ENHANCED THERMOELECTRIC FIGURE OF MERIT IN NANOSCALE ITO FILMS: EXPERIMENT AND SIMULATION

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It is shown that nanoscaled oxide In_2O_3:Sn is a promising material for thermoelectric applications. Thin films prepared by spray pyrolysis due to their specific grain structure demonstrate the enlarged values of thermo-power and ultra-low thermal conductivity at temperature range 600—700 K. These two factors provide a considerable increase of power factor and figure of merit of thermal conversion in comparison with ordinary n-type semiconducting metal oxides. We have developed numerical models describing electron filtering effect and reduced thermal conductivity in such films.

Keywords: nanoscale indium tin oxide, thermoelectric parameters, filtering effect, chemisorption.

Search of new *n*-type metal oxides, suitable for thermoelectric converters, is considered as a promising way to improve the efficiency of thermoelectric conversion. The conversion efficiency is usually expressed through the dimensionless factor of merit *ZT*, which is linearly dependent on the temperature:

$$ZT = S^2\sigma\, T/\kappa = PF\, T/\kappa, \qquad (1)$$

where S, σ, κ and T are the Seebeck coefficient or thermopower, electrical conductivity, thermal conductivity, absolute temperature and *PF* is a power factor. So far studies of bulk indium tin oxide revealed low values of *PF* and *ZT* primarily because of high electron concentration n and therefore due to the low values of thermopower S. This issue is in agreement with well-known general trend for $S(n) \sim n^{-2/3}$ in degenerated semiconductors when n exceeds values $\sim 10^{20}$ cm^{-3}. A filtering of low energy electrons is one way to overcome this circumstance and to increase the thermopower without any significant reducing of electrical conductivity. Nanoscale structure of ITO allows achieving this under certain conditions of the film growth. Furthermore, such structure leads to considerable decrease of thermal conductivity. Both a nature of aforementioned effects providing the significant improving of thermoelectric parameters in nanoscale ITO and their simulation are the aim of present report.

Our previous study [1] of In_2O_3:Sn films obtained by spray pyrolysis method for deposition temperature ~623 K and Sn content near 5 at.% with a growth rate ~0.5 nm/s showed abnormally high values of Seebeck coefficient and *PF* (4.5 mW·m^{-1}·K^{-2}) at operation temperature 600—700 K that by a factor of 4—5 higher that in conventionally prepared ITO. Careful examination [1] of grain structure and morphology allows to establish a cubic-like shape of the grains with (100) surface faceting and average grain size no more than 20 nm. Combined XPS and Hall measurements confirm our hypothesis on specific Sn atoms segregation onto the (100) surface and upward band bending at the surface vicinity. DFT calculations of ITO (100) surface confirm such Sn behavior. The physical reason of Sn segregation is in the decrease of surface tension for this plane having own dipole moment and a gain in total crystallite energy. Next accompanying effect consists in atomic oxygen chemisorption on such surface and it negative charging by electron capture from conduction band. This ionosorbed charge is very stable at elevated temperatures (600—700 K). All this factors result in appearance of potential barrier at the intergrain boundaries. Barrier height U_S turns out to be optimal for the filtration of electrons with low energies. Our simulation within modified filtering model [2] based on the model of differential conductivity gives U_S around 0.4 eV that exceeds the Fermi level position by ~0.05—0.07 eV. The consideration included several mechanisms of electron scattering. The ionized impurity and polar optical phonons are mainly affected on electron scattering and are the mostly contributed to electron relaxation time. A spatial criterion of modified filtering model applicability was established. This means existence of high limit for a distance between potential barriers or in other words a grain size when the filtering effect does work. Above this limit the S and σ are approaching to their bulk values. On the basis of experimental data the temperature dependence of effective intergrain potential barrier was calculated within the filtering model. The value U_S has a maximum near 650 K that indicates atomic nature of chemisorbed oxygen.

Our recent efforts were directed on experimental elucidation of thermal conductivity of such films and mechanisms responsible for low values of κ. A series of thermal conductivity experiments of samples deposited on silicon substrate were performed [3] using the laser flash method (Netzsch LFA) in conventional cross-plane configuration. The measurements gave $\kappa = 0.84 \pm 0.12$ W·m^{-1}·K^{-1} at room temperature that is below the amorphous limit for ITO. This value is approximately by one order of magnitude lower than that in bulk ITO. The simulation of phonon and electronic transport was done employing Boltzmann transport equation approach and modified filtering model. Total phonon relaxation time was calculated taking into account a three-phonon Umklapp scattering and phonon scattering on grain boundaries. The calculation of phonon part of κ included consideration of 2D and 3D cases of phonon density of states. Using effective medium approximation we have estimated the effect of the film porosity. Evaluation of porosity from refractive index measurements yield values in the range 20—35%, depending on the film thickness. Optimal intergrain barriers decrease the electronic part of thermal conductivity by a factor of 5—6 in comparison with bulk ITO. However, even with all these features calculation gives a value of thermal conductivity by 30% more than in the experiment. The lower values of experimental κ can be attributed to irregularity and scattering in size, shape and orientation of grains, resulting in possible trapping of phonon modes in grain segments. This effect is similar to phonon modes trapping in segmented and cross-section modulated nanowires, leading to the drastic reduction of phonon thermal conductivity.

The important part of the research is concerned with thermal stability of *PF*. The temperature stability tests (up to 973 K) were carried out and showed some degradation of *PF* (~30%) from the initial values [4]. However the structure control did not reveal any fundamental morphology changes. Apparently the cause of *PF* decrease is related to diffusion of some Sn atoms from the surface worsening the filtering effect.

Based on experimental values of *PF* and κ at $T \sim 573$ K obtained in thermal stability tests we can roughly estimate $ZT \sim 1.9$ for optimally doped and grown ITO films. This result shows that ITO films with optimal nanogranular structure may be very prospective for thermoelectric applications.

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Повышенные значения термоэлектрического фактора добротности в наноразмерных пленках ITO: эксперимент и моделирование

Показано, что наноразмерный оксид на основе In_2O_3:Sn является перспективным для термоэлектрических применений. В температурном диапазоне 600—700 К тонкие пленки, полученные методом спрей-пиролиза, демонстрируют увеличенные значения термо-эдс и ультранизкие величины теплопроводности вследствие их специфичной структуры нанозерен. Эти два фактора обеспечивают значительный рост коэффициента мощности и добротности термопреобразования по сравнению с обычными полупроводниковыми оксидами n-типа. Разработаны численные модели, описывающие фильтрационный эффект электронов и пониженную термическую проводимость в таких пленках.

Ключові слова: наноразмерный ITO, термоэлектрические параметры, фильтрационный эффект, хемосорбция.