Seebeck effect in ZnO nanowires for micropower generation

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Abstract

The Seebeck effect of ZnO nanowires has been investigated with the future aim of building thermoelectric devices based on nanowire arrays for energy harvesting and using them in low-power portable electronics and autonomous sensor systems. Quasi monodimensional (1D) ZnO nanowires have been deposited on alumina substrates according to the recently proposed thermal evaporation process, which involves Vapour-Phase and Vapour-Liquid-Phase growth mechanisms. The Seebeck coefficient of ZnO nanowires has been successfully measured with a purposely-developed experimental set-up, confirming that the ZnO nanowires exhibit high thermoelectric coefficient.

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1. Introduction

Achieving high efficiency thermoelectric generators requires materials with large figure of merit \(ZT\) that depends on the Seebeck coefficient. The \(ZT\) of the best bulk thermoelectric materials is about 1 [1]. Recently, it has been shown that Si-based quasi monodimensional (1D) nanowires can be designed to achieve extremely large enhancements in thermoelectric efficiency, but only at low temperature (\(T < 350\) K) [2-4]. Quasi 1D metal oxide nanowires would indeed provide the benefits of reduced dimensionality with their excellent durability at high temperatures and are promising candidates to develop high temperature thermoelectrics [5].

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2. ZnO nanowires deposition

ZnO nano-crystals have been prepared at Sensor Lab according to the recently proposed thermal evaporation process, which involves Vapour-Phase and Vapour-Liquid-Phase growth mechanisms [6]. The experimental set-up for the growth of ZnO nanostructures consists of an alumina furnace capable of achieving temperatures as high as 1500 °C, essential to initiate the decomposition of the metal oxide powder and to promote its evaporation. The controlled pressure of the inert atmosphere and the temperature gradient within the furnace allow condensation and nucleation of the nanostructures downstream the gas flow. Such a peculiar thermodynamic condition promotes formation of nanosized 1D structures. The pressure, gradient and carrier flux have to be strictly controlled in order to guarantee the reproducibility of deposition. Alumina 20 x 20 mm² substrates have been used with Au-nanoparticles deposited by RF sputtering as catalyst.

Samples of ZnO nanowires have been realized at different substrate temperatures as described in Table 1, while the temperature of the furnace has been set at 1370 °C; therefore they show different morphologies as reported in the Scanning Electron Microscopy (SEM) pictures of Fig. 1.

Fig. 1. Scanning Electron Microscopy (SEM) images of two different morphologies of ZnO nanowires, prepared at 700 °C (a) and 870 °C (b).

3. Measurement of the thermoelectric coefficient

The fabricated ZnO nanowire samples have been experimentally characterized in order to measure the thermoelectric coefficient. An experimental set-up has been assembled, including two Peltier cells with driver stages as heaters, two reference Pt100 temperature sensors to monitor the temperature profiles and a PC-based acquisition system, as shown in Fig. 2 (a).

The Peltier cells and the associated controllers have provided the temperatures $T_A$ and $T_B$ at the edges of the tested samples. With the approximation that the temperatures $T_A$ and $T_B$ could be considered uniform on the entire Peltier cells, the temperature difference $\Delta T$ has been numerically calculated from measured temperature data $T_A$ and $T_B$ according to the following equation:

$$\Delta T = T_A - T_B$$

The measurements on the nanowire samples have been performed by means of two pairs of probing tips. Connecting the sample with the probes, a thermocouple, which consists of the tested material and the probe material, is established. Therefore, the voltage generated by the nanowires with the probing tips provides a measurement of the relative Seebeck coefficient of the ZnO nanowire bundles with respect to the probe material. Two different thermoelectric materials have been used for the probing tips: Chromel (labeled $a$), an alloy of nickel and chromium, which exhibits a positive absolute Seebeck coefficient of about 28.1 $\mu$V/K [7] and Alumel (labeled $b$), an alloy of nickel, manganese, aluminium and silicon with a
negative absolute Seebeck coefficient of about \(-12.9 \mu V/K\) \([7]\). Chromel and Alumel have been chosen because they are typical reference materials, commonly used to form K-type thermocouples.

The voltages measured at the ends of the tips are proportional to the temperature difference applied at the tested sample in accordance with the following relationships:

\[
\begin{align*}
\Delta V_{ma} &= \alpha_{ma} (T_A - T_B) = \alpha_{ma} \Delta T \\
\Delta V_{mb} &= \alpha_{mb} (T_A - T_B) = \alpha_{mb} \Delta T
\end{align*}
\]

where \(\alpha_{ma}\) is the Seebeck coefficient of the tested material, labeled \(m\), i.e. the ZnO nanowires, with respect to the reference material \(a\), i.e. Chromel; while \(\alpha_{mb}\) is the Seebeck coefficient of the tested material \(m\) with respect to the reference material \(b\), i.e. Alumel. The voltages \(\Delta V_{ma}\) and \(\Delta V_{mb}\) have been amplified with low-noise instrumentation amplifiers INA128 and measured as a function of the temperature difference \(\Delta T\) applied across the sample.

4. Experimental results

The measured voltages \(\Delta V_{ma}\) and \(\Delta V_{mb}\) are reported as a function of time with the applied temperature difference \(\Delta T\) in Fig. 3 (a) and versus the applied temperature difference \(\Delta T\) in Fig. 3 (b).

Fig. 3. Trends of the applied temperature difference \(\Delta T\) and the thermoelectric voltages \(\Delta V_{ma}\) and \(\Delta V_{mb}\) Alumel versus time (a) and the generated voltages \(\Delta V_{ma}\) and \(\Delta V_{mb}\) versus the applied temperature difference \(\Delta T\) (b) for the sample deposited at 870 °C.
The thermoelectric voltages $\Delta V_{\text{ma}}$ and $\Delta V_{\text{mb}}$ and the applied temperature difference $\Delta T$ have the same trend as predicted by equations (2) and (3).

The relative Seebeck coefficients estimated by linear fitting of the experimental data are reported in Table 1 from which the absolute coefficients can be derived.

Table 1. Measured Seebeck coefficients of three ZnO nanowires samples deposited at different temperatures.

| Deposition temperature [°C] | Seebeck coefficient $\alpha_{\text{ma}}$ [ȝV/°C] | Seebeck coefficient $\alpha_{\text{mb}}$ [ȝV/°C] |
|-----------------------------|----------------------------------|----------------------------------|
| 700                         | -216                             | -143                             |
| 870                         | -140                             | -102                             |
| 1085                        | -210                             | -88                              |

The coefficient sign is negative, as expected for an $n$-type semiconductor. The experimental results are in agreement with the early values of Seebeck coefficient recently reported in the literature for ZnO thin-films [8] and nanostructures [9].

5. Conclusions

ZnO nanowire bundles have been deposited, proposed and experimentally characterized for energy harvesting applications. The Seebeck coefficient of the fabricated samples has been successfully measured around room temperature. The measured thermoelectric coefficients result in good agreement with the values recently reported in the literature.

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