

STRUCTURE AND ELECTRICAL PROPERTIES OF AMORPHOUS Ge—Mo FILMS

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Coevaporated amorphous $\text{Ge}_{1-x}\text{Mo}_x$ films ($0.07 \leq x \leq 0.32$) were investigated by means of electron microscopy, electron and X-ray diffraction and electrical measurements. Inhomogeneity in the Mo concentration has been found only in the samples of high metal content.

Mo causes drastic changes in the ED and XRD patterns of a-Ge. The experimental interference functions for $x \leq 0.22$ are well matched by those calculated on the basis of a structural model for a relaxed a-Ge random network in which the Mo atoms fill part of the empty space.

In the range 80–470 K both samples with $x = 0.07$ and 0.16 display activation energies ΔE 6 times less than those of a-Ge and close to $k_B T$, which is indicative of hopping on high density localized states. Below 80 K for the samples of high Mo content ΔE becomes very small suggesting the presence of metallic regions, which dominate conduction at low T .

Introduction

Cermets, consisting of a metal dispersed on atomic scale into a dielectric matrix, represent a new class of materials of technical interest, their physical properties being still hardly understood. Cermets are stable materials with controllable electrical resistivity ρ and small thermal coefficient of the electrical resistance TCR ($\pm 5 \cdot 10^{-5} \text{ K}^{-1}$). They are good candidates for passive resistors with small TCR in microelectronics. Also, cermets with optimized profiles of the metal concentration are much explored nowadays as absorbers for solar cells. Cermets are usually obtained as thin films, by co-deposition of the components.

The system investigated in the present work represents an alteration of amorphous Ge, which is a reference material in the physics of amorphous semiconductors, by introducing a metal, thereby modifying its electrical properties and its structure. Thus, by lowering the electrical resistivity the range of conduction measurements can be extended below 10 K. Also, the relatively high Debye temperature of Mo (360 K) suggests a slow diffusion of Mo in Ge, without formation of metallic Mo islands. At higher Mo concentrations a superconducting behaviour is expected, Mo having a critical temperature T_c of 0.98 K, while Ge shows no superconductivity at normal pressure.

Preparation

$\text{Ge}_{1-x}\text{Mo}_x$ films with $0.07 \leq x \leq 0.32$ were obtained by coevaporation from two independently controlled sources, under a residual pressure of 1.10^{-4} Pa. Mo was evaporated from an electron gun while Ge from a W filament. The deposition rate was controlled by means of a calibrated photodiode. The composition parameter x was varied by changing the deposition rate of Mo. The films were deposited on fused silica substrates maintained at room temperature, on which Mo electrodes in planar configuration had been deposited. The deposition rate was 6–11 nm/min. Samples for electrical conduction, thermopower and piezoresistance measurements (thickness 80–100 nm), for electron microscopy and diffraction (thickness 30–80 nm) as well as for X-ray diffraction (thickness 0.25–0.6 μm) were deposited at the same time.

Electron microscopy

Electron micrographs of the samples Mo concentrations $x < 0.16$ show a microstructure very similar to that of pure amorphous Ge (Fig. 1) [1]. This means that a quasi-periodic density fluctuation is present in the films which causes a weak phase contrast on the micrographs. The mean period length is 10–15 nm without any remarkable change with composition. The amplitude of these fluctuations, however, becomes higher with increasing Mo content. It can be supposed that in the samples $x \geq 0.22$ fluctuations occur not only in density but also in concentration. Probably Mo-rich regions are formed without any crystalline Mo precipitation, and pointing to increasing separation tendency of two different amorphous phases with increasing metal content.

Electrical properties

Electrical resistance measurements in the wide temperature range 1,9–760 K showed a semiconducting behaviour ($\text{TCR} < 0$) for $x < 0.16$. The electrical properties were described by the variation of the activation energy ΔE with temperature T . The activation energies were calculated from the $\varrho(T)$ data and from the $S(T)$ (thermopower) data by a numerical differentiation program.

The samples with $x = 0.07$ and 0.16 show activation energies of the conduction ΔE_σ smaller by a factor of ≈ 6 as compared to an evaporated a-Ge sample (Fig. 2). For $T > 80$ K ΔE_σ is practically equal to $k_B T$ (k_B is the Boltzmann constant) which is indicative of a hopping conduction mechanism on high density localized states [2]. These states should be attributed to Mo

dispersed on an atomic scale in the a Ge matrix which seems to be a characteristic feature of the cermets [3].

The Mo concentration determines the ΔE_σ values for $T < 80$ K. For $x = 0.07$, ΔE_σ is almost coincident with $k_B T$ while with increasing x ΔE_σ

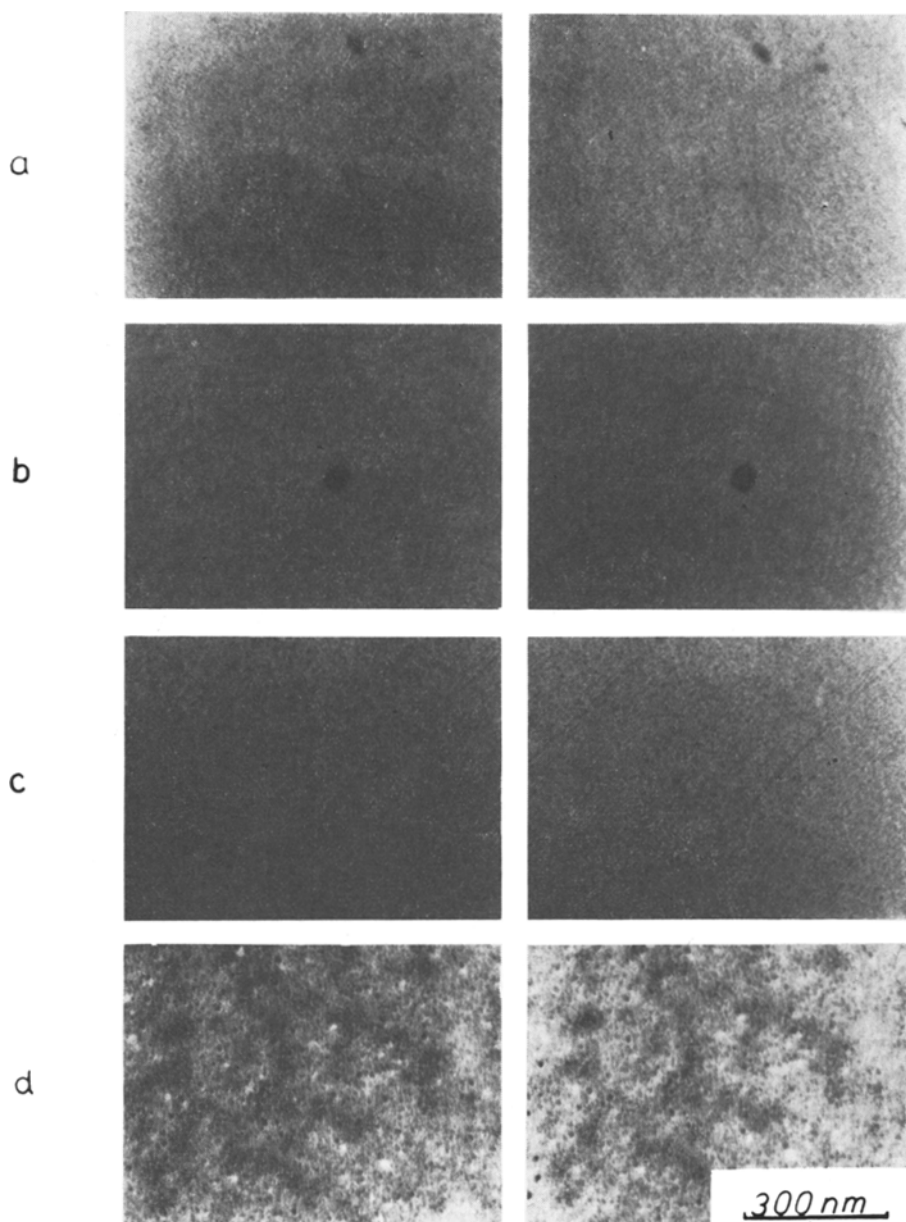


Fig. 1. Electron micrographs of the $\text{Ge}_{1-x}\text{Mo}_x$ samples. Left: focussed. Right: 100 nm under-focussed, a) $x = 0.07$; b) $x = 0.16$; c) $x = 0.22$; d) $x = 0.32$

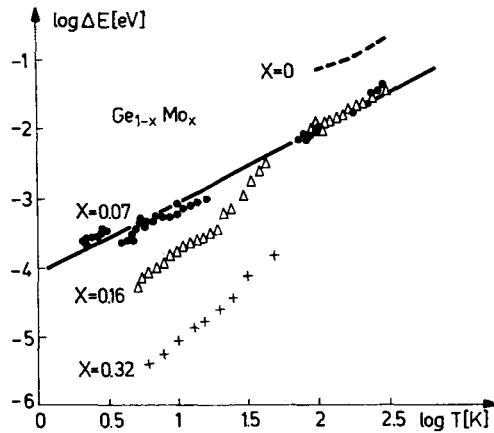


Fig. 2. Activation energy of electrical conduction. Full line: $\log k_B T$

decreases below $k_B T$ (Fig. 2). This fact could be explained by the formation of “filaments” with metallic-type conductivity for $x \geq 0.16$ which take over the electrical transport at low T . These “filaments” must be related to the Mo-rich zones observed by electron microscopy for $x > 0.16$.

The sample with $x = 0.32$ shows a superconducting transition at $T_n = 2.9$ K, which agrees with its metallic-type conduction at very low T ($\text{TCR} \simeq 2 \cdot 10^{-3} \text{ K}^{-1}$ between 3 and 6 K). Piezoresistance measurements also show the metallic character of the conduction increasing with x .

The ΔE_s thermopower activation energies are systematically lower than ΔE_σ . This fact is characteristic for other cermetes too [4] and suggests different mobilities for electrons and holes in the hopping conduction.

Structure

Coevaporated $\text{Ge}_{1-x}\text{Mo}_x$ alloys ($0 \leq x \leq 0.32$) have been found to have an amorphous structure both by electron and X-ray diffraction. A characteristic change in the electron diffraction patterns of the samples with increasing Mo-content are shown in Fig. 3. The trends of these changes are very similar to those observed by NOWAK et al [5] in amorphous Ge—noble metal alloys and suggest changes in the short range order towards metallic coordination of atoms. For a more exact study the diffracted electron intensity was recorded directly and the interference function

$$F(k) = k \cdot \frac{I(k) - \langle f^2 \rangle}{\langle f \rangle^2}, \quad k = 4\pi \frac{\sin \vartheta}{\lambda}$$

has been calculated. Experimental $F(k)$ functions are compared with those calculated from a model in Fig. 4.

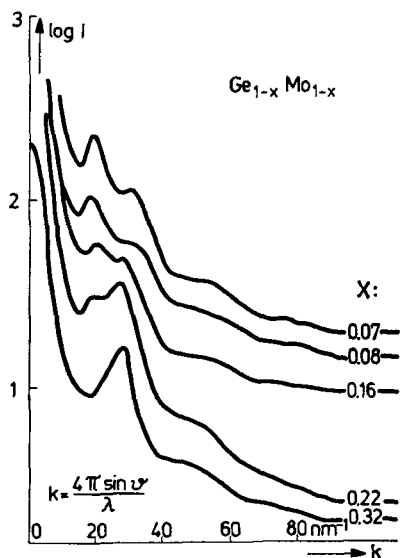


Fig. 3. Densitometric traces of electron diffraction patterns of $\text{Ge}_{1-x}\text{Mo}_x$ films

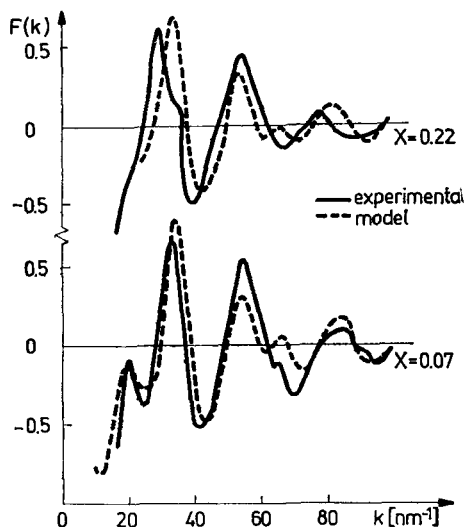


Fig. 4. Reduced interference functions $F(k)$ experimental and model calculated

Structural model for the $\text{Ge}_{1-x}\text{Mo}_x$ system

The structure of a-Ge is correctly represented by spatial models based upon local satisfaction of hybrid sp^3 bonds [6, 7]. These models satisfactorily account for the experimental atomic radial distribution (RDF) and for the diffracted intensity distribution.

A closer examination of such a model reveals much free space. On the basis of the a-Ge density ($\cong 4.92 \text{ g} \cdot \text{cm}^{-3}$) and covalent radius of Ge atom (0.122 nm) this free space can be calculated to comprise about 70% of the total volume. A fraction of it ($\sim 18\%$) is concentrated in zones large enough to accommodate a Mo atom (metallic radius 0.139 nm). The filling of the large zones corresponds to an atomic concentration of Mo $x = 0.22$. This value is remarkably close to the threshold concentration $x = 0.16-0.22$ at which marked changes in the diffraction pattern occur. Threshold concentrations around 0.20 were also noticed in the systems a-Ge-Cu [5] and a-Si-Fe [8].

On the other hand, the Mo solubility in crystalline Ge is unmeasurably small [9] due partly to the Mo being unable to form sp^3 hybrid bonds and to enter substitutionally into the Ge lattice. In a rather crude image we can assume that during the co-deposition the a-Ge network develops preferentially, enclosing the Mo atoms.

On the basis of the above arguments the modelling of the a-Ge-Mo system has been started by placing the Mo atoms in the large free zones of a 155-atoms a-Ge model [6]. In this way one can accommodate up to 22% Mo atoms without Mo-Mo repulsive contacts.

The Mo atoms were initially placed as being tangent to 3 of the Ge atoms bordering a large free zone. On the other hand, this positioning does not correspond to the maximum interaction between Mo and Ge. We assumed for this interaction a Lennard-Jones-type potential

$$V_{\text{GM}} = R^{-12} - AR^{-6},$$

where R is the interatomic distance, $A = 2R_{\text{GM}}^{-6}$ and R_{GM} is the equilibrium distance between Ge and Mo (0.261 nm). The Mo positions were submitted to a minimization program for the bond energy which yielded the energetically most favourable Mo positions.

The atomic pairs distributions were obtained up to $R_{\text{max}} = 2 \text{ nm}$ from the coordinates of the Ge and Mo atoms (Fig. 5). The first-order distances Mo-Ge range between 0.2 and 0.7 nm with a strong maximum at 0.261 nm (sum of the covalent Ge radius and of the metallic Mo radius). The distribution of Mo-Ge distance shows relatively sharp peaks at 0.495 and 0.630 nm too. The distribution of Mo-Mo distances displays broad maxima centred upon 0.49 and 0.75 nm which are characteristic for the topology of the "free space network" complementary to the network of the Ge atoms.

On the basis of the pairs distributions Ge-Ge, Ge-Mo and Mo-Mo the total interference function of the model $F(k)$ was computed. The pairs distributions were previously corrected for the limited size of the model and damped by a Debye-Waller-type factor in order to reduce the cut-off errors. These model interference function were computed for different x ranging between

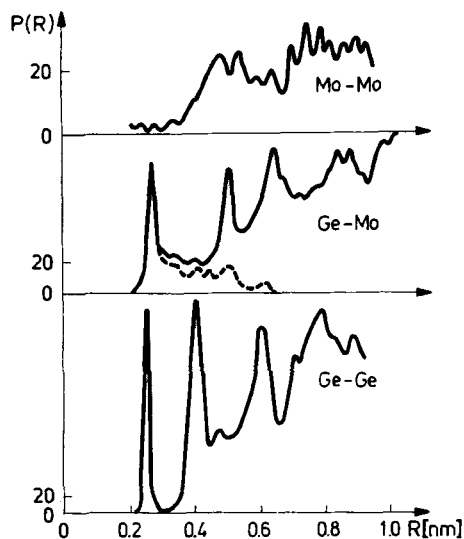


Fig. 5. Model pair density distribution (Ge-network not relaxed)

0.07 and 0.22 and checked against the experimental ones as determined from electron diffraction [1]. They account for the main changes brought about in the $F(k)$ of a-Ge by increasing the Mo concentration (Fig. 4). For example the first maximum at $k = 19.5 \text{ nm}^{-1}$ becomes a broad shoulder for $x = 0.22$. This blurring is due to the smaller concentration of Ge—Ge pairs but also to maxima due to the Mo—Mo pairs (at $k = 9.5$ and 16.2 nm^{-1}) and Ge—Mo pairs at $k = 15 \text{ nm}^{-1}$). This change in the diffracted intensity distribution is similar to and of the same order of magnitude as that noticed in the a-Ge—Au, Cu [5], a-Ge—Fe [10] and a-Si—Fe [8] systems suggesting the similarity of these structures. Characteristic changes show up with increasing x also in the regions $k = 66$ and 82 nm^{-1} in agreement with the experimental $F(k)$'s.

This structural model for the a-Ge—Mo system is a rather crude description of the process of network formation during the codeposition process. A better picture will be obtained by a general relaxation computing procedure including all the interactions between the present atoms. This procedure takes into account the bond stretching and bond-bending potentials of the Ge—Ge bonds as well as a Lennard-Jones potential for the Ge—Mo bonds. It minimizes the corresponding distortion energies E_S , E_B and E_{LJ} related to the distortion of the bond lengths and angles from their equilibrium values.

Preliminary results of this relaxation show that the Ge—Mo interactions distort rather heavily the Ge—Ge distances, thereby increasing E_S while E_B is less enhanced. The effect on the computed $F(k)$ is a shift in the peak at $k = 34 \text{ nm}^{-1}$ towards smaller k improving the agreement with the experiment in this region.

It is worth mentioning that the two constants which enter the Lennard-Jones potential are related to the equilibrium length of the Mo—Ge bond and to its relative strength, respectively. A correct assessment of these constants by an optimal fitting of the experimental $F(k)$'s will give a new and quite important insight into the nature of the metal-semiconductor bond in cermet. This problem is related to the total density and to the energy distribution of the localized levels in the energy gap.

The above described model should be generally valid for all amorphous tetrahedral semiconductor—metal systems with low metal solubility, provided an adjustment of the interaction parameters is made.

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