

## In<sub>2</sub>O<sub>3</sub>-based Thin Films Deposited by Spray Pyrolysis as Promising Thermoelectric Material

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**Abstract.** Structural, electrophysical and thermoelectric properties of nanoscaled In<sub>2</sub>O<sub>3</sub> films doped by Sn and Zn were studied. Thin films based on In<sub>2</sub>O<sub>3</sub>-SnO<sub>2</sub> and In<sub>2</sub>O<sub>3</sub>-SnO<sub>2</sub>-ZnO systems were prepared by spray pyrolysis method from water solutions of metal chlorides. It was confirmed that In<sub>2</sub>O<sub>3</sub>-based films, especially the In<sub>2</sub>O<sub>3</sub>:Sn ones, are promising material for applications related to thermoelectricity. The power factor of obtained films was found to be on the level of the best samples prepared on the base of ITO system.

### Introduction

At present time parameters such as the figure of merit  $ZT$  ( $ZT = \sigma \alpha^2 T / \kappa$ , where  $\sigma$ ,  $\alpha$ ,  $\kappa$ , and  $T$  are electrical conductivity, the Seebeck coefficient or thermopower, thermal conductivity and temperature, correspondingly) and power factor  $PF$  ( $PF = \sigma \alpha^2$ ) are the main parameters, which are usually used for characterization of materials designed for application in thermoelectric generators. There is an opinion that materials suitable for the use in thermoelectric devices must have  $ZT \sim 1$ . Currently, conventional thermoelectric materials such as PbTe, Bi<sub>2</sub>Te<sub>3</sub>, BiSbTe, Sb<sub>2</sub>Te<sub>3</sub>, AgSbTe<sub>2</sub>, SiGe, etc. have a highest value of the figure of merit  $ZT$  [1]. However, these materials are easily decomposed and oxidized in the air at high temperature. This greatly limits the application of these materials at elevated temperatures needed for increasing the efficiency of energy conversion. It is known that the efficiency of energy conversion is being increased with the operating temperature in linear mode if the other parameters remain at least unchanged. Therefore, during last decade a great interest was shown in the searching a new materials that do not have these drawbacks. The experiment showed that the use of conductive metal oxides is the best possible way meet these requirements. Metal oxides, in addition to high conductivity and high chemical stability in the air at increased temperature, also exhibit superior structure stability of nanostructured films during high temperature operation [2]. It was found that the last mentioned property of metal oxides is also important for thermoelectric applications because while using nanoscale effects, the thermoelectric materials are able to obtain enhancements in thermoelectric properties, which cannot be achieved in traditional bulk materials [3]. This enhancement of  $ZT$  is achieved due to a large decrease of thermal conductivity without a considerable decrease in thermopower and electrical conductivity, caused by a decrease in the phonon mean free path due to the grain boundary scattering.

Currently a large number of metal oxides, including  $p$ -type Na<sub>2</sub>CoO<sub>2</sub>, BiCuSeO, Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub>, has been tested, and the results proved that this study has great potential [2]. The experiment has shown that the conventional  $n$ -type transparent conducting oxides such as ZnO, SnO<sub>2</sub>, CdO, and In<sub>2</sub>O<sub>3</sub> may also be of interest for such applications. There is a necessity to obtain good  $n$ -type thermoelectric materials, since they usually are used as a partner for  $p$ -type materials in thermoelectric generators. From our standpoint,  $n$ -In<sub>2</sub>O<sub>3</sub> among the above mentioned metal oxides is the most promising one for thermoelectric applications. Parameters and properties that determine the advantages of In<sub>2</sub>O<sub>3</sub> are the followings: (1) For the film deposition one can use any of the known methods; (2) In tin-doped In<sub>2</sub>O<sub>3</sub> (ITO) one can realize the maximum electron concentration and maximum conductivity among studied metal oxides; (3) The lattice thermal conductivity in In<sub>2</sub>O<sub>3</sub> is sufficiently lower than

in SnO<sub>2</sub> and ZnO because of more complicated lattice structure of indium oxide and heavier metal atom in its unit cell; (4) In<sub>2</sub>O<sub>3</sub> is characterized by excellent thermal stability and can operate at temperatures up to 1400 °C in the oxygen containing atmospheres; (5) The films exhibit high adaptability to manufacture, because In<sub>2</sub>O<sub>3</sub> allows applying the technology of wet chemical etching, used in the conventional microelectronic technology. The only major drawback of In<sub>2</sub>O<sub>3</sub> is the cost of the raw materials. Indium's concentration in minerals is too low, and therefore indium is rare and expensive element that is obtained as a byproduct of the mining of ores of other metals such as zinc and lead. Thus, the supply of indium cannot be increased sufficiently without a large increase in price. This means that the In<sub>2</sub>O<sub>3</sub> prospects depend on thermoelectric parameters, which would be achieved while using it. However, due to the limited information available, there is no clarity in the answer to the question - how effective the use of In<sub>2</sub>O<sub>3</sub> in thermoelectric applications it may be in the reality? First of all it refers to the results related to the In<sub>2</sub>O<sub>3</sub> doping and the search of optimal dopants concentrations necessary for achievement maximal thermoelectric effect. As it is known, doping is the most effective method for controlling electrophysical and structural parameters of the films.

### Experimental details

Studied In<sub>2</sub>O<sub>3</sub>, In<sub>2</sub>O<sub>3</sub>:Sn ( $C_{\text{Sn}}=0-50$  at%) and In<sub>2</sub>O<sub>3</sub>:(Zn+Sn) ( $C_{(\text{Sn}+\text{Zn})}=10-100$  at%) films were obtained using the method of spray pyrolysis. Among the possible technologies of deposition methods the spray pyrolysis is characterized by a number of advantages. The details and features of this method one can find elsewhere [4-6]. 0.2 M water solutions of InCl<sub>3</sub>, SnCl<sub>4</sub> and ZnCl<sub>2</sub> were used as precursors. Films were deposited on polished alumina or silicon (with natural layer of silica) substrates. During our experiments we used films deposited at  $T_{\text{pyr}}$  of 350°C and 450 °C. Film thickness varied in the range of 90-120 nm.

For structural characterization of the films X-ray diffractometer ARL X'TRA ( $\lambda=1.5405$  Å) for the diffraction angle range 10-90° was used. Surface morphology was studied by scanning electron microscopy (SEM) using JSM-7001F (Jeol). The film thickness was measured by using the instrument F-20 (Filmetrics). Composition of the films was controlled by using an energy dispersive X-ray spectroscopy (EDAX) microanalysis (Quanta 3D FEG microscope).

Experimental home-made setup with linear temperature gradient  $\Delta T/\Delta x$  along one axis provided simultaneous measurements of the resistance and Seebeck voltage of a thin film in the temperature range of 20-450 °C with an accuracy of  $\Delta T/\Delta x$  measuring better than 0.5%. Measurements were carried out in the mode of slow heating ( $\sim 10^\circ\text{C}/\text{min}$ ). Two thermocouples in the vicinity of the each electrode were used for the measurement of sample temperatures and their difference,  $\Delta T$ , between electrodes. Temperature difference did not exceed of 20°C in the whole temperature range. Electrodes of silver paste applied to samples with deposited films on alumina substrate (dimensions of 10 x 4 x 0.5 mm) and annealed at stabilization temperature  $T_{\text{an}}=550$  °C for 0.5 h.

### Results and discussions

Fig. 1 shows the doping influence on the thermoelectric properties of the In<sub>2</sub>O<sub>3</sub>-based films deposited by spray pyrolysis. It is seen that a significant improvement is observed only for parameters of In<sub>2</sub>O<sub>3</sub> films doped by donor-type impurities, which is consistent with the results already obtained.

The results of a more detailed study of the In<sub>2</sub>O<sub>3</sub>:Sn and In<sub>2</sub>O<sub>3</sub>:(Zn+Sn) films are shown in Fig. 2. Studied In<sub>2</sub>O<sub>3</sub>:(Zn+Sn) films correspond to the incision of 50% in the phase diagram shown in Fig. 3. The In<sub>2</sub>O<sub>3</sub>:Zn films are not of interest to the study since Zn is an acceptor. The results presented in Fig. 2 indicate that the parameters of the In<sub>2</sub>O<sub>3</sub> films were strongly dependent on both the Sn and Zn content and the deposition temperature. In particular, the In<sub>2</sub>O<sub>3</sub>:Sn film conductivity had maxima near  $x=0.05$  and 0.20 for the films deposited at 350°C and 450°C, correspondingly. The power factor ( $PF$ ) as function of the Sn content also demonstrated the non-monotonous behavior with two maxima. For films deposited at 350 °C these maxima were observed near  $x=0.05$  and 0.20.

Maximal value of  $PF$  at operation temperature  $450^{\circ}\text{C}$ , which reached of  $4.7 \cdot 10^{-3} \text{ W/m}\cdot\text{K}^2$ , was observed at 5 at% of Sn. Such result is one of the best for metal oxides in the given temperature range. The  $\text{In}_2\text{O}_3:(\text{Zn}+\text{Sn})$  films also have a complicated dependence of the parameters on the film composition. Conductivity of the  $\text{In}_2\text{O}_3:(\text{Zn}+\text{Sn})$  films has maxima near  $x \sim 0.2$  and  $x \sim 0.5$ . At that the maximum  $PF$  value was obtained for the films with composition corresponding to the ratio of  $(\text{Sn}+\text{Zn})/(\text{Sn}+\text{Zn}+\text{In}) = 0.5$ .

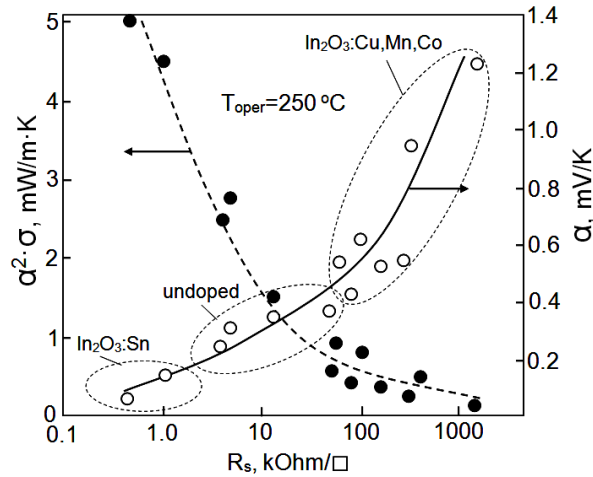


Fig. 1. Doping influence on the resistance, Seebeck coefficient and power factor of the  $\text{In}_2\text{O}_3$  films.

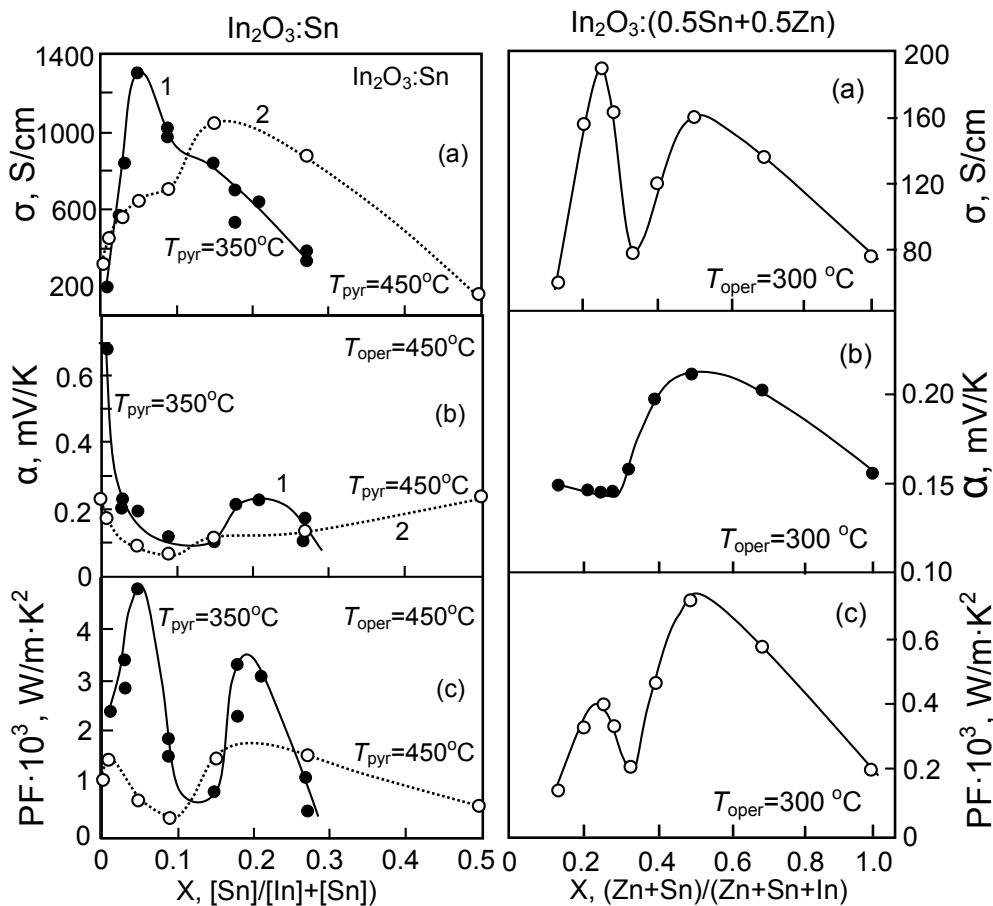


Fig. 2. Doping influence on electrophysical and thermoelectric parameters of the  $\text{In}_2\text{O}_3:\text{Sn}$  and  $\text{In}_2\text{O}_3:(\text{Sn}+\text{Zn})$  films ( $T_{\text{pyr}}=450^{\circ}\text{C}$ ).

Unfortunately at the moment we cannot explain all features of the composition influence on the film parameters. More studies are required. We can only state that there is a correlation between microstructure and thermoelectric properties of the  $\text{In}_2\text{O}_3$ -based films. For example, the shift of the

conductivity maximum in the range of concentrations exceeding limited tin solubility in the  $\text{In}_2\text{O}_3$ , observed for the films deposited at  $T = 450^\circ\text{C}$ , we associate with the film densification taking place at these doping levels. This is clearly seen in the SEM images shown in Fig. 4.

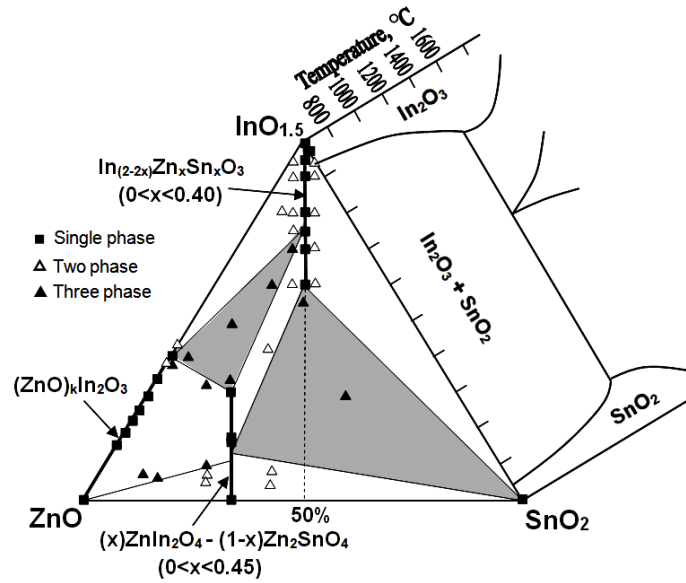


Fig. 3. Phase diagram for the  $\text{In}_2\text{O}_3$ - $\text{SnO}_2$ - $\text{ZnO}$  system (data from [7]).

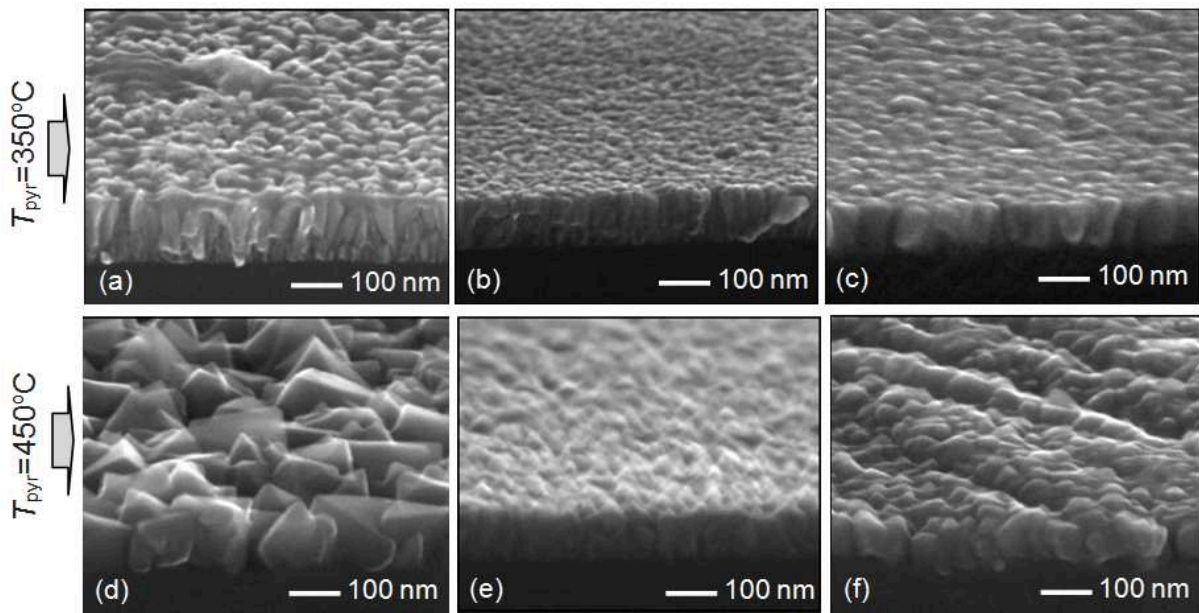


Fig. 4. Doping influence on the SEM images of the  $\text{In}_2\text{O}_3$ :Sn films deposited at  $T_{\text{pyr}}=350^\circ\text{C}$  (a-  $x=0.05$ ; b-  $x=0.16$ ; c-  $x=0.27$ ) and  $T_{\text{pyr}}=450^\circ\text{C}$  (a-  $x=0.06$ ; b-  $x=0.27$ ; c-  $x=0.50$ ):

For the films deposited at  $T=350^\circ\text{C}$  such strong structural change does not occur and therefore the position of the maximum on the  $\sigma=f(C_{\text{Sn}})$  dependences corresponds to the limited tin solubility in  $\text{In}_2\text{O}_3$ . Apparently, the same effect is responsible for the appearance of a second maximum in the  $\sigma=f(C_{\text{Sn}+\text{Zn}})$  dependence obtained for the  $\text{In}_2\text{O}_3$ :(Sn+Zn) films (see Fig. 2a,c). We also supposed that a nature of enhanced magnitude of  $\alpha$  relates with nanocomposite structure of the film. Due to the formation of fine high-resistance crystallite phases of ZnO and  $\text{SnO}_2$  on the surface of the main phase the potential barriers can be with upward band bending, results in filtering of low energy electrons and therefore to the  $\alpha$  increase. It is clear that its height is about the  $k_{\text{B}}T$ ; the higher barrier will constrain the current transport.

We have also concluded that the strong decrease in conductivity of heavily doped materials was great due to the decrease of the charge carrier mobility caused by an increased scattering at the grain boundaries and structural defects. Appearance of a second and even a third phase (see Fig. 3) and its segregation on the surface of the crystallites of the main metal oxide are a principle factors contributing to this effect.

A comparison of the  $\text{In}_2\text{O}_3:\text{Sn}$  and  $\text{In}_2\text{O}_3:(\text{Sn}+\text{Zn})$  films parameters presented in Fig. 2 showed that the power factor for  $\text{In}_2\text{O}_3:\text{Sn}$  is much greater than for  $\text{In}_2\text{O}_3:(\text{Sn}+\text{Zn})$ . It should be noted that the values obtained for  $PF$  are among the highest values given in the literature [8]. This fact should be considered as a significant advantage of the  $\text{In}_2\text{O}_3:\text{Sn}$  films aimed for thermoelectric applications. This statement is being primarily applied to films grown at  $T=350\text{ }^\circ\text{C}$  and having the composition corresponding to  $x\sim 0.2$ . Experiment [9] showed that  $\text{In}_2\text{O}_3:\text{Sn}$  with such composition had considerably smaller thermal conductivity than  $\text{In}_2\text{O}_3:\text{Sn}$  with  $x\sim 0.05$ . The last conclusion is especially important for thermoelectric materials.

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