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1988 Phys. Scr. 38 426

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Influence of the Interface on the Crystallization of Amorphous Ge in Pb/Ge Multilayers*

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Received August 10, 1987; accepted March 22, 1988

Abstract

The amorphous to crystalline phase transition of Ge in contact with Pb has been extensively investigated in Pb/Ge multilayers. We find that the Ge crystallizes at reduced temperatures in the range of 100–200°C depending on the thickness of the Ge and the Pb. Simultaneously the texture of the Pb improves and the layered structure completely disappears. It is suggested that the basis for the reduction of the crystallization temperature is the enhanced diffusion kinetics at the interface, caused by the adjacent Pb layer.

1. Introduction

During the last years metal/semiconductor multilayers have received considerable attention [1]. This has been stimulated by the development of new preparation techniques, the prediction of unusual superconducting properties [2], the study of the melting behaviour in reduced dimensionality [3], etc. We have undertaken a series of experiments in order to investigate the influence of a metallic interface on the crystallization of amorphous Ge. This is a problem of considerable interest for the understanding of fundamental kinetic processes. Moreover, the precise mechanism for the nucleation of a crystalline film starting from an amorphous layer is not well understood [4, 5].

The study of the amorphous–crystalline transition is quite favorable in the Pb/Ge multilayer configuration. This is because (a) the melting and crystallization temperatures of Pb and Ge are well separated [6], (b) there is a minimal interdiffusion between the constituents [6], and (c) the equilibrium thermodynamic phase diagram is eutectic [7] so the formation of compounds does not complicate the studies. Moreover, the multilayer geometry not only provides larger volumes of sample for the X-ray diffraction studies and avoids questions relating to surface contamination and oxidation, but it also provides precise information on the layer thicknesses (from small angle scattering) otherwise not available [1].

We present here extensive measurements on the crystallization of amorphous Ge sandwiched between crystalline Pb, in a multilayer geometry. The results show that far below the crystallization temperature of bulk Ge ($\sim 600^\circ\text{C}$) the a-Ge layers crystallize ($90^\circ\text{C} < T_x < 180^\circ\text{C}$). As a consequence the Pb texture improves and the layered structure breaks up.

* Paper presented at the 7th General Conference of the CMD-EPS, Pisa, 7–10 April 1987.

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The crystallization temperature strongly depends on the individual Ge as well as the Pb layer thickness.

2. Experimental

2.1. Sample preparation and structural analysis

The Pb/Ge multilayers were prepared in a load-locked Molecular Beam Epitaxy (MBE) apparatus equipped with two electron beam guns [8]. The evaporation rates (8 Å/s for Pb, 5 Å/s for Ge) were controlled using a quadrupole mass spectrometer in feedback mode. In this fashion, the evaporation rates could be controlled to better than 5% with a time constant of 3 ms. Pb/Ge multilayers were prepared from 99.999% Pb and 99.9999% Ge starting materials, using a microprocessor controlled shutter, to alternately expose the liquid nitrogen cooled sapphire substrates to the flux of evaporant.

X-ray $\theta - 2\theta$ diffractometer scans were performed in air, Ar atmosphere and vacuum (10^{-6} Torr) on a 2 kW DMax II Rigaku diffractometer, equipped with a high (up to 1500°C) temperature stage which has a control of better than 1°C . The orientation of the sample is such that the scattering vector is always perpendicular to the layers.

From the positions of the peaks of a spectrum taken at small angle X-ray diffraction (SAXD), one can calculate the periodicity of the multilayered structure. Due to dynamic corrections [9] Fourier analysis of the spectrum will not offer useful information about the composition profile. Therefore only qualitative conclusions can be drawn. Fig. 1 shows the SAXD from a Pb/Ge (50 Å/50 Å) multilayer. Up to the 9th order diffraction peaks can be observed, implying that the layered crystalline/amorphous structure is well developed.

We have shown earlier [10] that the thickness variation of the amorphous Ge layer is continuous and of the order of 2 Å and more. This thickness variation limits the perpendicular coherence length to the thickness of one Pb layer. In this way the typical finite size diffraction pattern is observed: one broad peak with secondary fringes. From the FWHM of the central peak (corresponding to the Pb (111) texture) using Scherrer's equation and the positions of the secondary fringes one can calculate the thickness of one Pb layer. The diffraction pattern in Fig. 2, of a Pb/Ge (45 Å/45 Å) multilayer, taken at wide angles clearly shows what has been described above. Since the Ge layer is amorphous no coherent scattering from it is observed.

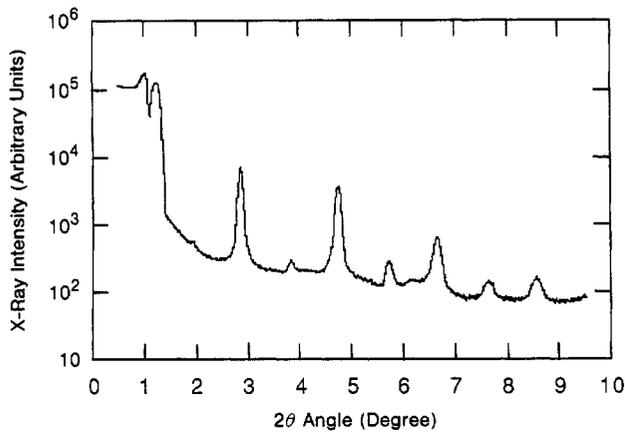


Fig. 1. Small angle diffraction spectrum of a Pb/Ge (50 Å/50 Å) multilayer.

2.2. Crystallization of the amorphous germanium

When heating the sample during the diffraction experiment the a-Ge crystallizes at an extremely low temperature (Fig. 3). Simultaneously, the Pb(111) texture improves and the layered structure disappears. The destruction of the layered structure has not been measured by Willens *et al.* [3] in virtually identical samples. An extended discussion concerning the discrepancy will be published elsewhere [11]. The crystallization temperature T_x is defined as the midpoint of the transition shown in Fig. 3. TEM clearly shows a substantial mass transport during the crystallization, producing a random network of Pb and Ge. It should be pointed out that Debye-Scherrer powder diffraction experiments on heated samples, scraped off the substrate, ruled out the formation of oxides or alloys during heating up to 250°C. All the diffraction lines could be indexed with pure Pb and Ge lattice planes [12].

In order to understand this unusual crystallization behaviour two sets of samples were prepared, one keeping $d_{\text{Pb}} = 50 \text{ \AA}$ and another keeping $d_{\text{Ge}} = 50 \text{ \AA}$. The crystallization was examined by recording the temperature dependence of the Pb(111) peak intensity since its increase always coincides with occurrence of the Ge(111) peak and the signal-to-noise ratio of the Pb(111) peak is much better. The results of this study are summarized in Fig. 4, where the crystallization temperature T_x is plotted as a function of d_{Ge} for constant Pb thickness (Fig. 4a) and d_{Pb} for constant Ge thickness

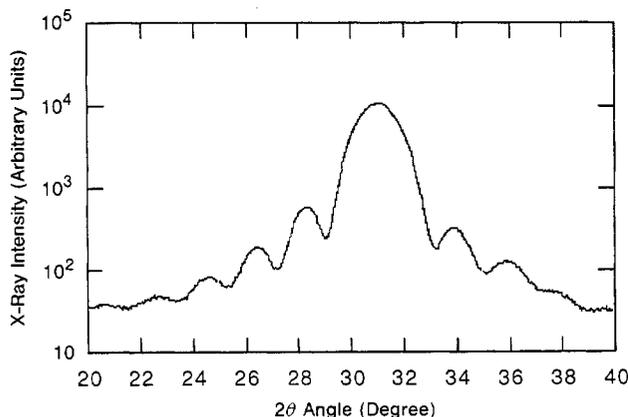


Fig. 2. Wide angle diffraction spectrum of a Pb/Ge (45 Å/45 Å) multilayer. The thickness variation in the a-Ge layers broadens the multilayer reflections in such a way that the coherence is limited by the thickness of one Pb layer.

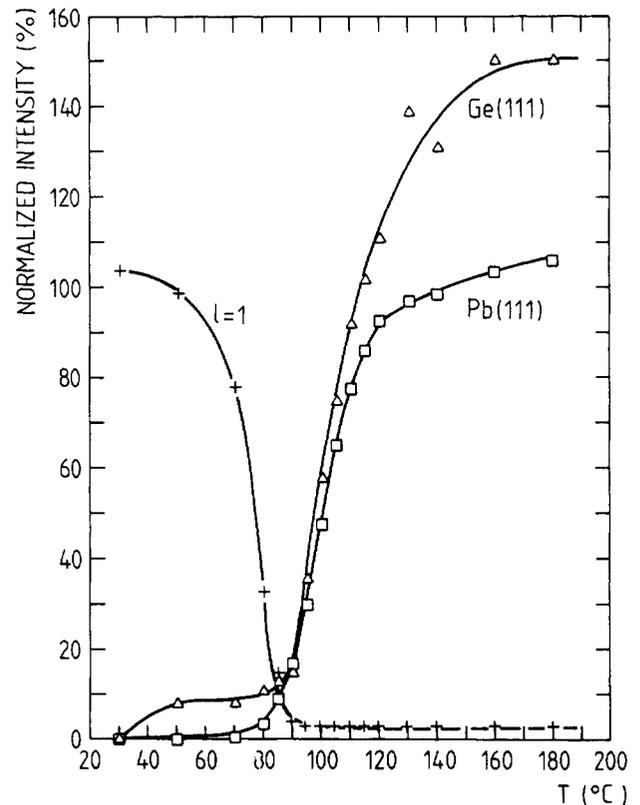


Fig. 3. Evolution of the peak intensity of the first order Bragg peak ($l = 1$) of the multilayered structure, the Pb(111) peak and the Ge(111) peak as a function of temperature. For the $l = 1$ peak the intensity (in percent) is plotted. The normalised Pb(111) and Ge(111) peak intensity is given by $(I(T) - I(0))/I(0)$, with $I(0)$ the intensity at room temperature.

(Fig. 4b). For decreasing Ge thickness T_x clearly goes down whereas for decreasing Pb thickness T_x goes up.

3. Discussion

The crystallization temperature for single a-Ge films ($d > 1000 \text{ \AA}$) was found to be in the range of 350–600°C [13]. In a number of studies [14–16] a-Ge and a-Si was put in contact with a metal (mostly transition and noble metals) and it was found that a relationship exists between T_x and the eutectic phase diagram of Ge, respectively Si and the considered metal. Herd *et al.* [16] concluded from their work that the crystallization is controlled by the kinetics of the diffusion along the metal/semiconductor interface. These kinetics are enhanced due to the decrease of the eutectic temperature, caused by the amorphous semiconductor [17]. No rigorous explanation for this mechanism however was given.

In an extended TEM and ED study [18] about contact reactions between amorphous Si and single-crystal Au films, crystallization was observed at about 100°C, surprisingly low compared with that of about 550°C for an unsupported a-Si film. It was stated by the authors that Au interstitials at the interface weaken the covalent bonds in the a-Si by increasing the number of nearest neighbours Si atoms, thereby lowering the activation energy allowing the diffusion process and the reconstruction of the diamond lattice to take place at this low temperature.

Hiraki *et al.* [19] reported on the metallic state of Si in Si-noble metal vapor-quenched alloys studied by Auger electron spectroscopy. From the observation of two additional peaks at 92 eV and 95 eV in the LVV spectrum of Si replacing

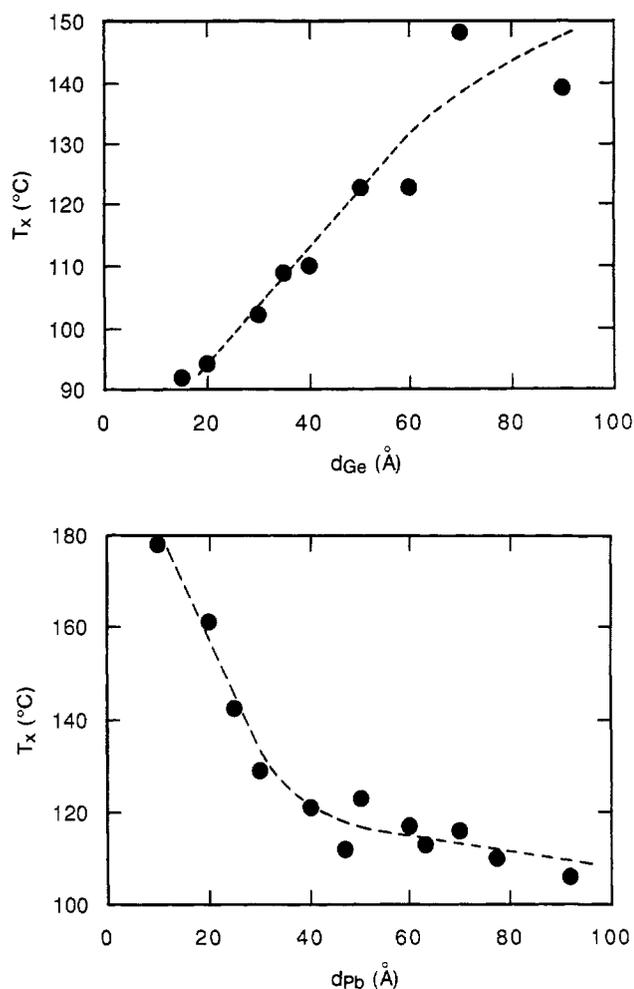


Fig. 4. Dependence of the crystallization temperature T_x on (a) the germanium layer thickness d_{Ge} , keeping $d_{Pb} = 50$ Å and (b) lead thickness d_{Pb} , keeping $d_{Ge} = 50$ Å.

the typical Si Auger peak at 92 eV, it was concluded that the a-Si is metallic when put in contact with Au, thereby supporting the above statement. These two "metallic" peaks were also observed in the Auger spectrum of a-Si/noble metal bi-layers [20].

In view of these observations and the fact that a high density of states near the Fermi level in Ge in Pb/Ge multilayers was observed [21], we believe that the a-Ge in our Pb/Ge multilayers is also metallic, allowing the diffusion to take place at "low" temperatures. Due to the low mutual solubility of Pb and Ge [7] the diffused Ge will precipitate in the Pb crystals.

The thickness dependence of T_x (Fig. 4) can be explained considering that T_x always goes down with increasing d_{Pb}/d_{Ge} ratio. Indeed, for an increasing number of Ge atoms (Fig. 4a) more covalent bonds have to be weakened. This initiates a delay in the diffusion mechanism and therefore an increase in T_x . A higher amount of Pb atoms (Fig. 4b) enhances the free electron density at the interface and increases the number of weakened covalent bonds. Therefore the diffusion starts at a lower temperature and T_x decreases.

4. Conclusion

The present X-ray diffraction study has shown that the crystallization temperature of a-Ge is strongly affected by the presence of a metallic interface. A plausible explanation for the substantially lowered crystallization temperature is the enhanced kinetics of the diffusion at the interface, caused by the metallic-like character of the Ge atoms.

Acknowledgements

We thank M. H. Brodsky, F. Spaepen and M. Van Rossum for useful discussions. This work has been supported by the Belgian Interuniversity Institute for Nuclear Sciences project number 4.0004.80, U.S.D.O.E.-BES-Material Sciences under contract # W-31-109-ENG-38, the Office of Naval Research contract number N00014-83F-0031. International travel was provided by the Belgian National Science Foundation and by NATO grant number RG85-0695.

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