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PROPERTIES OF SnO_2:F FILMS PREPARED BY INTERRUPTED SPRAYING ONTO GLASS SUBSTRATES BY EMPLOYING THE CARRIER GAS SPRAYER

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The properties of films prepared by spraying ethanol solution of $SnCl_4 \cdot 5H_2O$ *onto glass substrates* ($T_s = 385^0C$) *in ambient air atmosphere (spraying angle* $\alpha = 45^0$; *sprayer-to-substrate distance of ≈ 50 cm) are studied.*

Investigated film proprerties strongly depend on film thickness, d. The thickness dependence of sheet resistance $R_\square(d)$ *and optical energy gap* $E_g(d)$ *at specific film thickness* $d = d_f$ *obtain minimal values.*

At $d = d_f$ *the thickness dependence of X-ray diffraction intensitities ratio* $\frac{I(hkl)}{I(200)}(d)$ (hkl = *110,211,301) and Haacke's "figure of merit"* ϕ *receive maximal values* ($\phi = T^{10}/R_\square$; *T - film transmittance).*

1. INTRODUCTION

The properties of SnO_2:F films prepared by spraying method depend on more spraying parameters and circumstances [1,2,3,4,5,6]. The mainly used

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sprayed solutions are methanol, ethanol or water solution of $SnCl_4 \cdot 5H_2O$ doped with CH_3F or HF [1,5,7,8]. Optimal glass substrate temperatures T_s are about 400^0C.

The experimental results of previously investigated SnO_2:F films, [5, 7, 8] sprayed onto glass substrate (T_s=300, 400 and 430^0C) by employing the airless sprayer (spraying intervals 1-2 s with pauses of about 60 s in between) certified very remarkable thickness dependence of their properties.

The plots of optical refractive index n(d), $\frac{I(hkl)}{I(200)}$ (d) and E_g(d) at $d = d_f$ have minimum, but electrical conductivity σ(d) and ϕ(d) has maximum.

The experimental results of investigated SnO_2:F films prepared in the same spraying conditions are presented in this work, but employing the carrier gas sprayer (Fig. 1), ambient air atmosphere and spraying intervals of 1-2 s with pauses of about 30 s in between. The sprayed ethanol solution is: 200 g $SnCl_4 \cdot 5H_2O$; 90 ml C_2H_5OH; 10 ml HCl; 2,8 ml 50% HF; $[F/Sn]_{at}$ = 0.147. The thickness dependence of film properties is also strongly expressed.

2. EXPERIMENTAL RESULTS

The film thickness d has been determined [9] from the interference maxima and minima in spectral transmissivity T(λ) (Spestrometar Pye Unicam SPG-300). The film optical energy gap Eg was determined by spectral absorptivity $\alpha(\lambda)$, i.e. T(λ) measurements, and presented as $(\alpha h\nu)^2$ v.s. $h\nu$ [10,5]. The sheet resistance $R_\Box = \frac{\rho}{d}$ of the films was calculated by the use of the film resistivity (four point method). The diffraction intensity ratio I(hkl)/I(200) is based on X-ray diffractograms (Fig. 2; CuK_α; λ=1.54 Å; YEOL YDX7E).

The diffraction peaks of hkl = 110,211,301 and 200 were chosen with regard to some previous reports [1,3,8,11,12,13], where they are shown to be the most pronounced lines.

X-ray diffractograms (Fig. 2) verified that:

- film with d = o.56 μm is amorphous
- increase of the film thickness d is related to the increase of

the (101) diffraction intensity (beside the increasing of the half-width)

- "thicker" films (d > 0.7 μm) possess preffered (200 orientations, especially pronounced at d = 1.1 μm
- at d = 0.7 μm the smallest differences between diffraction intensities of (110), (211), (200) and

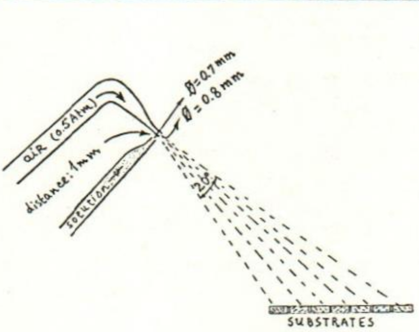

Fig. 1.

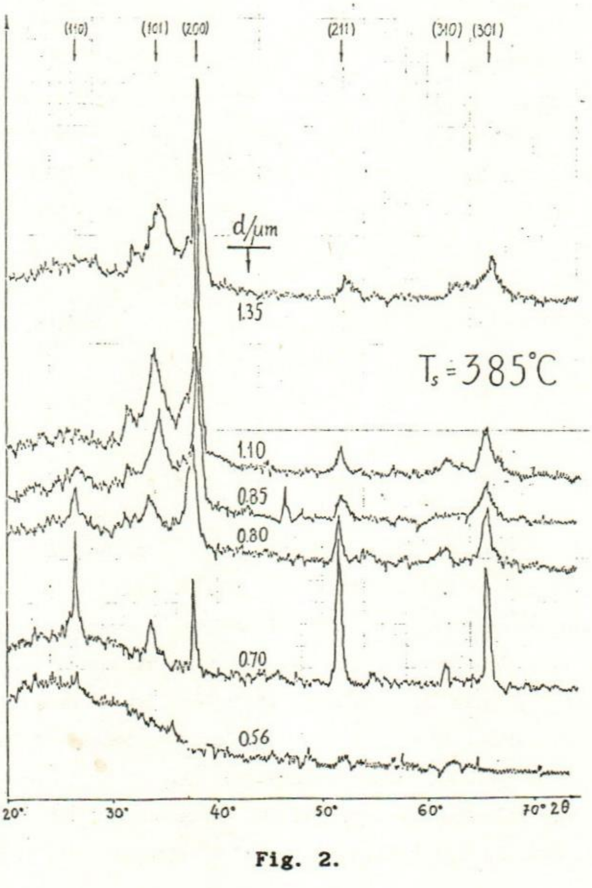

Fig. 2.

(301) lattice planes are pretty evident

- only at "thicker" films a feeble presence of suboxides ($2\vartheta = 31.4^0$; [6]) is evident.

On Fig. 3 the plots of $R_\square(d)$, $E_g(d)$ and $\phi(d)$ are presented. They show:

- existing of minimum in the course of $E_g(d)$
- existing of minimum and maximum in the course of $R_\square(d)$
- E_{gmin}, $R_{\square min}$ and ϕ_{max} are obtained for a specific film thickness $d = d_f = 0.7\ \mu m$
- good transparent - conductive properties are found between d - 0.6 and d = 0.8 μm.

Fig. 4 in fact is Fig. 3 with projected plots of $\frac{I(hkl)}{I(200)}(d)$ (hkl = 110, 211 and 301) over it.

It can be noted that:

- the courses of $\frac{I(hkl)}{I(200)}$ are very similar to those od $\phi(d)$
- smaller values of I(hkl)/I(200), after d = 0.85 μm ("thicker" films) indicate greater preffering of I(200) (Fig. 2)
- for $d = d_f$, when $\phi = \phi_{max}$ is obtained, the differences between I(hkl) and I(200) are the smallest (I(hkl)/I(200) ≈ 1.0; see Fig. 2).

In the case of employing the airless sprayer [8], this condition at $d = d_f$ is expressed by minimum in the course of $\frac{I(hkl)}{I(200)}(d)$.

3. DISCUSSION

The previous studies [1,4] of sprayed SnO_2 films verified the existence of minimum in $\rho(T_s)$ [4] and $R_\square(T_s)$ [14] which corresponds to the maximums in Sn concentration, i.e. to the maximal concentration of oxygen vacancies O^{2+}. ρ as a function of the dopant concentration [1, 15] exhibits similar behaviour (ρ has a minimum at specific dopant concentration $[F/Sn]_{at} \approx 0.25$). The resistivity dependence of the oxygen flow rate f [15] possess minimum at f = 1.8 l/min. Because of linearity between f and film thickness d, ρ_{min} is related to a specified value of d. The decreasing of ρ (increasing of conductivity) before it attains its minimum is ascribed to:

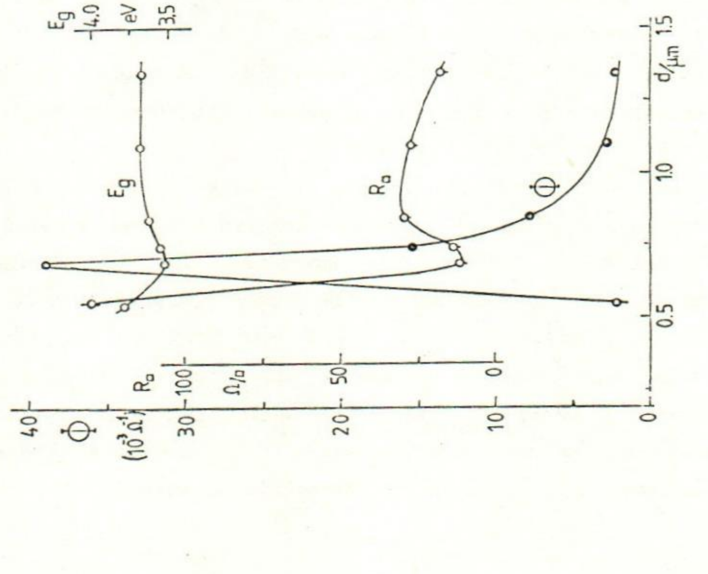
Φ
$(10^{-3}\Omega^{-1})$
40
30
20
10
0
R_a
100
$\Omega/\square$
50
0
E_g
4.0
eV
3.5
E_g
R_a
Φ
0.5
1.0
d/μm 1.5

Fig. 3.

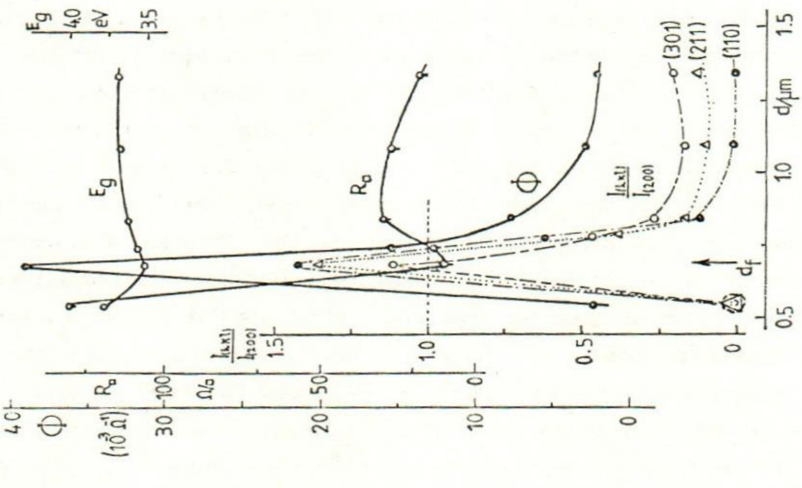
Φ
$(10^{-3}\Omega^{-1})$
40
30
20
10
0
R_a
100
$\Omega/\square$
50
0
$I_{(hkl)}/I_{(200)}$
1.5
1.0
0.5
0
E_g
4.0
eV
3.5
E_g
R_a
Φ
$I_{(hkl)}/I_{(200)}$
(301)
(211)
(110)
d_f
0.5
1.0
d/μm
1.5

Fig. 4.

the increase of carrier concentration (doping) stoichiometric deviation, intrinsc stresses, oxidation of SnO to SnO_2), the increase of carrier mobility with the increase of grain sizes and the change of the grain boundary potentials. The increasing of ρ after ρ_{min} is mainly ascribed to the changes of the film structure (increase of disorder). For SnO_2 film ρ_{min} corresponds to the optimal stoichiometric deviation and its dependence on the film structure. In our studies [5,7,8]. the thickness dependence of the film properties was confirmed. It would be in close relation with the change of F/Sn ratio (F/Sn in the films can be higner for as much as 1.5 - 2.0 than the one in the sprayed solution [16]), the stoichiometric deviation and the film structure which enables the changing of ρ. Other factors like intrinsic stresses, T_s, substrate coefficient of thermal expansion, implantation of alkalies from glass substrate (at higher T_s) have also an influence on the film conductivity. All of them cause structural and other changes which finally lead to alteration of the film conductivity and transmittivity. With an exception of the film with d = 0.56 μm (Fig.2), all films are polycrystalline, with mainly preferred orientation of (200) lattice plane [1, 13, 16]. It is attributed [16] to the preferential crystalline growth combined with modification of the structural factor of (200).

The existing minimum [8] in the course of $\frac{I(hkl)}{I(200)}(d)$, i.e. maximum Fig. 4 when $d = d_f$, represented also with $\phi = \phi_{max}$ is related to the smaller differences between X-ray diffraction intensities and would correspond to the optimal doping of F/Sn and Cl/Sn and optimal stoichiometric deviation, i.e. order/disorder in the film.

The optical energy gap E_g for sprayed SnO_2 films is between 3.7-3.8 eV (for single crystals E_g = 3,6 eV [1]). For sprayed SnO_2 films [4] E_g = 3.7 eV was found and E_g = 2.4 eV for flash evaporated films. By doping (Sb) [3,17], E_g increases by the increase of the dopant concentration (E_g = 3.95 - 4.62 eV). The small values of E_g (E_g = 2.95 - 3.35 eV) [8] may be related to the periodical (interrupted) process of the spraying. At this spraying procedure [8 and this work], E_{gmin} at $d = d_f$ would also be in relation with the obtained optimum between order/disorder (film structure) and optimal dopant concentration, i.e. optimal stoichiometric deviation.

4. CONCLUSION

Using interrupted (periodical) spraying process for preparation of SnO_2:F films onto glass substrates by employing the carrier gas (air) sprayer (Fig. 1), the film properties are with similar behaviour as those when airless sprayer is employed [5, 7, 8], i.e. their properties strongly depend on the film thickness. The best transparent-conductive properties (for given T_s) exist at the specified film thickness $d = d_f$. For given T_s the films possess good transparent-conductive properties only in narrow thickness interval Δd. Then the preferred orientation between the latice planes are not greather ($\frac{I(hkl)}{I(200)} \sim 1$).

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ОСОБИНИ НА Sn_2O:F ФИЛМОВИ ВРЗ СТАКЛЕН СУПСТРАТ, ДОБИЕНИ СО ИСПРЕКИНАТО СПРЕИРАЊЕ ОД СПРЕЕР СО НОСЕЧКИ ГАС (ВОЗДУХ)

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Резиме

Студирани се особините на SnO_2:F филмови добиени со спреирање на етил-алкохолен раствор на $SnCl_4 \cdot 5H_2O$ врз стаклен супстрат (T_s = 385^{0}C) во амбиент на воздушна атмосфера (агол на спреирање $\alpha = 45^0$; растојание спреер - супстрат 50 cm; Fig. 1).

Испитуваните особини на филмовите силно зависат од дебелината на филмот d. Зависностите од d на површинскиот отпор $R_\square$ и оптичкиот енергетски гап E_g постигаат минимум при определена дебелина $d = d_f$ (Сл. 3). При $d = d_f$

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зависноста од d на односот на интензитетите на дифракцијата на рентгенските зраци (Сл. 2), т.е. $\frac{I(hkl)}{I(200)}$, (hkl = 110, 211, 301; Сл. 4) и Haacke-овиот "Figure of merit" (индекс за споредба) ϕ постигнуваат максимум ($\phi = T^{10}/R_{\square}$ и T-трансмисивност на филмот).

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