الخواص البصرية والتركيبية لأغشية ثنائي اوكسيد القصدير المحضرة بطريقة الرش الكيماوي الحراري

ضحى مولود عبد اللطيف
قسم الفيزياء،كلية التربية ابن الهيثم، جامعة بغداد

الخلاصة

حضرت أغشية ثنائي اوكسيد القصدير (SnO_2)الرقيقة باستخدام تقنية الرش الكيماوي الحراري.وظهر من طراز حيود الأشعة السينية طبيعة التركيب البلوري وانمائها، اذ ظهرت انها ذو تركيب ثلاثي وبأتجاهية(110)،(101)،(211)،فعند تسليط حزمة من الأشعة السينية (احادية الموجه)على سطح الغشاء سوف تظهر لنا قمم (peaks) عند زوايا معينة نتيجة لأنعكاسات براك عن السطوح البلورية المتوازية. سجل طيف النفاذية والامتصاصية في مدى nm(300-900) إن الطيف اعتمد على معامل الامتصاص الذي حسب من خلال طيف النفاذية وحسبت فجوة الطاقة المباشرة المسموحة من خلال المنحني البياني $(\alpha h\upsilon)^2$vs.$(h\upsilon)$ وكانت قيمتها تتراوح بين 2.4 −2.6eVحسبت الثوابت البصرية المتضمنة معامل الخمود(k) ومعامل الامتصاص (α) .

Optical Properties & Structural of Dioxide Thin Films Prepared by Chemical Spray Pyrolysis

D. M. A. latif
Department of Physics ,College of Education, Baghdad University

Abstract

X-ray diffraction pattern reveled the tetragonal crystal system of SnO2 Thin films of SnO_2 were prepared on glass substrates using Spray Pyrolysis Technique. The absorption and transmition spectra were recorded in the rang of 300-900nm, the spectral dependences of absorption coefficient were calculated from transmission spectra. The direct and allowed optical energy gap has been evaluated from plots of $(\alpha h\upsilon)^2$ vs. $(h\upsilon)$. The energy gap was found to be 2.4-2.6eV. The optical constant such as extinction coefficient(k) and absorption coefficient (α) have been evaluated.

Introduction

Tin dioxide thin films are semiconductors with high transparency and very good conductivity. Their films are chemically inert, mechanically hard and can resist high temperature (1). Owing to its low resistivity and high transmittance, thin oxide thin films are used as a widow layer in solar cells(2). And as heat reflectors in solar cells (3), various gas sensors (4) liquid crystals displayers (5). Doped or undoped tin oxide films can be prepared by many methods such as spray pyrolysis (5), electron beam evaporation (6), Vapor deposition (7), Magnetron sputtering (8). Penichi method (9). There is much current interest binary compounds semiconductor for use in variety of solid-state devices. SnO_2 is an important semiconductor material for the development of devices (laser diodes, solar cells, micro wave devices. etc) (9). The study of the optical constant of material is interesting for many reasons. Firstly, the use of materials in optical applications such as interference filters ,optical fibers , and reflective coating which requires accurate knowledge of their optical constant over a wide range of wavelengths. Secondly, the optical properties of all materials may be related to their atomic structure , electronic band structure and electrical properties , thus , the study of the optical constant, would enable correlation to be made with the band structures derived by other methods (10). The performance of the optical devices strongly depends on the wavelengths dependence of the optical constants α and k of their layers and on their thickness . knowledge of these parameters is necessary to understand the fundamental aspects of the materials. Optical constants of thin films are influenced by various factors such as film thickness rate of deposition ,substrate temperature and crystallanity(11).The method of chemical spray pyrolysis is also suitable for preparing doped thin films where the rcentage of doping materials may be very accurately determined (12).

Experimental

The experimental set up, the spray nozzle and other experimental details are demonstrated elsewhere (13). SnO_2 films were deposited by spraying 0.1molar aqueous Solution of $SnCl_4$ +$9H_2O$ solved in 100ml H_2O in the required proportion on a glass substrate maintained at 550 ℃. Air was used as a carrier gas with a constant flow rate of 6 ℓ/m In particular experiment, the $Sn:O_2$ ratio was (1:1)(22)

$$SnCl_4+2H_2O \rightarrow SnO_2+4HCl$$

The clear white solution is sprayed on preheated borosilicate glass substrate to about 550 ℃. The spraying process lasts for about (15s). The period between spraying processes is about (1min). This period is enough to avoid excessive cooling of glass substrates. In order to get uniform thin films, the height of the spraying nozzle and the rate of spraying process are adjusted to 35cm and 10 cm^3/min respectively. All thin films prepared by spray pyrolysis were quite uniformed, free of pin holes, well fixed on the substrates. The film thickness was measured using laser interferometric method. All films had nearly about or equal to thickness (220nm).

Optical measurements on the thin films, prepared with different molarities 0.1-0.4, are carried out using a recording Pye-Unicam sp-8800 Spectrophotometer. The transmission ratio is obtained by placing two thin films of different thicknesses at the two windows of the spectrophotometer, the thinner one in front of the reference beam. This automatically eliminates the reflection effects (13).

Neglecting reflection effects, absorption coefficient is determined by the well-known relationship (15):

$$[1] \qquad \alpha = \frac{1}{d}\ln\frac{1}{T}$$

where (d) and (T) represent the film thickness and transmission coefficient, respectively.

Results and Discussion

By studying optical properties (transmission and absorption spectra , refractive index dispersion) of SnO_2 films, information can be obtained about energy band-gap, characteristics of optical transitions, etc(10).The optical transmission spectra as a function of wavelength in the range of (300-900) nm for more than one sample are shown in Figures(1-5). Fig. (1) Shows typical transmissions spectra with the aid of Eqn. (1) . It is obvious from Fig. (2) that SnO_2 films have good transmittance especially in low solutions concentrations (molarities). The absorbance of the films as a function of wavelength is presented in Fig.(2). Experiments showed that heat treatment influenced the shape of absorption spectra (16). The extinction coefficient k and the absorption α of the films were calculated from the relation(20):

$$[2] \quad k = \frac{\ln(1/T)\lambda}{4\pi d}$$

The dependence of the extinction k on the wavelength for as –prepared SnO_2 films is shown in Fig (3). It could be noticed that k decreases linearly as photon wavelength increases followed by slight increase at wavelengths greater than 900nm (3). The calculated value of α and k for SnO_2 films plotted as a function of incident wavelength. It is known that if the multiple reflections are neglected the transmittance of the film is given by(11)

$$T = (1-R)^2 \exp(-A) = (1-R)^2 \exp(-\alpha d) \qquad [3]$$

Where R is the reflectivity and A is the absorbance can determined from measurements of both t and a. Eqn. (3) can be rewritten in the form:

$$R = 1 - \{T \exp(\alpha d)\}^{1/2} \qquad [4]$$

Fig. (4) Shows variations of reflectance with the incident wavelength for SnO_2 thin film. The absorption coefficient (α) is related to the energy gap (Eg) by using the relation(21):

$$\alpha = (h\upsilon - Eg)^{1/2} / h\upsilon \qquad [5]$$

Using Eq.(5) the energy gap of the film can be extracted for the direct transition when $(\alpha h\upsilon)^2$ =0. Fig (5) shows the typical absorption edge at photon energies which correspond to the forbidden energy gap respective semiconductor.

From Eq. (5), when $(\alpha h\upsilon)^2$ =0, the value of intercept points for each curve at hυ-axis gives the value of energy gap. The values of energy gaps extracted from the figure were 2.4-2.6 eV.

Structural Properties

The prepared sample SnO_2 thin films deposited on borosilicate (thin glass slides) substrates reveal that the nature of crystal structure tetragonal. The dominating structure of these films is polycrystalline and the maximum reflected intensities were from the faces (110), (101), and (211).

Applying Brag's law using (hkl Miller indices) these faces showed agreement with (ASTM) standards card as well as previous studies (17-19). Figure (6) shows the x-ray diffraction spectra of (SnO_2). Moreover (XRD) revealed strong diffraction peaks at(27^o, 33.6^o, 51.8^o). for the crystal faces (110), (101), and (211) respectively.One of the benefits for this structure is employing in the solar cell and light as instate of the silicon cell because it is cheap (low price) in addition to that it is very easy to prepare in a shape of thin film with very good quality and with the room temprture as well as it is available in the form of comical solutions.

Conclusion

SnO_2 thin films deposited by chemical spray pyrolysis onto preheated glass substrate to 550 C^o revealed a good uniformity and homgeneousity. The SnO_2 films prepared by spray pyrolysis have good transmittance and the values of the energy gap, calculated from the absorption spectra.

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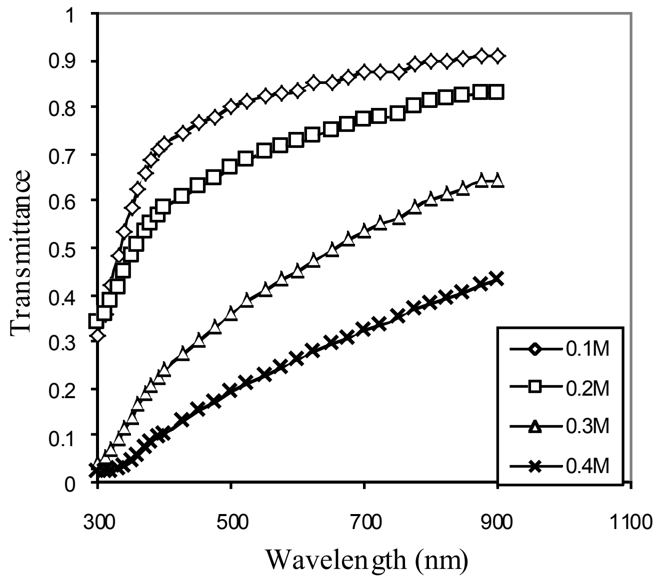

Fig.(1): Transmittance as a function of wavelength for various values of preparation molarities

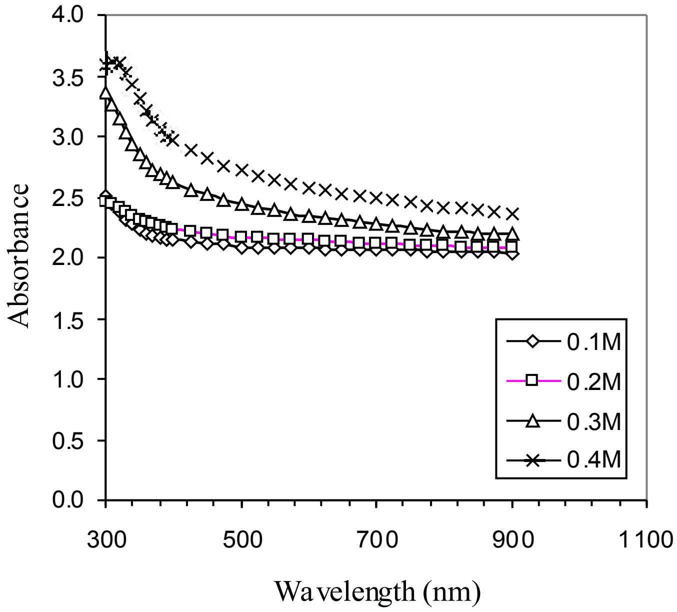

Fig.(2): Absorbance as a function of wavelength for various values of preparation molarities.

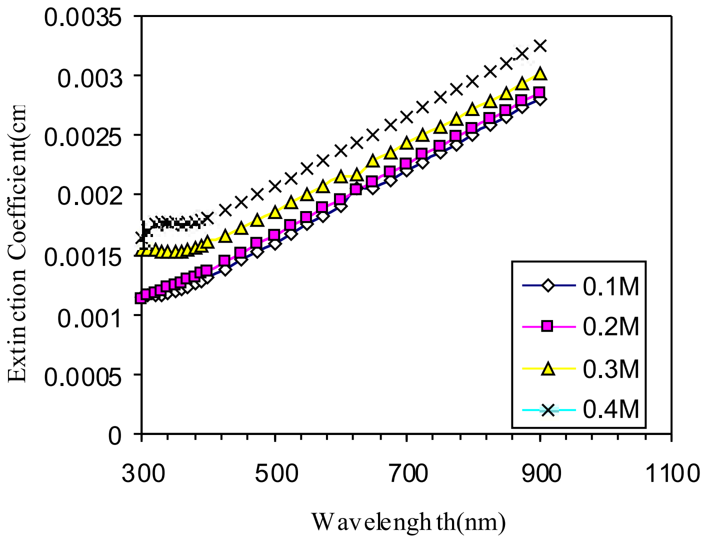

Fig. (3): Extinction coefficient as a function of wavelength for various of preparation molarities.

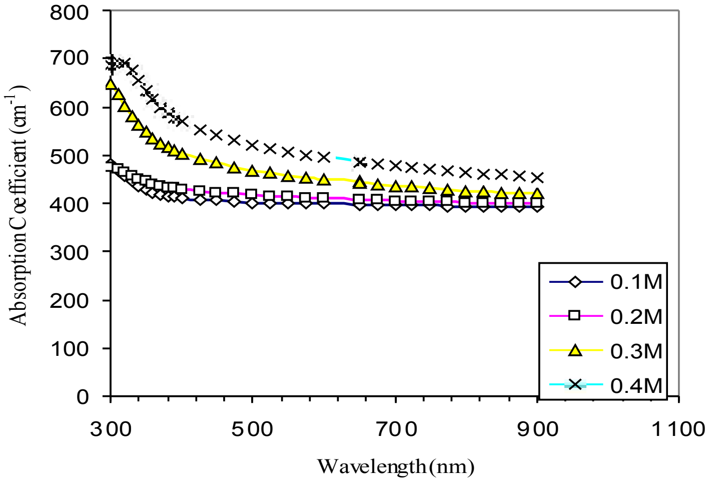

Fig.(4): Absorptio
preparation molar

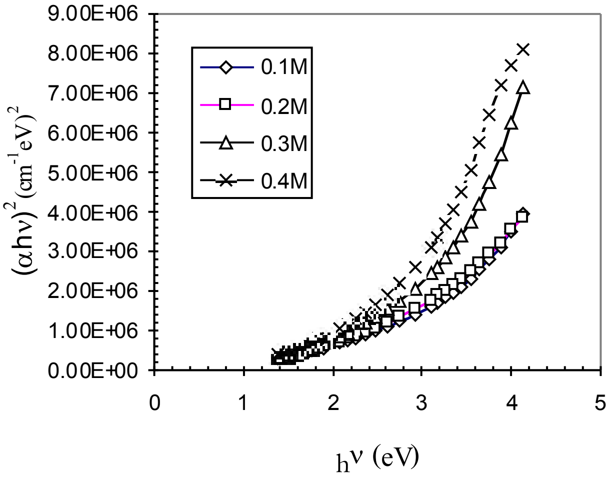

Fig.(5): Absorption edge as a function of photon energy for various values of preparation molarities.

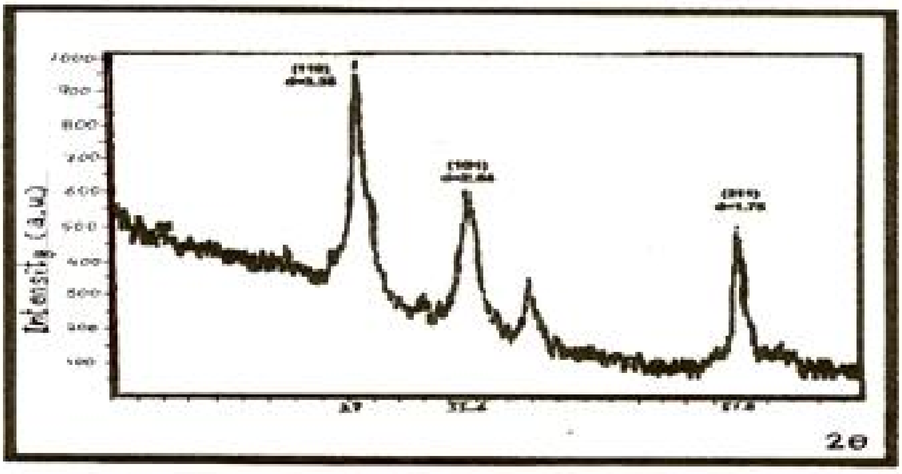

Fig.(6): Plot of X-Ray diffraction for (SnO_2) thin film prepared by spray pyrolysis