source with excitation wavelength of 325 nm. PL measurements were performed using the 325 nm line from a Xenon pulse lamp as the excitation source and a UV–vis photomultiplier tube as detector to the PL signals. The surface morphology profiles of the films were recorded using atomic force microscopy (AFM). Electrical measurements have been performed by Keithley 2601A System Source Meter four probe measurement systems.

3. Result and discussion

The transmission and reflectance spectra in ultraviolet and visible regions have been depicted in Fig. 2 for the set of ZnO films studied. Fig. 2 (a) illustrates the experimental transmission (T) of the films formed with different annealing temperature. From the data we can see that all films exhibit a strong UV sharp edge with annealing process and that the transmittance in the visible range varied from 65% to 45% as annealing temperature increased from 350 °C to 550 °C. It is clear from the curves that the absorbance is high for photons of energy greater than the band gap. On the other hand, the annealed films exhibit a sharp fundamental absorption edge. As the annealing temperature increases from 350 to 550 °C, the transmittance increases gradually at the same wavelength in the 300-900 range while the reflectance shows a concomitant decrease (Fig. 2 (b)).

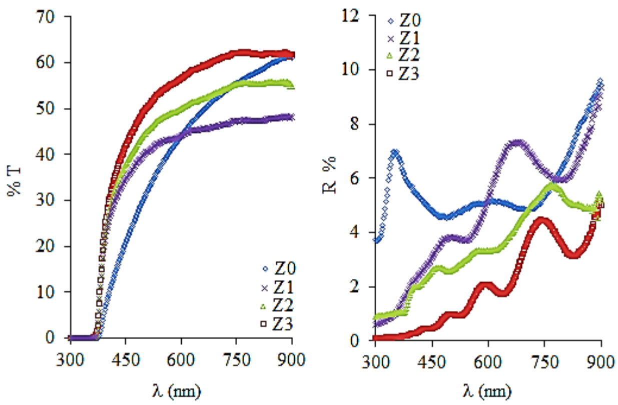


Figure 2. (a) Transmittance and (b) reflectance spectra of ZnO films

The optical absorption coefficient (α) was evaluated from the transmission spectra. The optical band gap of the films is determined by the following relationship:

$$\alpha = A(h\nu - E_g)^{1/2}/h\nu \quad (1)$$

for the allowed direct transition, where A is a constant and E_g is the optical band gap. The optical band gap values are obtained by extrapolating the linear portion of the plots of $(ah\nu)^2$ versus $h\nu$ to $\alpha = 0$. The variation of $(\alpha h\nu)^2$ with $h\nu$ of the as-deposited and annealed ZnO films formed at various temperatures are shown in Fig. 3. The optical band gap of the sprayed ZnO films varied from 3.24 eV to 3.27 eV and influenced with the annealing process. These values of optical band gap are in good agreement with the reports on spray pyrolysis (Lokhande vd., 2000), dc reactive magnetron sputtered (Subramanyam vd., 1999), rf sputtered (Qu vd., 1994), ion beam sputtered (Ma vd., 1996) and ultrasonic sprayed (Zang vd., 2001) films.

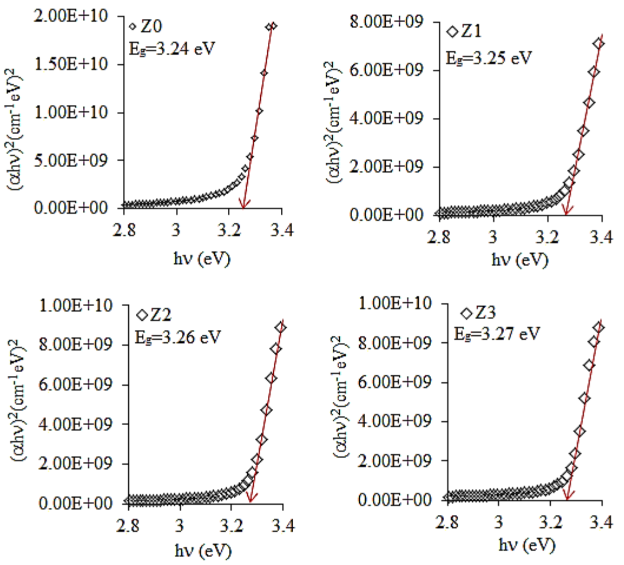


Figure 3. Variation of $(\alpha h\nu)^2$ with photon energy of sprayed ZnO films

For the analysis of the experimental ellipsometric spectra of the ZnO films and hence obtain their thicknesses and optical constants such as refractive index (n), extinction coefficient (k). The experimental ellipsometric measurements were performed under indicate angles of 70° and the measured data were fitted using the Cauchy-Urbach (CU) model. The measured SE data, Ψ (the relative amplitude change) of ZnO films over the spectral range 330–1600 nm are shown in Fig. 4.

From the Fig. 4 it is clear that there is a good correlation between the experimental and the model curves for the desired wavelength range, 300–900 nm. Hence, the optical constants of the ZnO films can be described adequately by using the CU model over a visible wavelength range. The values of ZnO film thickness and data of spectroscopic ellipsometry are given in Table 1. Fig. 5 shows the optical constants (index of refraction n and extinction coefficient k) of ZnO films. The index of refraction and the extinction coefficient exhibit a strong dispersion and decrease monotonically with increasing wavelength. Refractive indices of ZnO films in this study were found to be in the range 2.11–2.60. The extinction coefficients were very small from 7.34×10^{-4} to 1.19×10^{-3} over the chosen wavelength range. Also, from the Fig. 5 it can be seen that the refractive index shows a strong spectral dependence for λ<500 nm (near the band edge), indicating that ZnO thin film becomes absorbent in the ultraviolet region.

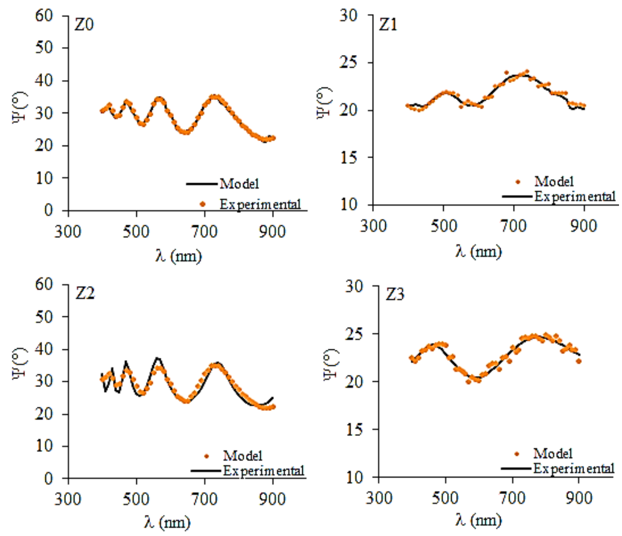


Figure 4. SE data of ZnO films

Table 1. The thickness and spectroscopic parameters of ZnO films

Film	Thickness (nm)	A_n	B_n $(nm)^2$	C_n $(nm)^4$	A_k	B_k $(eV)^{-1}$
Z0	390	2.45	0.081	0.001	0.051	1.51
Z1	382	2.30	0.065	0.001	0.052	1.45
Z2	360	2.28	0.032	0.004	0.034	1.48
Z3	425	2.25	0.017	0.003	0.030	1.41

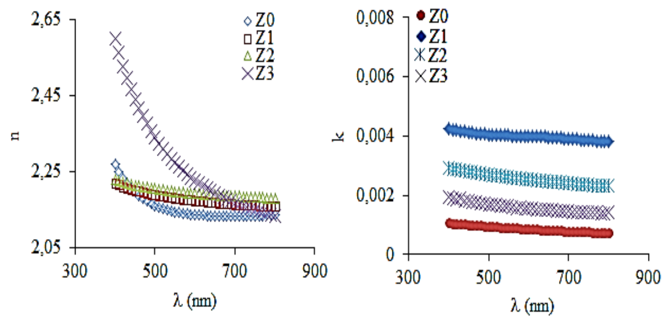


Figure 5. Refractive index and extinction coefficient of ZnO films

The PL spectra of the ZnO films are measured in the wavelength range of 200–900 nm with an excitation wavelength of 325 nm and shown in Fig. 6, from which we can see that the UV peak is weak for all ZnO films. PL spectra of the films shows identical emission peak positions different defect states and their formation energies have been calculated theoretically (Zang vd., 2001; Janotti vd., 2006).

The relative intensity normalized at 375 nm, which is reported originated from the conduction band to valence band combination, is plotted in Fig. 6 inset. However, we find that the intensity ratio of ZnO films is weaker than other studies. Besides, It is well known that different types of defects are responsible for violet, blue, green, yellow and orange–red emissions. However, the origin of the defects responsible for these emissions is not fully clear but still there are lots of controversial explanations for these emissions in ZnO films (Mo vd., 1998; Yao vd., 2000; Wu vd., 2001). Using the full-potential linear muffin-tin orbital method, Sun (Sun vd., 2000) determined the defects in ZnO films as shown in Fig. 6, such as oxygen vacancy (V_O), zinc vacancy (V_{Zn}), interstitial oxygen (O_i), interstitial zinc (Zn_i) and antisite oxygen (O_{Zn}).

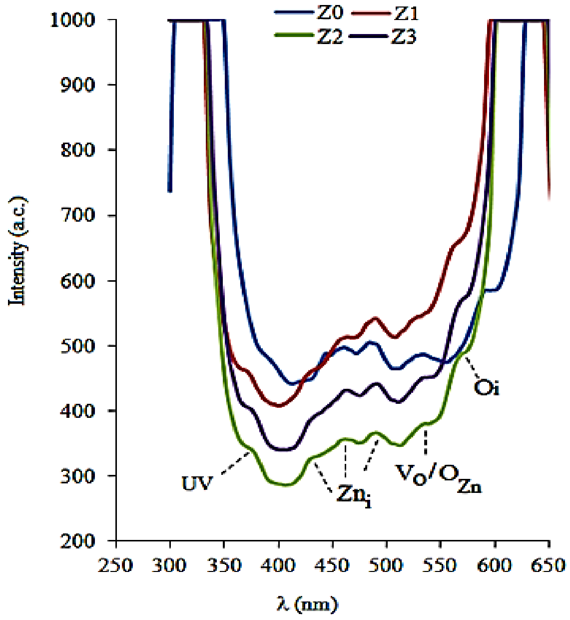
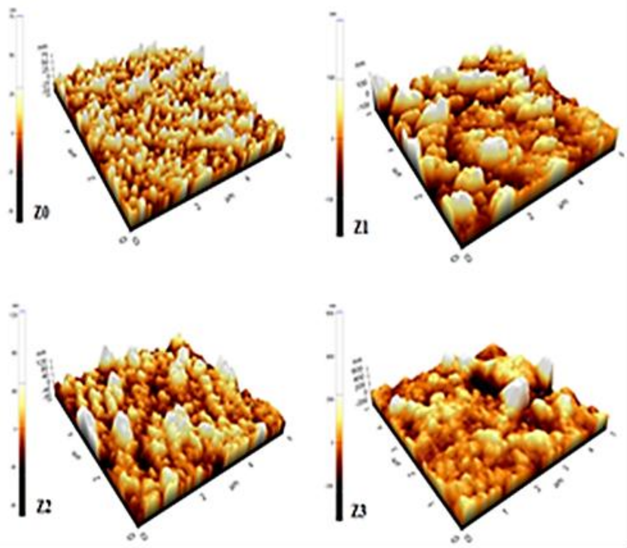


Figure 6. PL spectra of ZnO films

Fig. 7 shows the AFM images of the ZnO films. The AFM images are obtained by 5×5 μm² scan. AFM images are examined, hill-type formations are observed which have scattered randomly in different widths and heights and white areas are. The reason of this situation is different horizontal and vertical arrangement of neighboring atoms. Also black areas are formed due to grain boundaries which have accumulated by reaching the surface atoms. Moreover, another reason for the formations of different color may be formed height differences due to atoms which are come to rest in glass surface of roughness. The AFM images are shown clearly the influences of the annealing on the morphology of the film. For the unannealed film have the best granulous structure but granular structure of annealed films is disrupted. Consequently; the surface morphology of ZnO films that unannealed has the best of granulous structure. But after two hours annealing the surface morphology of ZnO films have high roughness values.



These values were shown Table 2.

Figure 7. AFM images of ZnO films

Table 2. Roughness vaules of ZnO films

Film	R_q (nm)	R_a (nm)	R_{pv} (nm)
Z0	15	12	132
Z1	25	20	215
Z2	48	37	304
Z3	54	49	354

In this study, the resistivity of ZnO films depends on two parameters, the deposited and annealing temperature. The dependence of resistivity on the deposited and annealing temperature is shown in Fig. 8. As shown from this figure, the electrical resistivity is influenced with the annealing temperature. The minimum value of resistivity of about 2.13×10³ Ωcm has been obtained at 550 °C annealing temperature. It is clear that the resistivity of ZnO films shows decrease with annealing process.

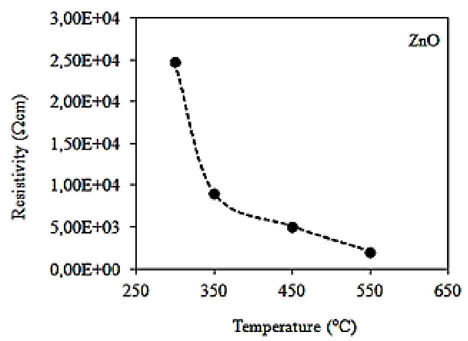


Figure 8. Electrical resistiviy of ZnO films

4. Conclusion

In summary, the influence of annealing temperature on the electrical, optical and surface properties of ZnO films is presented. The average transmittance of the films is over 60 % in the visible range. The lowest resistivity of 2.13×10^3 Ωcm was obtained at an annealing temperature of 550 °C. The results show that the resistivity decreases as the annealing temperature increases. The determined refractive index was decreased as the annealing temperature increased. The deduced roughness was increased noteworthily with annealing process. The films exhibited a direct transition in the range 3.24–3.27 eV. The room temperature photoluminescence spectra of the annealed films showed near band-edge emission and defect related visible emissions. The presence of interstitial zinc (Zn_i) and interstitial oxygen (O_i) induced the dominant blue and orange red emissions in the films.

Kaynaklar

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Symbols

T	transmission
α	absorption coefficient
A	constant
E_g	optical bant gap (eV)
ν	frequency (s^{-1})
h	planck constant (j.s)
n	refractive index
k	extinction coefficient
R_q	root mean square roughness (nm)
R_a	average roughness (nm)
R_{pv}	peak-valley roughness (nm)
Zn	zinc
O	oxygen
V_O	oxygen vacancy
V_{Zn}	zinc vacancy
O_i	interstitial oxygen
Zn_i	interstitial zinc
O_{Zn}	antisite oxygen

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a	average
q	root mean square
pv	peak valley
g	gap
o	vacancy
i	interstitial