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DETERMINATION AND ANALYSIS OF THE DISPERSIVE OPTICAL CONSTANTS OF THE NON-CRYSTALLINE ZnO THIN FILM

M. Caglar, S. Ilican* and Y. Caglar

Anadolu University, Faculty of Science, Department of Physics, Eskisehir, Turkey

**silican@anadolu.edu.tr*

Abstract. In this work, non-crystalline ZnO thin film has been successfully deposited by the spray pyrolysis method onto glass substrate. The structure of the film was analyzed by X-ray diffraction and the results obtained showed that the structure of the film is non-crystalline. The Urbach tail parameter, the optical band gap, and the optical constants such as refractive index, extinction coefficient and dielectric constants of the deposited non-crystalline thin film have been investigated by optical characterization method. The dispersion curves of the refractive index of the non-crystalline film obey single-oscillator model. The dispersion parameters such as E_o (single-oscillator energy) and E_d (dispersive energy) of the non-crystalline film was determined.

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1. INTRODUCTION

There exists a worldwide strong interest in realizing inexpensive transparent conducting films to be used, for example, in solar cells, as sensor devices or as coating to heat glass windows. ZnO is one of the few metal oxides which can be used as a transparent conducting oxide. It has some advantages over other possible materials such as In_2O_3, Cd_2SnO_4 or SnO_2 due to its unique combination of interesting properties: non-toxicity, good electrical, optical and piezoelectric behavior, stability in a hydrogen plasma atmosphere and its low price [1-3]. Additionally, ZnO is suitable for many different applications, such as optoelectrodes, surface acoustic wave devices (SAW) and sensor materials. The ZnO films can be deposited by several techniques including, sputtering, metal organic chemical vapour deposition, sol gel and spray pyrolysis. Among these, the spray pyrolysis method has the advantages of low cost, easy-to-use, safe, and can be implemented in a standard laboratory.

The refractive index is one of the fundamental properties of a material, because it is closely related to the electronic polarizability of ions and the local field inside the material. The evaluation of refractive indices of optical materials is of considerable importance for applications in integrated optic devices such as switches, filters and modulators, etc., where the refractive index of a material is the key parameter for device design [4].

There have been extensive studies on the crystalline structure and optical transmittance of ZnO thin films. There are, however, few studies on the optical constants of non-crystalline ZnO thin films. In this work, we deposited non-crystalline ZnO thin film successfully onto glass substrate. We also investigate the optical properties (the band gap, optical constants such as refractive index, extinction coefficient, and dielectric constant, the Urbach energy and the dispersion parameters).

2. EXPERIMENTAL

The ZnO non-crystalline film was deposited onto glass slices, chemically cleaned, using the spray pyrolysis method at 475 ^oC substrate temperature. 0.2 M solution of zinc acetate dehydrate [$Zn(CH_3COO)_2.2H_2O$] diluted in methanol and deionized water (3:1) was used for the film. A few drops of acetic acid were added to improve the clarity of solution. Nitrogen was used as the carrier gas, pressure at 0.2 bar. The ultrasonic nozzle to substrate distance was 30cm and during deposition, solution flow rate was held constant at 4 mlmin^{-1}. The deposition time was about 5 min. The substrate temperature was measured using an Iron-Constantan thermocouple. The thicknesses of the films were determined with Mettler Toledo MX5 microbalance by using weighing method. The film thickness value was found to be 87 nm.

The structural analysis of the thin film was performed with a RIGAKU RINT 2200 Series X-Ray Automatic Diffractometer with CuK$_\alpha$ (λ=1.54059Å) radiation. The diffractometer reflections were taken at room temperature and the value of 2θ were swapped between 20^o and 70^o with a scanning speed of 0.02^o/s at 40 kV and 30 mA. The optical absorption and transmittance spectra of all the thin films at room temperature were recorded on a SHIMADZU UV-2450 UV-VIS Spectrophotometer in the wavelength range 190nm-900nm. The reflectance data were calculated using these data.

3. RESULT AND DISCUSSION

The crystal structure and orientation of the ZnO thin film were investigated by X-ray diffraction (XRD) patterns. Fig.1 shows the diffraction pattern of the ZnO thin film. XRD pattern indicates that the film has almost non-crystalline phase.

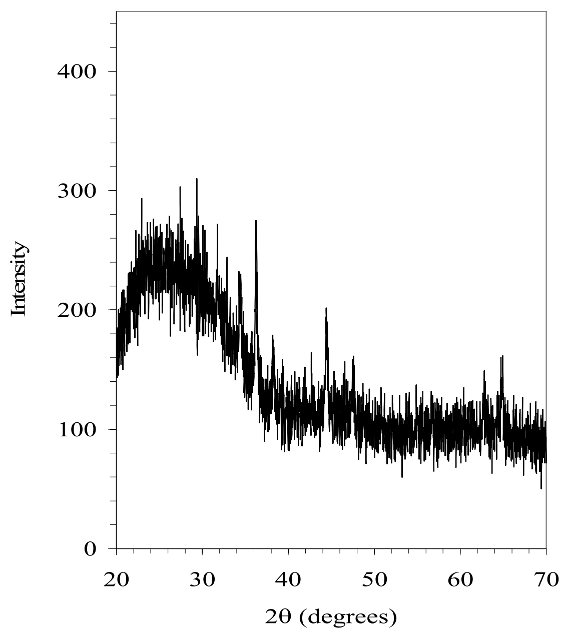

Fig.1. X-ray diffraction spectrum of ZnO thin film.

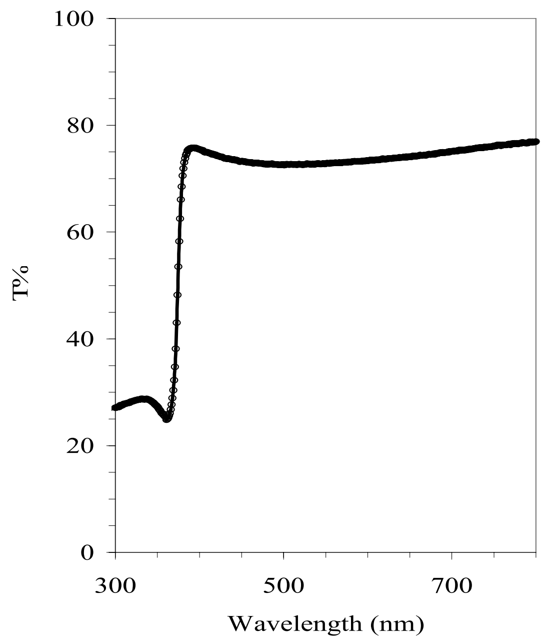

Fig. 2. Transmittance spectrum of non-crystallineZnO thin film.

The most direct and perhaps the simplest method for probing the band structure of semiconductors is to measure the absorption spectrum. The transmission spectrum of non-crystalline ZnO thin film is shown in Fig.2. The data for the non-crystalline film shows peculiar characteristics that we will attribute to inhomogeneities in the film. The average transmittance is almost 74%.

In order to determine the optical band gap of the non-crystalline ZnO thin film, the absorbance spectra of the film was recorded at room temperature. The absorption coefficient (α) was calculated from the absorbance spectrum using the formula

$$\alpha(\upsilon) = 2.303\frac{A}{d}, \qquad (1)$$

where *d* is the film thickness and *A* is the optical absorbance. The optical absorption edge was analyzed by the following equation [5],

$$\alpha h\upsilon = A(h\upsilon - E_g)^m, \qquad (2)$$

where *A* is a constant, *m* value is respectively 1/2 and 2 for direct and indirect transitions. The variation of $(\alpha h\upsilon)^2$ with photon energy $h\upsilon$ non-crystalline ZnO thin film is shown in Fig.3a. It has been observed that the plot of $(\alpha h\upsilon)^2$ versus $h\upsilon$ are linear over a wide range of photon energy indicating the direct type of transition. The intercept (extrapolation) of this plot (straight line) on the energy axis gives the energy band gap. The direct optical band gap E_g was determined 3.295eV.

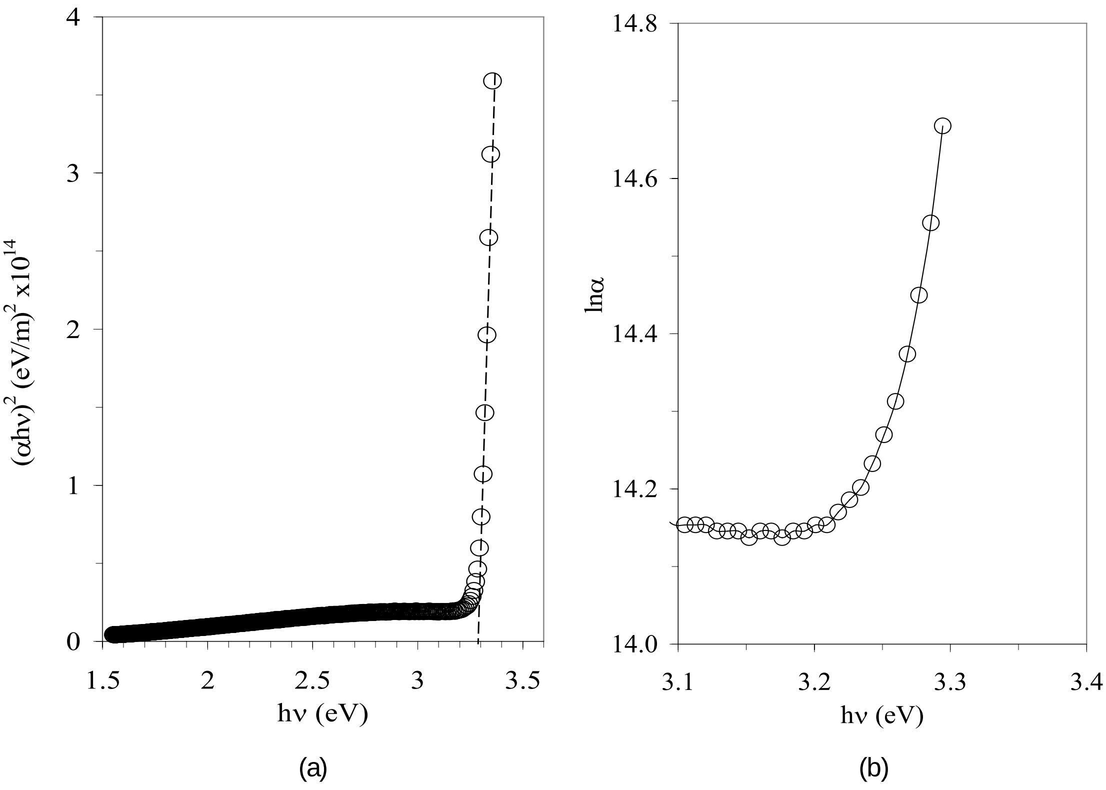

Fig. 3. (a)The plot of $(\alpha h\upsilon)^2$ vs. photon energy and (b) the Urbach plot of the non-crystalline ZnO thin film.

It is also assumed that the absorption coefficient near the band edge shows an exponential dependence on photon energy and this dependence is given as follows [6],

$$\alpha = \alpha_o \exp\left(\frac{h\upsilon}{E_u}\right), \quad (3)$$

where α_o is a constant and E_U is Urbach energy interpreted as the width of the tails of localized states, associated with the amorphous state, in the forbidden gap. The $ln\alpha$ vs. photon energy plot for non-crystalline ZnO thin film is shown in Fig.3b. The value of E_U obtained from this figure is 121meV. It is believed that the exponential dependence of α on the photon energy may arise from random fluctuations of the internal fields associated with the structural disorder in many amorphous materials.

The refractive index of the sample can be obtained from the following equation [7],

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}, \quad (4)$$

where k ($k = \alpha\lambda / 4\pi$) is the extinction coefficient. The refractive index value was calculated by using equation (4). The variation of the refractive index and the extinction coefficient with photon energy for the non-crystalline thin ZnO film is shown in Figures 4.a and 4.b.

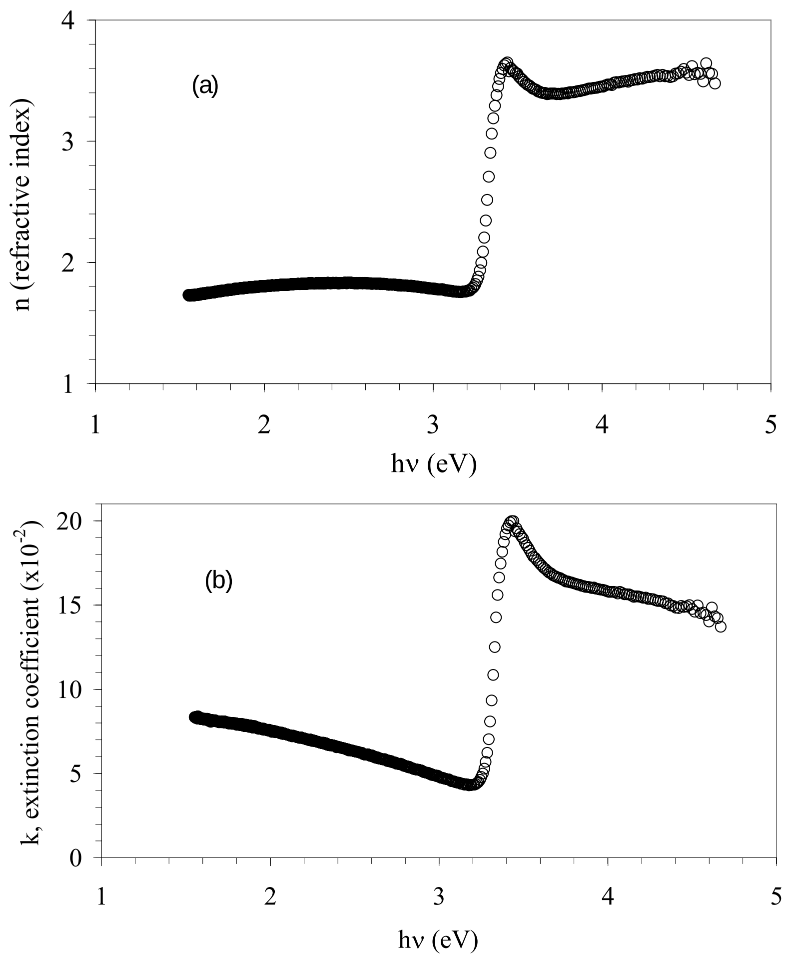

Fig. 4. The variation of (a) refractive index and (b) extinction coefficient of the non-crystalline ZnO thin film with photon energy.

On the other hand, if the refractive index and extinction coefficient are known, the real and imaginary parts of dielectric constant of the film can be also estimated. The real and imaginary parts of complex dielectric constant are expressed as [8],

$$\varepsilon_1 = n^2 - k^2 \quad , \quad \varepsilon_2 = 2nk \, , \tag{5}$$

where ε_1 is the real part and ε_2 is the imaginary part of the dielectric constant. The dependence of the real (ε_1) and imaginary (ε_2) parts of dielectric constant on photon energy are shown in Fig.5.a and b for non-crystalline ZnO thin film. The real and imaginary parts follow the same pattern and it is seen that the values of real part are higher than the imaginary parts.

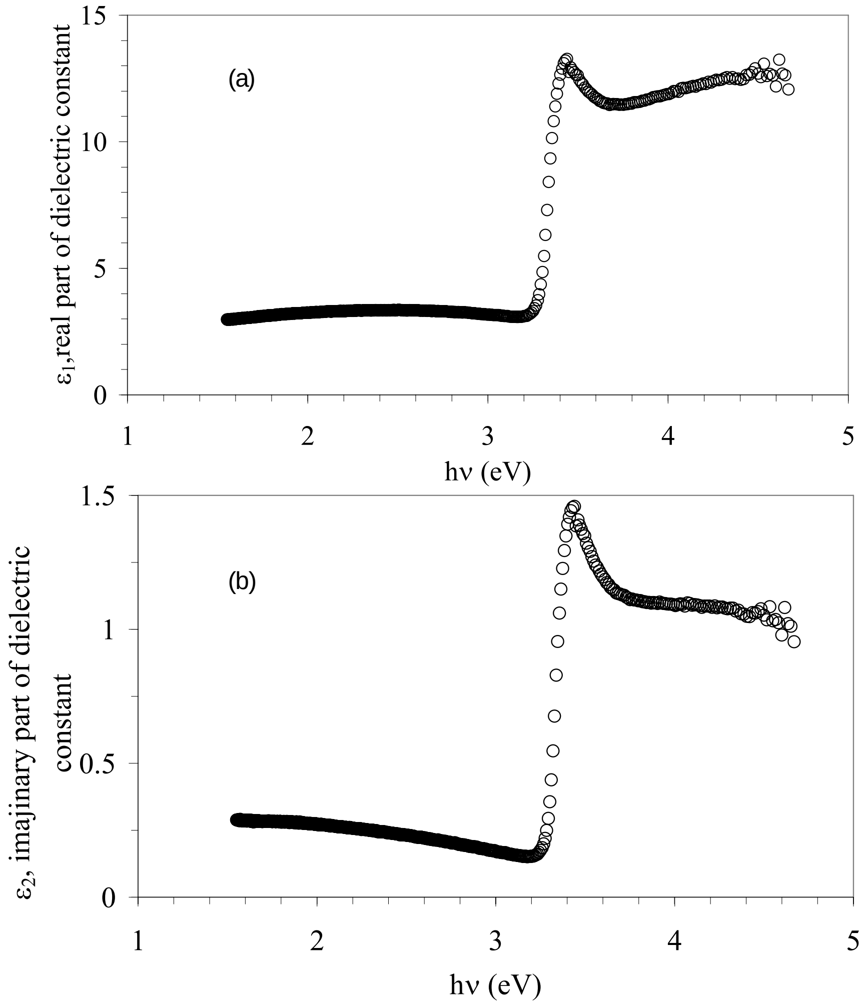

Fig. 5. The variation of (a) real and (b) imaginary parts of the dielectric constant of the non-crystalline ZnO thin film with photon energy.

The data on the spectral dependence of refractive index were evaluated according to the single-oscillator model proposed by Di-Domenico and Wemple [9]. The dispersion parameters of various materials (both non-crystalline and crystalline) were investigated by using this model in the literature [10-13]. This model describes the dielectric response for transitions below the optical gap. It plays an important role in determining the behaviour of the refractive index. The dispersion data of the refractive index can be described by a single-oscillator model [9]:

$$n^2 = 1 + \frac{E_d E_o}{E_o^2 - (h\nu)^2}, \tag{6}$$

where E_o and E_d are single-oscillator constants. E_o is the average excitation energy for electronic transitions and E_d is the dispersion energy which is a measure of the strength of interband optical transitions. The oscillator energy E_o is an average energy gap.

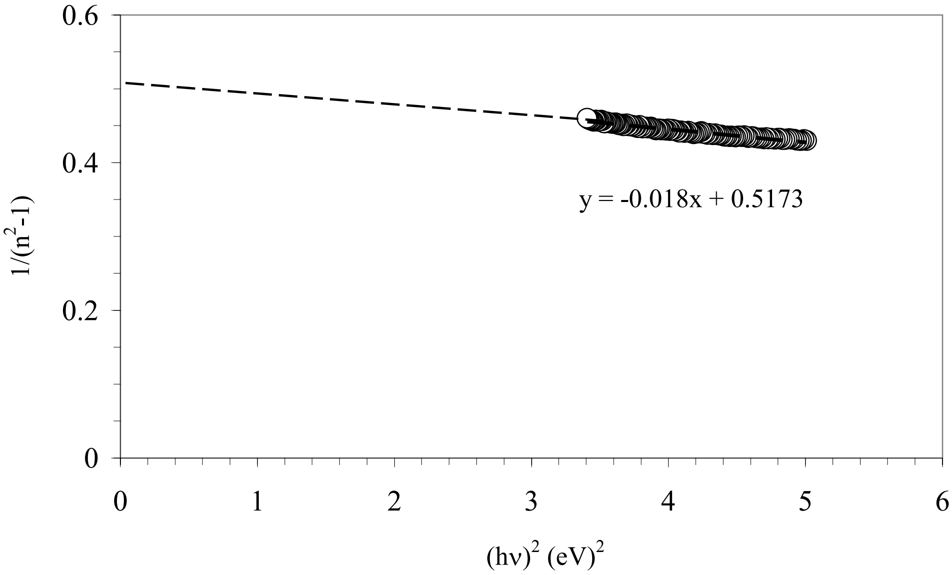

Fig. 6. The plot of $(1/(n^2\text{-}1))$ vs. $(h\upsilon)^2$ of the non-crystalline ZnO thin film.

Fig.6 shows plots of $(1/(n^2-1))$ versus $(h\upsilon)^2$ for the non-crystalline film. E_o and E_d are determined directly from the gradient, $(E_o\ E_d)^{-1}$ and the intercept (E_o/E_d), on the vertical axis. Also, the long wavelength refractive index (n_∞) for the non-crystalline thin film was determined from the interception of the vertical axis in Fig.6. The values of E_o, E_d and n_∞ for the non-crystalline ZnO thin film are 5.36 eV, 10.36 eV and 1.71, respectively.

4. CONCLUSION

The optical constants and optical band gap of the non-crystalline zinc oxide thin film deposited by the spray pyrolysis method onto glass substrates have been investigated by optical characterization method. X-ray diffraction result showed that the ZnO film had non-crystalline structure. The direct band gap E_{gi} of non-crystalline thin film was determined 3.295eV. The optical constants, such as refractive index, extinction coefficient and dielectric constants, and Urbach energy value of non crystalline film were also determined. The dispersion curve of the refractive index of the non-crystalline film obeys single-oscillator model. The dispersion parameters of the non-crystalline film were also determined.

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ОПРЕДЕЛУВАЊЕ И АНАЛИЗА НА ДИСПЕРЗНИТЕ ОПТИЧКИ КОНСТАНТИ НА НЕ-КРИСТАЛЕН ТЕНОК ФИЛМ ОД ZnO

М. Каглар, С. Илицан и Ј. Каглар

Факултет за природни науки, Анадолија Универзитет,
Институт за физика, Ескисехир, Турција

Апстракт. Во рамките на ова истражување успешно е нанесен филм од не-кристален ZnO со помош на методата на спреирање врз стаклен супстрат. Структурата на филмот беше анализирана со рендген дифракција, која потврди дека структурата на филмот е не-кристална. Параметарот на Урбаховата опашка, широчината на оптички забранетата зона, оптичките константи, како што се индексот на прекршување, коефициентот на апсорпција и диелектричната константа на нанесениот филм беа испитани со метод на отпичка карактеризација. Дисперзионата крива на индексот на прекршување на не-кристалниот филм се потчинува на моделот на единечен осцилатор. Беа определени дисперзионите параметри на филмот, како што е E_0 (енергијата на осцилаторот) и E_d (енергијата на дисперзија) на филмот.