

Grain boundary scattering contribution to the thermopower in Cr-Si nanocrystalline films

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Abstract. We study transport properties of $\text{Cr}_{1-x}\text{Si}_x$ films ($x = 0.65, 0.67, 0.72, 0.85$), produced by magnetron sputtering of composite targets on unheated Si/SiO₂ substrates. The as-deposited films have amorphous structure, which can be converted by isothermal annealing into nanocrystalline state with the average crystal grain size of about 15 nm. We found that in the nanocrystalline composites there is an additional large contribution to the thermopower due to energy dependent scattering of the charge carriers on the nanocrystal interfaces. This contribution to the thermopower is strongly dependent on the film composition. The maximum contribution have the films of stoichiometric CrSi_2 composition.

1. Introduction

Thermoelectric energy conversion has a large potential to increase power system efficiency by utilization of the waste heat. Recently, considerable efforts were directed to investigate the prospects of the thermoelectric converters for utilization waste heat from the internal combustion engines, garbage incinerators, metallurgical furnaces, and so on. In order to be economically viable the thermoelectric converters should be efficient and cheap. The efficiency of the converters to a large part is determined by the properties of the thermoelectric materials from which the active parts of the converters are made. The thermoelectric efficiency of a material is characterized by parameter Z :

$$Z = \frac{S^2}{\rho\kappa}, \quad (1)$$

where S - Seebeck coefficient or thermopower, ρ - resistivity and κ - thermal conductivity. The nanostructurization is considered as a promising way to increase the efficiency [1, 2]. One of the practically important types of the nanostructured materials is the nanocrystalline (NC) composites. It is commonly agreed that the NC materials are the polycrystalline substances with average crystal grain size below about 100 nm [3]. Two main effects are expected to contribute to the enhancement of the efficiency in the NC thermoelectrics: a strong reduction of thermal conductivity, and increase of the thermopower due to energy-dependent scattering (energy filtering) of the charge carriers at the boundaries of nanoparticles.

The preparation of NC materials with well defined properties is quite a challenging task. The main difficulty is to get the NC state with clean nano-crystal interfaces. In this work, the



NC state is prepared by crystallization of amorphous material in the course of annealing at a certain temperature, i.e. via solid state reaction. The NC state can be further transformed into conventional microcrystalline state (MC) by long annealing at sufficiently high temperatures. In this way it was possible to compare thermoelectric properties of amorphous, NC and MC states of the same sample.

2. Experimental procedures

The amorphous films were deposited by magnetron sputtering of composite targets onto unheated Si/SiO₂ substrates. The deposition procedures were carried out in a high-vacuum chamber equipped with a turbo-molecular pump and with a mass flow controller for maintaining Ar working pressure at $4 \cdot 10^{-3}$ mbar. The deposition rate was in the range 20-60 nm/min.

Cr_{1-x}Si_x films with composition x=0.65; 0.67; 0.72; 0.85 with thickness from 20 to 300 nm were prepared. The film composition was determined with Rutherford Backscattering Spectroscopy (RBS) and Energy Dispersive X-ray Spectroscopy (EDXS). The films were further transformed into nanocrystalline state by annealing with in-situ thermopower and electrical resistivity measurements. The resistivity and thermopower were measured simultaneously. 4-point, DC procedure was used in the resistivity measurements, while a differential method was employed for measurement of thermopower. The measurement set-up was described elsewhere [4]. The measurements were done in the inert helium gas atmosphere.

3. Results and discussion

Amorphous films were transformed into nanocrystalline state during thermal annealing. The crystallization of Cr_{1-x}Si_x films into the NC state was confirmed by structural analysis [5]. At isothermal annealing the crystallization rate is strongly dependent on the annealing temperature and can be experimentally observed above about 450 K. Below this temperature the crystallization rate is too low for experimental observation. The crystallization temperature increases with increasing silicon content in the Cr_{1-x}Si_x composite films [6].

The evolution of the resistivity and thermopower during the isothermal annealing at T_{ann}=495 K is shown in Fig. 1. Both, the resistivity and the thermopower have a characteristic sharp increase at the onset of the crystallization.

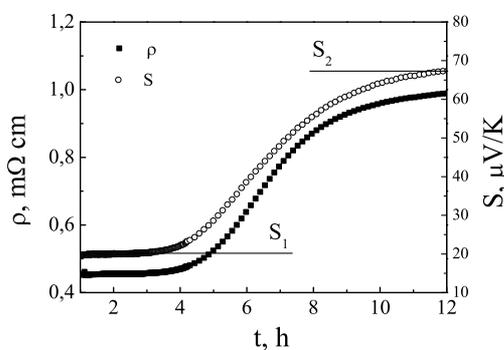


Figure 1. Dependencies of thermopower and resistivity on annealing time at T_{ann} = 495 K of CrSi₂ film.

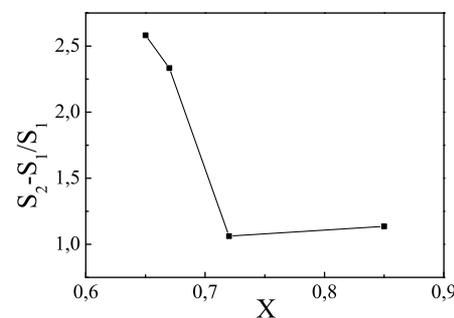


Figure 2. Change of the thermopower due to the crystallization versus film composition. Thickness of the films is 100 nm.

According to the film structure investigation [5] the crystallization starts with the nucleation of nanocrystals of CrSi₂ with the average size of 15 nm. In the course of the crystallization the number of the nanocrystals increases, while the average grain size remains in the range

10–20 nm. At the early stages of the crystallization process the film consists mainly of the amorphous phase with diluted inclusions of the CrSi₂ nanocrystals. With annealing time the amount of the NC phase increases.

Interaction between charge carries and nanocrystals depends on ratio of crystalline size and the de Broglie wavelength λ . λ is given by

$$\lambda = \frac{h}{m^*V},$$

where h - Planck's constant, m^* - effective mass, V - thermal mean velocity. The effective mass of holes for this material $m_h^* = 3.2m_0$ [7].

The thermal mean velocity can be calculated from:

$$\frac{3}{2}kT = m^*V^2/2,$$

where k - Boltzmann constant, T - absolute temperature. Thus $\lambda = 5$ nm, so the nanocrystal can be regarded as a point defect or point-like scattering center because the average grain size comparable to de Broglie wavelength.

Accordingly, the increase of the resistivity and thermopower (Fig.1) is related to the increasing number of the scattering centres with selective scattering of the charge carriers at the boundary of the nanocrystals. This scattering gives essential contribution to both, to the resistivity and to the thermopower Figs.1 and 2. Of course, at later annealing stages the NC grains can not be considered as independent point-like scattering centres, they even can form a percolating cluster of NC phase, nevertheless the scattering on the grain boundaries remains the dominating scattering mechanism for charge carries as long as the grain size is comparable to the mean free path of the carriers. In accord with this our earlier experimental observation demonstrated that the power factor S^2/ρ of the Cr-Si and MnSi_{2.2} compounds in the nanocrystalline state exceeds the power factor in the microcrystalline state due to enhancement of thermopower [8].

More detailed analysis of the resistivity and thermopower during crystallization can be based on the Matthiessen's rule for resistivity Eq. 2, and Nordheim-Gorter rule for thermopower [9]:

$$\rho = \rho_a + \rho_b, \tag{2}$$

$$S = (S_a - S_b) \frac{\rho_a}{\rho_a + \rho_b} + S_b, \tag{3}$$

where S and ρ are the total thermopower and resistivity of the sample, $S_a \equiv S_1$ and ρ_a - thermopower and resistivity arising from charge carriers scattering in amorphous phase, S_b and ρ_b - thermopower and resistivity arising from charge carriers scattering at the NC grain interfaces.

The Matthiessen's rule Eq. 2 and the Nordheim-Gorter rule Eq. 3 are valid for diluted alloys, i.e. under the condition that the interaction of charge carriers with the alloy matrix and with the impurity scattering centres are independent processes. In the context of the presents work this corresponds to the initial stages of the annealing, Fig.3. According to the Eq. 3 the total thermopower, measured during annealing should be a linear function of the reciprocal total resistance. Fig.3 shows that, indeed, the linear function law is realized on the first stage of annealing. S_b was found from slope of Fig.3. Fig.4 shows value of S_b for different film compositions.

It was found that grain boundary scattering contribution to the thermopower of the nanocrystalline state depends on compositions. S_b is comparable to thermopower of bulk crystalline CrSi₂ [10]. The maximum thermopower of selective scattering have films of stoichiometric composition.

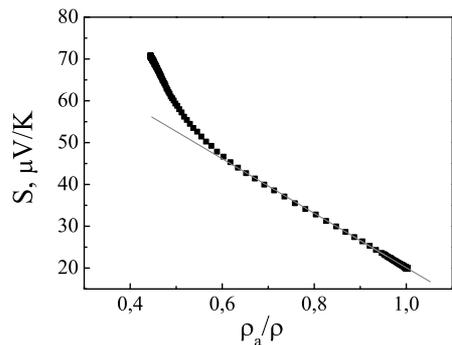


Figure 3. Dependence of the total thermopower on inverse total resistivity for CrSi₂ film.

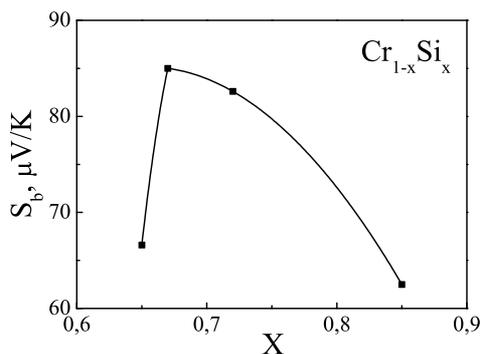


Figure 4. Dependence of the thermopower arising from charge carriers scattering at the boundaries on composition. Thickness of the films is 100 nm.

4. Conclusions

Grain boundary scattering contribution to the thermopower due to selective scattering is large. For this reason, the power factor of the nanocrystalline state is larger than power factor of microcrystalline state. Stoichiometric composition of Cr-Si has maximum grain boundary scattering contribution to thermopower.

Acknowledgments

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