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PHYSICAL PROPERTIES OF TIN OXIDE THIN FILMS DOPED WITH BORON

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ABSTRACT

Thin films of tin oxide doped with 10 % boron were prepared using the spray pyrolysis technique . The deposited films were carried out at substrate . temperature ranges from 425^{o} C to 525^{o} C with 25^{o} C step. A highly transparent films are produced .

The investigation included the transmittance in the wavelength region 200 -- 900 nm,film thickness estimation , figure of merit , refractive index ,energy gap, sheet resistance and X -- ray diffraction analysis .

X - ray diffraction analysis showed that the crystallinity of films deposited at 425^{o}C is generally poor and a good improvement in the crystallinity is observed for films deposited at higher temperature. The temperature of deposition as well as doping of boron affects greatly the preferred orientation of the microcrystallites along (211) and (301) planes in polycrystalline films .

INTRODUCTION

Tin oxide thin films have been considered as one of the most successful and valuable transparent conducting oxides. These transparent thin films have found major applications in a numerous fields either in passive and active electronics or in optoelectronic devices, applications based on transparent conductors including resistors, heating windows of aircrafts and cars, heat reflecting mirrors for glass windows and incandescent lamps, anti reflection coatings, selective absorber components in solar heat collectors, gas sensors, electrodes for liquid crystals, electrochromic and ferroelectric photoconductor storage and display devices, SIS heterojunction, protective and wear - resistant coatings for glass containers [1].

To get a good transparent conductor, we can create electron degeneracy in a wide band gap oxide by introducing non-stoichiometry and / or appropriate dopants.

Tin oxide thin films verified such condition, which can be prepared by a lot of deposition techniques. The need has emerged to modify and improve the electrical and optical properties to meet the application demands. The aim is always directed towards increasing transmittance of thin films together with minimizing its resistivity. This can be verified through selecting of suitable technique, controlling the deposition parameters as well as doping with the suitable dopant and concentration.

Since the electrical and optical properties of these films depend strongly on their micro structure, stoichiometry and the nature of the impurity present, so, each deposition technique with its associated parameters yields films of different properties. The techniques used are fluctuating from low temperature deposition as in sputtering and reactive ion plating that permits to deposit thin films on polymers and plastics to, a high temperature technique as in spray pyrolysis. In addition there are the evaporation, CVD, the dip technique, laser deposition technique and the chemical solution growth.

Spray pyrolysis involves spraying of an aqueous solution containing soluble salts of the constituent atoms of the desired compounds onto heated substrates. A hydrolysis reaction is normally involved. The spray pyrolysis method is very simple and adaptable for mass production and large area coatings for industrial applications. Moreover, it needs no sophistication in a form of high vacuum or controlled atmosphere, etc.

Earlier, we have gotten a transparent conducting films of pure and doped tin oxide thin films. The doping was by incorporating fluorine -FTO-[2] , indium-ITO-[3] and cadmium-CTO-[4]. In all these depositions, an alcoholic solution of $SnCl_4$ was used.

In this work, efforts have been devoted towards the properties improvement of tin oxide thin films through doping with Boron and investigation of the effect of substrate temperature.

II - EXPERIMENTAL

Thin films of tin oxide doped with boron were deposited using the spray pyrolysis technique. The solution (0.6 M) of $SnCl_4$ in ethyl alcohol was prepared with 10 % of boric acid of the same molarity. A home made apparatus was used which was described elsewhere [2]. The process of pyrolysis tooks place according to the reaction :

$$SnCl_4 + 2\,H_2\,O \rightarrow Sn\,O_2 + 4\,H\,Cl$$

Glass substrates of dimension (26 mm x 12 mm x 1mm) were used.

The substrate temperature ranged from 425^{o} C to 525^{o} C with a step of 25^{o}C.

A deposition was carried out at each temperature with different spraying time of duration from 2 min. to 10 min. .The rate of flow of compressed filtered air as a carrying gas was 5 lit. / min. The temperature of the used furnace was electronically controlled within + 1^{o} C.

The sheet resistance were measured using the four - probe method at room temperature.

Investigation includes the measurment of the transmittance within the range 200 - 900 nm. The measurment was carried out using a double beam spectrophotometer of type Lambda 4B UV-VIS [Perkin - Elmer]. While structural investigation was carried out using Phillips X - ray diffraction equipment model PW/1710 with a Ni filter and Cu K_{α} radiation (λ = 0.1542 nm) at 40 KV and 30 mA.

III - RESULTS AND DISCUSSION

The boron-doped tin oxide thin films were spectrophotometrically scanned to obtain T - λ curves in the region 200 - 900 nm. Generally, it is noticed that the number of interference extrema are in proportion with the film thickness. The deposited films of 10 % BTO possesses a high optical transparency in the visible (and near IR) region of solar spectrum. This is due to its wide band gap ($\cong$ 4.1 eV). Fig. 1 shows the transmittance spectra for the BTO thin films at 525 ^{o} C as a substrate temperature.

A useful figure that helps in many applications and gives a quick comparison is the figure of merit Φ by Haacke [5], which is defined as $\Phi = T^{10}/R_{\square}$.

Where T is the transmission and $R_{\square}$ is the sheet resistance.

Table **I** summarizes the obtained values of transmission at solar maximum (550 nm) and the thickness of the thin films with its corresponding sheet resistance. This can interrelate the optical and electrical parameters.

It is clear from table **I** that the sheet resistance decreases by increasing thicknesses and by doping.

The reduction of the sheet resistance values for the doped TO is referred to the increasing of the crystallinity of the films as seen from the X - ray diffraction results. The increasing in crystallinity leads to decreasing the disorder and therefore increases the carrier mobility [6]. Accordingly, due to the increase of the crystallite size, the scattering at the boundaries decreases [7]. The effect of the dopant (boron) is clear, since adding foreign atoms to the TO matrix with the aim of improvement its quality have led to such improvement that is clearly seen from figure of merit values. This means that boron is already incorporated in TO matrix. This may be due to the proper ionic radius of the dopant (0.097 nm)[8]. Accordingly, we may also interpret the reason of the effectiveness of some dopants as fluorine (ionic radius = 0.136 nm) and the failure of some other dopants such as chlorine and bromine (0.181 nm, 0.196 nm) to substitute the divalent oxygen anion of ionic radius 0.14 nm.

Table I

Substrate temp. (^oC)	Time (min.)	Thickness (t) (nm)	Transmission (T) (at 550 nm)%	R □□	Φ x10^{-3}
525	2	------	99	600	1.5
	3	------	93	130	2.4
	4	390	88	25	11.2
	5	540	93	14	34.5
	10	770	88	22	12.6
500	2	-----	----	----	----
	3	-----	88	95	2.9
	4	225	91	62	4.3
	5	285	90	53	6.5
	10	740	90	10	15.5
475	2	----	95	295	3.0
	3	----	95	110	5.4
	4	220	92	54	8.0
	5	305	97	40	18.4
	10	740	93	12	40.2
450	2	----	----	----	----
	3	----	80	330	3.2
	4	157	86	130	3.7
	5	335	92	95	3.7
	10	610	92	40	4.5
425	2	----	----	----	----
	3	----	99	450	2.2
	5	210	82	220	1.5
	10	400	82	138	1.1

Energy gap is determined by plotting $(\alpha\Delta\ T)^2$ as a function of photon energy $h\nu$ as in fig. (2) . The intersection of the straight lines with the $h\nu$ axis at $(\alpha\ \Delta\ T)^2 = 0$ indicates the value of the direct energy gap, which lies here at $\cong 4.11$ eV, so there is no effect on the direct energy gap by either doping with boron or deposition temperature.

Determination of the refractive index (n) was based on the analysis of T - λ curves in the weak absorption region using the method described in [9].

Applying this method, the refractive indices for all the doped samples were calculated. Fig. (3) shows the refractive index spectrum of some samples which indicates that it ranges between the values 1.75 and 2.1.

X- ray diffractogram shown in fig. (4) indicates the pattern of the deposited BTO thin films at deposition time of 5 min. and substrate temperature range 425 - 525^o C. Lattice constants **a** and **c** of the thin films were determined using high - angle reflections [10]. The values obtained in this investigation were tabulated in table **II**. The d-spacings calculated from 2θ and the relative intensities (I / I_0) for the various planes are estimated from the recorded counting rate. The d-values agree with ASTM data for SnO_2 powder [11]. The intensity of the diffraction planes shows an appreciable increase at doping with boron and with increasing of substrate temperature as in fig. (4). In addition some of the planes of B- doped films orient themeselves to give maximum reflection and hence maximum intensity is observed for planes (211) and (301) as prefered orientation. Table **II** indicates that the crystallite size values are in agreement with the unit cell volume.

The average crystallite size **D** for crystallites perpendicular to the (211) and (301) planes were calculated from Scherrer formula [12]:

$$D = 0.94\,\lambda / \Delta(2\,\theta)\cos\theta$$

where, $\Delta\ (2\theta)$ is the half- peak width of the diffraction lines in radians.

Table II

Sample no.	Substrate temp., C	Lattice const., a (nm)	Lattic const.,c (nm)	Unit cell volume (nm)^3	Crystallite siz D (nm) (301)	(211)
34	525	0.47792	0.3180	0.726404	12	17.6
40	500	0.47838	0.3187	0.729336	10	16.1
58	475	0.47977	0.3185	0.733305	8.6	12.3
46	450	0.48117	0.3171	0.734094	8	11.5
52	425	0.48187	0.3122	0.724854	6.2	8.4
undoped TO	450	0.47151	0.3154	0.701202		
ASTM spec.pure powder		0.4738	0.3188	0.71566		

IV - CONCLUSION

Glass like thin films of BTO are produced at different substrate temperatures and thicknesses. It was observed that doping with boron influenced positively the conductivity of the produced films, as well as the increasing of the substrate temperature, while transmittance is kept high. The large values of figure of merit indicate its suitability for applications in solar cells as electrodes or as antireflection coating as it have a low refractive index (1.75).

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FIGURE CAPTIONS

Fig. 1 -- Tansmission T(%) of BTO thin films as a function of wave length λ from 200-900 nm. for 5 min. deposition time at substrate temperature 500^{o} C

Fig. 2 -- Variation of the square of ($\alpha\Delta t$) as a function of photon energy $h\nu$ of BTO thin films for substrate temperature 475 ^{o}C [(o) = 4min., (o) = 5 min., (Δ) = 10 min], and for substrate temperature 425^{o} C [(x) = 5 min., (Δ) = 10 min.]

Fig. 3 -- Refractive index n as a function of wave length λ from 200 - 900 nm.

(1) = 4min.at substrate temperature 450^{o} C;

(2) =5min. at substrate temperature 475^{o} C;

(3) = 4min. at substrate temperature 525^{o} C.

Fig. 4 -- X-ray diffraction pattern of 10 % BTO films with deposition time 5 min. and substrate temperature (a) 425, (b) 450, (c) 475, (d) 500, and (e) 525^{o} C.

Fig. 5 -- Effect of substrate temperature on the crystallinity of BTO films with substrate temperature (a) 425, (b) 450, (c) 475, (d) 500, and(e)525^{o}C.

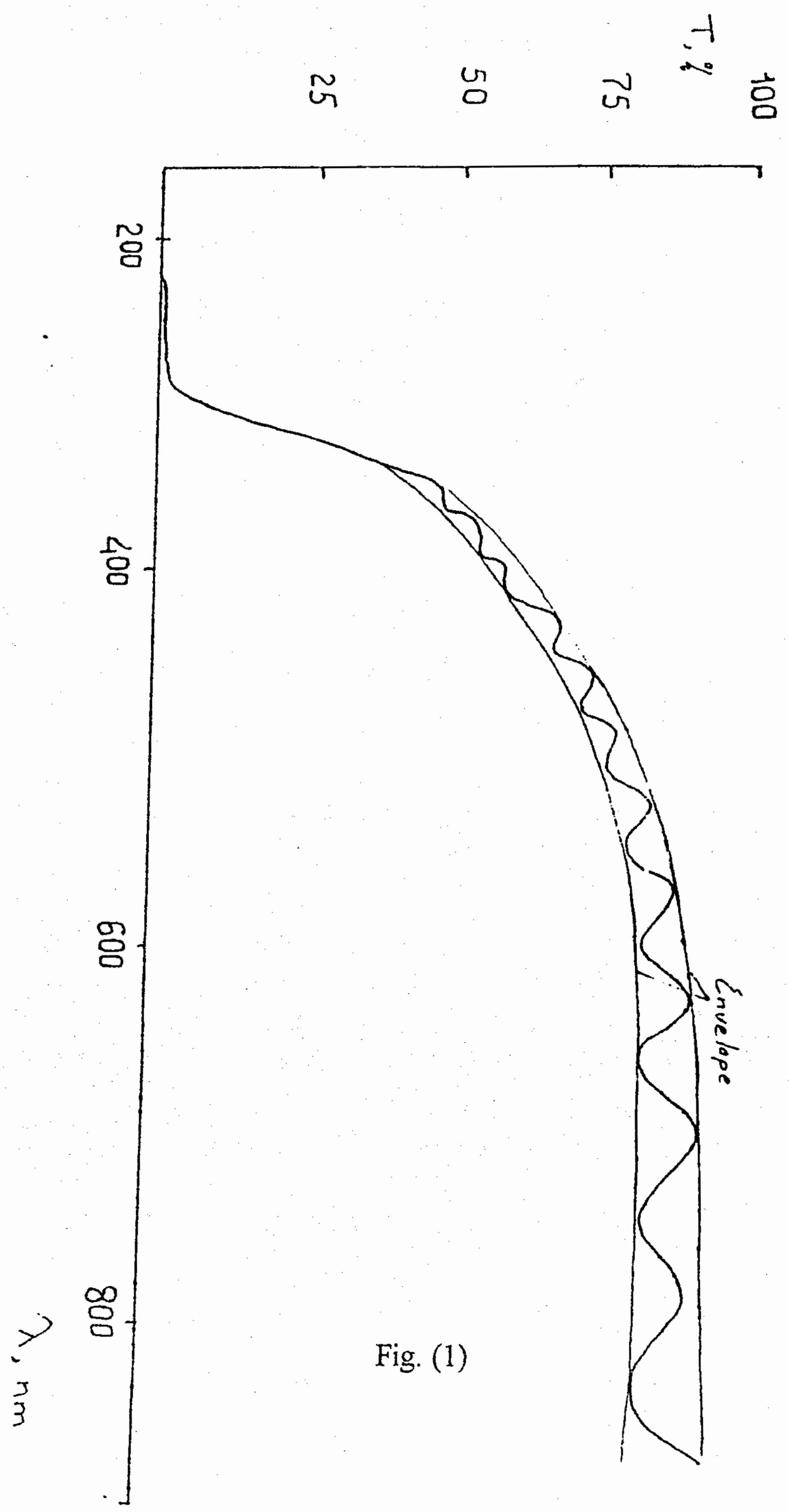

Fig. (1)

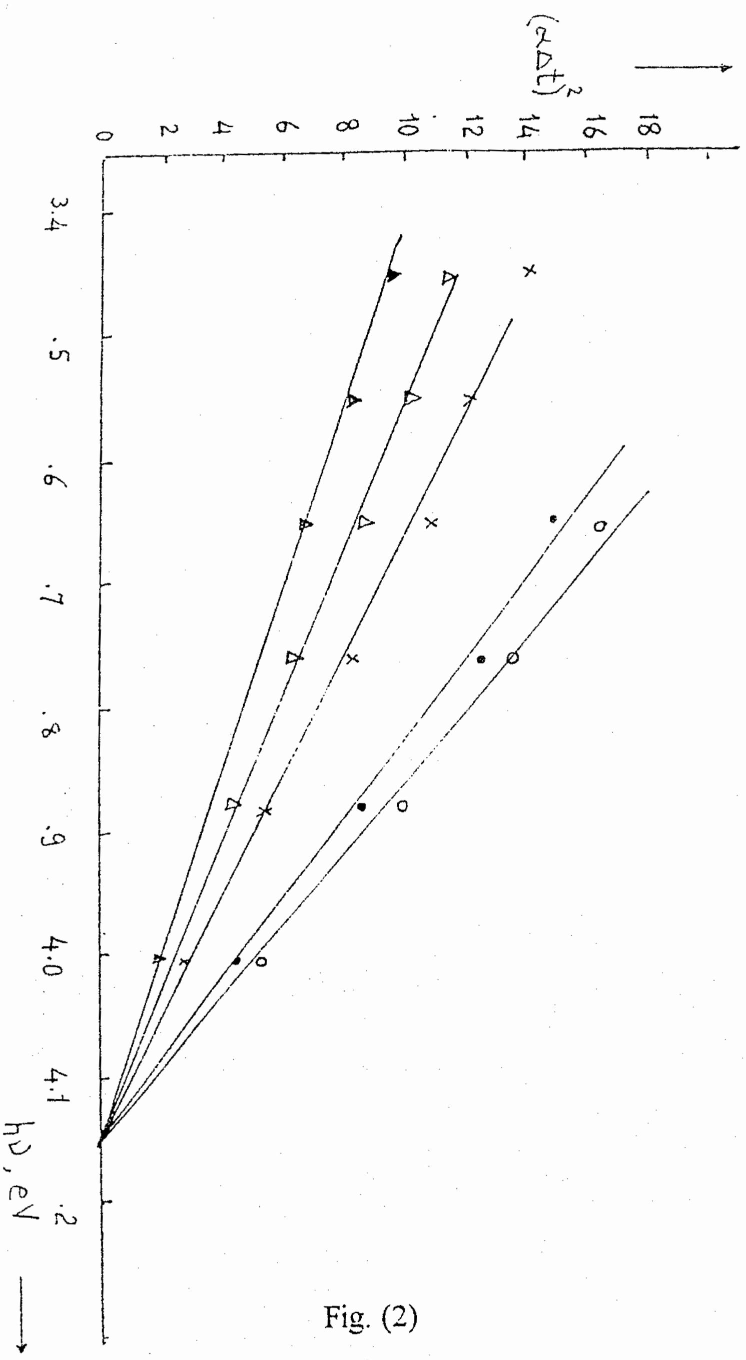

Fig. (2)

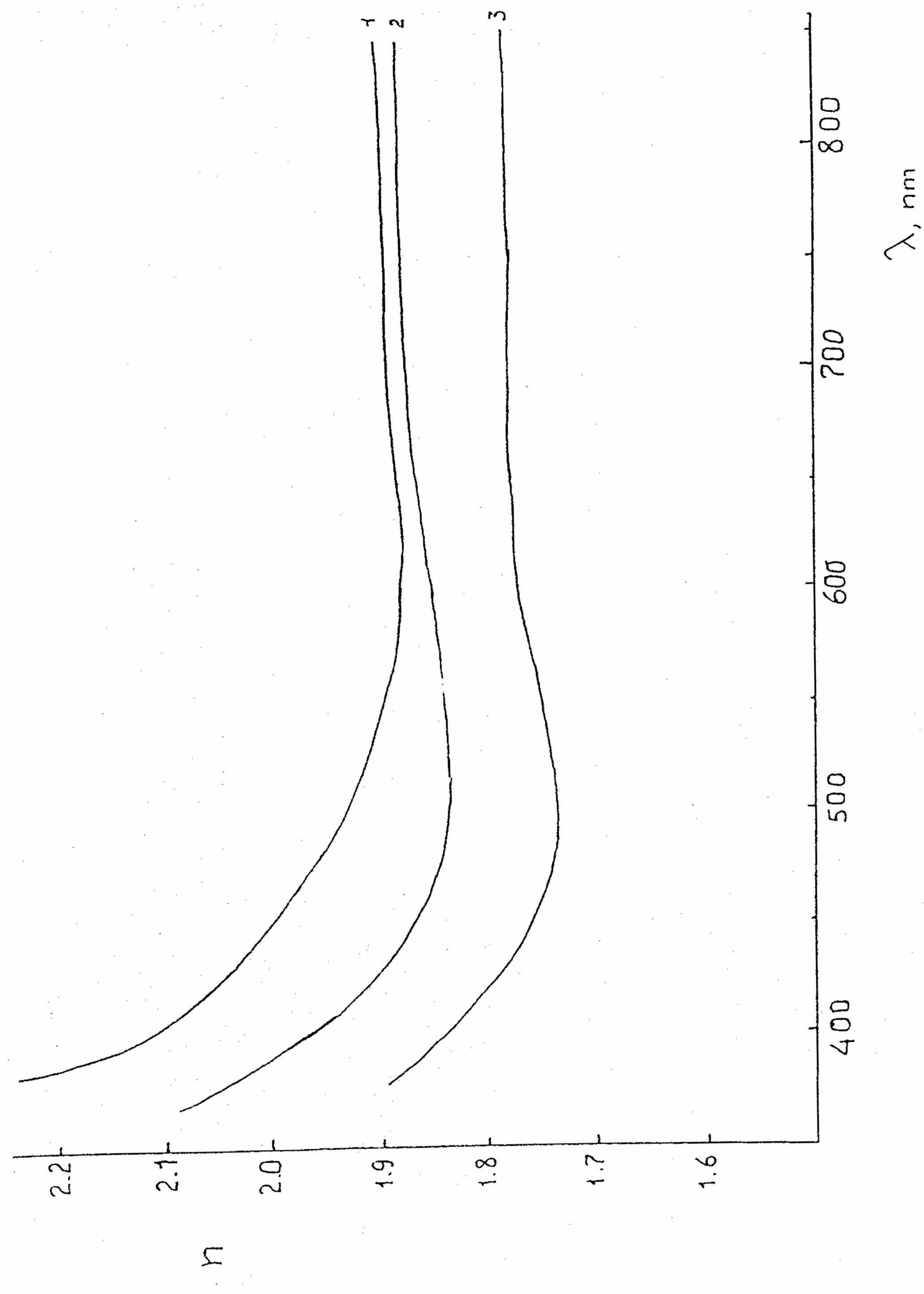

Fig. (3)

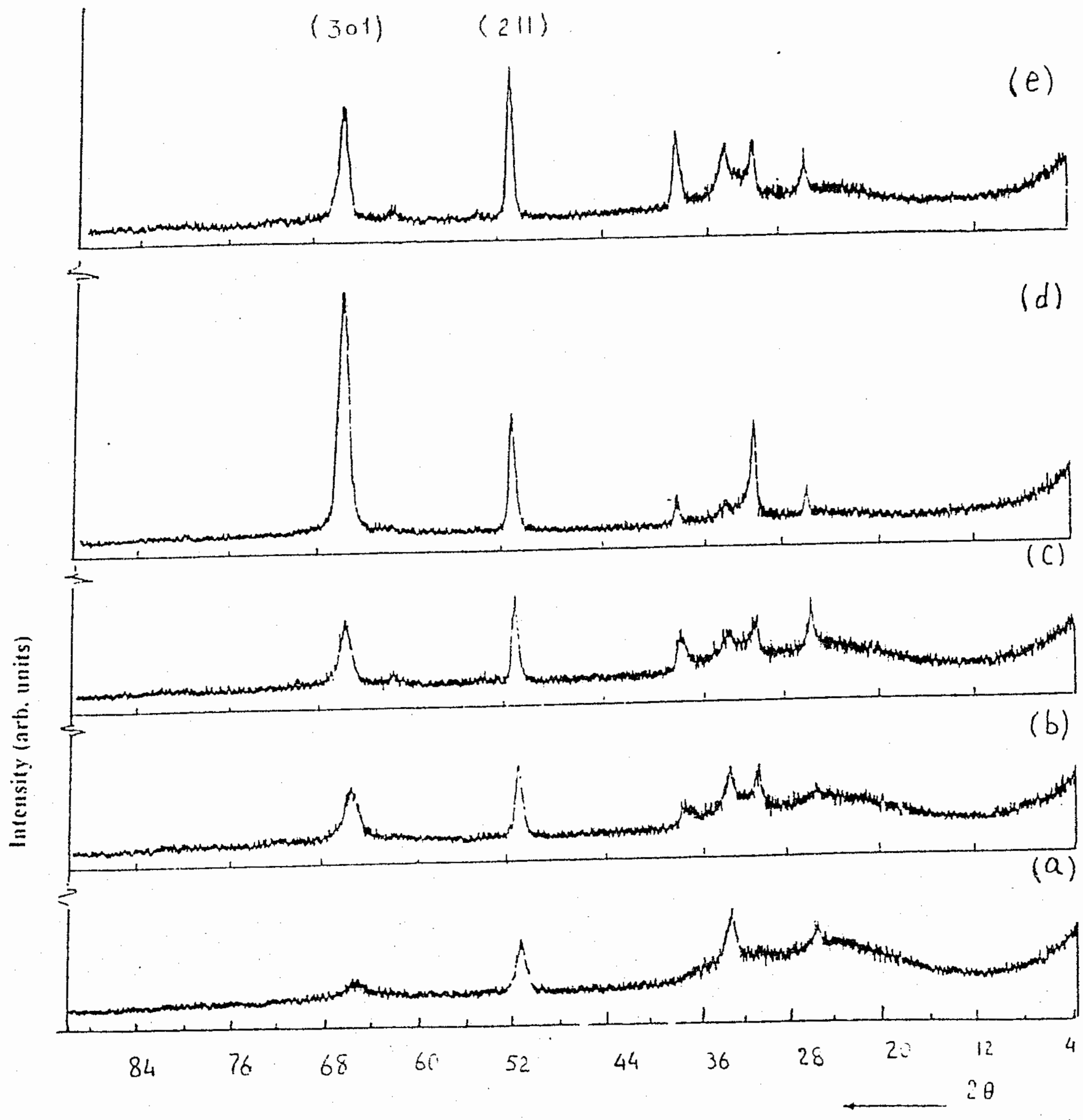
(301)
(211)
(e)
(d)
(c)
(b)
(a)
Intensity (arb. units)
84
76
68
60
52
44
36
28
20
12
4
2θ

Fig. (4)

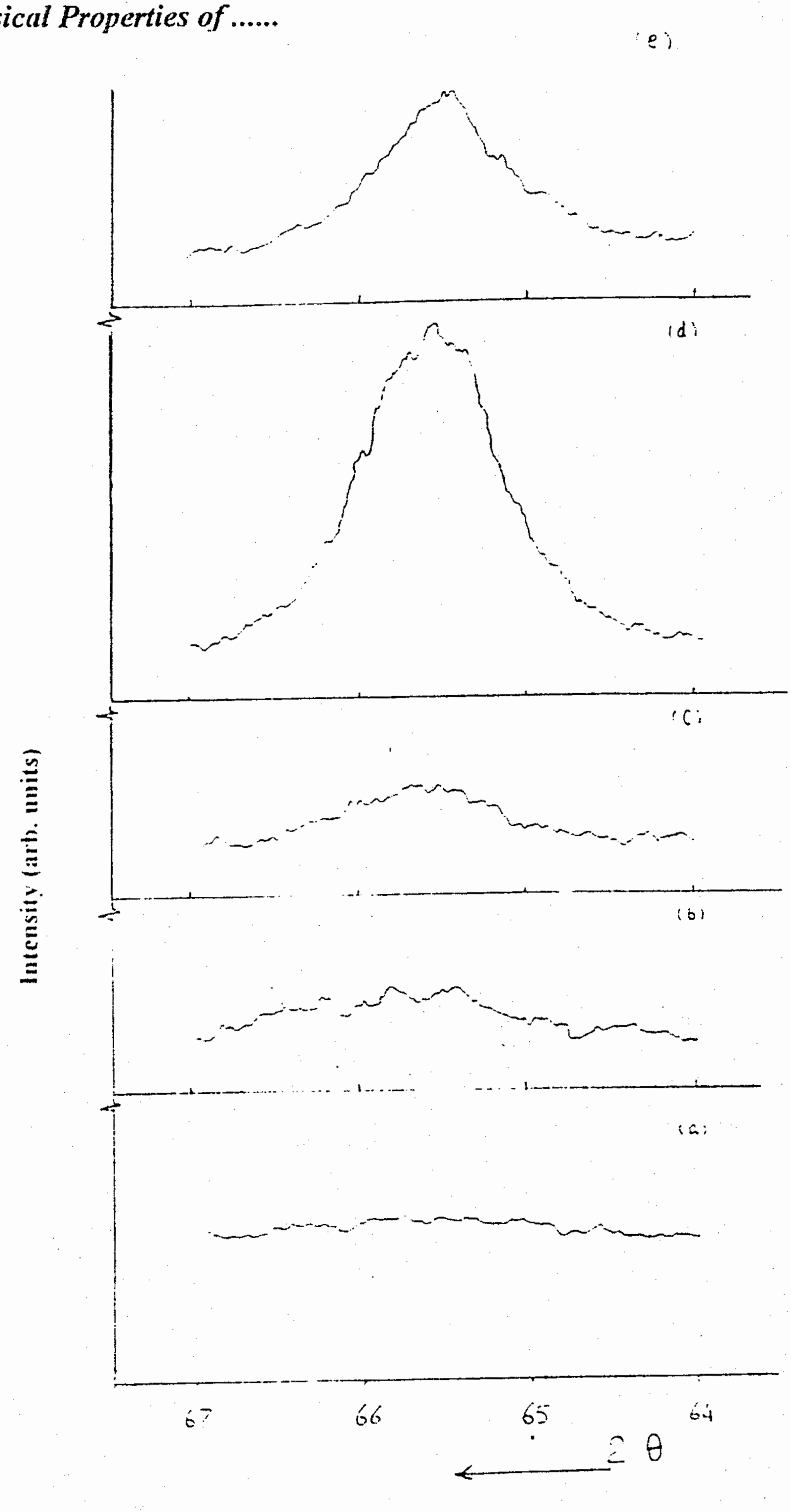

Fig. (5a)

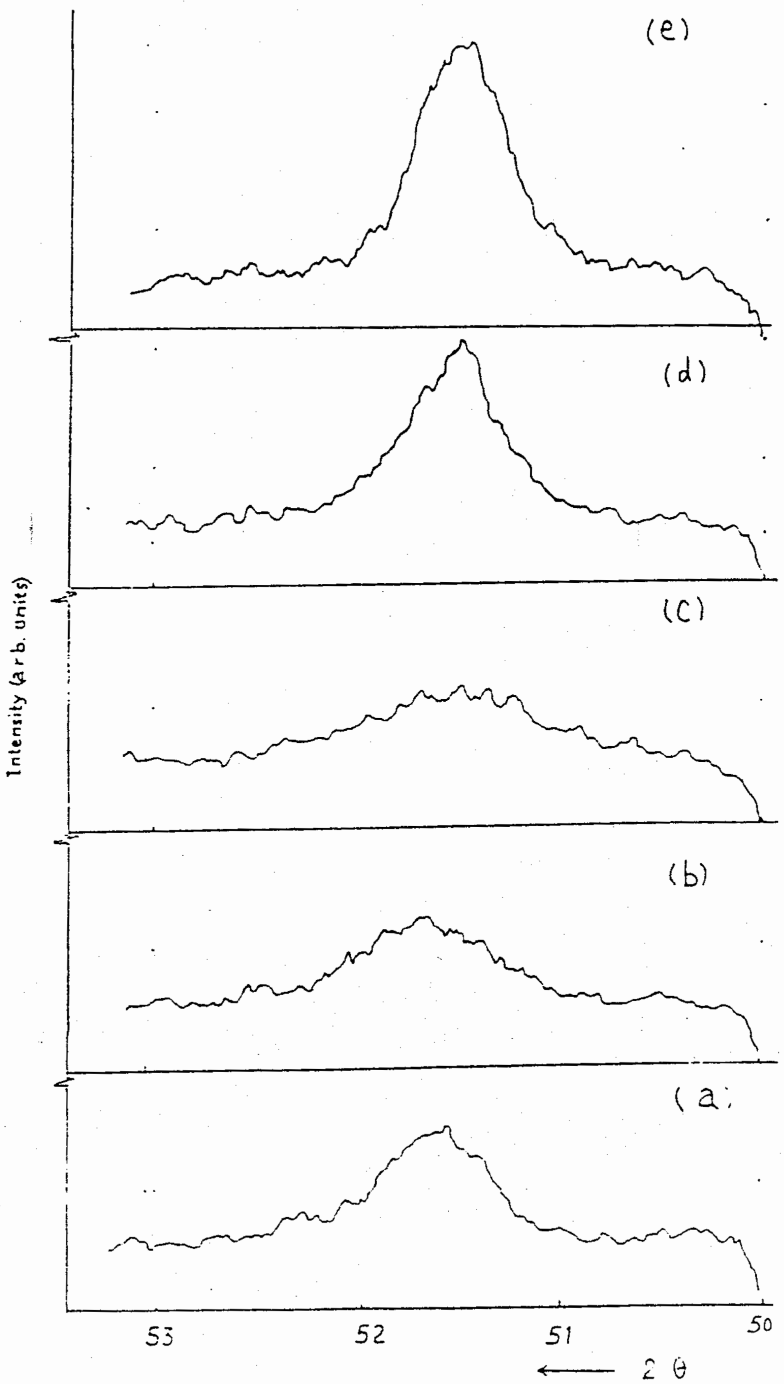

Fig. (5b)

الخواص الفيزيائية لأغشية
أكسيد القصدير المطعم بالبورون

يتناول البحث طريقة تحضير أغشية أكسيد الرصاص المطعم ب ١٠٪ بورون وذلك عند درجات حرارة تتراوح بين ٤٢٠°م ، و ٥٢٥°م بطريقة .spray tech وقد تمت دراسة الأغشية الرقيقة الناتجة وذلك بعمل مسح لشفافية هذه الأغشية عند ظروف التحضير المختلفة وكذلك عند أزمنة تحضير (سمك) مختلفة وبربط (المقاومة السطحية) مع الشفافية يتبين تأثير ϕ fig. merit. ومنه يتبين خواص الغشاء البصرية والكهربية معا. تحت أيضا دراسة تأثير العوامل السابقة من درجة الحرارة والسمك فى وجود البورون فى منظومة اكسيد القصدير حيث تأثر معامل الإنكسار وتم تعيين السمك المقابل لكل زمن ترسيب للغشا الرقيق يتبين تأثير درجة الحرارة من حيث حجم البللورة وذلك عن طريق دراسة حيود الأشعة السينية (XRo) حيث بينت انه عند درجات الحرارة المنخفضة تكون ذو تأثير سلبى على تكون حجم البلورات فى الغشاء عديد التبلر وأظهر المستوى المفضل يكون عند (٢١١) ، (٣٠١).