

The Optical Properties of Cadmium Stannate (Cd_2SnO_4) Thin Films Prepared by Chemical Spray Pyrolysis Technique

Mazen N. Al-Dileamy and Sabah M. Alnaimi
Physics Department, University of Qatar, Qatar

دراسة الخواص البصرية لأغشية استينات الكاديوم (Cd_2SnO_4) الرقيقة المحضرة بطريقة الرش الكيميائي الحراري

مازن الدليمي و صباح النعيمي

قسم الفيزياء - جامعة قطر

أغشية استينات الكاديوم (Cd_2SnO_4) الرقيقة حضرت باستخدام تقنية الرش الكيميائي الحراري على قواعد زجاجية وبدرجة حرارة الغرفة وبأسماك مختلفة في حدود (3000A - 6000A). الخواص البصرية للأغشية العشوائية التركيب درست قبل وبعد التلدين (Annealing) حيث تم تعيين نوع الانتقالات الإلكترونية وحساب قيمة فجوة الطاقة البصرية ولوحظ إن قيمة فجوة الطاقة البصرية تقل مع زيادة سمك الأغشية وأن عرض ذيول الطاقة ومعامل الخمود ومعامل الانكسار ومعامل الانعكاس تتناسب طردياً مع زيادة درجة حرارة التلدين وسمك الأغشية المحضرة.

Keywords: Cadmium stannate, UV/Vis.

ABSTRACT

Thin films of cadmium stannate were prepared using thermal chemical spray pyrolysis. Cadmium stannate' solution (0.2M) was prepared by dissolution of $CdCl_2 \cdot 5H_2O$ in $C_2H_5 \cdot OH$ and tin stannate' solution ($SnCl_2 \cdot 3H_2O$ in CH_3COOH at molar 2:1, respectively). The Cd_2SnO_4 solution was sprayed on substrate that was kept at $300^\circ C$. The studies of structure showed that the prepared thin film was amorphous. After annealing, no changes observed in the films' structure. The type of electronic transition was determined by studying the Ultra Violet/Visible (UV/Vis) spectrum. Energy's gap, width of band tail, refraction coefficient, reflection index, and extinction coefficient were calculated before annealing. The optical constants were increased by increasing annealing's temperature and thickness.

1. Introduction

The thin film technique is one of the most recent fully-fledged technologies that greatly contribute to developing the study of semi-conductors by giving a clear indication of their chemical and physical properties.

Thin films are also particularly important for their use in a great number of optical fields such as the manufacturing of ordinary and thermal mirrors, of highly specialized filters and solar cells.

The study of optical properties of semi-conductors of both crystalline and amorphous structures is extremely essential for an understanding of the mechanism by means of which optically-induced transitions and the structures of bands are carried out.

Optical transitions [1, 2] start in semi-conductors when energy of photons is absorbed at a quantity higher than the forbidden energy gap or equal to it. When the required energy is almost equal to the difference between the lowest level of conduction band and the highest level of covalent band, electrons will transfer from covalent band to conduction.

Mott, Davis, and Tauc [3, 4] have proposed a mathematical equation to represent the relationship between optical energy gap and the energy of the incident photon.

$$\alpha (h\nu) = (h\nu - E_{\text{opt}})^r \quad (1)$$

where α is the optical absorption coefficient,

$h\nu$ is the energy of the incident photon,

E_{opt} is the optical energy gap,

r is the logarithm index taking different variables according to electronic transitions.

As for amorphous semi-conductors, the basic absorption edge slightly differs from crystalline structure. In this case, the value of the optical absorption coefficient could be expressed by the following mathematical relations [5-7]:

$$\alpha = \alpha_o \exp\left(\frac{h\nu}{\Delta E}\right) \quad (2)$$

$$\alpha = \alpha_o \exp\left(\frac{h\nu}{E_o}\right) \quad (3)$$

where α_o is the correlation constant,

and ΔE , E_o represent the tail width of localized states within the optical energy gap.

Moreover, the optical properties of semi-conductors can also be expressed by using the concepts of refraction index (n_o) and extinction coefficient (k) through the following relations:

$$n_o = \left(\left[\frac{4R}{(R-1)^2} \right] - k^2 \right)^{\frac{1}{2}} - \frac{(R+1)}{(R-1)} \quad (4)$$

$$k = \frac{\alpha \lambda}{4 \pi} \quad (5)$$

where λ is the wave length of incident photon,

and R the reflection index, which could be calculated from the relation: $R + A + T = 1$, with A and T representing absorption and transmission respectively.

Studies of the optical properties of cadmium stannate started in the early 1970s. Al-Ani [8] dealt with the optical properties of a variety of semi-conductors including cadmium stannate, obtaining under preparation circumstances the energy gap values and the optical absorption of the variety of phases for the material. Mohammed [10] also studied thin films of cadmium stannate prepared by thermal spraying and pointed out that one of the drawbacks of this approach was the difficulty of obtaining the homogeneity of thin films.

Procedure

The thin films of cadmium stannate were prepared by using a solution of cadmium stannate of (0.2M) concentration. The solution results from dissolving $\text{CdCl}_2 \cdot 5\text{H}_2\text{O}$ in $\text{C}_2\text{H}_5 \cdot \text{OH}$ and $\text{SnCl}_4 \cdot 3\text{H}_2\text{O}$ in CH_3COOH at molar 2:1, respectively. Mixing them by leaving the solution of cadmium stannate for 72 hours to make sure that no residues were left and to ensure the homogeneity of the resultant solution followed this dissolution process. Glass substrates were thoroughly cleaned and placed on a hotplate at 300°C . The used hotplate was rotating to ascertain that the spraying process was properly done.

Following the same procedure, several thin films of cadmium stannate with varying thickness $3000\text{\AA} - 6000\text{\AA}$ were prepared. The mass method was used to calculate the thickness of prepared thin films. Annealing (thermal treatment) of the prepared samples were carried out at different temperatures $300^\circ\text{C} - 600^\circ\text{C}$ and lasted 90 minutes.

Results and Discussion

Using X-ray diffraction, the structural properties of thin films of cadmium stannate prepared by thermal-chemical spraying were studied before and after annealing. Thus, it turned out that the structure of the prepared thin films was amorphous.

The UV/ Visible technique was used to study the structure of transmission and absorption of the prepared samples before and after annealing, Figure 1. By observing the spectrum of transmission and absorption of the prepared samples, no major changes occurred before and after annealing. This was compatible with aforementioned result, i.e. the structure of the prepared thin films stayed almost the same, but still amorphous.

Using equation (1) and giving different values for logarithm index (r), the types of electronic transitions and the calculation of optical energy gap were specified: it was clearly observed that the direct allowed transition was dominant, Figure 2. This is in line with previous studies [8-12]. We conclude that

1. In general, the value of optical energy gap E_{opt} decreases as thin films thickness increases, since the increase in the thickness leads to filling structural gap and hence increasing localized states within the gap, something that results in a decrease in the value of optical energy gap (E_{opt}), Table 1 and Figure 2.

2. When annealing thin films, it was noticed that the value of optical energy gap increased in accordance with the increase in the annealing temperature. This can be attributed to the fact that an increase in the annealing temperature leads to minimizing structural imperfections in the prepared thin films. This in turn leads to maximizing the value of optical energy gap. Table 1 and Figure 3.

3. Using equation (3) and figures (4a) and (4b), the tail width of localized states were calculated. It was noticed that the value of the tail width of localized states (ΔE) within optical energy gap increased with the increase in film's thickness, Table 2. That is, the relationship between them is directly proportional. This can be explained in the light of the fact that the increase in film's thickness could lead to an increase in the structural imperfections of the film. This directly affects the decrease in the optical energy gap.

4. Given Table 2, we noticed that the value of the tail width of localized states within the energy gap decreased with the increase in the annealing temperature. An increase in the annealing temperature leads to improving the order of the atoms constituting the prepared thin films, which will result in a decrease in the number of localized states within the energy gap, thus, amounting to an increase in the value of the energy gap.

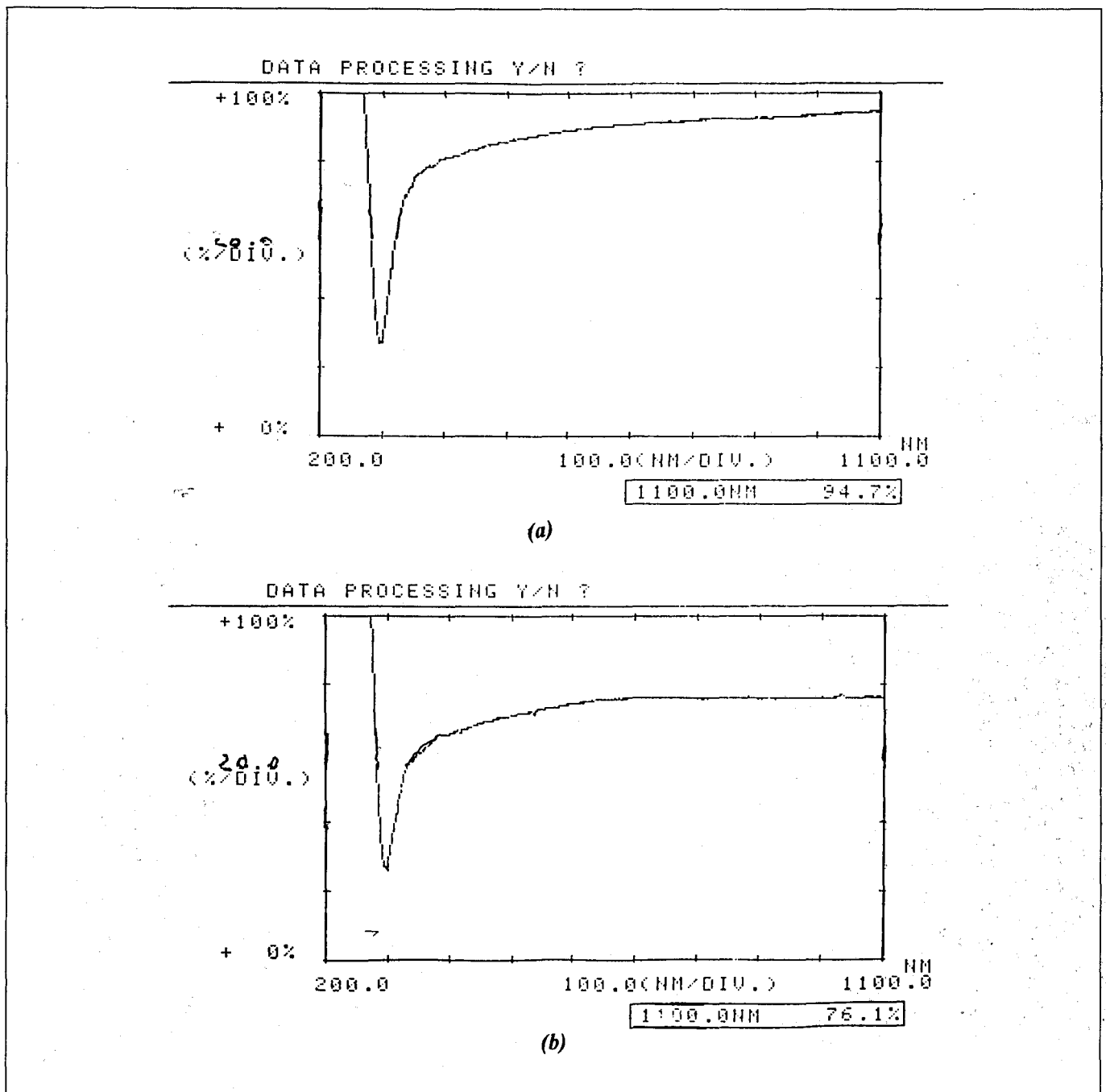


Figure 1: UV / Visible spectrum for prepared sample: a) before annealing b) after annealing.

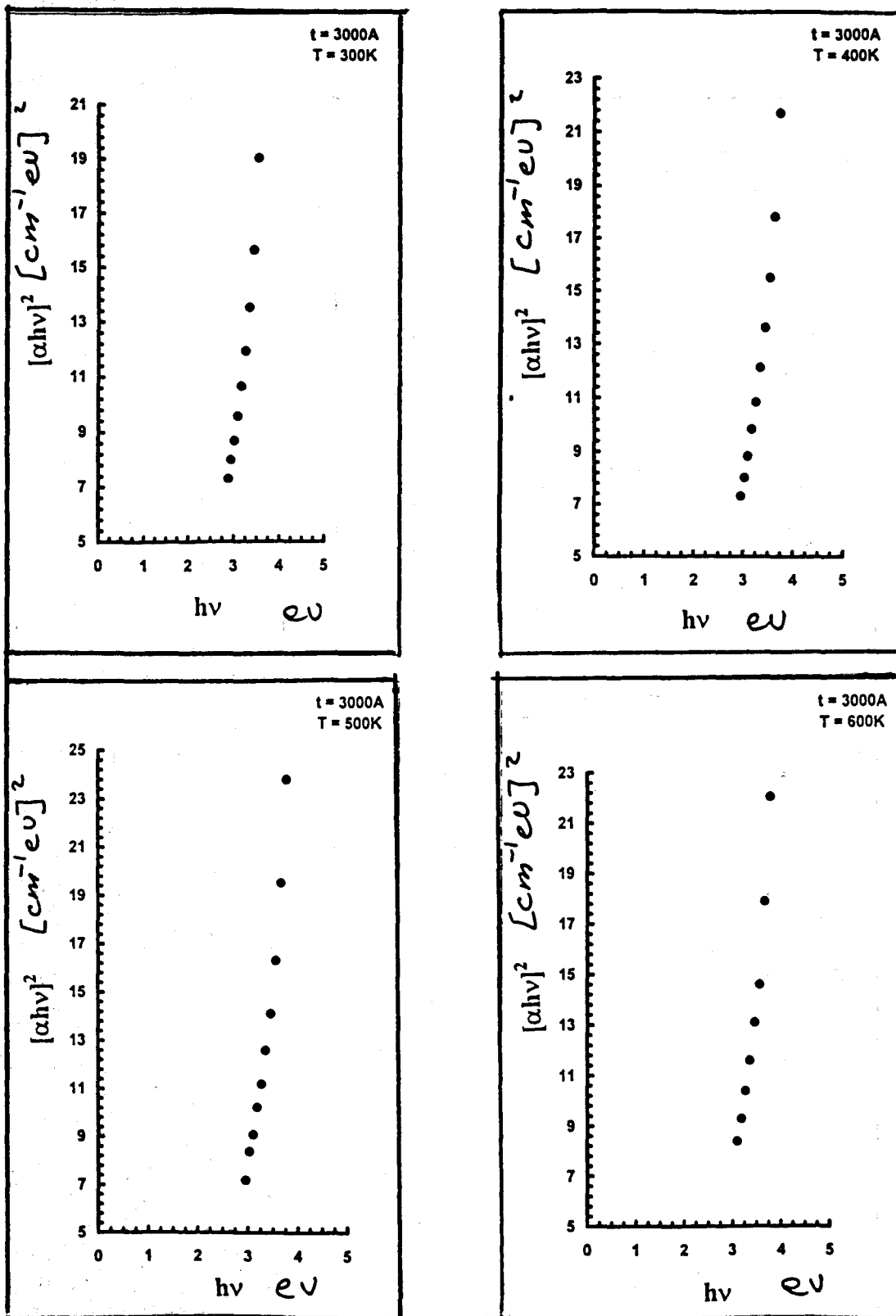


Figure 2: $(\alpha h\nu)^2$ versus photon energy of 3000 \AA with different thickness.

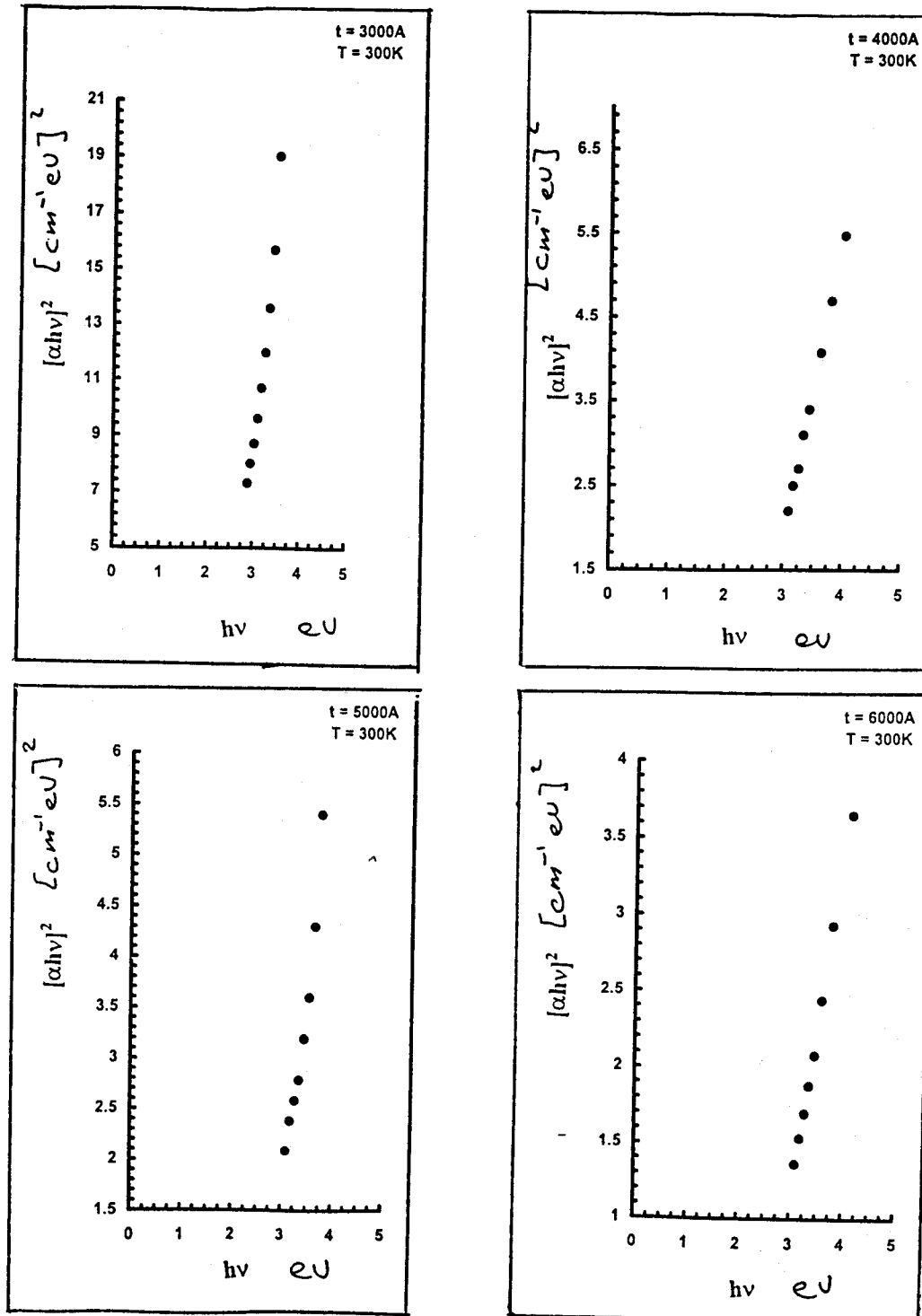


Figure 3: $(\alpha h\nu)^2$ versus photon energy of 300°K at different thickness.

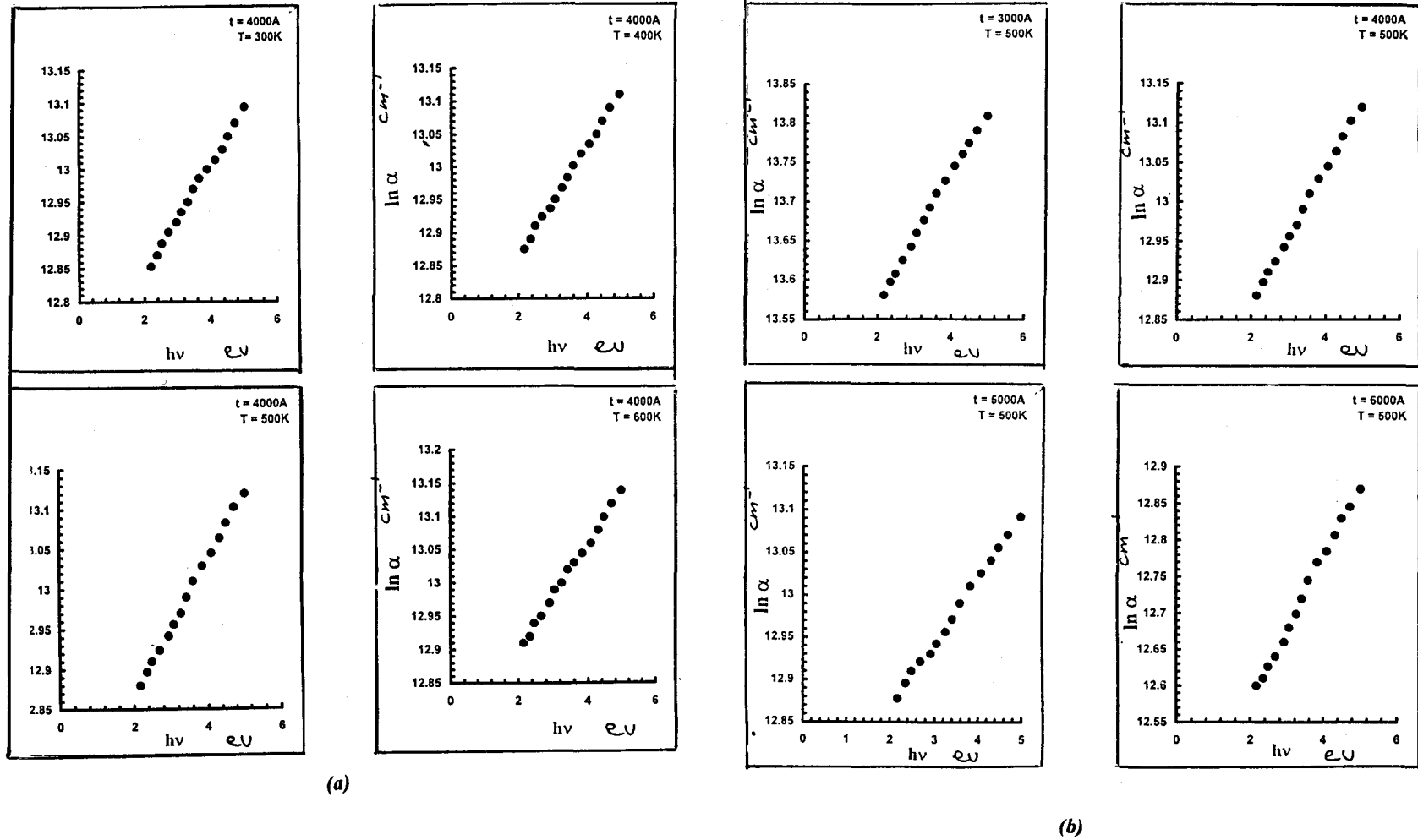


Figure 4: $(Lh\alpha)$ versus photon energy: a) at different temperature b) with different thickness.

Temperature (K)	Thickness (Å)	E _{opt} (eV)
300	3000	2.95
	4000	2.892
	5000	2.851
	6000	2.8
*****	*****	*****
400	3000	3.197
	4000	3.075
	5000	3.05
	6000	3.023
*****	*****	*****
500	3000	3.21
	4000	3.17
	5000	3.15
	6000	3.125
*****	*****	*****
600	3000	3.251
	4000	3.238
	5000	3.231
	6000	3.225

Table 1: The values of optical energy gaps (E_{opt}) for all substrates at all annealing temperatures.

Temperature (K)	Thickness (Å)	ΔE (eV)
300	3000	3.303
	4000	3.516
	5000	4.037
	6000	4.291
*****	*****	*****
400	3000	3.287
	4000	3.323
	5000	3.381
	6000	3.401
*****	*****	*****
500	3000	3.205
	4000	3.303
	5000	3.333
	6000	3.4
*****	*****	*****
600	3000	3.103
	4000	3.213
	5000	3.316
	6000	3.333

Table 2: The values of tail width of the localized states (ΔE) for all substrates before and after annealing.

5. Figures 5-7 represent a variation in the extinction coefficient (k) being a fraction of photon energy for the prepared films at different thickness and different annealing temperatures. It was observed that the value of the extinction coefficient (k) gradually decreased with the increase in thickness, whereas it increased with the increase in the annealing temperature. This can be interpreted by saying that an increase in temperature leads to an increase in the value of the absorption coefficient (α). The increase in the value of the absorption coefficient directly affects the value of the reflection index, as illustrated in equation (4). Also, the refraction index (R) was calculated by using an equation relying on the principle of energy conservation. Finally, it was noticed that the highest refraction and reflection index value is approximately 22eV, and the peaks of refraction and reflection index moves towards the lowest energy values when film's thickness increases. However, the peaks slightly move towards the highest energy values when the annealing temperature increases. All issues raised in point (5) match the results calculated for the optical energy gap mentioned at the outset.

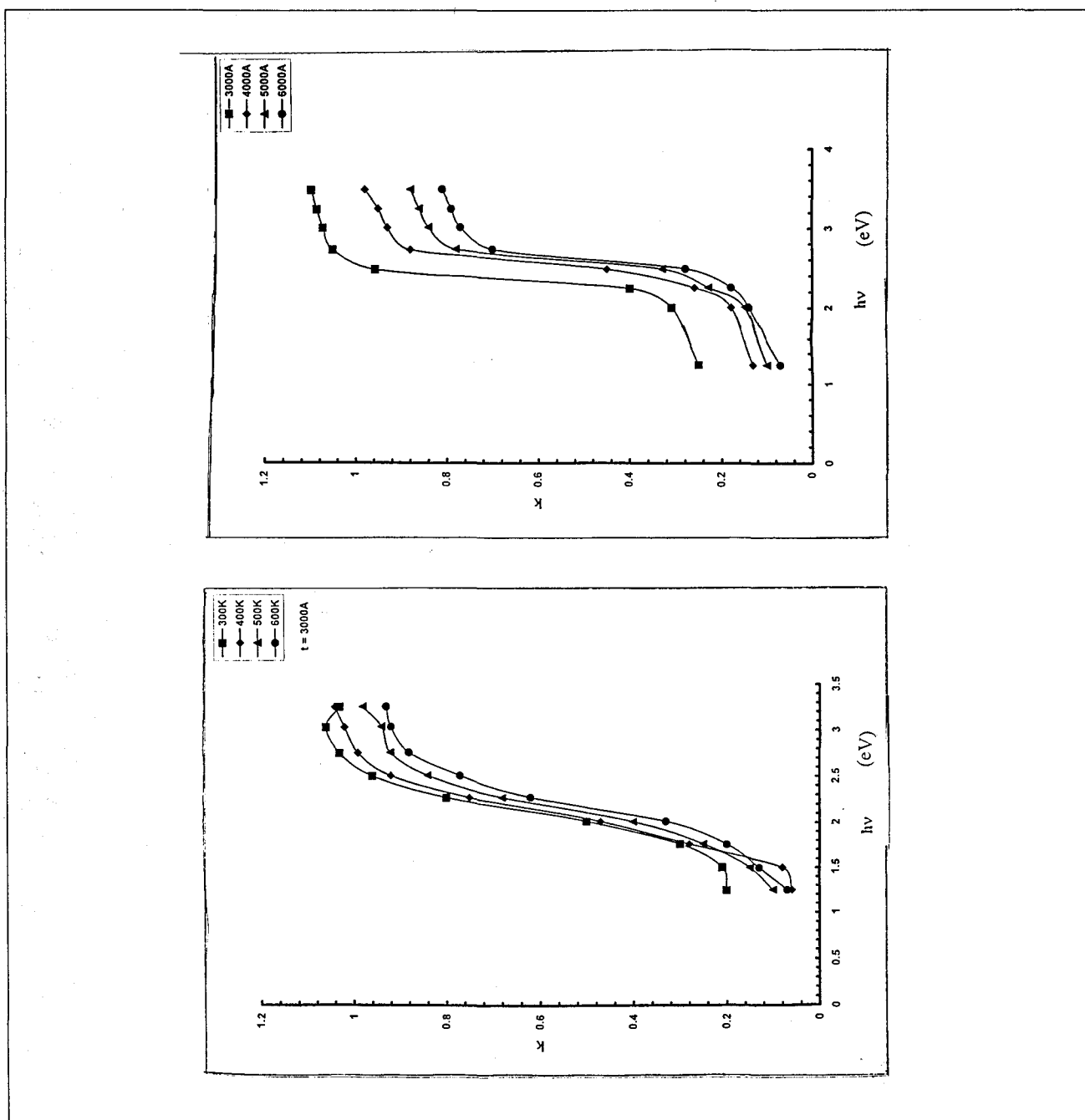


Figure 5: extinction coefficient versus photon energy: a) at different temperature b) with different thickness.

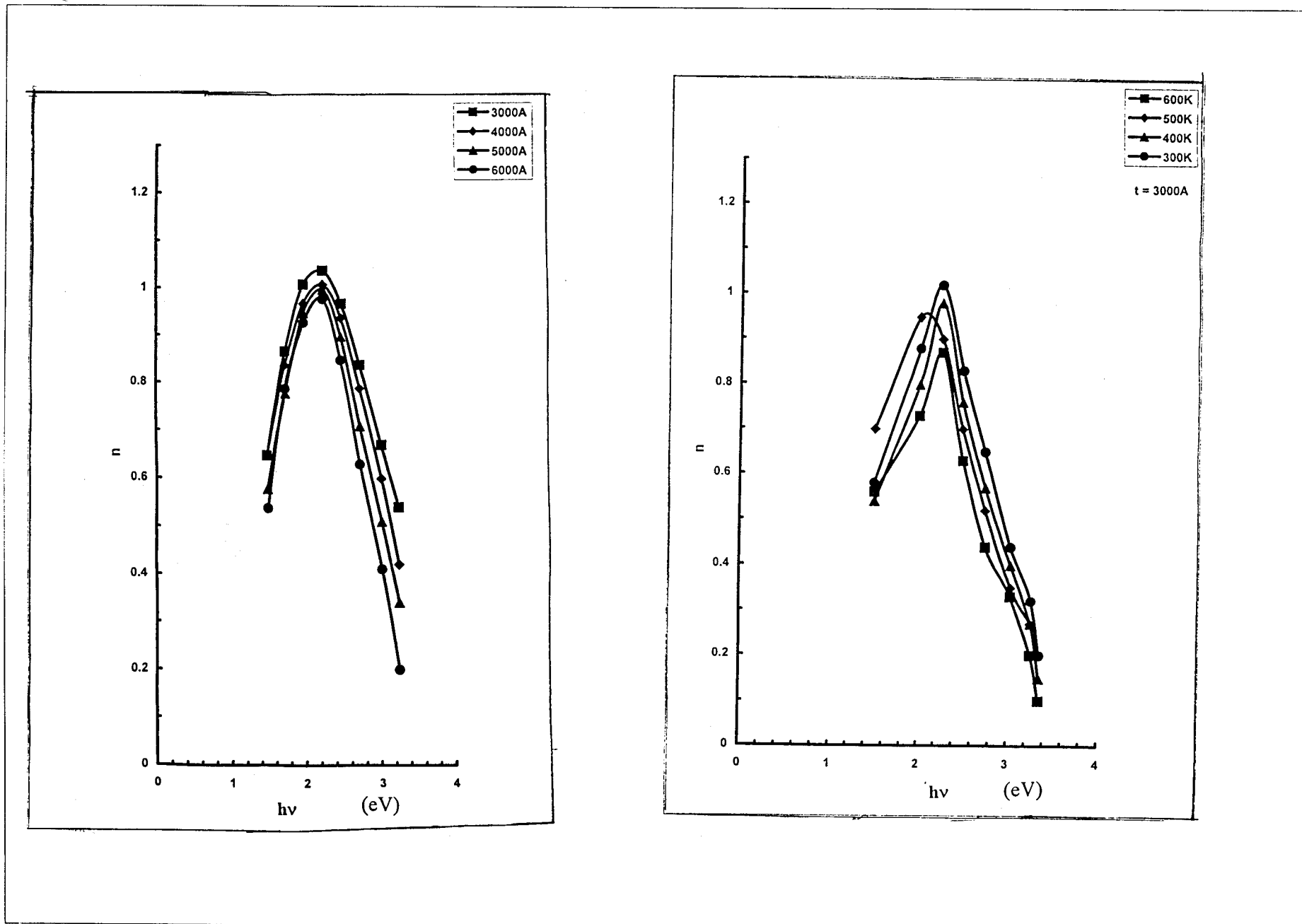


Figure 6: Reflection coefficient versus photon energy: a) at different temperature b) with different thickness.

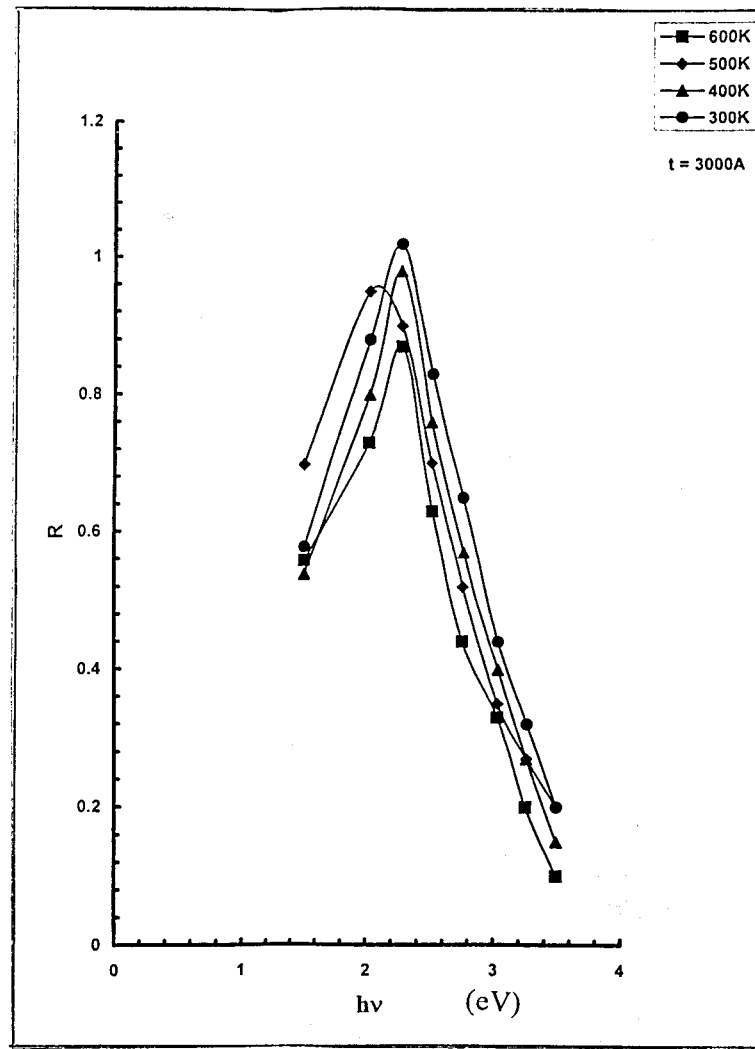
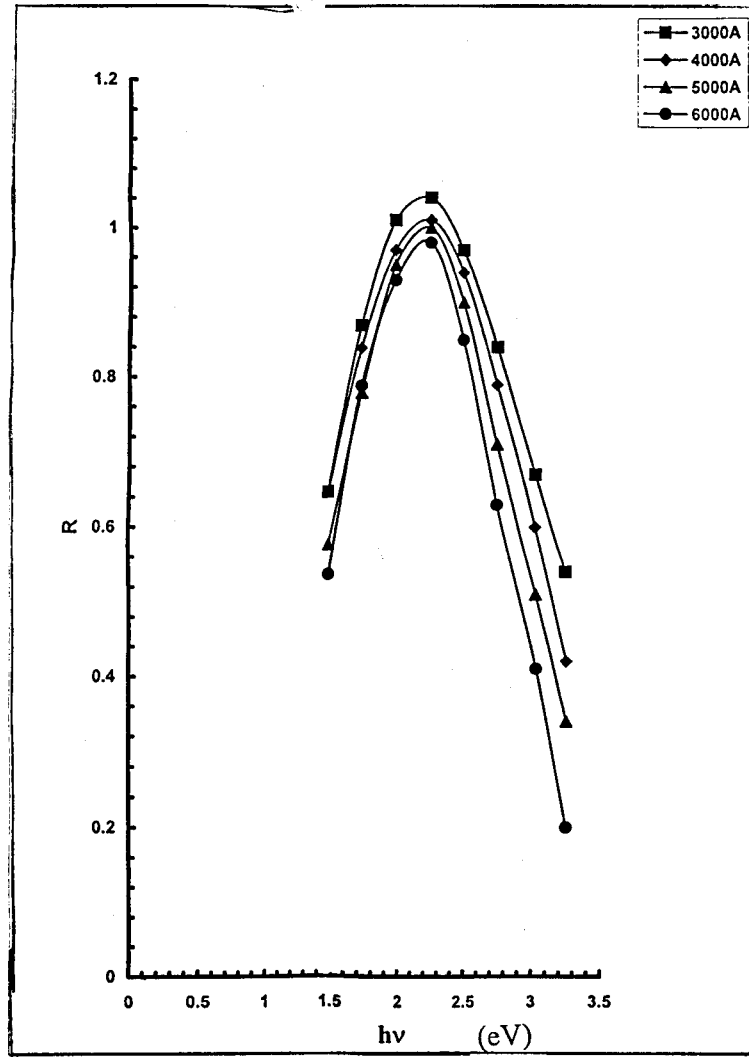


Figure 7: Refraction index versus photon energy: a) at different temperature b) with different thickness.

CONCLUSIONS

- Structural examinations of thin films of cadmium stannate prepared by thermal chemical spraying technique have shown that the structure is amorphous before and after annealing.
- UV/ Visible spectrum test has shown that the direct allowed transition is the dominant electronic transition.
- Calculations of optical energy gap (E_{opt}) have shown that its value decreases as thickness of thin films increases, and increases as the annealing temperature increases.
- Calculations of the tail width of the localized states (ΔE) have shown that its value increases as thickness of thin films increases, and decreases as the annealing temperature increases.
- Calculations of the extinction coefficient (k) have shown that its value decreases as thickness of thin films increases, and increases as the annealing temperature increases.
- The peaks of reflection and refraction indices have approximately a value of 22eV. The peaks move towards the lowest energy value when the thickness of thin films increases. The peaks move slightly towards the highest energy value when the annealing temperature increases.

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