Temperature Dependence of the Seebeck Coefficient in Zinc Oxide Thin Films

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Abstract. Thermoelectric devices are reliable tools for converting waste heat into electricity as they last long, produce no noise or vibration, have no moving elements, and their light weight makes them suitable for the outer space usage. Materials with high thermoelectric figure of merit ($zT$) have the most important role in the fabrication of efficient thermoelectric devices. Metal oxide semiconductors, specially zinc oxide has recently received attention as a material suitable for sensor, optoelectronic and thermoelectric device applications because of their wide direct bandgap, chemical stability, high-energy radiation endurance, transparency and acceptable $zT$. Understanding the thermoelectric properties of the undoped ZnO thin films can help design better ZnO-based devices. Here, we report the results of our experimental work on the thermoelectric properties of the undoped polycrystalline ZnO thin films. These films are deposited on alumina substrates by thermal evaporation of zinc in vacuum followed by a controlled oxidation process in air carried out at the 350-500 °C temperature range. The experimental setup including gradient heaters, thermometry system and Seebeck voltage measurement equipment for high resistance samples is described. Seebeck voltage and electrical resistivity of the samples are measured at different conditions. The observed temperature dependence of the Seebeck coefficient is discussed.

Keywords: thermoelectric, Seebeck coefficient, polycrystalline semiconductor, temperature dependence, ZnO thin film.

1. Introduction

Thermoelectric (TE) effect directly converts heat to electricity. TE devices have recently attracted considerable attention because of their potential applications in cooling units, power generator, sensors, and waste heat recovery system [1,2]. TE devices are advantages in that they have no mechanical moving parts, no greenhouse gas release, good stability, high reliability and long life. These features make TE devices suitable choices for portable, military and aerospace applications [3-5].

The performance of a TE device depends on the TE material; hence, for decades, researchers have tried to figure out the most efficient TE materials. The efficiency among TE materials is quantitatively...
Metal oxide semiconductors are promising candidates as TE materials [12-14]. Zinc Oxide is an important II-IV metal oxide semiconductor with wurtzite crystal structure and a good candidate TE material owing to its high chemical stability, high electrical conductivity and acceptable Seebeck coefficient [15]. Oxide semiconductors, because of their remarkable characteristics have various applications such as transparent conductor for solar cells/displays, surface acoustic wave devices, chemical sensors and etc. [16-18]. Here, we report the results of our experimental work on the thermoelectric properties of the undoped polycrystalline ZnO thin films. It is shown that as the temperature increases, the Seebeck coefficient of ZnO increases in absolute value.

2. Experimental

ZnO thin films are deposited on 10 mm × 5 mm alumina substrates by the thermal evaporation of zinc powder in vacuum followed by the controlled oxidation process in air carried out at the 350-500 °C temperature range. Two different types of samples are fabricated, which are produced in the same conditions, but are different in the utilized oxidation temperature. Sample A is oxidized at 450 °C but sample B has experienced 500 °C. Oxidation temperature profiles utilized are shown in figure 1. After oxidation, both samples are transparent indicating the completion of the oxidation process [19].

![Figure 1. Oxidation temperature profile of the zinc layers deposited on alumina.](image)

A chromium thin film microheater is deposited on the back side of the alumina substrate covering a third of its length. By passing different currents from the heater, temperature differences of different magnitude are created across the sample. All contacts to the microheater and ZnO thin film are made by silver paste printing and silver wire segments (figure 2.a and b) [20,21]. A Ni-Cr wire heater placed on the sample holder under the sample can increase the average sample temperature. This will allow sample
resistance measurements at different temperatures. Hence, we are using two different heaters; the first one determines the average temperature of the sample and the second heats up the one third of the sample to create the temperature gradient and generate Seebeck voltage.

**Figure 2.** (a) The schematic diagram of the sample positioned on the sample holder. (b) The photograph of the ZnO thin film sample on the sample holder.

The main requirement for an accurate Seebeck coefficient measurement is to make the temperature and voltage readouts simultaneous from the same locations on the sample [22]. To meet this condition, two fine type S thermocouples are placed on ZnO electrical contacts as show in figure 3.b.

The prepared ZnO samples’ resistance is in the $10^6 \, \Omega$ range. Thus, the correct measurement of the Seebeck voltage across our samples requires an ultra-high input impedance voltmeter [23,24]. In the case of a high resistance sample, an alternative method is used in the present work, which is schematically presented in figure 3 [25]. As shown in figure 3.a, a variable power supply and a resistor are connected in series with the sample. Seebeck voltage along the sample is measured by adjusting the voltage source $V_s$ (see figure 3.a) manually till the voltage drop over the resistor $R$ becomes zero. At this point, the power supply voltage is equal to the Seebeck voltage [26].

**Figure 3.** (a) The circuit utilized for the measurement of the Seebeck voltage. (b) The schematic diagram of the sample.
To measure the sample resistance at different temperatures, a dc voltage is applied to Ni-Cr wire heater. The sample temperature becomes stable in a few minutes. The resistance of sample is, then, recorded after 2 minutes. The temperature difference across the sample is require for Seebeck coefficient measurements. This is created by applying a dc voltage to the chromium microheater. Time is allowed for the temperature profile along the sample to become stable. The Seebeck voltage is read a few minutes after this stability.

3. Results and discussion

The variations of the resistance and Seebeck coefficients of the undoped polycrystalline ZnO samples are shown in figure 4.a-c. In figure 4.a the resistance variations in the A and B samples are presented, showing that the span of changes is wider in the A samples. The Arrhenius diagram for resistance is shown in figure 4.b. The conduction activation energy deduced for the sample is 0.50 ± 0.05 eV. As shown in figure 4.b, the activation energy of sample B is marginally lower than that of the sample A. This means that by increasing the oxidation temperature, carriers meet a slightly smaller energy barrier in passing from one grain to another.

Figure 4.c shows the variation of the Seebeck voltage versus the temperature difference across the sample. The slope of the plotted line in figure 4.c determines the Seebeck coefficient. It is clear that the Seebeck coefficient of sample B is larger than that of the sample A. The variations of the Seebeck coefficient of ZnO samples with respect to the average sample temperature is presented in figure 4.d, showing that the Seebeck coefficient in both sample categories increase in absolute value with temperature. That is more profound in the B sample.

![Figure 4.](image-url)

Figure 4. Resistance variations with temperature presented in linear (a) and logarithmic scales (b). (c) Seebeck voltage variations with respect to the established temperature differences across the sample and (d) the variations of the measured Seebeck coefficient with regards to the average sample temperature.
4. Conclusion
The maximum annealing temperature of the ZnO thin films is important in determining the Seebeck effect and $zT$ of the undoped polycrystalline ZnO thin films. In fact, this parameter affects both electrical resistivity and Seebeck coefficient. Samples with higher annealing temperature of 500 °C have lower resistance and higher Seebeck coefficient than those annealed at 450 °C. Therefore, the figure of merit in B sample becomes significantly higher than that in A sample.

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