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Thermoelectrical properties of spray pyrolyzed indium oxide thin films doped by tin

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ABSTRACT

The search for materials with thermoelectric parameters capable of operating at high temperatures continues to be of great interest; *n*-type metal oxides are promising candidates. Here, two series of thin (~100 nm) indium oxide films doped by tin (from 0 to 50 at.%) were deposited by spray pyrolysis at 350 °C and 450 °C. Characterization of the films was performed using X-ray diffraction, scanning electron microscopy and atomic force microscopy. Thermoelectric properties, i.e., the conductivity and the Seebeck coefficient, were then studied over a temperature range of 20–450 °C. It was shown that these parameters as well as their nanostructure were strongly dependent on the Sn content and deposition temperature. Specifically, the conductivity had maxima near 5% and 20% for films deposited at 350 °C and 450 °C, respectively. The power factor (*PF*) as a function of Sn content also demonstrated non-monotonous behavior with two maxima; for films deposited at 350 °C these maxima were again observed near 5% and 20% of Sn content. The maximal *PF* value equaled to 4.7 $\text{mW}/(\text{m}\cdot\text{K}^2)$ at a temperature of 450 °C was observed at 5 at.% Sn. This result is one of the best ever obtained for metal oxides in a given temperature range. The optimal films were characterized by a cubic-like crystallite nanostructure with {400} surface faceting. A model explaining such high parameters was subsequently proposed. We also determined the effect of ambient humidity on the thermoelectric properties of nanostructured In_2O_3:Sn films at an operating temperature range below 400 °C, which is caused by the change of surface conductivity under the influence of water vapor.

1. Introduction

Thermoelectric materials such as PbTe, BiSbTe, SiGe [1–3], and transition metal disilicides show a high figure of merit *ZT* (non-dimensional figure of merit) value, where

$$ZT = \sigma\alpha^2 T/\kappa, \quad (1)$$

with σ, α, κ, and *T* being the electrical conductivity, Seebeck coefficient or thermopower, thermal conductivity, and temperature, respectively. In these materials, the electrical contribution to the heat transducer efficiency is described by the power factor *PF*, which is the product of the conductivity and the thermopower squared, i.e.,

$$PF = \sigma\alpha^2. \quad (2)$$

However, such materials are easily decomposed or oxidized at high temperature in air. As a result, the practical utilization of the above mentioned thermoelectric materials as power generators has been limited and the search for materials with thermoelectric parameters capable of operating at high temperatures continues to be of great interest. Experiment has shown that metal oxides are promising candidates for the decision of this problem. Metal oxides have attracted attention due to their high thermal and chemical stability at high temperatures in air, ease of manufacturing, and low cost. In these materials, the efficiency of energy conversion is increased with the operating temperature in linear mode, if other parameters are unchanged. Thus, the increase of working temperature is a promising method for improving the parameters of thermoelectric generators, such as for heat engines. At present, among metallic oxides, *p*-type oxides such as Na_2CoO_2 exhibit the highest figure of merit value: Z ($\sim 1 \times 10^{-3}$ K^{-1}) and

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$ZT \sim 1$ at $T = 1000$ K [2,4]. In the research community, the consensus is that $ZT = 1$ is the criterion for practical applications.

The demand for 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 such as ZnO, SnO_2, In_2O_3, and their various binary and ternary compounds, also known as transparent conducting oxides (TCO), have been proposed for use in elaboration and study of thermoelectric materials [1,2]. An extremely large figure of merit ($ZT = 1.64$ at $T = 1073$ K) was reported in [5] for non-stoichiometric $TiO_{1.1}$; however, no other evidence has appeared after this publication. Another aspect of interest in such metal oxides is their ease of fabrication in the form of nanostructured materials. By exploiting nanoscale effects, these materials are able to improve thermoelectric properties that cannot be achieved in traditional bulk materials, resulting in a large ZT increase [3,6]. It is posited here that this enhancement of ZT is due to a large decrease of thermal conductivity without incurring a considerable decrease in the thermopower and electrical conductivity.

It is known that In_2O_3 films have a maximum conductivity among wide-bandgap metal oxides. However, only a limited number of works have dealt with the thermoelectric properties of In_2O_3-based oxides [7–15]. In particular, for indium tin oxide (ITO), the current TCO benchmark, there have been few attempts to optimize the composition and microstructure, and thereby obtain appropriate electronic and thermoelectric parameters suitable for heat conversion. Of note, estimations based on the Jonker and Ioffe analysis done in [16] and fragmentary testing of rather weakly doped ITO support the potential use this material.

Experiment has shown that as a rule, the Sn/In composition ratio of ~10% provides the reasonable conductive and optical transmittance properties of ITO films [17]. However, for thermoelectrical applications, the optimum composition may differ from the traditional ratio. This means that the Sn content needs to be varied over a wide range to determine the best composition of ITO films for thermoelectrical applications. It is posited here that by controlling of Sn/In ratio, the electron concentration can easily be varied over a wide range, which is one of the basic parameters of n-type thermoelectric materials. The range of electron concentration should provide the conditions required for electron gas degeneration [2]. The lattice thermal conductivity of ITO is sufficiently lower than for SnO_2 and ZnO because of more complicated indium oxide lattice structure and heavier metal atom in the unit cell. In addition, ITO is characterized by its excellent chemical and thermal stability in air and can operate at temperatures up to 1400 °C [18] in harsh environments, such as gas turbines and jet and rocket engines. It should be understood, however, that a noticeable nanostructure transformation indicates that the growth of nanocrystallites and their agglomeration under heat conditions may occur at lower temperatures (~700–1000 °C) [19].

Therefore, the aim of this paper is to close this knowledge gap by studying the thermoelectric properties of nanostructured In_2O_3:Sn films while varying Sn contents over the range of 0–50 at.%. For this task, we use In_2O_3:Sn films deposited by spray pyrolysis. Among the possible deposition methods, spray pyrolysis has a number of advantages [20]; the details and features of this method can be found elsewhere [21].

2. Experimental details

The spray pyrolysis setup allowed for film deposition on polished alumina and silicon (with a natural layer of silica) substrates. The synchronous rotation (40 rpm) of the sample holder and a nozzle swing (120 min^{-1}) provided improved uniformity of the deposited films. The nozzle was positioned vertically above the substrate holder at a distance of 20 cm. The rotating stainless holder with diameter of 110 mm could load up to 16 samples (1 cm × 1 cm in size). The holder along its perimeter was surrounded by cylindrical framing to provide better conditions for the deposition. Quartz lamps, used as heaters, were placed at the bottom of the holder inside the annular cavity on a fixed platform. The motor rotating the sample holder was placed on bottom side of this platform. Then, 0.2 M water solutions of $InCl_3$ and $SnCl_4 \cdot 5H_2O$ were used for the deposition of thin films (thickness: ~100 nm). The deposition of the ITO films was carried out using a mixture of these solutions, and the ITO film composition was controlled by the quantity of stannic chloride added in spraying solution. Several cycles, each lasting no more than 30 s (sprayed solution volume did not exceed 1.5 ml) were used to prevent sufficient holder cooling (<30 °C). Two pyrolysis temperatures (T_{pyr}) of 350 °C and 450 °C were chosen for deposition of two series of samples. The average growth rate of the films was subsequently in the range of 0.5–1 nm/s. Silver paste electrodes were applied to samples having films deposited on the alumina substrate (dimensions: 10 mm × 4 mm × 0.5 mm) and were annealed for stabilization of parameters at $T_{\text{an}} = 550$ °C for 0.5 h. The current–voltage measurements showed that the used contacts are ohmic. Moreover, the samples with Ag electrodes displayed good repeatability in the temperature measurements.

Deposited films were characterized for their structural properties using an X-ray diffractometer (ARL X'TRA; $\lambda = 1.5405$ Å) using Cu K_α radiation within a diffraction angle range of 10–90°. The surface morphology was studied by scanning electron microscopy (SEM) using a JSM-7001F (Jeol); this instrument also allowed the thickness of the films to be measured. Here, scans were performed on the cleavage surface of the sample at a tilt angle of 90°. An energy dispersive X-ray spectroscopy (EDAX) microanalysis was then performed using a Quanta 3D FEG microscope. The surface roughness was measured by atomic force microscopy (AFM) using a NT-MDT SOLVER HV-MFM instrument.

The homemade experimental setup provided simultaneous measurements of the resistance and the Seebeck voltage of a thin film over a temperature range of 20–450 °C, with an accuracy of better than 0.5%. A special stainless holder (dimensions: 70 mm × 20 mm × 4 mm), suspended on four needle supports, had two resistive autonomic heaters on opposite ends of the holder. The sample holder, clamp contacts and thermocouples mounted on the metallic support were covered by special cap coated on the inner side by reflecting metal film. Such a design allowed to provide practically linear temperature gradient along the main direction of a holder near its center at the area approximately equal to sample size and also—sealed space under the cap. The cap had an input and output to change the atmosphere inside it. The clamp contacts had underlying silver strips that were connected to a measuring circuit out of the hot zone. Such a configuration allowed the parasitic thermo-emf and contact resistance to be notably reduced. Two thermocouples in the vicinity of each electrode were used to measure the sample temperature and the temperature difference (ΔT) between the electrodes. The additional check and calibration of $\Delta T = f(T)$ was performed by measuring the Seebeck voltage using a silver strip having the same in-plane dimensions as our samples. Knowing the absolute Seebeck coefficient dependence of silver on temperature [22], we then calculated ΔT and found a sufficient agreement with the thermocouple readings (within 5%); ΔT did not exceed 20 °C over the entire temperature range. As the operating temperature we took its value at the middle part of the sample. Voltage and resistance measurements were carried out under heating at an average temperature increase of ~5–10 °C per minute. Each sample was measured several times under various time intervals between testing cycles, and error in determination of the Seebeck coefficient did not exceed 5–6 μV/K. Thermoelectric measurements were performed on the two sample sets for two T_{pyr}, each of which included 11 ($T_{\text{pyr}} = 350$ °C) and 7 ($T_{\text{pyr}} = 450$ °C) samples of various compositions. Some depositions and sample preparations were repeated to confirm the reproducibility of the experiment, particularly for $T_{\text{pyr}} = 350$ °C. All samples were tested over the entire temperature range (T_{oper} =20–450 °C) of the experimental setup.