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Grain growth and morphology of In_2O_3:Pd nanocomposite films

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ABSTRACT

Thin film nanocomposites based on semiconducting oxides and palladium have been systematically studied using combinatorial chemistry techniques to optimize their thermoelectric properties. These nanocomposites have considerable potential for energy harvesting applications in harsh environments and were prepared by embedding palladium nanoparticles into an indium oxide matrix via co-sputtering from metal and ceramic targets. The as-deposited films were largely amorphous and thus were subsequently heat treated in nitrogen ambients to produce crystalline nanocomposites. These nanocomposite films were screened for their thermoelectric properties at room temperature as a function of composition, and the resulting films exhibited thermoelectric power factors that were significantly greater than the semiconducting oxides deposited directly from ceramic targets. Based on these rapid screening protocols employing hundreds of micro-thermocouples, the most promising nanocomposite films in terms of thermoelectric power factor were down-selected. Transmission electron microscopy, selected area electron diffraction, and scanning electron microscopy were then used to study the microstructural changes in these films as a function of temperature. When thermally cycled to 800 °C, an abrupt transition from normal, equiaxed grain growth to abnormal (spherulitic growth) was observed at a threshold palladium loading which was also optimal for thermoelectric energy harvesting.

1. Introduction

Energy-harvesting devices capable of operating in harsh environments to power active wireless sensors are needed in power plant and gas turbine engines applications. Severe thermal gradients are often observed in these environments, which make them ideally suited for energy scavenging approaches using thermoelectrics. However, conventional SiGe alloys oxidize in these environments, and many of the promising telluride and selenide based thermoelectric materials suffer from limited stability at these elevated temperatures or in oxidizing atmospheres [1,2]. Alternative materials based on oxide semiconductors have more recently been considered for these higher temperature applications [3]. Thermoelectric materials are often compared using their dimensionless figure of merit, which is defined according to Eq. (1) as,

$$ZT = \frac{S^2\sigma}{\kappa}T \tag{1}$$

where S is the Seebeck coefficient, σ is electrical conductivity and κ is thermal conductivity. Frequently, in the case of thin films, the thermoelectric power factor, defined as $\zeta = S^2\sigma$, is used as a performance metric since the thermal conductivity of thin films is difficult to measure. Also, in the case of devices where the thermal gradient is out of plane, the thermal conductivity is almost entirely dictated by the substrate [4]. High-temperature thermoelectrics were first realized in n-type Al-doped ZnO and p-type $Na_xCo_2O_4$. However, these materials exhibit poor thermoelectric efficiency and are extremely expensive to manufacture [5,6]. More recently, several groups have made progress in improving the figure of merit in bulk oxides, for example, ZnO ceramics co-doped with Al and Ga exhibit figures of merit as high as 0.74 at 1000 °C [7]. However, these ceramics were prepared by sintering in nitrogen ambients and subsequent investigations have suggested that the thermoelectric efficiency of ZnO is greatly reduced after cycling at high temperatures in oxidizing environments [8]. Since one of the sources of charge carriers in n-type oxides are the doubly charged oxygen vacancies, diffusion of oxygen into the bulk ceramic causes compensation of the charge carriers and can reduce the figure of merit by increasing the electrical resistivity. Despite the stability issue in bulk and thin film oxides, thin film thermoelectric materials capable of operating efficiently at very high temperatures are still of great interest since they can be used to power wireless sensors operating in harsh environments, i.e., instrumentation in gas turbine engines and power plants.

Many groups have studied the effect of nanostructured materials to improve the performance of thermoelectric devices, which has yielded two viable options: one, to reduce the thermal conductivity through selective phonon scattering, and two, to increase the Seebeck coefficient through filtering out low energy electrons [9]. Both of these methods rely on interfacial scattering over a very large number of boundaries and have been demonstrated in both experiments and simulations. For example, experimental studies on

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PbTe/PbTeSe quantum dot super lattices and the incorporation of metallic nanoparticles into similar structures has led to significant improvements in power factor and figure of merit, which have been reported to be as high as 3.5 [10,11]. While these techniques clearly provide the opportunity to make significant improvements to the overall efficiency of thermoelectric devices, the stability of nanostructured materials especially during extended exposure at high temperatures has not been sufficiently investigated. At high temperatures, microstructural changes including secondary grain growth, Ostwald ripening, spinodal decomposition and other thermally activated phenomena may come into play and will ultimately degrade the materials thermoelectric properties [12]. As a result, the microstructure of various In_2O_3:Pd nanocomposite films was investigated as a function of heat treatment using transmission electron microscopy (TEM) and scanning electron microscopy (SEM) [13].

2. Experimental procedure

Thin film combinatorial libraries consisting of 800 micro-thermocouples were prepared by rf sputtering using an MRC model 8667 sputtering system where the rf power was divided between an In_2O_3 target and a Pd target. The micro-thermocouple library was prepared on a 96% pure alumina substrate, measuring 4 in. × 4 in. that was patterned with high purity platinum reference electrodes. The nanocomposite films were deposited at a total rf power of 400 W at 25 °C in an argon plasma at a total pressure of 1.83 Pa. The chamber was evacuated to a background pressure of less than 1.13×10^{-4} Pa prior to the deposition. The nanocomposites were also prepared on an SiO_2 substrate using identical sputtering conditions, so that the spatially dependent thickness of each thermoelement could be accurately measured using surface profilometry. Samples for TEM were prepared by growing films on 10 nm thick, amorphous silicon nitride grids.

The resulting library was heat treated for 5 h at 500 °C in a high purity nitrogen atmosphere and characterized in terms of its thermoelectric properties. The micro-thermocouples were tested by measuring the voltage drop across each micro-thermocouple while applying a constant temperature difference of 7.7 K with a special hot probe. The output voltage was then determined by fitting the thermoelectric response to a second-order autoregressive function using the least squares method. To determine the Seebeck coefficient of each thermocouple, the surface temperatures of the hot and cold junction were monitored using thin film type K thermocouples sputtered directly on the alumina wafer. The resistivities of the films were determined by measuring the resistance and thickness of each micro-thermocouple leg after deposition and heat treatment. Micrographs of the nanocomposite films were obtained using a JEOL 5900 SEM operating at 20 keV. The compositions of the films were determined using SEM in combination with energy dispersive x-ray spectroscopy (EDS) with an acquisition time of 5 minutes per sample. TEM and selected area electron diffraction (SAED) was performed on the selected compositions using a JOEL JEM-2100 operating at 200 keV as a function of heat treatment. EDS was also used in conjunction with SEM to study segregation effects. The refractory nature of the Si_3N_4 grids permitted the direct observation of microstructural changes in the specimens could as a function of temperature. However, these grids were only heated in a >99.9% purity nitrogen atmosphere since they can oxidize and degrade in air at elevated temperatures. Quantitative stereology of the TEM images was also utilized to confirm the volume fraction of palladium in the nanocomposite films. Based upon room temperature screening results, selected materials were characterized from room temperature to 800 °C. The Seebeck coefficient was characterized as a function of temperature for these down-selected materials using the integral method; i.e., by placing one end of a 120-mm-long alumina beam containing a nanocomposite and platinum junction in a tube furnace while maintaining the other end of the beam at 20 °C using a recirculating chiller [14]. The electrical conductivity of the film was determined as a function of temperature using the van der Pauw method. All high-temperature measurements were conducted on films that were exposed to air ambients.

3. Results and discussion

The as-deposited nanocomposite films were chemically homogenous and largely amorphous, as shown in Fig. 1. This was likely due to the relatively low growth temperatures and non-equilibrium nature of the sputtering process as well as the separation distance from the targets when co-sputtering which tends to produce amorphous films. Furthermore, the films exhibited a monotonically decreasing Seebeck coefficient with increasing palladium content. After heat treatment of the films, crystallization of the In_2O_3 was induced as well as precipitation of the palladium nanoparticles. The room temperature Seebeck coefficient as a function of the volume fraction of palladium in the film after annealing at 500 °C is shown in Fig. 2. At zero palladium loading, the Seebeck coefficient was in good agreement with literature value for un-doped In_2O_3 films grown in reducing environments [15,16]. However, as the palladium content was increased, the Seebeck coefficient also increased, due to scattering of low energy electrons at the In_2O_3/Pd interfaces. When the palladium content was increased beyond 10 vol%, the Seebeck coefficient started to decrease due to coalescence of larger palladium particles. This coalescence resulted in an increased electrical conductivity of the films, indicating that they were no longer acting as traps for low energy electrons.

Backscatter SEM micrographs of several films from the thermoelectric library obtained after annealing in nitrogen at 500 °C are shown in Fig. 3. At very low palladium contents (<8 vol% Pd), large clusters were observed with no distinguishable features. However, as the palladium content was further increased, microcracking was observed in the clusters. High-resolution SEM micrographs of a film containing 12 vol% Pd, exhibited significant microcracking as shown in Fig. 4. Moreover, the maximum Seebeck coefficient observed in the In_2O_3:Pd library corresponded to thermocouples containing significant, although not the greatest extent of microcracking. As the palladium content was further increased (Fig. 3f and g), virtually no cracks were observed and segregation of the palladium was observed in the backscatter mode SEM micrographs. These SEM micrographs suggest that Ostwald ripening and coalescence of the palladium nanoparticles occurred when the palladium content is >15 vol% Pd.

Since the SEM investigation showed significant variation in morphology and microstructure as a function of palladium content, several nanocomposites were grown on TEM grids and examined in the as-deposited and annealed condition (500 °C and 800 °C) to determine the grain growth mechanism and final palladium particle size and particle size distribution. Low magnification TEM micrographs of the specimens after

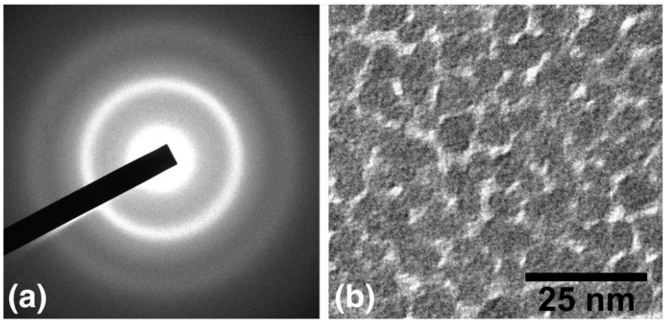

Fig. 1. Large area electron diffraction pattern (a) and TEM micrograph of an as deposited 6 vol% Pd nanocomposite; light areas in the image are voids in the film and are a result of the sputtering processes.