

SEMICONDUCTING SnO_2 FILMS WITH In AND Sb IMPURITIES

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Thin SnO_2 films have been deposited on glass substrates by d.c. cathode sputtering of metallic tin in argon-oxygen mixture. The films obtained by means of this method are conducting and have polycrystalline structure. The conductivity of the films was changed within 10 orders of magnitude by introducing In and Sb impurities to the material of the cathode. Indium decreased the conductivity of the films while the presence of antimony increased it to saturation at sufficiently large concentration values. The activation energies of donor levels have been determined from the temperature dependences of the conductivity. A simple band model of SnO_2 containing impurities is presented.

1. Introduction

The aim of the work was to investigate some fundamental electric properties of thin tin dioxide films obtained by reactive cathode sputtering and the determination of the influence of In and Sb on these properties. According to literature [1], [2] tin dioxide is a wide band semiconductor with the energy gap amounting to about 3.4 eV. Owing to the existence of donor levels in the forbidden energy gap the conductivity of SnO_2 is considerable and therefore this material is used for the production of conducting coatings on glass and ceramic materials. The crystal structure and the electric properties of thin SnO_2 films have been the subject of many experimental papers [3-8], the results, however, have shown considerable differences dependings on the method by which the films were obtained. It is the opinion of the author of the present paper that the reactive cathode sputtering method applied in the present work permits films with properties very close to those of SnO_2 single crystals to be obtained, and the results will allow some already known properties of the material to be elucidated.

The reactive cathode sputtering method has been applied in case of thin SnO_2 films by Holland and Siddal [9]. In their experiment the tin cathode was "activated" for about 30 minutes in a mixture composed of 95% Ar and 5% O_2 . After the initial stage of sputtering the films had a brown colour and a comparatively high resistivity (about 50 $\text{k}\Omega/\square$). However, after annealing for several hours at about 673°K the resistivity decreased while at the same time the transmissivity of light increased. The recrystallization of SnO_2 films has been studied by Sinclair *et al.*, [10], [11]. The sputtering conditions which have been used by these

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authors were the following: The samples were oxygen-deficient. Immediately after sputtering the films were amorphous and nonconducting. The state of normal conductivity which depended on the concentration of In and Sb impurities was reached after annealing at 973°K. The influence of the presence of impurities was considerable since the conductivity could be changed within seven orders of magnitude. The authors of the discussed paper used only high impurity concentrations (above 2%). Similar results have been obtained by Baillon *et al.* [12]. However, in all these papers the authors pointed out the necessity of using thermal treatment of the films after their deposition by sputtering in order to stabilize the electric parameters.

After preliminary experiments the author of the present paper has come to the conclusion that a suitable choice of sputtering conditions permits the deposition of films whose properties are very similar to SnO₂ single crystals without the necessity of thermal treatment. The results of the above-mentioned preliminary experiments were published in 1966 [12].

2. Apparatus

The construction of the apparatus for cathode sputtering designed by the author exhibits no essential differences compared to the standard equipment described in literature [14], [15]. The cathode block cooled with water is fastened in the steel cover of the chamber of the diameter 0.3 m (Fig. 1). The material to be sputtered was pressed into cathodes of 0.092 m diameter. The construction of the substrate support permitted the control of its temperature as well as the control of the potential with respect to the earthed anode by means of a suitable supply. The use of a positive potential of the support (with respect to the anode) resulted in increased oxygen concentration in the film whereas negative potential resulted in an opposite effect. The influence of this potential on the properties of oxide and metallic films has been proved in Refs [13], [14] and [15]. The chamber was filled with oxygen-argon mixture by means of two needle valves which permitted a continuous change of the oxygen contents in the mixture.

3. Preparation of samples

The films were deposited on substrates of boron-silicon glass. Preliminary stage of cathode sputtering the aim of which was to remove eventual contaminations from its surface was carried out for about 30 minutes. The use of such preliminary sputtering ensured the repeatability of the film properties. In order to separate the influence of foreign impurities on the film conductivity from the influence of impurities resulting from the non-stoichiometric composition, the sputtering conditions had to be such that the concentration of oxygen in the film would be maximum. The choice of the sputtering conditions was such that the conductivity of the films would be minimum, however, with the preservation of the polycrystalline structure of the film. The conditions selected by the author were the following:

- pressure in the chamber: 8 N/m².
- cathode-to-substrate distance: 20 mm,

- concentration of oxygen in the oxygen-argon mixture: greater than 10%,
- cathode voltage: 1700 V,
- potential of the substrate support with respect to anode: +50 V,
- substrate temperature: 580°K.

In these conditions the density of the current was 1.5 mA cm^{-2} and the rate of film growth about 2.5 \AA s^{-1} . 24 cathodes composed of Sn—In and Sn—Sb alloys have been used with In and Sb-contents covering the range between $1.8 \times 10^{-3}\%$ and 10% atom/atom. The thickness of the film samples used in the measurements was 4700 \AA . The measuring electrodes made of gold were deposited by means of the cathode sputtering method.

4. Measurements of the conductivity and mobility

The stability of the conductivity of the films in time has been checked during the period of several weeks. Changes in the conductivity have been found only in case of samples with conductivity values less than $10^{-3} \Omega\text{m}^{-1}$; they ranged within one order of magnitude. These changes were associated with varying humidity of air and can be explained in terms of chemisorption of hydrogen at the film surface, similarly as is in case of TiO_2 [16]. The

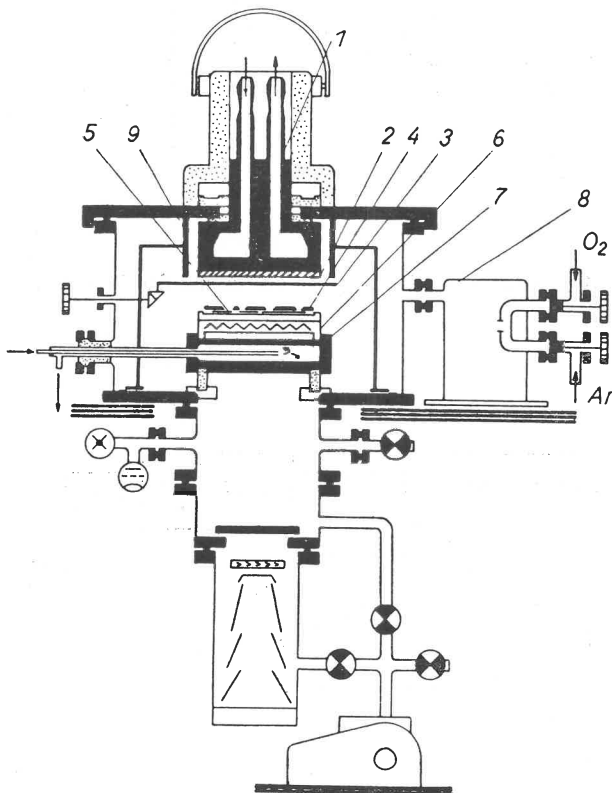


Fig. 1. Chamber for reactive cathode sputtering. 1-cathode block, 2-sputtered material, 3-diaphragm, 4-mask, 5-substrate, 6-electrically heated support, 8-vessel—containing the gas mixture with needle valves 9-screen insulating the cathode block

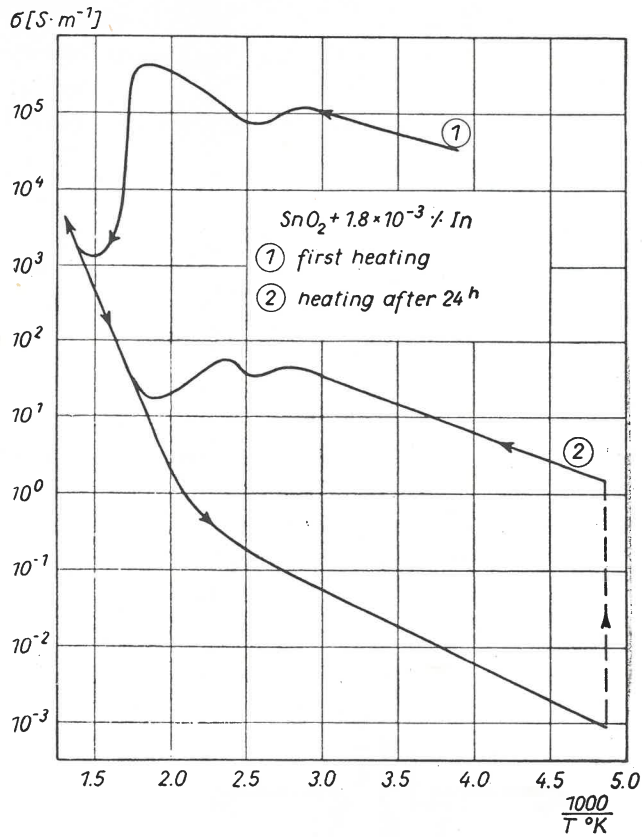


Fig. 2. Changes in the conductivity of SnO_2 during the thermal treatment.

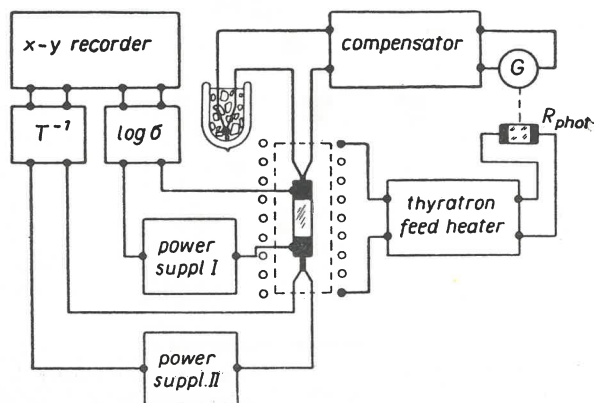


Fig. 3. Block diagram of the circuit for studies of the temperature dependence of the conductivity.

changes in the resistivity of SnO_2 films which occur during the thermal treatment are shown in Fig. 2. These are reversible changes, however, the time needed for return to the state before thermal treatment is of the order of fifty hours. The temperature dependence of the conductivity was measured by means of a device which directly plotted the function $\ln \sigma = f(T^{-1})$.

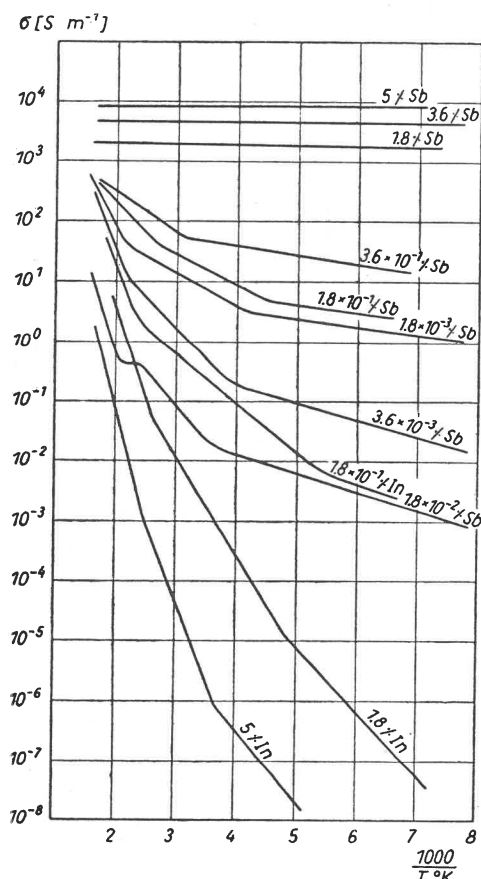


Fig. 4. Temperature dependence of the conductivity of SnO_2 films containing In and Sb impurities

The block diagram of this device is shown in Fig. 3. The temperature was stabilized by means of a thermo-control system with a thyatron supply. The reciprocal temperature was recorded by means of a converting four-terminal network with resistance probe.

The Hall mobility at room temperature was measured by means of the method proposed by Van der Pauwe [17].

5. Results of measurements

The results of the measurements of the dependence of conductivity on temperature are shown in Fig. 4. This figure illustrates the most characteristic results obtained from the series of 24 samples containing various concentrations of In and Sb impurities. A complete

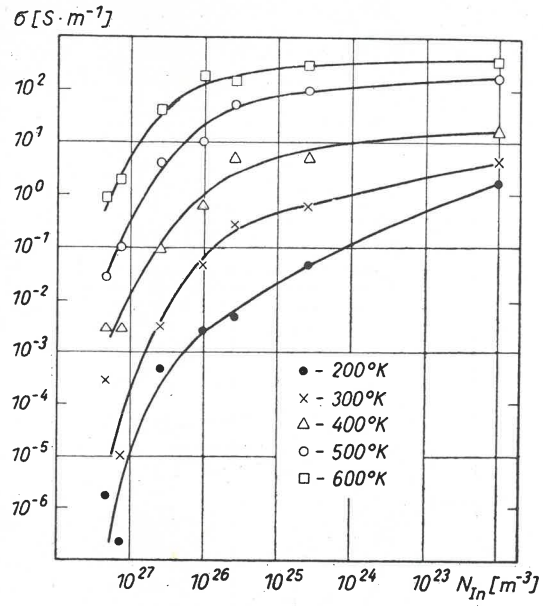


Fig. 5. Dependence of the conductivity of SnO₂ films on the concentration of In impurities

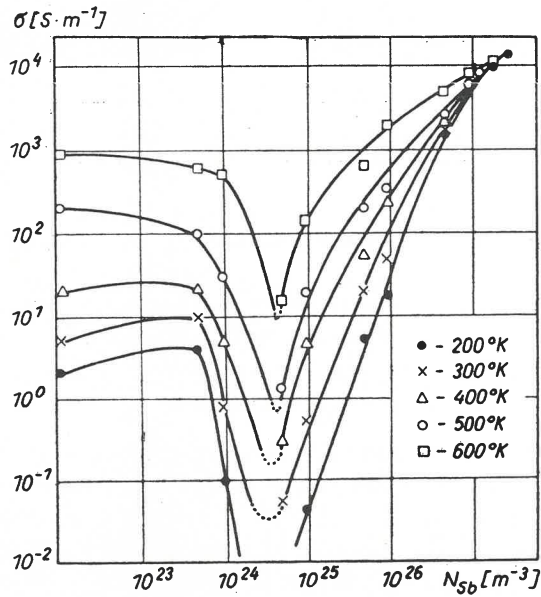


Fig. 6. Dependence of the conductivity of SnO₂ films on the concentration of Sb impurities

list of all measurements is not necessary for getting an overall picture of the effect. The activation energies of the electrons have been determined from the slope of the $\ln \sigma$ vs. T^{-1} curves. The dependence of the conductivity of the films on the concentration of impurities in the cathode is shown in Figs 5 and 6. The concentrations of impurity atoms in the SnO_2 film with respect to the concentration of Sn atoms are plotted on the abscissa axes under the assumption that the cathode sputtering process does not occur selectively. This assumption seems to be justified since the sputtering parameters of the particular components of the Sn—In—Sb alloys are similar.

The measurements of the Hall mobility have been carried out only for those samples whose conductivity was greater than 10^{-5} Sm^{-1} . The mean value of mobility $3 \cdot 10^{-4} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ shows no significant difference from the values obtained by other authors [1], [7]. The sign of the Hall constant indicates that the conduction is of the electronic type. A careful examination of the curves presenting the temperature dependence of the conductivity permits us to distinguish three rectilinear parts. Two of those obviously correspond to

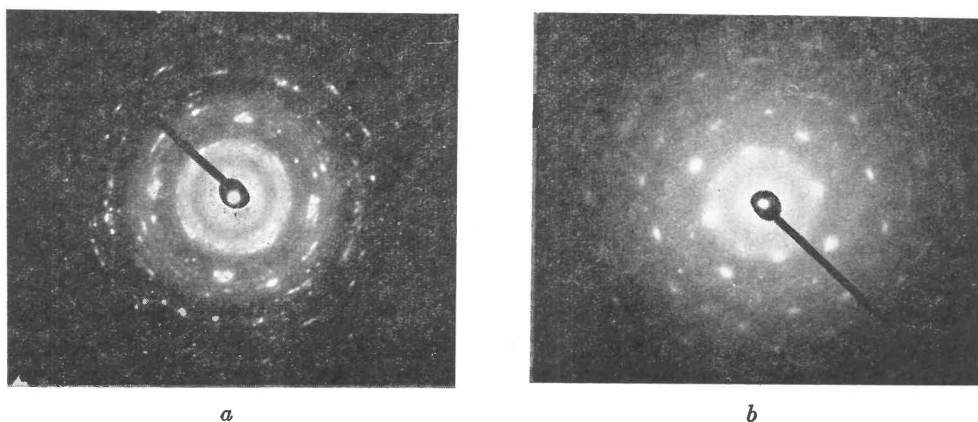


Fig. 7. Electron diffraction patterns of SnO_2 films deposited on NaCl single crystal substrates; *a* - film not subjected to thermal treatment, *b* - film annealed for four hours at the temperature of 673°K

excitation energies of electrons from donor levels lying in the forbidden band. The excitation energies corresponding to these levels amount to $E_1 = 0.3 \text{ eV}$ and $E_2 = 0.03 \text{ eV}$, respectively. The third rectilinear part of the curves in Fig. 4 whose slope is the greatest may be connected with the ionization of the Sn—O system or with the conduction of the glass substrate occurring at high temperatures. Therefore all further consideration will comprise only two components in the expression for the conductivity of SnO_2 films.

The crystal structure of the films was determined by means of the X-ray and electronographic method. In the latter method the films were deposited on substrates made of NaCl single crystals. Fig. 7 shows electron diffraction patterns of a sample which was not subjected to thermal treatment and another sample which was annealed for four hours in air at 680°K . Both the X-ray and the electron diffraction patterns correspond to tetragonal structure of SnO_2 .

6. Interpretation

6.1. Film containing no impurities

The comparatively large conductivity of SnO_2 films with no impurities is the consequence of the deviation from stoichiometry. The conduction electrons come from the donor levels associated with oxygen vacancies. This conclusion can be justified by comparing the conductivities of films obtained under different partial pressures of oxygen in the sputtering chamber. Films obtained under greater partial pressures of oxygen had smaller conductivities. The depth of the donor level connected with the oxygen vacancies is about 0.3 eV below the bottom of the conduction band. Each oxygen vacancy is connected with two electrons. The concentration of donor levels is thus twice as large as the concentration of oxygen vacancies. It seems that in thin SnO_2 films it is not possible to obtain stoichiometric composition like in single crystals. The smallest density of donor levels connected with oxygen vacancies obtained in optimum conditions by the author of the present paper was 10^{23}m^{-3} . This value was calculated on the basis of the temperature dependence of the conductivity in case of a film containing no impurities. This density of donor levels does not significantly depend on the thermal treatment on the film after its deposition.

6.2. Films containing indium impurities

The indium atoms are embodied into the SnO_2 lattice as trivalent ions. As a result of this the In ions should play the role of acceptor centres with the acceptor level below the middle of the forbidden band. However, hole conduction was not observed even at a high concentration of In atoms (10%) in the material of the cathode. The conductivity of the films decreases with increasing concentration of these impurity atoms in the cathode. This happens due to the compensation of donor levels associated with oxygen vacancies by acceptor levels associated with trivalent In ions. The ionization of the acceptor levels is thus impossible even at high temperatures since all acceptor levels are occupied by electrons coming from donor levels.

6.3. Films containing antimony impurities

The antimony atoms embodied in the SnO_2 -lattice give up four out of their five electrons of the outer shell to the lattice bonds, while the fifth electron which is only loosely bound can be dissociated from the Sb^{+4} ion by thermal excitation. In the framework of the band model this effect corresponds to the transition of the electron to the conduction band. The binding energy of this electron is not greater than 0.03 eV, and hence the samples with Sb impurities are conducting already at room temperature and even at the temperature of liquid nitrogen. It was found that the conductivity becomes minimum for Sb concentrations between 10^{24} and 10^{25}m^{-3} . This effect may be caused by the neutralization of oxygen vacancies by antimony ions whose valency is greater than that of tin ions in the tetragonal SnO_2 lattice. This is connected with a decrease in the effective concentration of donor levels since a fraction of the tin atoms is reduced from Sn^{+4} to Sn^{+2} . If the concentration of antimony atoms increases to a value greater than the concentration of donor levels in SnO_2 containing no impurities then the conductivity of the films enormously increases. Such an increase in

conductivity has also been observed by other authors [10], [11]. For concentrations of Sb-atoms of about $5 \cdot 10^{26} \text{ m}^{-3}$ the conductivity of the films is already independent of temperature. For greater concentrations the conduction band becomes degenerate and the properties of semiconducting SnO_2 become similar to the properties of metals.

6.4. Energy band model of SnO_2 containing impurities

In order to calculate the concentration of electrons in the conduction band a simplified band model of SnO_2 containing In or Sb impurities in the lattice has been assumed (Fig. 8). The width of the forbidden band in pure SnO_2 is about 3.4 eV [2]. In the forbidden energy band there is a donor level associated with the presence of antimony impurities and with the acceptor level associated with In. The energies of the donor levels have been determined

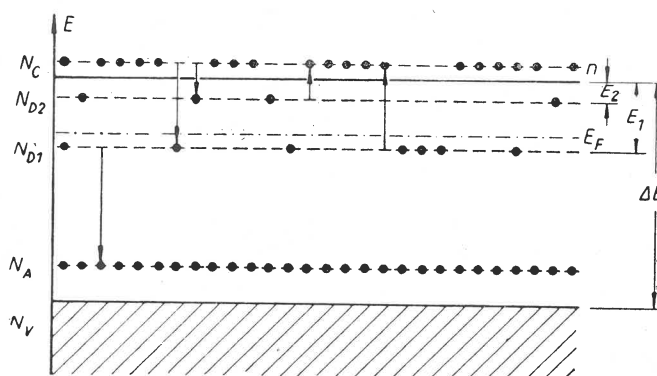


Fig. 8. Energy model of semiconducting SnO_2 containing In, and Sb impurities

experimentally from the measurement of the temperature dependence of the conductivity. The position of the acceptor level has been assumed quite arbitrarily, however, below the middle of the forbidden band. The conductivity of the films is thus the result of excitation of two donor levels:

$$\sigma = \sigma_{01} \exp\left(-\frac{E_1}{kT}\right) + \sigma_{02} \exp\left(-\frac{E_2}{kT}\right) \quad (1)$$

where

$$E_1 = 0.3 \text{ eV} \quad \text{and} \quad E_2 = 0.03 \text{ eV}.$$

The concentration of electrons in the conduction band for partly compensated semiconductors can be expressed by means of the equation derived by de Boer and van Geel [18]:

$$n = \frac{N_D - N_A}{2N_A} N_C \exp\left(-\frac{E}{kT}\right) \quad (2)$$

For $N_D \gg N_A$

$$n = \frac{1}{\sqrt{2}} (N_D \cdot N_C)^{1/2} \exp\left(-\frac{E}{2kT}\right) \quad (3)$$

where: n — is the concentration of electrons in the conduction band, N_D — is the density of donor levels, N_A — is the density of acceptor levels, $N_C = 2 \left(2\pi m^* \frac{kT}{h^2} \right)^{3/2}$ — density of levels in the conduction band.

By applying Eq. (2) for $N_D \approx N_A$ and Eq. (3) for $N_D \gg N_A$ it is possible to express the conductivity of SnO_2 films containing In and Sb impurities by means of the equation

$$\sigma = e \cdot u \sqrt{\frac{N_C}{2}} \left\{ (N_{D1} - N_A)^{1/2} \exp\left(-\frac{E_1}{kT}\right) + \left(N_{D2} - \frac{1}{2} N_{D1}\right)^{1/2} \exp\left(-\frac{E_2}{2kT}\right) \right\},$$

where:

u — is the electron mobility, e — is the elementary charge, N_{D1} — is the density of donor levels associated with oxygen vacancies, N_{E2} — is the density of donor levels associated with Sb impurities, and N_A — is the density of acceptor levels associated with In impurities.

The numerical conductivity values calculated from Eq. (4) are in good agreement with the experimental results for In and Sb concentrations up to 10^{27} m^{-3} in the temperature range from the temperature of liquid nitrogen up to 500°K . A detailed quantitative description of the dependence of the conductivity on temperature and on the concentration of impurities will be possible after the consideration of changes in the mobility and effective mass of electrons in a very wide concentration and temperature range. In the calculations made by the author both the effective mass and mobility were treated as constant.

7. Conclusions

The results of the present work indicate that the reactive sputtering method permits the deposition of polycrystalline oxide films on amorphous substrates. Such films can be easily doped with various impurities. The control of the impurity concentration in the film essentially consists in the control of the composition of the alloy from which the cathode is made. The conductivity of the films containing In and Sb impurities for concentrations less than 5% is in agreement with that calculated under the assumption that each impurity atom contained in the material of the cathode becomes embodied into the SnO_2 structure. It follows from the observations made in this experiment that in case of SnO_2 it is not possible to change the type of conduction from the electron to hole conduction since the concentration of donor levels in the material which does not contain impurities is too high. This does not rule out the possibility of application of SnO_2 films in the production of elements for integrated circuit electronics. In particular owing to the possibility of compensation of donor levels by acceptors coming from the presence of In impurities it is possible to produce junctions with a high gradient of electron concentration whose nonlinear current-voltage characteristics may be of considerable importance in integrated circuit electronics. On the other hand from

the purely scientific point of view tin dioxide is a rather convenient material for studies on the mechanism of current carriers coming from foreign impurities transport.

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REFERENCES

- [1] K. Ishiguro, T. Sasaki, T. Arai, I. Imai, *J. Phys. Soc. Japan*, **13**, 296 (1958).
- [2] T. Arai, *J. Phys. Soc. Japan*, **15**, 916 (1960).
- [3] A. J. Kuzniecov, *Fiz. Tverdogo, Tela*, **2**, 35 (1958).
- [4] W. K. Miloslavsky, S. P. Liashenko, *Optika i Spektrosk.*, **8**, 868 (1960).
- [5] E. E. Kohnke, *J. Phys. Chem. Solids*, **23**, 1557 (1962).
- [6] H. Koch, *Phys. Status Solidi*, **3**, 1059 (1963).
- [7] J. F. Tigane, *Fiz. Tverdogo Tela*, **7**, 276 (1965).
- [8] L. D. Loch, *J. Electrochem. Soc.*, **110**, 1081 (1963).
- [9] L. Holland, G. Siddal, *Vacuum*, **3**, 375 (1953).
- [10] R. W. Sinclair, F. G. Peters, S. E. Koonce, *J. Electrochem. Soc.*, **110**, 56 (1963).
- [11] R. W. Sinclair, F. G. Peters, S. E. Koonce, D. W. Stillinger, *J. Electrochem. Soc.*, **112**, 1096 (1965).
- [12] E. Leja, M. Jachimowski, *Acta Phys. Polon.*, **30**, 45 (1966).
- [13] J. Baillou, P. Bugnet, J. Deforges, S. Durand, G. Batailler, *Rev. Phys. Appl.*, **3**, 1 (1968).
- [14] E. Krikorian, *Proc. Int. Conf. Single-Crystal Films*, Pergamon Press, Oxford 1964.
- [15] R. Glang, R. A. Holmwood, P. C. Furois, *Trans. Third Intern. Vacuum Congress*, Pergamon Press, Stuttgart 1965.
- [16] J. P. Suchet, *Bull. Soc. Franc. Electr.*, **5**, 274 (1955).
- [17] L. J. Van der Pauw, *Philips Res. Rep.*, **13**, 1 (1958).
- [18] J. H. de Boer, W. C. Van Geel, *Physica*, **2**, (1935).