THERMOELECTRICAL PROPERTIES OF NANOSCALE INDIUM THIN OXIDE-BASED THIN FILMS

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Abstract. *The thermoelectrical properties of indium tin oxide-based nanoscale films deposited by spray pyrolysis method have been investigated. Different metal additives were used to modify the electronic properties of the base oxide. Rh doped films have demonstrated the highest value of power factor ~ $1.4 \cdot 10^{-3}$ W/mK^2 among the studied nanostructured films. Further optimization of film composition and a rise of operation temperature promise the sufficient improvement of thermoelectrical efficiency of given materials.*

Keywords: *thermoelectrics, indium tin oxides, thin films, spay pyrolysis*

I. Introduction

Thermoelectric materials can be used to convert thermoelectrical energy to electrical energy directly via the Seebeck effect induced by temperature difference. Thermoelectric materials such as PbTe, BiSbTe, SiGe [1-3], and transition metal disilicides show a high value of the figure of merit ZT (non-dimensional figure of merit), where $ZT= \sigma\alpha^2T/\kappa$, with σ, α, κ, T being electrical conductivity, the Seebeck coefficient or thermopower, thermal conductivity and temperature. However, such materials are easily decomposed or oxidized at high temperature in air. Therefore the practical utilization of these materials as power generators has been limited. Metal oxides have attracted attention as a promising thermoelectric materials due to their high thermal and chemical stability at high temperature in air, ease of manufacturing an low cost. As one can see the efficiency of energy conversion is increased with the operating temperature in linear mode if the other parameters are unchanged at least. Thus, the increase of working temperature is a promising way for thermoelectric generators like other heat engines. Among the known metallic oxides the p-type oxides exhibit the highest value figure of merit. Z (~$1x10^{-3}$ K^{-1} for Na_2CoO_2) [2]. The demand to have a good n-type thermoelectrical oxide proceeds from the fact that it usually utilized as a p-type partner for thermoelectric module production. N-type oxide materials as ZnO, SnO_2, In_2O_3 and their binary and ternary various compounds have been investigated and proposed to decide this problem [1,2]. Other aspect which gained the interest to such metal oxides is the ability to create them rather easily in the form of nanostructured material. By exploiting nanoscale effects these materials are able to obtain enhancements in thermoelectric properties which cannot be achieved in traditional bulk materials, resulting in large increase of ZT [3]. As a rule the most enhancement of ZT is due to a large decrease of thermal conductivity without considerable decrease of thermopower and electrical conductivity.

In principle the nanograin structure with its inherent numerous interfaces should suppress the heat transport by phonons more strongly than the electronic ones if some relations between grain size and characteristic length of phonon and electron transport are adhered [1,3]. However the state of art in this area is far enough from quantitative predictions and many efforts should be done for the better understanding of phonon and electron transport and scattering mechanisms in nanostructures.

Among the possible technologies of deposition methods the spray pyrolysis is distinguished

by a number of advantages [4]. The details and features of this method one can find elsewhere [5]. The aim of this study was to elucidate the possibilities of such method of deposition for obtaining of nanostructured indium tin oxide-based films perspective for thermoelectric applications.

II. Results and discussions

The spray pyrolysis setup allowed the deposition on alumina substrates with synchronous rotation of sample holder and a nozzle swing to provide the better uniformity of the deposited films. For the deposition we used 0.2 M water solutions of the $SnCl_4 \cdot 5H_2O$ and $InCl_3$ varying the pyrolysis temperature between T_{pyr}= 350-500 ^oC. As doping additives the Co, Fe, Cu, Au, Rh were used in the form of water solutions of corresponding chlorides, added to main component. The content of additive in all cases did not exceed 20 vol.% in sprayed solution. Typical thickness of our films were in the range 80-100nm with a grain size dependent on T_{pyr}, type and content of additive. Some AFM morphologies of In_2O_3 films on T_{pyr} are shown in fig.1.

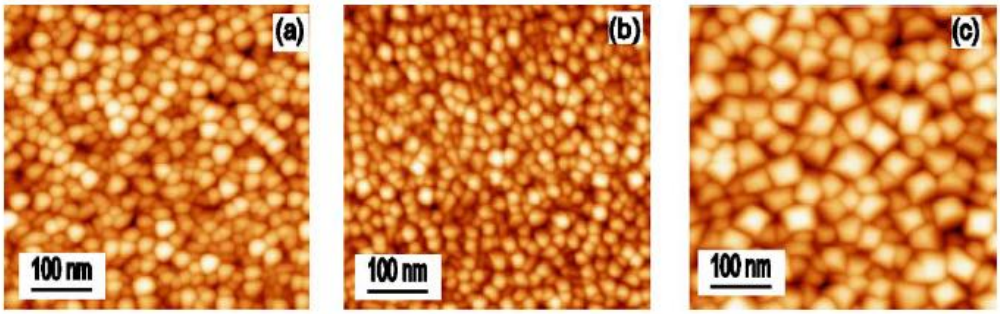

Fig.1 AFM images of In_2O_3 films deposited at T_{pyr}=360 ^oC (a), 430 ^oC (b), 500 ^oC

Experimental test setup provided the simultaneous measurements of resistivity and Seebeck voltage of a thin film deposited on alumina substrate with two gold electrodes in the range of 20-300 ^oC. Special stainless holder has a temperature gradient along one direction. Two thermocouples in the vicinity the each of electrode were used for the temperature difference measure.

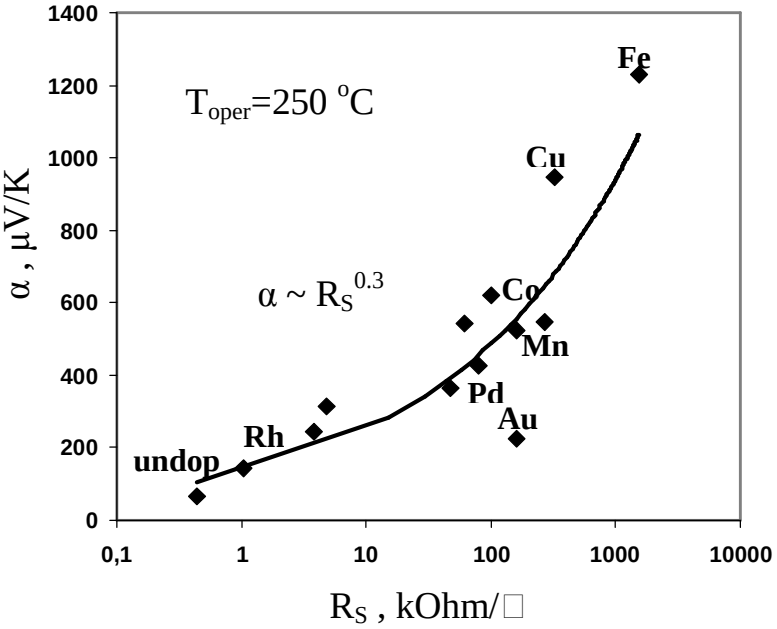

Fig.2. Seebeck coefficient vs layer resistivity of indium-tin oxide films with various additives

Here, in fig.2 we are presenting the Seebeck coefficient vs layer resistivity for various films of indium and tin oxides both doped and undoped. The trend of this dependence reflects the general law and is determined first of all by Fermi level position relatively to conduction band or by electron concentration, because in all cases the films are of n-type conductivity. The lower electron concentration, the higher Seebeck electric field and parameter α is. Our numerical estimations showed that electron concentration ranged by more than three orders of magnitude (from ~10^{16} to ~$3 \cdot 10^{19}$ cm^{-3}) what means that the situation changes from heavily compensated semiconductor (E_C-E_F~0.5 eV, that means Fermi level is inside band gap) to slightly degenerated one (E_C-E_F~-0.05 eV). The power factor that is the product $\alpha^2\sigma$, i.e. it is more close to thermoelectrical efficiency than Seebeck coefficient, as function of operation temperature is shown in Fig.3 for indium oxide films doped by Rh. Such films revealed the best thermoelectric conversion among our films. Note that the best to now known value of power factor obtained for metal oxides (p-type conductivity) is equaled to 8.6×10^{-3} W/mK^2. One can see that after 250 ^oC the sharp decrease of the power factor is observed. One of the reasons of such behavior may be is due to surface adsorption effect related with transformation of chemisorbed forms of oxygen ($O_2^- \rightarrow O^-$). As a result some increase of intergrains barrier and depletion layer in their surface vicinity is observed providing a noticeable peak in the film conductivity with it decline after 250 ^oC especially for Rh doped sample. The experimental observations [6] allow to suppose that after 400 ^oC such tendency changes in opposite direction. This will be next immediate task in our future tests of these films. To estimate the value of ZT of our films the thermal conductivity of nanostructure should be known. Lattice component of it rather strongly depends on grain size and porosity and total thermal conductivity ranged between k~1.5-4 W/(m K) [7] for submicron films. In conditions of high limit (lower limit) of the k we have ZT≈0.2 (0.5) at T_{oper}=250 ^oC for Rh doped In_2O_3 film.

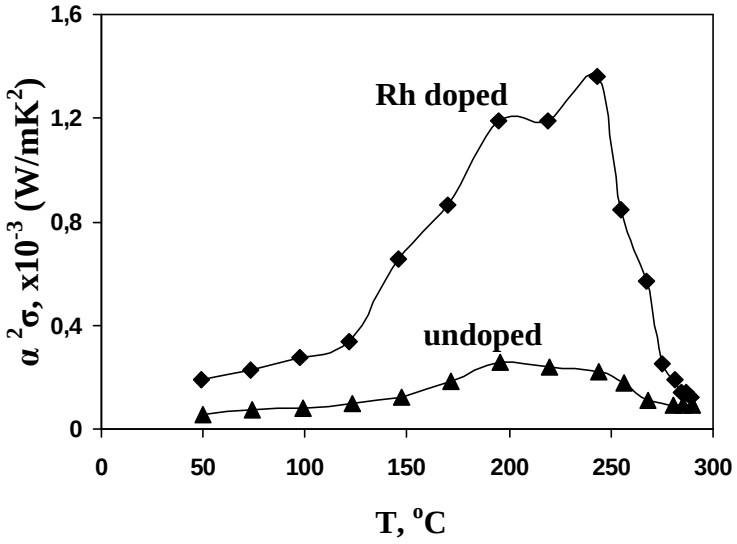

Fig.3. The power factor of In_2O_3 films vs. operating temperature

III. Conclusion

The obtained value of ZT for n-type metal oxide is good enough if to take into consideration the further search in optimizations of the material composition and a possible shift to higher operation temperatures. Here we also imply the introduction of other elements which can substitute the In atoms in the atomic lattice, for example Zn [8] and may considerably decrease the total thermal conductivity of a nanostructure. Therefore the studying of such kind metal oxides may

bring to a new route in the real applications of thermoelectric materials.

IV. References

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