Ion Beam Assisted Deposition Enhanced Thermoelectric Properties (With Figure of Merit Above 3.0)

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Abstract

Ion Beam Assisted Deposition (IBAD) was used to process a thermoelectric materials system, with high volume fraction and high thermoelectric figure of merit, based on the interaction of composites of two metal nanocrystals in silica substrate prepared by a multilayer structure having alternate layers of metal/material mixture. The alternate layers component of this work either has gold or silver content. The deposited layered structure was bombarded during deposition by 500eV to 10keV argon ions in order to produce nanoclusters in each layer. Using the IBAD method we obtained a much larger volume fraction, compared to our previous work, and a resulting thermal conductivity as low as 1.2 (W/m.k), electrical conductivity nearly as high as 90,000 (1/Ohm.m), square of Seebeck Coefficient as high as 1.37 x 10^-7 (V/k)^2 at 350K, which translates to a Figure of Merit as high as 3.6.

Introduction

Thermoelectric (TE) materials are used to fabricate devices in order to convert heat directly to electrical power, or conversely, to create cooling directly from electrical power. These devices are entirely solid state, very rugged with no moving parts to wear out, and thus can last indefinitely. Nowadays, the thermoelectric devices are used in a variety of applications such as cooling electronics and electrical devices, cooling seats in cars, recharging batteries in cell phones and cars from wasted heat, and in home appliances [1].
During the past few years, the potential for thermoelectric devices has expanded since the operational temperatures have reached as low as room temperature [2-5] and the Figure of Merit has been increased to well above 2.0. If the scale-up cost is reduced, it may become more attractive to replace mechanical compressor refrigeration systems and gasoline generators with thermoelectric devices, which can be utilized in conjunction with geothermal power production. High figure of merit thermoelectric devices, with an operational range from room temperature to a few-hundred degrees Celsius, can play a significant role in energy production, home heating/cooling and general energy management for the future.

Recent advances in TE devices, including our most recent work [2], have shown that quantum dot and superlattice structures combined with semiconductor technology can produce even higher efficiency factors [6]. These findings infer the creation of pseudo-quantum dot lattices which have been shown in a series of research works initiated during the past decade. The researchers have theoretically shown the enhancement of the thermoelectric figure-of-merit in regimented quantum dot super lattices [6-8].

In this work, we have achieved the highest thermoelectric figure of merit by creating highly dense alternate layers of a metal/silica mixture containing nanocrystals of silver and gold in each layer. The alternate layers were constructed by the ion beam assisted deposition (IBAD) [9] process in order to have differing metal content: Au and Ag. In our previous work, the differing metal content served to quench and isolate nanoclusters along the 5.0 MeV Si beam irradiation track, as described in our publications over the past 16 years [2, 10-14]. In the present work the metal nanocrystals were formed during each layer formation by IBAD, as a result of which we achieved a larger volume fraction [15 and16] and significantly reduced the thermal conductivity (τ), increased the electrical conductivity (σ) and increased the absolute value of the Seebeck coefficient (S) resulting in a higher figure of merit (ZT) at room temperature and at 350K. The IBAD system used is an in-house developed system consisting of an e-beam evaporator, an ion evaporator, and an argon ion gun where the distance between the evaporating materials and the substrate is adjustable between 10 cm to 20 cm.

Using IBAD, we successfully improved the figure of merit of the materials system in our previous work [2]. The periodic deposition of Au+ SiO2 and Ag+SiO2 was bombarded by 500eV to 10keV argon ions in order to produce nanoclusters in each layer during the deposition, one layer at a time. The dual layering process was repeated 100 to 1000 times.

**Background information and Experimental procedures**

To identify the effectiveness of a thermoelectric material, one must measure the following properties: the Seebeck coefficient, the electrical conductivity, and the thermal conductivity of such materials in order to calculate the figure of merit, ZT, which is related to the physical properties of the device that determine the potential efficiency of the device, as indicated in Equation 1:

$$ZT = S^2\sigma T/\tau$$  \hspace{1cm} (1)

where,

- S is the Seebeck coefficient,
- σ is the electrical conductivity,
- T is the absolute temperature, Kelvin
- τ is the thermal conductivity.

Equation 1, shows, that ZT is increased as the Seebeck coefficient or electrical conductivity is increased or as the thermal conductivity is decreased. Increasing the temperature of operation may also increase the figure of merit if there is no change in the structure, no change in the phase of the material used in the device, or if there is no negative change in other properties of the TE material.

The Seebeck coefficient is related to the voltage achieved by a temperature difference across the thermoelectric device and is typically expressed in microvolts per degree Kelvin (μV/K). The electrical conductivity refers to the conductivity parallel to the direction of heat transfer, where the units are (ohm-cm)^1. For a multilayer structure having alternate layers of metal/material mixture, the electrical conductivity was measured cross plane rather than...
using the traditional Van der Paw technique, in order to include effects from each layer in our measurement, which is also in the same direction as the temperature difference across the device.

Measuring the thermal conductivity of thin films is a challenge since in such a measurement one should consider the effects of the contacts and the substrate. For such measurement, we used cross plane third harmonic technique (also referred to as a three omega, 3-Omega technique) which is used to determine the thin film thermal conductivity [17], where the units are mW/(cm°K). The thermal conductivity measurement was performed starting at room temperature (300K) and at steps of 50K to as high as 500K. The detail for the third harmonic measurement and sample preparation is indicated in our most recent applied surface science publication [2].

In our previous work [2] the layers were deposited using co-deposition of gold and silica then silver and silica, repeating the bi-layer deposition 100 to 1000 times, then bombarded by 5 MeV Si ions, in order to create nanocrystals of Au and Ag in the path of the Si beam. In the present work we used IBAD, co-depositing gold and silica while bombarding by 500eV to 10keV argon ions, then silver and silica while bombarding by 500eV to 10keV argon ions, and repeating the bi-layer IBAD process 100 to 1000 times to produce nanoclusters in each layer during the deposition. This technique allowed us to increase the volume fraction well above our previous work [2], increasing the electrical conductivity and reducing thermal conductivity, while increasing the Seebeck coefficient and the figure of merit, even at 300K (room temperature). The detail of increased volume fraction for formation of nanocrystals of gold in silica and other host materials using IBAD is discussed by Hubler et al in their 1997 publication [15 and 16].

In our approach, we used three evaporators, one for gold deposition, one for silver deposition and one for silica deposition, in addition to an ion gun in order to produce 500eV to 10keV argon ions creating100 to 1000 bi-layers containing nanocrystals of gold in silica and silver in silica. The gold contact layers and the co-deposited composite layers of Au	extsubscript{x}(SiO	extsubscript{2})	extsuperscript{(1-x)/Agy(SiO	extsubscript{2})}	extsuperscript{(1-y)} were formed by appropriately enabling and adjusting the three evaporators to produce each successive layer. The thickness of each layer was controlled and monitored by a quartz resonator deposition monitor.

The IBAD films were produced on a gold coated substrates were we used for variety of measurements, such as; Seebeck coefficient measurements, cross-plane electrical conductivity measurement and thermal conductivity measurements (using 3 omega technique “3ω”) and for Rutherford backscattering spectrometry (RBS) to study change in the layer composition and measure the metal content in layered stack. The geometry in Figure 1 shows two conducting contact layers, one each on the top and bottom of the multilayers.

These contacts, traditionally gold, could be any materials with good thermal and electrical conductivity, were used in the Seebeck coefficient measurement system and were also used when electric contact was needed.

**Results and data analysis**

Rutherford Backscattering Spectrometry study the concentration of silver and gold in order to have fine control on the deposition shows an RBS spectrum for four layers of depositing the composite layers on a carbon nitrogen as incident beam. A large number produced by co-depositing gold and silica argon ions, then silver and silica while ions.

Table 1 shows the measured electrical conductivities, measured thermal conductivities, and measured Seebeck coefficients at 300K, 350K, 400K, 450K, and 500K. Also shown is the figure of merit calculated using Equation 1 at these measured parameters at each temperature, and the theoretical value of figure of merit, if we consider that there would have been no change in electrical conductivity, thermal...
conductivity and Seebeck coefficient as we increase “T” in Equation 1. The ZT=3.7 was taken arbitrarily as the starting point for the theoretical calculation of figure of merit. Any ZT point from the experimental data may be selected as a comparison to theoretical plot, in order to show that the theoretical value of figure of merit (ZT = (S²eT)/k) can’t be used for predicting the change in the figure of merit at higher temperature in such a materials system, as shown in figure 6.

Table 1. Shows electrical conductivities, thermal conductivities, Seebeck coefficients and both experimental and theoretical figure of merit

| Temperature | ZT (Theory) | ZT (Experiment) | Seebeck Coefficient | Electrical Conductivity | Thermal Conductivity | Figure of Merit (Calculated) |
|-------------|-------------|------------------|---------------------|------------------------|----------------------|-------------------------------|
| K           |             |                  |                     |                        |                      |                               |
| 300         | 3.2         | 3.4              | 1.6E-7              | 95600                  | 1.35                 | 3.36566                       |
| 350         | 3.7         | 3.7              | 1.6E-7              | 95600                  | 1.45                 | 3.70756                       |
| 400         | 4.2         | 3.75             | 1.6E-7              | 96100                  | 1.65                 | 3.75081                       |
| 450         | 4.8         | 3.8              | 1.6E-7              | 96120                  | 1.83                 | 3.80541                       |
| 500         | 5.3         | 3.88             | 1.6E-7              | 96190                  | 1.99                 | 3.88787                       |

Figure 3 shows thermal conductivity (W/m.K) conducted at 300K, 350K, 400K, 450K, and 500K. The 47% increase in thermal conductivity at 500K compare conductivity at 300K could be due to increase in electron rapidly warming of the thin films (typically from 500 nm and thus a potential change in the materials property of the thin film.

Figure 4 shows the Electrical Conductivity (1/Ohm.m) measurements conducted at 300K, 350K, 400K, 450K, and 500K. Electrical conductivity at 350K compare to the electrical conductivity at 300K shows a minor increase of 0.5%, after which at higher temperatures such as 500K the electrical conductivity shows a small drop which might be due to the thin film reaching a rapid equilibrium temperature, changing the materials properties of the thin film and increasing the scattering.

Figure 5 illustrates a graph of the square of the Seebeck coefficient (V/K)², the measurements conducted at 300K, 350K, 400K, 450K, and 500K. Square of the Seebeck coefficient at 400 shows 0.6% increase compare to the square of the Seebeck coefficient at 350K. After 400K the square of the Seebeck coefficient transitions to a constant value similar to what was observed after 400K for electrical conductivity, as shown in figure 4.

Figure 6 illustrates a calculated (ZT) using the thermal electrical conductivity and}

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Seebeck coefficient at temperatures from 300K to 500K. It also shows, using Equation 1 and the measured thermal conductivity, electrical conductivity and Seebeck coefficient at 350K as a fixed point. We calculated the theoretical value of figure of merit at 300K and 400K. The deviation from the theoretical value of figure of merit from the calculated value using the measured physical properties at each temperature is due to thermal dependence of each of these properties for such a layered thin film.

Conclusions

The higher figure of merit for the IBAD synthesized multilayer thermoelectric materials compared to the results obtained using post bombardment by 5 MeV Si ion, as indicated in our previous publication, could be due to higher volume fraction of the nanocrystals obtained resulting in increased electrical conductivity, increased square of the Seebeck coefficient, and lowered thermal conductivity, as predicted by Hubler et al. The increase in thermal conductivity at higher temperature could be due to the ultra-thin film reaching the equilibrium temperature.

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