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# THE THICKNESS OF $SnO_2$: F FILMS AS PRINCIPAL FACTOR OF THEIR PROPERTIES*

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All of the studied properties of $SnO_2$ : F films prepared by spraying of ethanol solution of $SnCl_4 \cdot 5H_2O$ onto heated glass substrates (Ts = 300°C, 400°C, 430°C) in ambient air atmosphere (spreying angle $\alpha = 45°$, airless sprayer-to-substrate distance of $\approx 50$ cm) strongly depend on the film thickness d.

At given substrate temperature of preparation, the thickness dependences of the: refractive index n(d), optical gap Eg (d), and X-ray diffraction intensities ratio $\frac{I\,(hkl)}{I\,(200)}(d)$ (hkl = 110, 211, 301) exibit minimus at a concrete film thickness $d = d_f$. The thickness dependences of the electrical conductivity $\sigma$ (d) and the Haacke's „figure of merit" $\Phi$ (d) ($\Phi = T^{10}/R_\square$ ; T— transmittance, $R_\square$ — sheet resistance) obtain maximums at the same thickness $d_f$.

## INTRODUSTION

Our firts results were concerned to $SnO_2$ : F films [1] prepared by spraying of ethanol solution of $SnCl_4 \cdot nH_2O$ (200gr $SnCl_4 \cdot nH_2O$ 90ml $C_2H_5OH$ 10ml HCl 2.8ml 50%HF; F/Sn=0 147; solution A) in intervals 1—2s with pauses of about 60s in between A distance airless sprayer-to-substrate of $\approx$ 50 cm and a spraying angle of $\approx 45°$ were used together with substrate temperature Ts = 430°C. The experimental results pointed out the thickness dependence of n, $\Phi$, $\sigma$ i.e. for $d \approx 0.85\ \mu m$ n(d), $\Phi$(d) and $\sigma$(d) obtain maximums.

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The next study [2] was dealing mainly with the sprayed $SnO_2$ : F films prepared with ethanol solution of $SnCI_4 . 5H_2O$ (200gr $SnCl_4.5H_2O$, 90ml $C_2H_5OH$, 10ml HCl, 2.8ml 50% HF; soltuion A′) at Ts = 300°C, 400°C, and 430°C. In that case n(d) for all the films exibit minimums for $d=d_f$, while σ(d) and Φ(d) exibit maximums. $d_f = 0.6 - 0.8$ μm is different for different $T_s$. The comparation of the film properties prepared with solutions A and A′ was performed together with sprayed undoped $SnO_2$ films (solution $A'_0$:200gr $SnCl_45H_2O$, 90ml $C_2H_5OH$, 10ml HCl; $T_s = 430°C$). It affirmed the best transparent-conductive properties of the films prepared with solution A.

The results presented in this work (sol. A′), i.e. n(d), Φ(d), σ(d), Eg (d) and $\frac{I(hkl)}{I(200)} \sim$ (d) certify more completly the thickness dependence of the film properties.

## 2. EXPERIMENTAL RESULTS

a. — From the spectral transmittance measurements T(λ) (spectrophotometer Pye Unicam SPG—300) and their interference maxima and minima, the spectral refractive index n(λ) and the film thickness d have been determined [3].

The plots of n(d) for the studied films prepared at substrate temperatures $T_s = 300°C$, 400°C and 430°C are given in Fig. 1. Minimums in the courses of n(d) for $d=d_f$ are well expressed. d · is different for different $T_s$. The values of n are smaller than those reported in some former investigations [4—6]

b. — The optical gap was determined from the spectral apsorptivity α(λ) i.e. T(λ) measurements using the relation $(\alpha_\nu h\nu)^2 = \text{const.}(h\nu - E_g)$ ploted as $(\alpha h\nu)^2$ v.s. hν [7].

The plots $E_g(d)$ for the studied films are presented in Fig. 2. It is notable that the minimums in their courses correspond to those of n(d) (Fig. 1). All the Eg values are lower than the previously reported ones [4,8,9].

c. — Some results of the X-ray diffraction measurements (Cu $K_\alpha$; λ = 1.54Å; JEOL JDX—7E) for the investigated films are presented in Fig. 3 in form of intensity ratios $\frac{I(hkl)}{I(200)}$ (d) where hkl=110, 211, 301. These diffraction peaks were chosen refereing to some previous reports [4,9 — 12] where they are shown to be the most pronounced lines.

The comparison of the plots in Figs. 1,2 and 3 shows an obvious similarity i.e. they obtain minimums for the same film thickness $d=d_f$.

The minimums in $\frac{I(hkl)}{I(200)}$ (d) indicate that the differences between the compared intensities are the smallest when $d=d_f$. For this film thickness the preferred orientation of the crystallites diminisches.

In Fig. 3d are given two X ray diffractograms ($T_s$ = 300°C; d=0.54 µm, and 0.79 µm). Difraction A ($2\theta = 31{,}4°$) from [15] is asctribet to the presence of suboxydes (SnO, $Sn_2O_3$, $Sn_3O_4$)

d.— The thickness dependence of the film conductivity (measured by the four point method) is given in Fig. 4. The courses of $\sigma$(d) are inverse to those of n(d), $E_g$(d) and $\frac{I(hkl)}{I(200)}$ (d) (Figs. 1,2,3). At $d=d_f$ the film conductivity is maximal. In a pretty narrow interval of d, $\sigma$ is the highest for the films prepared at $T_s = 300°C$, while from the aspect of good conductivity in a wide thickness interval, the films deposited at $T_s$ = 430°C are more attractive.

Fig. 1

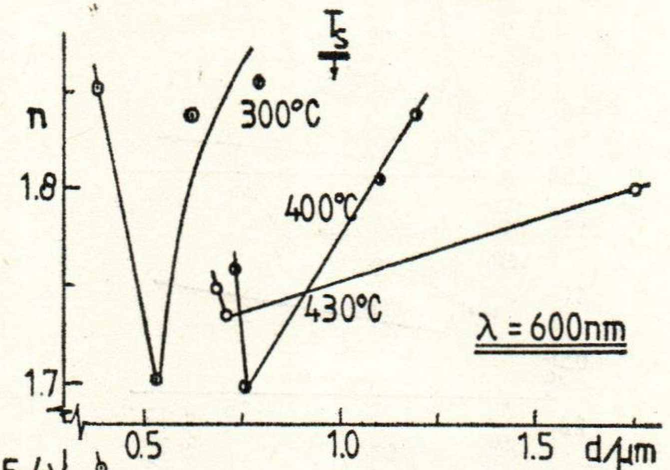
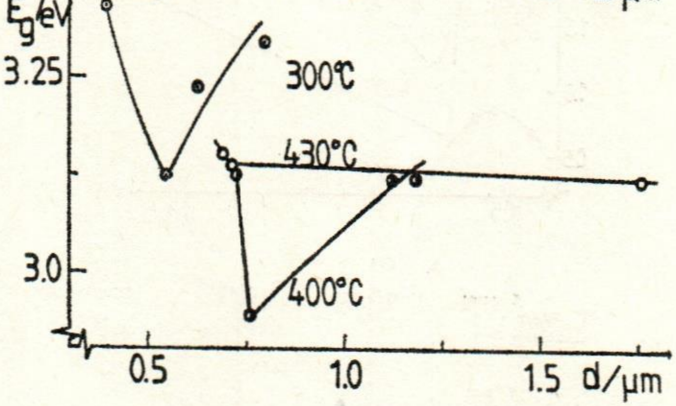


Fig. 2



e.— The optical-electrical properties of the studied films represented through the Haacke's „figure of merit" (Fig. 5) also certify the best quality of the spracyed $SnO_2$:F films whose thickness is $d=d_f$. The films deposited at $T_s = 430°C$ are preferable. The presented plots $\Phi_{max}$ (d) correspond to $T_{max}$ of the interference maximums in T(λ), ($\Phi_{max} = \frac{T^{10}_{max}}{R_\square}$).

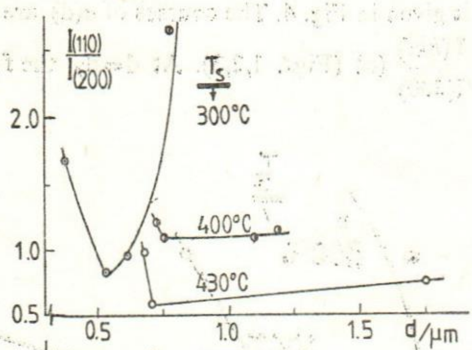


Fig. 3a

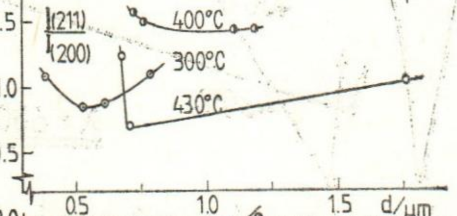


Fig. 3b

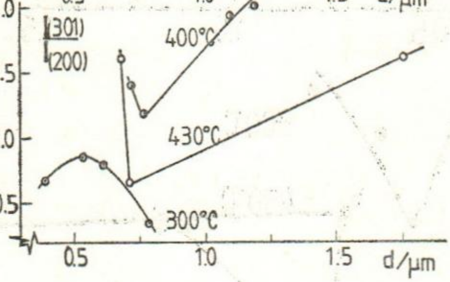


Fig. 3c

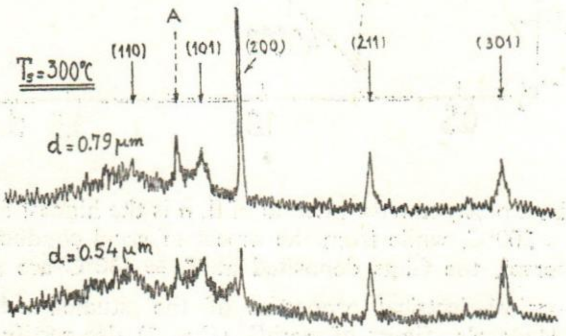


Fig. 3d

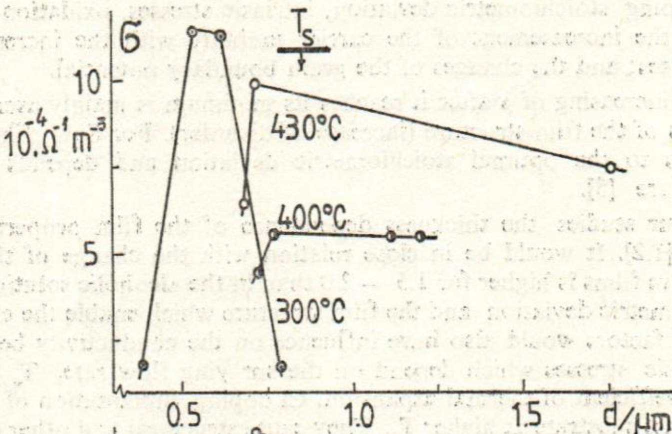


Fig. 4

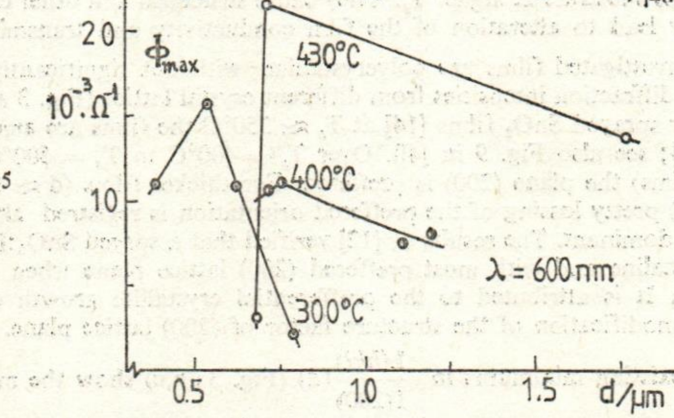


Fig. 5

## DISCUSSION

The previous studies (4,5,13) of sprayed $SnO_2$ films verified the existence of minimums in $\rho(T_s)$ [5] and $R_{\square}$ $(T_s)$ [13] which correspond to the maximums in Sn concentration $\bar{c}$ [4] i.e. to the maximal concentration of oxygen vacancies $0^{2+}$.

The resistivity ρ exibits similar behaviour as a function of the dopant concentration [14,4]. Namely, ρ obtains a minimum at specific dopant concentration [F]/[Sn] at. ≈ 0.25.

The resistivity dependence of the oxygen flow rate f (C.V.D. method) [15] posseses a minimum at f ≈ 1.8 lit/min. Because of the established linearity between the film thickness d and the flow rate f, $\rho_{min}$ is found to correspond to a concrete value of d. The decreasing of ρ (increasing of σ) before it attains its minimum is ascribed to: the increasment of the carrier concentration (doping stoichiometric deviation, intrinsic stresses, oxidation of SnO to $SnO_2$); the increasement of the carrier mobility with the increasing of the grain sizes; and the changes of the grain boundary potential.

The increasing of $\rho$ after it reaches its minimum is mainly ascribed to the changes of the film structure (increase of disorder). For $SnO_2$ films $\rho_{min}$ corresponds to the optimal stoichiometric deviation and depends on the film structure [5].

In our studies the thickness dependence of the film properties was confirmed [1,2]. It would be in close relation with the change of the F/Sn ratio (F/Sn in films is higher for 1.5 — 2.0 than in the alcoholic solution [14]), the stoichiometric deviation and the film structure which enable the changing of $\rho$. Other factors would also have influence on the conductivity behaviour like: intrinsic stresses which depend on the spraying flow rate, $T_s$ and the substrate coefficient of thermal expansion, Cl doping, inplantation of alkalies from the glass substrate at higher $T_s$. They cause structural and other changes which finaly lead to alteration of the film conductivity and transmittance.

All investigated films are polycrystalline with not significantly preffered X-ray diffraction intensities from different crystal lattice (Fig. 3 a,b,c,d) although for sprayed $SnO_2$ films [14] at $T_s \approx 350°C$ the films are amorhous (their Fig. 4; see also Fig. 9 in [4]). Over $T_s = 400°C$ to $T_s = 500°C$ (for not thick films) the plane (200) is preffered. For thicker films ($d \approx 1.5 \mu m$; $T_s = 500°C$) pretty lossing of the preffered orientation is registred although (200) is still dominant. The results of [12] verified that a spryed $SnO_2$:F films are polycrystaline and with most preffered (200) lattice plane when $280 < T_s < 450°C$. It is attributed to the prefferential crystallite growth combined with a modification of the structure factor of (200) lattice plane.

The existing minimums in $\frac{I(hkl)}{I(200)}$ (d) (Fig. 3a,b,c) show the minimal differences between the compared X-ray diffraction intensities (fig. 3d) and it would correspond to the optimal doping of F/Sn and Cl/Sn and optimal stoichiometric deviation when at $d = d_f \sigma_{max}$ is obtained (Fig. 4).

The behaviour of n depends on the film structure which is expressed not only in the courses of $n(\lambda)$ but also in the values of n. The polycrystalline sgprayed $SnO_2$ films [5] have smaller n tham the amporhous ones prepared by flash evfporation ($n = 2.15$). The similarity in the courses of n (d) (Fig. 1) and $\frac{I(hkl)}{I(200)}$ (d) (Fig. 3 a,b,c) and the obtained $\sigma_{max}$ (Fig. 4) for $d = d_f$ would relate to the condition when optimum in the processes of doping, oxidation stoichiometric deviation and order/disorder is achieved in the films.

The optical gap $E_g$ for sprayed $SnO_2$ films is between 3.7 — 3.8 eV (for single crystal $E_g = 3.6$ eV) [4]. For sprayed $SnO_2$ films $E_g = 3.7$eV was registred and $E_g = 2.4$eV for flash evaporated films [5]. By doping (Sb) [9,17] $E_g$ increases by increasing of the dopant concentration ($E_g = 3.95$ — 4.62 eV).

In our case (Fig. 2) $E_g$ would be in relation with the film structure. $E_{g,min}$ would correspond to optimums between order/ disorder, when also the dopant concentration, stoichiometric deviation and the film structure are optimal ($\sigma_{max}$).

Films with $\sigma_{max}$ posses maximal transmitivity T. It is (Fig. 5) expressed by $\Phi$ (d) $_{max}$ when $d = d_f$ is obtained.

## CONCLUSION

Thickness dependence of $SnO^2$:F film properties prepared by the described procedure and spraying conditions enable concretisation of the film thickness $d = d_f$ when the transparent-conductive properties of $SnO_2$:F films are the ebest.

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# ДЕБЕЛИНАТА НА $SnO_2$:F ФИЛМОВИ — ГЛАВЕН ФАКТОР ЗА НИВНИТЕ ОСОБИНИ

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и В. Јорданова

Експерименталните резултати од испитуваните $SnO^2$:F филмови добиени со спреирање при три температури на субстратот ($T_s = 300$, 400 и 430°C) и останатите назначени параметри на спреирањето покажуваат дека: 1.- индексот на прекршувањето n (Fig. 1). 2.— оптичката енергија на зафаќањето Eg(Fig. 2), 3.— односот на интензитетите на дифрагираните рентгенски зраци од поедини равнини ($I_{(h,k,l)}$) и равнината (200) т.е. ($I_{(h,k,l)})/I_{(200)}$ (Fig. 3a,b,c,d), 4.— електричната проводливост $\sigma$ (Fig. 4) и 5.— Haacke-овиот „figure merit“ $\Phi = \frac{T^{10}}{R}$ (Fig. 5) силно зависат од дебелината на филмот постигајќи минимум, односно максимум, при определена дебелина на филмот $d=d_f$. $d_f$ е во функција од температурата на субстратот $T_s$.

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