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Thermoelectric power factor of $\text{In}_2\text{O}_3\text{:Pd}$ nanocomposite films

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A nanocomposite exhibiting large thermoelectric powers and capable of operating at temperatures as high as 1100 °C in air was fabricated by embedding palladium nanoparticles into an indium oxide matrix via co-sputtering from metal and ceramic targets. Combinatorial chemistry techniques were used to systematically investigate the effect of palladium content in these nanocomposite films on thermoelectric response. Based on these rapid screening experiments, the thermoelectric properties of the most promising nanocomposites were evaluated as a function of post-deposition heat treatment at high temperatures. An n-type nanocomposite film was developed exhibiting a power factor of 4.5×10^{-4} W/m·K² at 1000 °C in air. © 2011 American Institute of Physics. [doi:10.1063/1.3607289]

Thermoelectric materials capable of operating at very high temperatures in oxidizing environments have drawn considerable attention in the realm of energy harvesting.¹ Since many of the promising tellurides and selenides suffer from limited stability at elevated temperatures and in oxidizing environments, alternative materials have been considered for higher temperature applications.² Significant advances have been made in enhancing the dimensionless thermoelectric figure of merit $ZT = S^2\sigma T/\kappa$ and power factor $\zeta = S^2\sigma$, in bulk oxides, where S is the Seebeck coefficient, σ is the electrical conductivity, and κ is the thermal conductivity. For example, ZnO ceramics co-doped with Al and Ga exhibit figures of merit as high as 0.74 at 1000 °C.³ However, these electroceramics were prepared by sintering in nitrogen, and recent studies have suggested that the thermoelectric efficiency of ZnO is greatly reduced when it is prepared in an oxidizing environment.⁴ 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 charge carriers and can reduce the figure of merit by increasing the electrical resistivity.⁵ In thin films, oxidation affects are even more important since the thickness is on the same order of magnitude as the oxygen diffusion length. Despite these stability issues, thin film thermoelectric materials capable of operating efficiently at very high temperatures are of great interest, since they can be used to power wireless sensors operating in harsh environments. For example, temperature gradients of 450 °C or greater can exist between the tip and root of the blades used in gas turbine engines that could be utilized for energy harvesting.

Significant improvements have been made to the figure of merit in conventional thermoelectrics by incorporating them into nanostructured material systems. Due to the large number of interfaces that exist in these cermets, the effective phonon scattering is increased, thereby reducing the thermal conductivity.^{6,7} For example, experimental studies on PbTe/PbTeSe quantum dot super lattices⁸ and the incorporation of

metallic nanoparticles⁹ have led to significant improvements in power factor and figure of merit, which have been reported to be as high as 3.5. Very few groups, however, have studied the thermoelectric properties of nanostructured materials based on oxide semiconductors. In this letter, we describe an $\text{In}_2\text{O}_3\text{:Pd}$ nanocomposite with a very large power factor that is stable at temperatures up to 1000 °C in air.

Combinatorial libraries containing 800 μ -thermocouples were deposited by co-sputtering from In_2O_3 and palladium targets to form gradients of nanocomposites with spatially varying compositions. The most promising libraries were screened in terms of thermoelectric response and Seebeck coefficient, where the imposed temperature gradient was calibrated utilizing thin film type K thermocouples prepared using the same footprint ($\Delta T = 7.7 \pm 0.43$ K). A detailed overview of the techniques utilized to rapidly characterize the thermoelectric properties of these nanocomposites near room temperature can be found in Ref. 5. Based on these rapid screening experiments, several nanocomposites exhibited very large and reproducible thermoelectric responses. These were subsequently fabricated into larger scale devices such that a reasonably large temperature gradient could be applied across the thermoelectric material. The Seebeck coefficients of these films were characterized in-plane at temperatures as high as 1100 °C using the integral method,¹⁰ relative to platinum reference electrodes, and the σ - T behavior was determined using a van der Pauw technique. Prior to the characterization of both Seebeck and electrical resistivity, the films were annealed for 10 h at 1000 °C. The composition of the films was determined using both energy dispersive x-ray spectroscopy (EDX) and auger electron spectroscopy (AES), and the volume fraction of palladium was determined using quantitative stereology¹¹ of the TEM images and had a measurement error of ± 0.94 vol. % Pd. Electron diffraction patterns of selected films deposited on SiO_2 grids were evaluated using TEM in an attempt to characterize the crystal structure and size of the nanoparticles as a function of heat treatment.

Due to its relatively small effective mass compared to other n-type semiconducting oxides such as SrTiO_3 ¹² as well

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as the unique defect chemistry associated with the bixbite crystal structure of In_2O_3 (unoccupied oxygen interstitial sites),¹³ it was chosen as the continuous phase in the nanocomposites. The optimal loading of palladium particles was experimentally determined using combinatorial chemistry techniques. Figure 1 shows the dependence of the Seebeck coefficient as a function of the volume fraction of palladium incorporated into the film. A maximum in the Seebeck coefficient was achieved for a nanocomposite containing 6 vol. % palladium. As the palladium content in the film was increased beyond this value, intergranular cracking was observed in the microstructure, which led to a decrease in both the electrical conductivity and Seebeck coefficient. Nanocomposites containing more than 20 vol. % palladium resulted in significant Ostwald ripening of the palladium nanoparticles, and a terminal particle size on the order of 200–300 nm. The microstructure of the 6 vol. % nanocomposite was examined using TEM (Figure 2), in the as-deposited and annealed condition. Figure 2(a) shows that the films were largely amorphous in the as-deposited condition and that little or no coalescence of the palladium particles had occurred. After the film was annealed at 500 °C in nitrogen for 2.5 h, phase separation of the bulk cermet into dark and light phases occurs and an average palladium particle diameter of 4 nm was obtained. Heating to 500 °C also produced an electron diffraction pattern with some lattice fringing, which indicated the onset of crystallization (Figure 2(d)). The film was further annealed at 700 °C in nitrogen for 2.5 h and showed significantly greater lattice fringing, and a diffraction pattern consistent with a relatively small number of crystallites. After heating to 700 °C, the average particle diameter increased from 4 to 6 nm. Furthermore, the diffraction pattern in Figure 2(e) indicated that there was a preferred orientation in the nanocomposite film and only discrete indium oxide and palladium phases were found. No In-Pd bimetallic phases were observed in the electron diffraction pattern after 700 °C exposure, consistent with other investigations where temperatures were maintained below 300 °C.¹⁴

The Seebeck coefficient and electrical resistivity as a function of temperature of the two most promising nanocomposites, along with that of In_2O_3 , are shown in Figure 3. A precipitous drop in the electrical conductivity was observed in composite films containing 20–40 vol. % Pd at 700 °C,

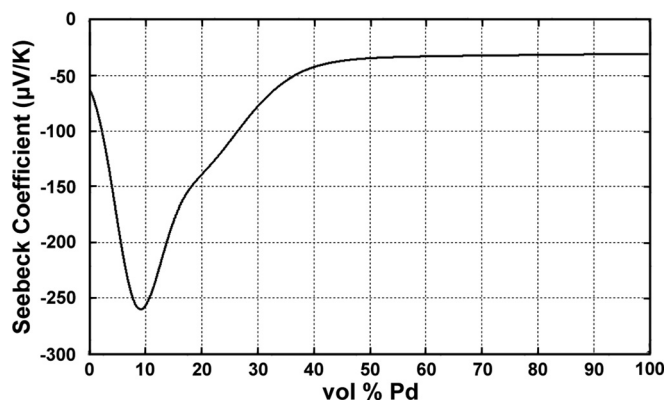


FIG. 1. Effect of palladium content on the room temperature Seebeck coefficient of In_2O_3 :Pd nanocomposite films after annealing at 500 °C for 5 h in N_2 .

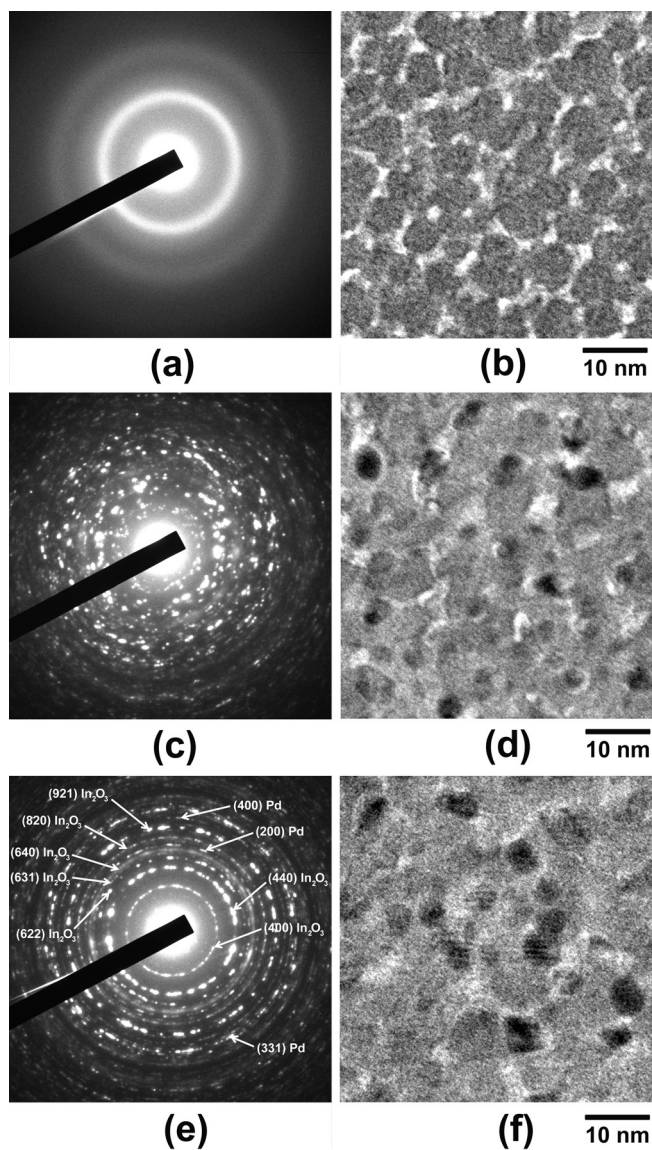


FIG. 2. TEM micrographs of 6 vol. % Pd nanocomposite and associated electron diffraction patterns after deposition (a), (b), annealing in N_2 at 500 °C (c), (d), and annealing in N_2 at 700 °C (e), (f).

which corresponds to the temperature where the excitation of all the thermally activated charge carriers in In_2O_3 to the conduction band occurred.¹⁵ Furthermore, this order of magnitude drop in resistivity was observed after repeated cycling and showed hysteresis between heating and cooling cycles, suggesting that a thermally activated metal-semiconductor transition had taken place in this compositional range. Scanning electron microscopy indicated that the palladium particles had coarsened from the nanometer scale to particles as large as 300 nm, most likely by an Ostwald ripening mechanism. A lower Seebeck coefficient in these samples was observed relative to the other two films, likely due to the contributions of the larger palladium particles. The power factor in these films (Figure 4) indicated that In_2O_3 films had power factors similar to those of bulk In_2O_3 sintered in oxidizing environments, as well as similar carrier concentrations, on the order of $1.2 \times 10^{19} \text{ cm}^{-3}$ at room temperature.¹⁶ On the other hand, Al doped ZnO films had a power factor that was two orders of magnitude lower than bulk samples sintered in reducing environments and an order of magnitude

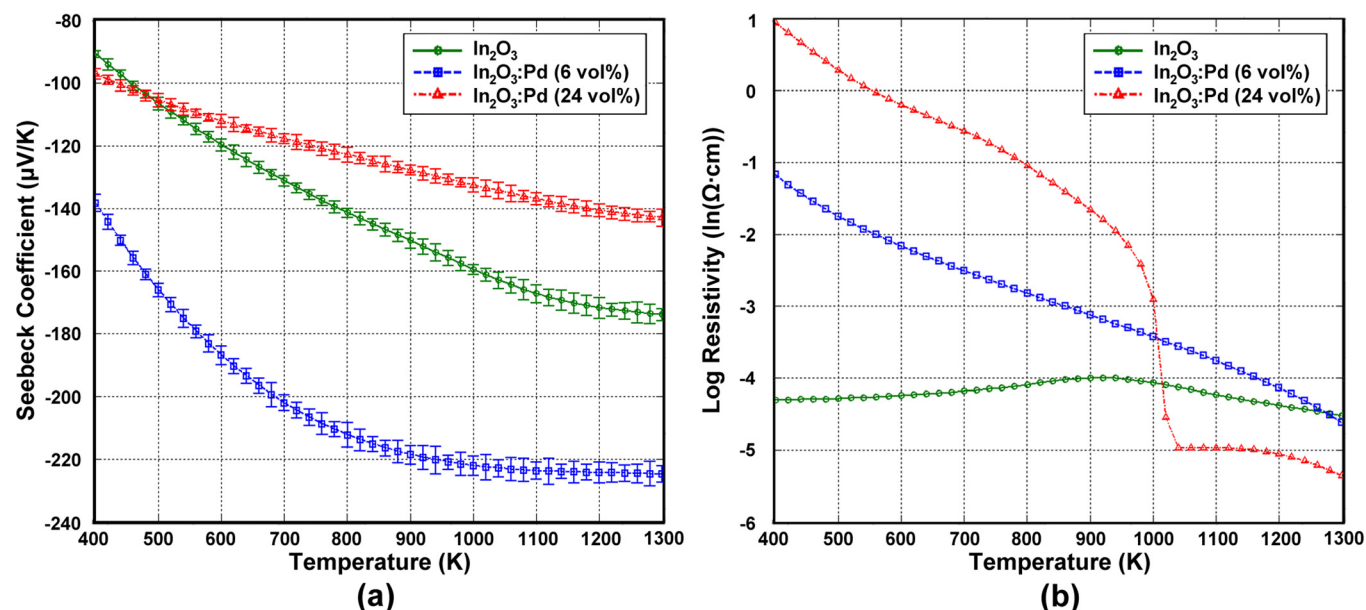


FIG. 3. (Color online) Temperature dependence of the Seebeck coefficient (a) and electrical resistivity (b) for In_2O_3 films and selected In_2O_3 :Pd nanocomposites, the lines are provided as guides for the eye.

lower than those sintered in oxidizing environments.³⁻⁵ The dramatic reduction in power factor observed for ZnO films was attributed to the compensation of charge carriers generated by doubly charged oxygen vacancies in air ambients and limits the use of many semiconducting oxide materials (ZnO , SnO_2 , SrTiO_3) for thin film thermoelectric generators.^{4,17}

In summary, In_2O_3 :Pd nanocomposites were investigated as thermoelectric materials for energy harvesting purposes. Co-sputtering from ceramic and metal targets was used to create palladium particles (<10 nm in diameter) dispersed in an In_2O_3 matrix. Combinatorial chemistry techniques were used to successfully screen the nanocomposite films for thermoelectric power. Films containing an optimal volume fraction of palladium in the In_2O_3 matrix (6 vol. %) produced a 47% increase in the thermoelectric power factor

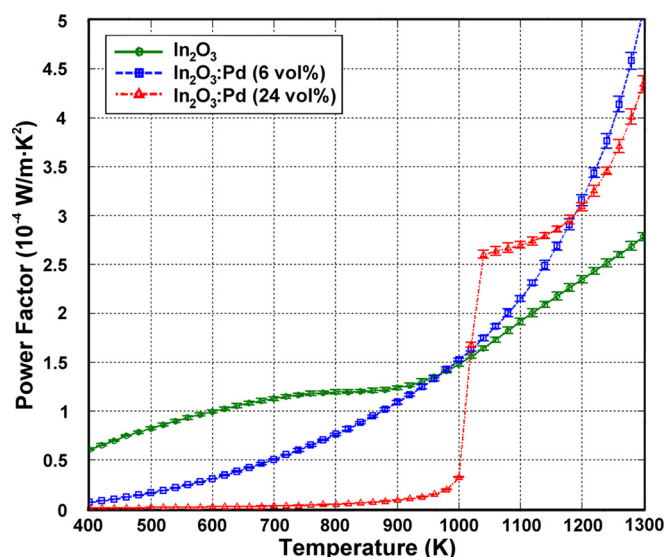


FIG. 4. (Color online) Temperature dependence of the power factor of In_2O_3 films and selected In_2O_3 :Pd nanocomposites, the lines are provided as guides for the eye.

at 1000 °C relative to bulk In_2O_3 and 65% increase in power factor relative to In_2O_3 thin films. Moreover, these films were stable in oxidizing atmospheres at 1000 °C and, thus, could be used to power active wireless sensors in harsh environments, provided that an equally stable high temperature p-type thermoelectric material can be identified.

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