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Effect of interphase boundaries on resistivity and thermopower of nanocrystalline Re-Si thin film composites

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The phase formation, electrical resistivity, and thermoelectric power of the thin film Re-Si composites have been investigated at different stages of the transformation from the amorphous to nanocrystalline state. The nanocrystallization was achieved by the annealing of amorphous films with the initial composition $Re_{0.34}Si_{0.66}$, which is equal to the composition of the crystalline $ReSi_2$ semiconductor. The composite films include only two phases: the amorphous phase and the nanocrystalline $ReSi_2$ with the mean grain size of about 10 nm; however, a large volume fraction of the composite films is occupied by interfaces and intergrain regions. The transport properties of this semiconductor-semiconductor system show nonmonotonic dependence on the volume fraction of the nanocrystalline phase. The role of the interfaces in this peculiar behavior is discussed. [S0163-1829(98)02636-8]

Nanocrystalline (NC) materials are polycrystalline substances with grain sizes of up to about 100 nm.[1] An important common feature of these materials is that they are structurally characterized by ultrafine grains and by a large volume fraction of interfaces. It has been found that the electronic transport properties of NC metals are strongly affected by the interaction of conduction electrons with the interfaces.[1–3] One can expect to find an even more distinct manifestation of this interaction in NC semiconductors and in semiconductor-semiconductor composites. In that case two additional effects may become important: (1) The band structure of the nanocrystals can differ from the band structure of the bulk semiconductor. (2) The screening length of the charge carriers, trapped at the interface, can be comparable with the size of the grains. The latter implies that the properties of the semiconducting component of a composite are dependent on the kind and amount of another component in the NC composite. As a consequence the effective medium approximation (EMA), commonly used for the theoretical analysis of composite materials, should fail in this case. This effect should be particularly strong near the composition at which the semiconducting component forms a percolating cluster.

A great deal of attention has been paid to the transport in metal-insulator or metal-semiconductor NC composites.[4,5] It has been found that, in these binary composites, both the resistivity (ρ) and the thermopower (S) are monotonic functions of the volume ratio of the components and that they always lie between the corresponding values of the pure components of a composite system, in agreement with EMA predictions.[6] These observations indicate that in the metal-insulator and in the metal-semiconductor composites, where the main phases have very different conductivity, either the interfaces do not play an essential role or their effect is difficult to observe. The situation can be quite different for those binary semiconductor-semiconductor systems in which both components have comparable conductivity. Here the interfaces can play an important or even dominant role in the electronic transport.

The aim of this work is to investigate the contribution of the interfaces to ρ and S of composite Re-Si films. Re-Si thin film composites are suitable for this study for the following reasons:

(1) Within the Re-Si system, $ReSi_2$ is a narrow-gap semiconductor. The forbidden gap was found to be of about 0.12–0.15 eV.[7,8]

(2) The composites can easily be produced in NC form by the crystallization from the amorphous state. Partially crystallized films consist of two phases: NC and amorphous. Both of these phases are semiconductors and have electrical conductivity of the same order of magnitude.

Among the variety of methods for synthesis of NC materials, crystallization from the amorphous state has features that are important for the present investigation: (1) It is simple and convenient in this method to control the crystallization process. Conventional annealing can achieve the nanocrystallization with different volume ratios of amorphous and crystalline components depending on the heat treatment conditions. (2) Because in this method the crystalline phase is formed from the amorphous state via a solid state reaction, the internal interfaces are clean.

Films with two initial compositions have been studied. In stoichiometric films, the Si to Re ratio was equal to the composition of the crystalline semiconductor $ReSi_2$. Since both the crystalline and the amorphous phases have the same composition, no other phases appear during crystallization. Therefore the films can be considered as true binary mixtures of the amorphous $Re_{0.34}Si_{0.66}$ and the NC $ReSi_2$.

Recently, the composition of the semiconducting Re silicide was discussed and suggested to be $ReSi_{1.75}$ rather than of $ReSi_2$.[9] Assuming this compound is formed also in our $Re_{0.34}Si_{0.66}$ films, we would have to take into account an excess of Si with respect to the stoichiometric composition. To be assured that the observed dependencies of ρ and S do not result from a small Si excess, we also measured the films with the initial composition $Re_{0.39}Si_{0.61}$, where there is an excess of Re with respect to both $ReSi_2$ and $ReSi_{1.75}$ composition.

The films were prepared by magnetron cosputtering from pure Re and Si targets on to unheated substrates. Thermally

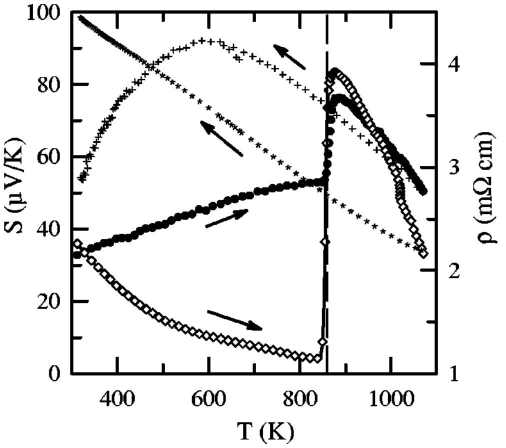

FIG. 1. Temperature dependence of electrical resistivity (◇: on heating; *: on cooling), and thermopower (●: on heating; +: on cooling) of a $Re_{0.34}Si_{0.66}$ film. The broken line indicates the crystallization temperature.

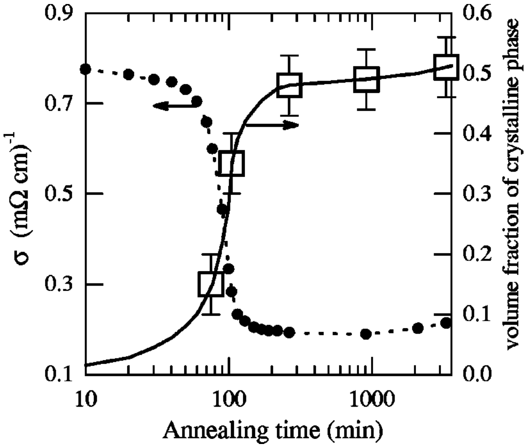

FIG. 2. The electrical conductivity σ, ●, and the volume fraction of the crystalline $ReSi_2$ phase, □, vs annealing time at the constant temperature $T=790$ K for a $Re_{0.34}Si_{0.66}$ film. The solid line is drawn by the spline interpolation between the experimental points and is used to plot the conductivity and the thermopower against the composition (Figs. 3 and 4).

oxidized Si wafers were used as substrates. The dense, 1 μm thick SiO_2 layer on the top of Si prevents a chemical reaction of the film with the substrate and provides electrical insulation. The film thickness was typically 100–150 nm. The composition analysis of the films was performed by Rutherford backscattering Spectroscopy (RBS) and energy dispersive x-ray spectroscopy (EDXS), the former with an accuracy of $\pm 1\%$. The structure of the films was determined by *in situ* x-ray diffraction measurements during annealing at temperatures of up to 1300 K, and also after *ex situ* annealing, at room temperature. The size of the crystalline grains was estimated from x-ray line broadening analysis. According to the x-ray data, the as-deposited films have an amorphous structure. S and ρ were measured during the annealing of the films in a high-purity helium atmosphere. Electrical resistivity was measured by the conventional dc four-probe method. In the case of the thermopower measurements, the differential method was used. Both properties were measured simultaneously during heat treatment of a sample as functions of the temperature and/or of the annealing time.

Figure 1 displays ρ and S temperature dependencies of a $Re_{0.34}Si_{0.66}$ film. The measurements were made with a continuous temperature variation at the rate of 2 K/min on heating and 10 K/min on cooling. The crystallization under these conditions takes place at a temperature of about 850 K. The temperature dependencies of ρ and S measured with the increasing temperature from 300 K to the crystallization temperature are characteristic for the amorphous film, whereas those measured during the cooling of the sample from about 1100 K down to room temperature are representative of the NC film. More detailed investigations of the films have been made in the course of annealing at a fixed temperature of 790 K.

Figure 2 presents the variation of the electrical conductivity ($\sigma=1/\rho$) and of the volume fraction of the crystalline $ReSi_2$ phase, x, as determined from the x-ray data, with the annealing time t. At $t=0$ the film is a single-phase amorphous compound. On increasing t the amount of the crystalline $ReSi_2$ phase increases, the film becomes a binary mixture consisting of NC $ReSi_2$ phase and the amorphous phase of the same atomic composition. Finally, at large t we obtained again a single-phase film but of crystalline $ReSi_2$. The x-ray measurements revealed that $ReSi_2$ is the only crystalline phase formed during annealing. The mean grain size of this phase was about 10 ± 5 nm. It remained constant, within the limits of experimental uncertainty, throughout the whole annealing procedure at $T=790$ K. That indicates that the crystallization makes progress not due to a growth of individual grains but by an increasing number of NC grains within the amorphous matrix.

As can be seen in Fig. 2, crystallization is almost complete in about 300 min, when the NC phase constitutes about 50% of the total film volume. With further annealing at a constant temperature there is almost no increase of the NC phase content. The results of the x-ray analysis imply that the rest of the film volume is occupied by the interfaces and intercrystalline regions. This amount of the interface volume agrees well with the average crystalline grain size.[1] A further increase of the crystalline phase content can be achieved by annealing at a considerably higher temperature—at about 1100 K. The increase of the crystalline phase content is accompanied in this case by a growth of the NC grains. The mean grain size was about 50 nm when the film contained nearly 100% of the crystalline phase.

A smooth interpolation between the x-ray data was used to obtain the calibration function $x=P(t)$ of the crystalline phase content x depending on the annealing time t. Using this function we plot σ and S, measured during the annealing of the film, against x. We should emphasize here that, because of the rapid variation of $P(t)$ between $x=0.1$ and $x=0.4$, the resulting dependencies of the transport properties on the composition in this range are very sensitive to experimental errors and to the interpolation procedure. Therefore, we should focus only on rather general features of these dependencies and will not discuss their details.

Figure 3 shows the dependence of σ and S of the stoichiometric $Re_{0.34}Si_{0.66}$ film on x. The most striking feature of these dependencies is that both σ and S reveal a nonmonotonic variation with the composition of the film, having a maximum (minimum in case of σ) at $x\approx0.5$. This behavior

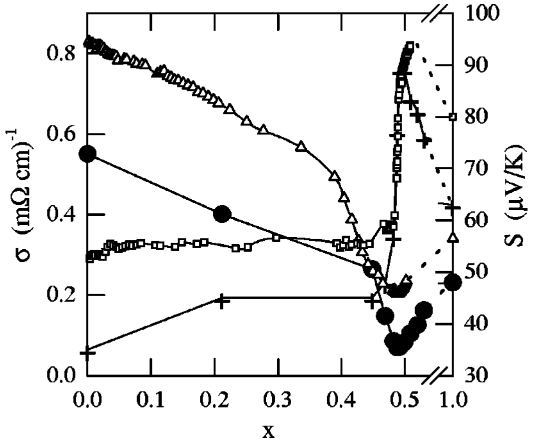

FIG. 3. Conductivity and thermopower of $Re_{0.34}Si_{0.66}$ thin film vs volume fraction (x) of the NC phase: ●: σ at $T=350$ K; △: σ at $T=790$ K. +: S at $T=350$ K; □: S at $T=790$ K. The data points on the right Y axis ($x=1$) show σ and S of the single-phase polycrystalline film with the mean grain size of about 50 nm (this film was annealed at higher temperature, about 1100 K).

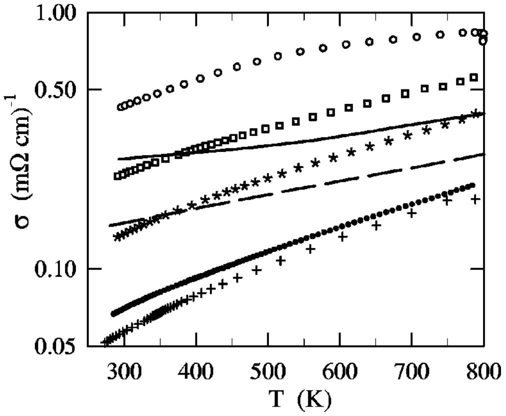

FIG. 5. The temperature dependence of the conductivity (in $\log_{10}$ scale) of a $Re_{0.34}Si_{0.66}$ film at different annealing stages: ○: amorphous film; □: $x\approx 0.21$; *: ≈ 0.45; +: ≈ 0.49; ●: ≈ 0.5; broken line: ≈ 0.53, and solid line: single-phase polycrystalline film with the mean grain size of about 50 nm.

is in a sharp contrast to the theoretical prediction of EMA for binary composites and with the experimental results for binary metal-insulator and metal-semiconductor composites.[4–6] This implies that the interfaces essentially affect the transport properties of the Re-Si NC compounds. One may argue that a small excess of Si as compared with the stoichiometric $ReSi_2$ or $ReSi_{1.75}$ ratio can result in this nonmonotonic variation of the transport properties. To check whether this might be the case we performed similar annealing experiments with a film that had an initial composition of $Re_{0.39}Si_{0.61}$. Films of this composition have an excess of Re in comparison with the stoichiometric composition not only of $ReSi_2$ but also of $ReSi_{1.75}$. Therefore one should expect an increase of the conductivity during the crystallization of this compound due to the appearance of free Re. However, $\sigma(x)$ and $S(x)$ of this composite, depicted in Fig. 4, show essentially the same nonmonotonic variation as those of the stoichiometric film.

Useful information about the conductivity mechanism can be obtained from the changes of the temperature dependence of the conductivity during annealing. These temperature dependencies are shown in Fig. 5 in $\log_{10}$ scale for the different stages of annealing. As can be seen, the ln $\sigma(T)$ dependencies are essentially parallel to each other when $x\leqslant 0.49$. That indicates that the conductivity mechanism is the same in this range of x. Comparison with $\sigma(T)$ of the single-phase films reveals that it is nearly the same as that of the as-deposited amorphous compound but different from that of the crystalline one. Therefore, we can suggest that at the early stages of annealing the NC phase does not contribute to the conductivity of the film being isolated within amorphous matrix by interfacial barriers. In this case the effective film cross section will decrease with an increase in the NC phase content. The measured conductivity of the film is determined by the conductivity of the amorphous phase σ_{am} and effective film cross section A_{am}:

$$\sigma=\sigma_{am}\frac{A_{am}}{A}, \tag{1}$$

$$\ln(\sigma)=\ln\left(\frac{A_{am}}{A}\right)+\ln(\sigma_{am}). \tag{2}$$

The decrease of the first term in Eq. (2) with the decreasing content of the amorphous phase results in the observed behavior of $\sigma(T)$. The composition dependencies $S(x)$ and $\sigma(x)$ (Fig. 3) at the early stages of the annealing are in agreement with this picture. The conductivity decreases with the NC phase content, while $S(x)$ shows a small variation. This is what one would expect from a pure geometrical effect.

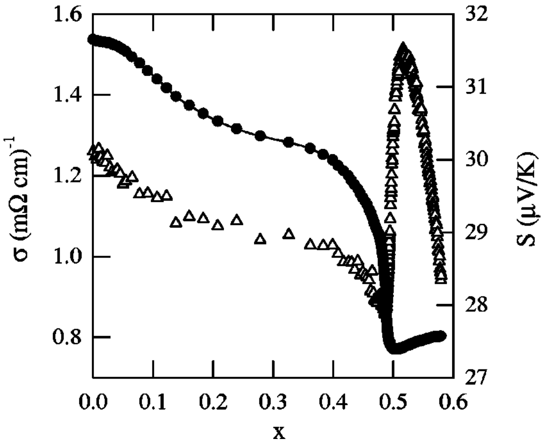

FIG. 4. Conductivity and thermopower of $Re_{0.39}Si_{0.61}$ thin film vs volume fraction of the NC phase: ●: σ at $T=830$ K; △: S at $T=830$ K.

At $x\geqslant 0.5$ the slope of the $\sigma(T)$ dependencies changes. This implies a change in the conductivity mechanism. The dependence of $\sigma(x)$ (Fig. 3) reveals that this change in the conductivity mechanism takes place at the same composition x_c where the conductivity reaches its minimum value. When the content of the NC phase increases beyond x_c, the conductivity increases. This increase suggests that x_c corresponds to the formation of a percolating cluster of the NC phase. The percolation threshold $x_c\approx 0.5$ is a characteristic of granular systems, including, for example, granular thin film Al-Ge composites.[5] Therefore, the Re-Si composites close to x_c can be visualized as the conductive ReSi$_2$ grains within the ‘‘insulating matrix’’ of interfaces and disordered intergrain regions. In contrast to the former granular systems, in the Re-Si composites the conductivity increases on both sides from x_c. If the volume fraction of the NC phase is lower than x_c, the conductivity is higher since the conductive amorphous phase is present. Above x_c the conductivity increases due to the formation and growth of the percolating cluster of the NC phase.

Concerning the interfacial barriers, we believe that the charge carriers trapped in the intergrain regions are mainly responsible for their formation. The mismatches in the band structure of the NC and amorphous phases, which both are narrow-gap semiconductors, should be too small to be effective at temperatures as high as 800 K.

In conclusion, we have found that the transport properties of Re$_{0.34}$Si$_{0.66}$ thin films consisting of amorphous and NC phases do not follow the EMA predictions. On the contrary, both $\sigma(x)$ and $S(x)$ reveal nonmonotonic variation. This implies that the interfaces between the amorphous and NC phases strongly influence the transport properties of the films. Below the percolation threshold, the NC phase is isolated within the amorphous matrix by interfacial barriers and gives only a minor contribution to the conductivity of the film. However, some details in σ and S behavior could not be understood within this simplified picture. One of the open questions is why the thermopower of the composites near the percolation threshold of the NC phase is considerably larger than the thermopower of both the amorphous and of the NC components. More detailed investigations of the compounds are now in progress.

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[1] C. Suryanarayana, Int. Metall. Rev. **40**, 41 (1995).

[2] A. E. Berkowitz, J. R. Mitchell, M. J. Carey, A. P. Young, S. Zhang, F. E. Spada, F. T. Parker, A. Hutten, and G. Thomas, Phys. Rev. Lett. **68**, 3745 (1992).

[3] A. Milner, A. Gerber, B. Groisman, M. Karpovsky, and A. Gladkikh, Phys. Rev. Lett. **76**, 475 (1996).

[4] B. Abeles, Ping Sheng, M. D. Coutts, and Y. Arie, Adv. Phys. **42**, 407 (1975).

[5] G. Hurvits, R. Rosenbaum, and D. S. McLachlan, J. Appl. Phys. **73**, 7441 (1993).

[6] D. J. Bergman and O. Levy, J. Appl. Phys. **70**, 6821 (1991).

[7] T. A. Nguyen Tan, J. Y. Veuillen, P. Muret, S. Kennou, A. Siokou, S. Ladas, F. Lahatra Razafindramisa, and M. Brunel, J. Appl. Phys. **77**, 2514 (1995).

[8] R. G. Long, M. C. Bost, and John E. Mahan, Thin Solid Films **162**, 29 (1988).

[9] O. Laborde, A. Sulpice, U. Gottlieb, and R. Madar, Solid State Commun. **97**, 323 (1996).