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CoSb₃ 纳米薄膜的制备与热电性能

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摘 要:通过对低压化学气相沉积制得的 CoSb₃ 纳米薄膜在 300~800K 温度范围内的热电性能测试, 发现其电阻率较其他单晶 CoSb₃ 块状样品低一个量级, 热导率值在 1.08~4.05 Wm⁻¹K⁻¹ 之间, 比单晶 CoSb₃ 低得多. 这表明纳米结构导致热导率显著降低, 最高热电优值在 773K 出现且为 0.114. 这种纳米薄膜材料在研制新型高效热电半导体方面极具应用前景.

关键词: 纳米材料; CoSb₃; 低压化学气相沉积; 热电性; 半导体

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Fabrication and Thermoelectric Performance of CoSb₃ Nanoparticle Films

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Abstract: The thermoelectric properties of the CoSb₃ nanoparticle films, which have been prepared via the Low Pressure Chemical Vapor Deposition, were measured in the temperature range from 300 to 800 K. The resistivity of the CoSb₃ nanoparticle films is one order of magnitude lower than the single crystal CoSb₃ bulk sample. The measured values of the thermal conductivity of the CoSb₃ nanoparticle films are in the range from 1.08 to 4.05 Wm⁻¹K⁻¹, which are much lower than that of the single crystal CoSb₃ samples. This suggests that the nano-structure results in a significant reduction of the thermal conductivity. The highest thermoelectric optimal value was 0.114 and obtained at 773 K. The discussed nanoparticle films are promising for realizing new types of highly efficient thermoelectric semiconductors.

Key words: Nanomaterials; CoSb₃; Low pressure chemical vapor deposition; Thermoelectric properties; Semiconductors

OCIS Codes: 160.4236;160.6000;160.6990

0 Introduction

Thermoelectric (TE) materials have many attractive applications in power generation and solid-state cooling. The efficiency of TE materials is defined as $ZT = S^2 \sigma T / \kappa$, where S , σ , T and κ are the Seebeck coefficient, electrical conductivity, absolute temperature and thermal conductivity respectively. ZT can be significantly changed by varying the Seebeck coefficient or the thermal conductivity^[1]. Both parameters can be manipulated by the nanotechnology. Nano-structure TE materials is considered to be one of

the most promising approaches to increase the ZT values, by incurring the quantum size effect and the increased phonon scattering^[2]. The decrease in the grain size of the material can lead to a drastic increase in the density of grain boundaries, which brings about a significant reduction in the thermal conductivity, and hence improve the values of ZT ^[3-4]. Specifically, nanoparticles have been predicted to show a strong scattering effect on phonons which is similar to that of atomic impurities or crystal boundaries^[5-6].

Among different types of TE materials, CoSb₃-based skutterudite compounds have a high ZT value and

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are regarded as one of the promising materials working at an intermediate temperature region^[7-11]. CoSb₃-based materials have been received much attention due to their large Seebeck coefficient and high electrical conductivity^[12-13]. However, their thermal conductivities are almost ten times higher than that of other state-of-the-art TE materials, such as Bi₂Te₃^[14]. Thus, it is desirable to decrease the lattice thermal conductivity and improve the ZT values of CoSb₃ material. One promising method is through Nanostructure. CoSb₃ nanostructures have been synthesized by various methods including Sol-Gel^[15], polyol process^[16-17], electrodeposition^[18] and solvothermal method^[19]. These methods have their own advantages. However, CoSb₃ nanostructures obtained via the above-mentioned methods are difficult to be directly integrated into TE device construction as they require the removal of the insulating surface capping ligands or inorganic templates. A simple approach to prepare CoSb₃ nanostructures with promising TE properties will be attractive.

Here, we report the synthesis of CoSb₃ nanoparticle films by using Low Pressure Chemical Vapor Deposition (LPCVD) and test their thermoelectric properties comprising electrical conductivity, Seebeck coefficient and thermal conductivity. This growth process holds promising potential to produce assembled nanocrystal samples with a high electrical conductivity and a low thermal conductivity, which are keys to enhance TE performance.

1 Experimental Details

The synthesis of CoSb₃ nanoparticle films was carried out in a horizontal vacuum tube furnace with a 2 cm inner-diameter quartz tube mounted inside. In experiment, 0.02855 g CoCl₂ · 6H₂O (purity 98%) powder loaded in a crucible was put into the quartz tube at 5 cm downstream of the center zone of the tube furnace, while 0.04392 g Sb (purity 99.5%) powder loaded in a crucible was placed into the quartz tube at 10 cm upstream of the center zone of the tube furnace. One piece of glass slide (0.5 × 1 cm²) was used as substrate and loaded at 16 cm downstream of the center zone of the tube furnace. Before starting the growth process, the quartz tube was evacuated to 10⁻³ mbar and then flushed with 95% Ar + 5% H₂ gas for 3 times to prevent possible oxidation of the samples. The furnace was heated to 1073K with a heating rate of 30K/min and kept for 60 min. During the growth, a constant mixture gas of 95% Ar and 5% H₂ was

maintained at 200 standard cubic centimeters per minute by a mass flow meter controller. The pressure inside the quartz tube was kept at 2.8 mbar. After the system was cooled down to room temperature, gray products were produced on the surface of the glass substrate.

The resulting products were characterized by X-ray Diffraction (XRD, Shimadzu 6000 X-ray Diffractometer), Field Emission Scanning Electron Microscopy (FESEM, JEOL JSM6340F) and Transmission Electron Microscopy (TEM, JEOL 2100). The Seebeck coefficient and electrical resistivity were determined by a standard four probe method using the Seebeck Coefficient/Electrical Resistance Measuring System ULVAC ZEM-3 in a He atmosphere.

CoSb₃ nanoparticle films deposited on glass slide (1 × 1 cm²) were used measuring the thermal diffusivity D and the specific heat capacity C_p by laser flash (NETZSCH LFA 457 Micro Flash Analyzer). Specific heat capacity C_p was determined using the ratio method by comparing the temperature rise of the sample to the temperature rise of a standard sample of known specific heat tested under the same conditions. Thermal conductivity, κ , is calculated from the thermal diffusivity D , density ρ , and specific heat capacity C_p by using the equation: $\kappa = D \times \rho \times C_p$.

2 Results and Discussion

Fig. 1 shows the XRD pattern of the resulting products. All the intensity peaks can be indexed by skutterudite-type CoSb₃ phase (JCPDS 78-0976). Without impurity phases, such as Co and Sb, were detected. FESEM images (Fig. 2(a), (b)) reveal that the products are CoSb₃ nanoparticles with diameters in a range from 200 to 400 nm. The CoSb₃ nanoparticles interconnect with each other and form a film with the thickness of about 1 μm. The energy dispersive X-ray spectroscopy (Fig. 2(c)) shows that Co and Sb were in atomic ratio of about 1 : 3. The interconnection of nanoparticles was furtherly verified in TEM images (Fig. 3(a)). Clear grain boundaries can be seen from Fig. 3(a). The present average grain size is about 300 nm. Such a fine-grained microstructure is in favor of TE materials requiring low thermal conductivity. The Selected Area Electron Diffraction pattern (SAED, inset Fig. 3(a)) suggests that the CoSb₃ nanoparticles possess polycrystalline structure. Lattice-resolved image (Fig. 3(b)) also reveals the polycrystalline structure of the CoSb₃ nanoparticles with the spaces of lattice planes of 0.286 nm, corresponding to (013) crystalline planes.

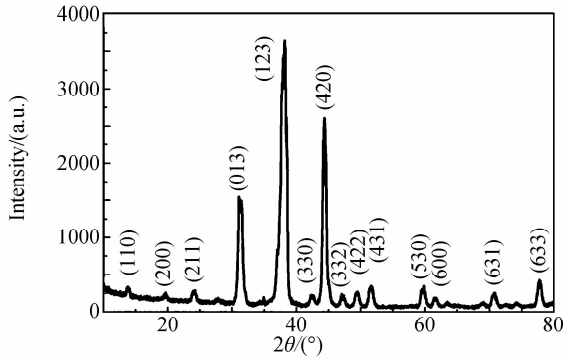
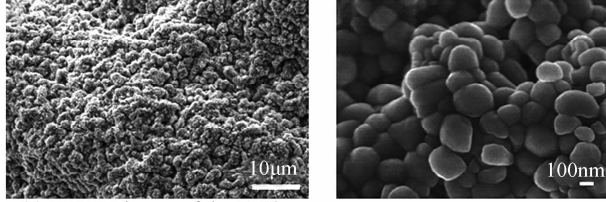
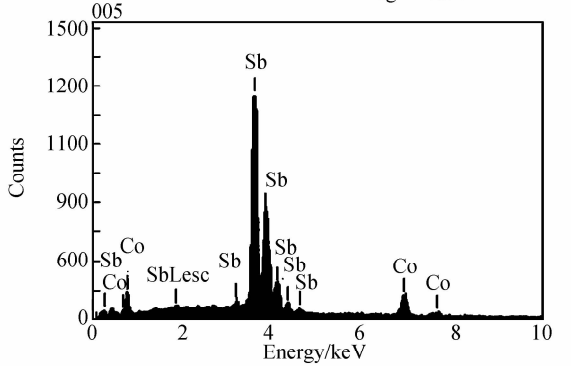

 Fig. 1 XRD pattern of the CoSb₃ nanoparticle films

 (a) FESEM image of the CoSb₃ nanoparticle films in low-magnification
 (b) FESEM image of the CoSb₃ nanoparticle films in high-magnification

 (c) EDX spectrum taken from the CoSb₃ nanoparticle films

Fig. 2 FESEM images and EDX spectrum

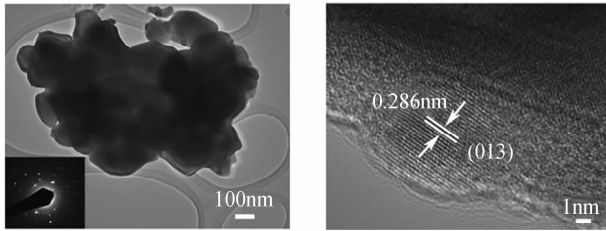

 (a) TEM image of CoSb₃ nanoparticles; inset: SAED pattern
 (b) High-resolution TEM image of a CoSb₃ nanoparticle

Fig. 3 TEM image and high-resolution TEM image

Fig. 4 shows the electric resistivity of the CoSb₃ nanoparticle films as a function of the temperature. The resistance of the CoSb₃ nanoparticle films decreases monotonically with the temperature increasing, exhibiting a semiconductor behavior. In the temperature range $323\text{K} \leq T \leq 773\text{K}$, the CoSb₃ nanoparticle films show very low electrical resistivity in the range from $10^{-4} \Omega \cdot \text{m}$ to $3.5 \times 10^{-4} \Omega \cdot \text{m}$, which is approximately an order of magnitude lower than that of bulk samples. This phenomenon indicates that the carrier concentration of the nanosized particles is much higher than that of the bulk samples^[16].

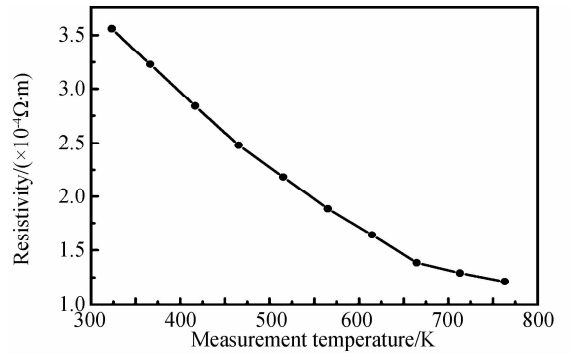
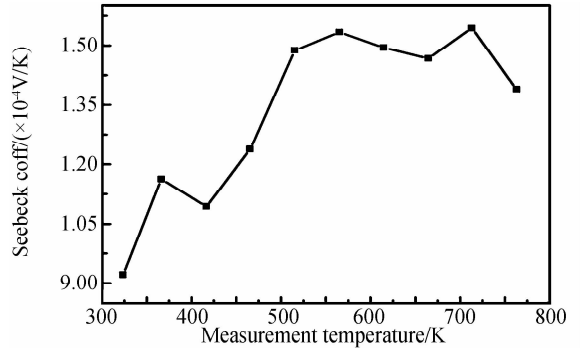

 Fig. 4 Temperature dependence of resistivity of the CoSb₃ nanoparticle films

Fig. 5 shows the Seebeck coefficient of CoSb₃ nanoparticle films as a function of temperature. The Seebeck coefficient is positive in the whole temperature range, indicating the dominant contribution of hole carriers. Many studies on CoSb₃ have reported a p-type behavior with a positive sign of the Seebeck coefficient^[20-21]. The Seebeck coefficient increases with the measurement temperature increasing, reaches a maximum at about 700 K, then decreases. The decrease is due to that the small polaron hopping activation within this temperature range. The increase in the carrier concentration due to small polaron hopping activation leads to a reduction in the Seebeck coefficients^[16].


 Fig. 5 Temperature dependence of Seebeck coefficient of the CoSb₃ nanoparticle films

The thermal diffusivity D and special heat capacity C_p were measured by a laser flash apparatus and a thermal analyzer. The thermal conductivity κ was calculated by $\kappa = D \times \rho \times C_p$. The thermal conductivity of material is often approximately described as $k = k_l + k_e$, where k_l is the heat conducted by photons traveling through the lattice and k_e is electrons and holes transporting heat^[22]. The carrier thermal conductivity was estimated using the Wiedemann-Franz's law, $k_e = L\sigma T$, where L is the Lorenz number, σ is electrical conductivity, and T is the temperature in kelvins. The nanosized particles play an important role in reducing the lattice thermal conductivity k_l which is the main contribution to the total thermal conductivity. Fig. 6

shows the thermal conductivity versus temperature for CoSb₃ nanoparticle films. The thermal conductivity κ decreases with the temperature increasing. The CoSb₃ nanoparticle films show much reduced values of κ at room temperature, e. g. $4.05 \text{ Wm}^{-1} \text{ K}^{-1}$, which is much lower than that reported for single crystal CoSb₃^[23], e. g. $10 \text{ Wm}^{-1} \text{ K}^{-1}$. This provides further evidence of the effect of nanostructuring on the lattice thermal conductivity of the material. The decrease in the thermal conductivity of CoSb₃ nanoparticle films is mainly due to the enhanced phonon scattering^[18]. The decrease in the grain size of the material lead to a drastic increase in the density of grain boundaries, which brings about a significant reduction in the thermal conductivity^[19]. It should be mentioned that the present data have not been corrected for density differences due to porosity.

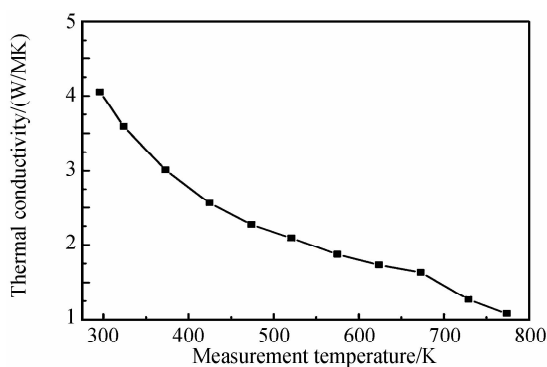


Fig. 6 Temperature dependences of thermal conductivity of the CoSb₃ nanoparticle films

Based on the measured electrical and thermal transport properties, dimensionless figures of merit ZT are calculated and showed in Fig. 7. The ZT values of CoSb₃ nanoparticle films increase with the temperature increasing and reach the highest value of 0.114 at 773 K. The ZT value is significantly larger than that of bulk sample, whose highest ZT value is 0.047. The decrease in the electrical resistivity of the CoSb₃ nanoparticle films is the most important contributor to the improvement in electrical property even though the improvement is slightly counteracted by the decrease in the Seebeck coefficient. Meanwhile, nanosized particle results in a reduction in the lattice thermal conductivity. Hence, due to the improvement in both the electrical and thermal properties, the ZT values of the CoSb₃ nanoparticle films are dramatically enhanced compared to bulk CoSb₃. These results show that nanostructuring approach can be an effective way to increase the ZT value by decreasing not only the thermal resistivity but also the thermal conductivity.

The corresponding power factors ($S\sigma$) as a function of measurement temperature increases to $1.848 \times 10^{-4} \text{ W/m} \cdot \text{K}^2$ with the temperature increasing and then

decreases slightly.

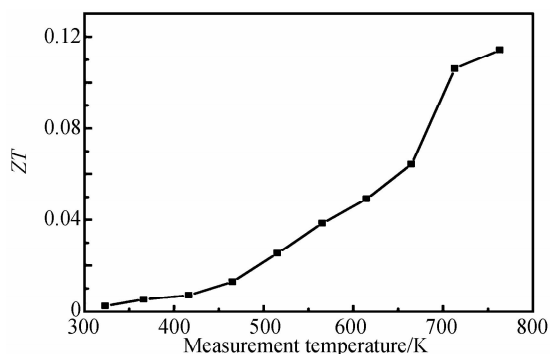


Fig. 7 Temperature dependences of dimensionless figure of merit ZT value for the CoSb₃ nanoparticle films

3 Conclusions

In summary, CoSb₃ nanoparticle films have been synthesized using LPCVD and their TE properties are investigated. The resultant CoSb₃ nanoparticle films show dramatic reduction in the thermal conductivity and electrical resistivity. The highest ZT value of 0.114 was obtained at about 773 K. This approach demonstrates a promising route to achieve new types of highly efficient TE semiconductors.

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