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Electrical Conductivity of M–Ge (M = Al, Sc, Y) Films

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Abstract—The microstructure and electrical conductivity of microcrystalline and granular M–Ge (M = Al, Sc, Y) films are studied. The results demonstrate that annealing of amorphous films gives rise to microstructural changes and influences the temperature ranges of different conduction mechanisms. The electrical properties of microcrystalline and granular films are compared.

INTRODUCTION

Aluminum and rare-earth (RE) germanides are ideal materials for the preparation of microcrystalline and granular alloys. The key features of the interaction between the components of such alloys manifest themselves in the structure of thin-film materials [1–3]. The possibility of depositing amorphous germanium and microcrystalline metallic inclusions allows one to tune the physical properties of deposits over a broad range.

The subject of this paper is the effect of annealing time and temperature on the microstructure and properties of microcrystalline and granular M–Ge (M = Al, Sc, Y) films of different compositions. The hop distance and the density of localized states in the films are calculated as a function of deposition conditions.

EXPERIMENTAL

Granular and microcrystalline films were produced by thermal coevaporation in a vacuum of 10^{-3} Pa. As source materials, we used semiconductor-grade germanium, electrolytic aluminum, and extrapure-grade yttrium and scandium. The films were grown on glass-ceramic substrates at room temperature. The deposition rate was varied from 2 to 10 nm/s. Amorphous films were heated in vacuum to 500–520 K and held there until microcrystals appeared (about 15 min). Film thickness, h = 100–200 nm, was determined using an MII-4 microinterferometer. Microstructures were examined on a UEMV-100K electron microscope. The temperature-dependent electrical conductivity of the amorphous and annealed films was measured in a helium cryostat in 5- to 10-K steps using a Shch34 multimeter.

RESULTS AND DISCUSSION

The volume fraction of crystalline phases in the films was determined by electron microscopy. After annealing of the amorphous films at 500–520 K for 15 min, the content of the crystalline phase was 20–25% in the RE–Ge films and 10–15% in the Al–Ge films (Fig. 1). In an earlier study [4], the content of the crystalline phase in 27 wt % Sc + 27 wt % Fe + Ge films annealed at 650 K was determined to be 5–7%. The annealed M–Ge deposits were found to contain metal microcrystals. Crystal growth ceased when a metastable equilibrium between the crystalline and amorphous phases was reached. The structure and size of the microcrystals depended primarily on the metallic component of the alloys. In the RE–Ge deposits, the RE crystallites were distributed at random over the amorphous matrix, and their maximum size did not exceed ≈0.26 μm (Fig. 1a). The Al crystallites in the annealed granular Al–Ge deposits were about 0.1 μm in size (Fig. 1b). Amorphous ternary Ge-based alloys produced by evaporation of separate sources offer a higher thermal stability and lower densities of microcrystals (Fig. 1c, 1d) [4, 5] compared to the M–Ge alloys. The crystallites in the ternary amorphous matrix were found to consist of $ScFeGe_2$, $Sc_4Fe_4Ge_{6.6}$, and $FeGe_2$.

At low temperatures, the electrical conductivity of the microcrystalline RE–Ge deposits varies smoothly, without breaks. Characteristically, the films have a negative temperature coefficient of resistance. This behavior fits well with the Mott–Davis theory of amorphous materials with allowance made for three conduction mechanisms: thermally activated conduction, hopping transport through localized states at band edges, and hopping transport through localized states near the Fermi level (Fig. 2). Annealing slightly increases the low-temperature conductivity and shifts the break in the Arrhenius plot to higher temperatures, which is related to changes in transport properties.

The conductivity of the granular Al–Ge films exhibits Arrhenius behavior, in contrast to that of the microcrystalline RE–Ge deposits (Fig. 2). Compositional variations in the range 62–66 wt % Al have little effect on the conductivity of the Al–Ge films (Fig. 3).

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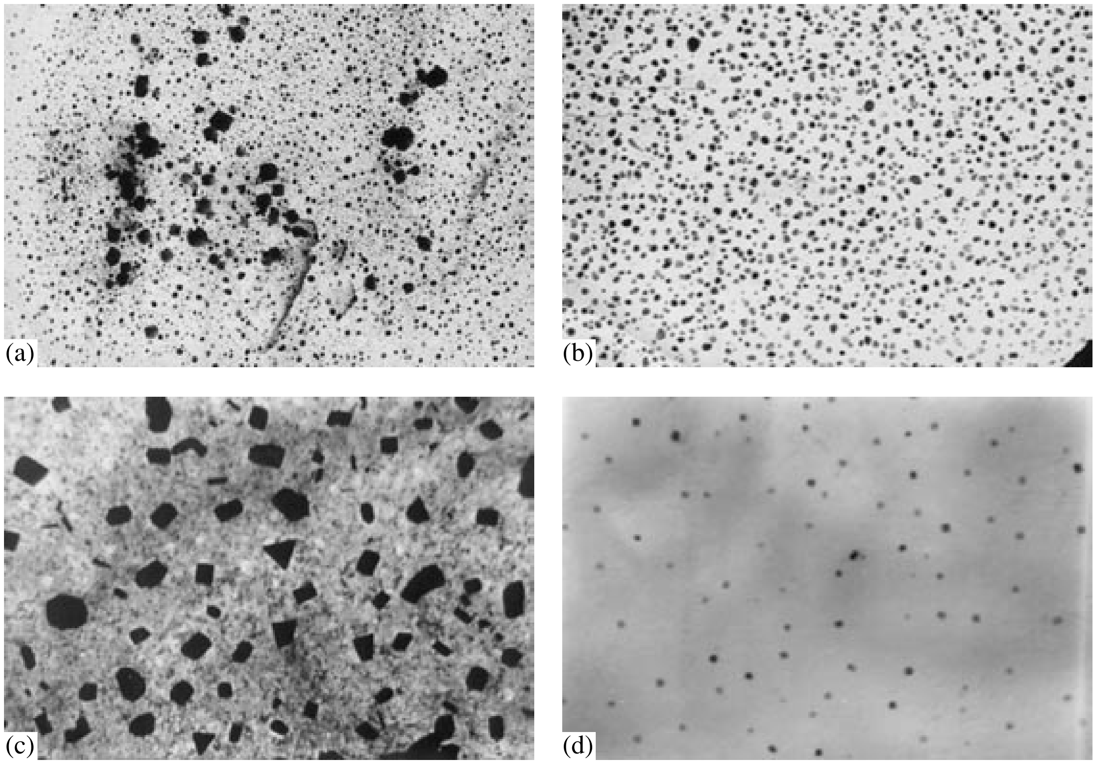

Fig. 1. Electron micrographs of microcrystalline and granular films on glass-ceramic substrates: (a) 15 wt % Y + Ge, annealing at 520 K (15000×); (b) 65 wt % Al + Ge, annealing at 500 K (10000×); (c) 35.5 wt % Fe + Ge, annealing at 520 K (15000×) [5]; (d) 27 wt % Sc + 27 wt % Fe + Ge, annealing at 650 K (19000×) [4].

Using techniques described in [6, 7], we analyzed the conductivity versus temperature data for the films studied here with the aim of determining some parameters of low-temperature electrical transport processes. From the plots of $\ln(\sigma T^{1/2})$ versus $T^{-1/4}$ (Fig. 4), we evaluated σ_0 and T_0 in the Mott formula

$$\sigma = \sigma_0 T^{-1/2}\exp\left(-\frac{T_0}{T}\right)^{1/4},$$

where $T_0 = \dfrac{18\alpha^3}{N(E_F)k}$ and $\sigma_0 = 3e^2\gamma_{ph}\left(\dfrac{N(E_F)}{288\pi\alpha k}\right)^{1/2}$.

This allowed us to estimate the low-temperature hop distance $R = \left(\dfrac{9}{8\pi N(E_F)\alpha kT}\right)^{1/4}$, the transfer energy $W = \dfrac{3}{8\pi R^3 N(E_F)}$, and the Fermi-level density of localized states $N(E_F) = 4.29 \times 10^{50} T_0^{1/2}\dfrac{\sigma_0^3}{\gamma_{ph}^3}$, where γ_{ph} is the frequency factor ($\gamma_{ph} = 10^{13}$), α is the damping constant of the wave function of localized states at the Fermi level ($\alpha = 10^{-7}$ cm), and k is the Boltzmann constant ($k = 8.16 \times 10^{-5}$ eV/K) [7].

In 25 wt % Sc + 25 wt % Fe + Ge films, the conduction mechanism changes from carrier transport through delocalized states to transport through localized states at band edges between 150 and 120 K. In the range 58–47 K, a gradual transition to hopping conduction occurs. The transition to variable range hopping takes place in a very narrow temperature range, between 14 and 11 K, independent of the thermal history of the

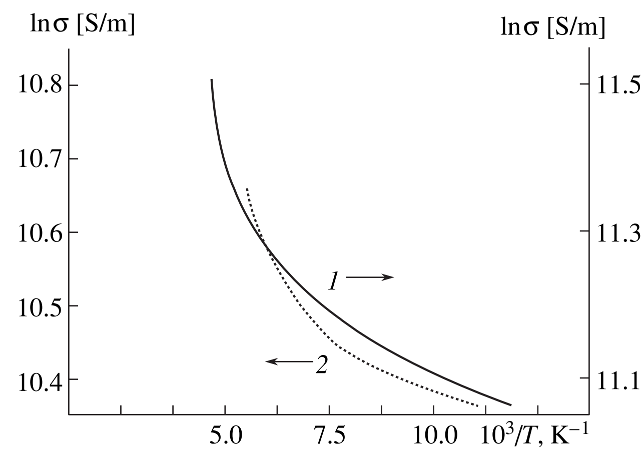

Fig. 2. Arrhenius plots of conductivity for 15 wt % Y + Ge films (*1*) annealed at 500–520 K and (*2*) amorphous.

4.2-K density of states at the Fermi level in amorphous and annealed 27 wt % Sc + 27 wt % Fe + Ge films

Microstructure	T_0, K	σ_0, S $K^{1/2}$/cm	$N(E_F)$, eV^{-1} cm^{-3}	R, Å	W, eV
Amorphous	5.80	9.2×10^3	8.05×10^{23}	10.5	1.28×10^{-4}
Microcrystalline (annealing at 500–520 K for 15 min)	5.69	7.2×10^4	3.81×10^{26}	2.3	2.72×10^{-5}

material (at $T_{ann} < 520$ K). Our results indicate that T_0 depends on film thickness, while σ_0, $N(E_F)$, and W do not (table) [8].

Changes in the Fermi-level density of localized states, hop distance, and transfer energy influence the parameters of low-temperature carrier transport. In the microcrystalline materials prepared by annealing amorphous deposits, the temperature ranges of different conduction mechanisms vary insignificantly. This finding is somewhat surprising since, according to earlier results, increasing the carrier mobility and the density of states related to structural defects at the Fermi level accelerates the transition from carrier transport through delocalized states to transport through localized states at the Fermi level [8]. Note that annealing increases the density of structural defects and dangling bonds in amorphous materials and gives rise to structural ordering, which results in specific microstructures and properties of the resulting films, consisting of nanocrystalline or granular alloys [9, 10].

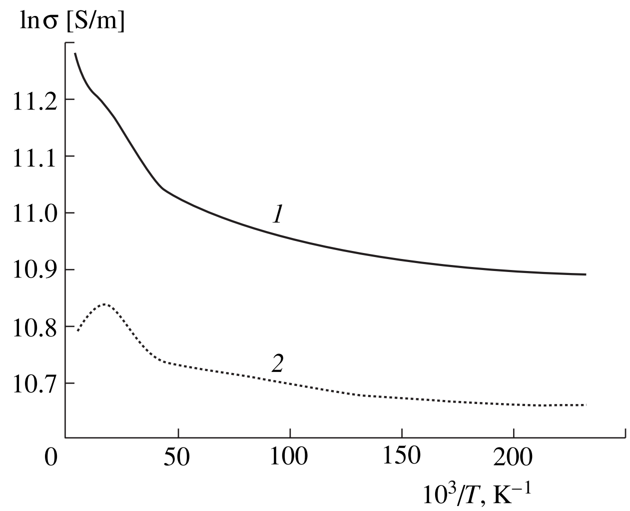

Fig. 3. Arrhenius plots of conductivity for granular ≈65 wt % Al + Ge deposits (*1*) annealed at 520 K for 15 min and (*2*) unannealed.

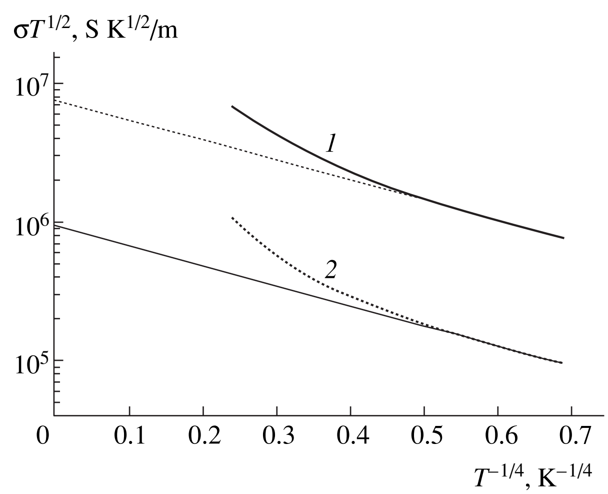

Fig. 4. Plots of $\sigma T^{1/2}$ (on a logarithmic scale) vs. $T^{-1/4}$ for 25 wt % Sc + 25 wt % Fe + Ge films (*1*) annealed at 500–520 K and (*2*) amorphous.

Annealing also influences the parameters of carrier transport in the amorphous Al–Ge deposits. As in the case of RE–Ge films, the effect is stronger for films grown in electric or magnetic fields [11, 12]. The transport parameters are governed by the even distribution of the metallic inclusions, even though their density in the amorphous matrix is rather low.

CONCLUSIONS

The present results on the microstructure and electrical properties of microcrystalline and granular films indicate that precrystallization annealing allows one to produce materials containing metallic nanoparticles embedded in an amorphous semiconductor matrix. The mechanism of microcrystallite nucleation depends on the nature of the components of the alloy, annealing conditions, and deposition procedure. The electrical conductivity of the films is determined by the properties of the amorphous matrix, which undergoes structural changes on heating. The annealing-induced changes in the microstructure and properties of microcrystalline films are more significant than those in granular films.

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