CRYSTALLIZATION AND MELTING IN MULTILAYERED STRUCTURES

W. SEVENHANS, H. VANDERSTRAETEN, J.P. LOCQUET, Y. BRUYNSERAEDE,
Laboratorium voor Vaste Stof-Fysika en Magnetisme, Katholieke Universiteit Leuven, B-3030 Leuven, Belgium
H. HOMMA,
Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439, U.S.A.
IVAN K. SCHULLER
Physics Departement-B019, University of California-San Diego, LaJolla, California 92093, U.S.A.

ABSTRACT

The stability of Pb/Ge and Pb/C multilayers has been studied over a broad temperature range by x-ray diffraction experiments. In the Pb/Ge system an amorphous to microcrystalline phase transformation of the Ge-layers was already observed at $\simeq 100\,^{o}$C. This transition destroys the modulation structure and improves the Pb(111) texture. In the Pb/C multilayers, the layered structure was still present at temperatures higher than the melting temperature of Pb. Contrary to recent publications, no depression of the melting temperature of the two-dimensional Pb layers could be observed.

1 Introduction

Metal/metal and metal/semiconductor multilayers and superlattices have received considerable attention in recent years [1]. This has been motivated by the development of novel preparation techniques which allow microscopic control of the thickness and structure of the layers, and by the prediction of unusual superconducting and magnetic properties [2]. More recently interesting phenomena where predicted and observed in the recrystallization [3] and melting [4] behaviour of those multilayered structures [4,5,6].

Amorphous Si and Ge in contact with certain metals appear to crystallize at temperatures much lower than the usual bulk crystallization temperature [7,8]. The precise mechanism for the nucleation and growth of a crystalline film starting from an amorphous layer is however not well understood.

In an interesting experiment [4] it is claimed that the melting temperature of Pb in Pb/Ge multilayers is suppressed and the transition changes from first to second order as the Pb layer thickness is reduced along the (111) growth direction. Ion-shadowing and blocking measurements [9] reveal a reversible order-disorder transition at the (110) surface of a Pb crystal well below its melting point T_m. This transition is however not present in the Pb (111) surface [10]. The orientation dependence of the degree of positional disorder appears to be directly correlated with the large anisotropy in surface free energy.

In this paper we report on a detailed study of the crystallization of a-Ge and the melting of Pb in Pb/Ge and Pb/C multilayers prepared by electron-beam evaporation. Both phenomena where studied using x-ray diffraction, transmission electron microscopy (TEM) and electron diffraction (ED).

2 Experimental techniques

The Pb/Ge and Pb/C multilayers were condensed on liquid nitrogen cooled sapphire substrates in a load-locked molecular beam epitaxy (MBE) apparatus equipped with two electron beam guns [11]. The evaporation rates were controlled using a quadrupole mass-spectrometer in feedback mode. After warming up to room temperature, the sample was brought into air and cut into pieces of $\simeq \frac{1}{12}$" $\times \frac{1}{2}$" enabling us to carry out different experiments on the same sample.

X-ray diffraction measurements were performed in air and vacuum (10^{-6} Torr) on a Rigaku Dmax II diffractometer (2 kW Cu K_α x-ray gun) equipped with a high-temperature stage. The

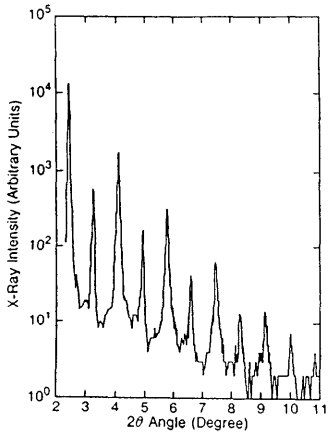

Figure 1: Small angle x-ray diffraction from a Pb (50Å)/Ge (50Å) multilayer. The fact that the even order peaks are smaller in intensity than the odd order ones shows that the modulation is almost square with minimal interdiffusion.

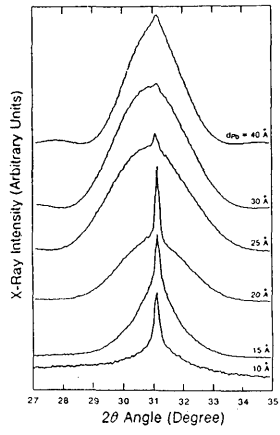

Figure 2: Evolution of the Pb (111) diffraction peak for different thicknesses of Pb in Pb/Ge(50Å) multilayers. For $d_{Pb} \geq$ 30Å, a typical broad peak shows up.

crystallinity and purity of the layers was checked by independent Debye-Scherrer measurements on samples scraped off the substrate. Transverse cross-sections for TEM and ED were prepared using standard thinning techniques. TEM and ED were performed on a Jeol 100 CX electron microscope equipped with high temperature capabilities.

3 Results and discussion

3.1 Initial structure

The multilayers are examined by $\theta - 2\theta$ small angle x-ray diffraction revealing the well developed layered structure, as shown in Fig. 1. The presence of a large number of small angle peaks clearly illustrates the quality of the resulting multilayer. At wide angles, no high order multilayer reflections [1] could be observed. Instead, a broad peak corresponding to the Pb (111) texture as well as secondary fringes were visible. As reported earlier [12] the wide angle spectrum is due to continuous thickness variation (interface roughness) of the amorphous Ge which limits the perpendicular coherence length to the thickness of an individual Pb layer. The evolution of the wide angle x-ray spectrum with Pb layer thickness is illustrated in Fig. 2. The smaller the individual Pb layer thickness the wider the Pb (111) peak becomes. The sharp peak on top of the broad one originates from the edge of the sample where the Pb layers can connect. This hypothesis was checked by removing the edges photolitographically.

3.2 Crystallization

After an examination at ambient temperature the substrate is heated while the small and wide angle x-ray scans are recorded. Far below the melting temperature of Pb, the a-Ge crystallizes, the Pb texture improves and the layered structure disappears [13]. The latter is clearly illustrated in Fig. 3 where the intensity of the first three observed small angle peaks of a Pb/Ge (49Å/59Å) multilayer is plotted versus substrate temperature.

To what extent the layered structure is destroyed is shown in Fig. 4. At room temperature the layered structure is clearly visible in the transmission electron micrograph (Fig. 4a) taken

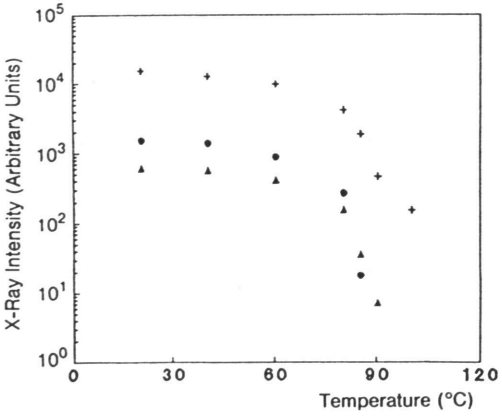

Figure 3: Evolution of the intensity of the first three observed (+ l3, △ l4, • l5) small angle peaks of a Pb/Ge (49Å/59Å) multilayer as a function of temperature by keeping a fixed temperature for 5 minutes.

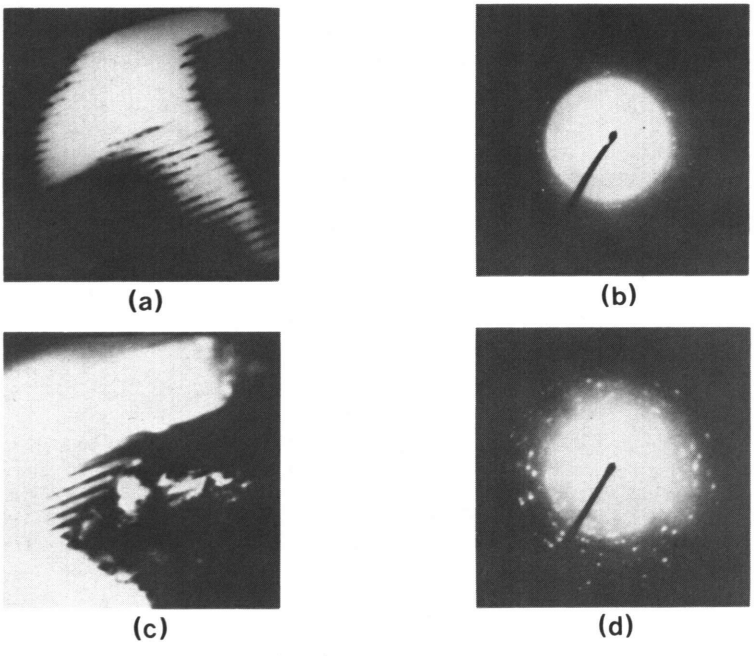

Figure 4: a) TEM of a Pb/Ge(120Å/80Å) multilayer clearly showing the layered structure. b) ED showing Pb (111) crystalline spots with no trace of crystalline Ge. c) TEM picture of the sample shown in a) after annealing. Note that the layered structure is absent. d) ED of the annealed sample showing crystalline Ge spots.

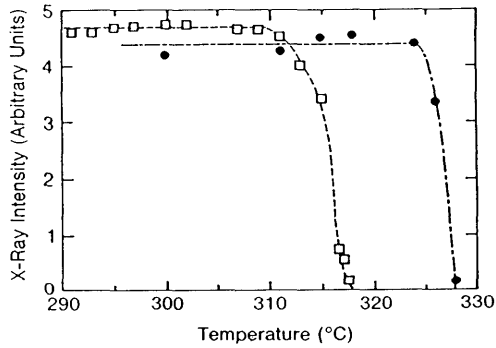

Figure 5: Pb (111) x-ray peak intensity as a function of temperature (by staying at a particular temperature for 5 minutes) for a Pb/Ge (25Å/50Å) multilayer near the Pb melting point. Data were taken in air (open squares) and in vacuum (closed circles).

from a transverse cross section of a Pb/Ge (120Å/80Å) multilayer. Moreover, no trace of crystalline Ge next to the Pb (111) spots shows up in the electron diffraction picture (Fig. 4b). During annealing the layered structure disappears (Fig. 4c) and crystalline spots of the Ge are showing up (Fig. 4d). This behaviour is seen in all the examined Pb/Ge multilayers. The temperature T_x at which the crystallization of the a-Ge occurs increases with increasing Ge layer thickness and decreases with decreasing Pb layer thickness [13]. A direct relationship between the crystallization temperature and the initial mosaic spread regardless of the Pb and Ge layer thickness was also found. The latter suggest that the crystallization is driven by the interface structure. Another explanation for the extreme low crystallization temperature and its functional behaviour with varying Pb and Ge layer thickness may be the enhanced kinetics of diffusion at the metal/semiconductor interface [14]. In the Pb/C multilayer no phase transformation was observed below the melting temperature T_m of bulk Pb.

3.3 Melting

According to Willens et al. [4] the onset of the melting of Pb in Pb/Ge multilayers decreases significantly and the transition becomes second order as the Pb layer thickness is decreased. This is in agreement with theoretical predictions [3]. The melting experiments conducted on our Pb/Ge multilayers, prepared in a similar way, however do not show any behaviour of that kind i.e. the melting transition of the Pb in these multilayers is very sharp (Fig. 5) and the melting temperature corresponds within 2 °C to the value of bulk Pb. This is not suprising in view of the fact that the multilayer is destroyed (Fig. 4c) at a temperature much lower than T_m. Indeed, as the layered structure disappears, the broad Pb (111) diffraction peak sharpens drastically [14] indicating that the crystal dimension of the Pb in the multilayer growth direction increases dramatically (a factor of 50 for the thinnest Pb layers). Therefore, no two dimensional melting behaviour of Pb can be expected in these multilayers.

A reasonable explanation can be given for these contradicting results. The melting of the Pb is in both cases measured by monitoring the decrease of the Pb (111) diffraction peak intensity. This intensity decrease may however be induced by other mechanisms.

Indeed, alloying of Pb and Ge as well as oxidation of Pb results in an intensity drop of the Pb (111) diffraction peak due to the fact that the amount of pure Pb decreases. Since Pb and Ge do not alloy in the bulk [15] we performed the melting experiments in air to allow oxidation. A decrease of T_m as reported in [4] was indeed observed. A typical transition of the Pb (111) peak of a Pb/Ge (20Å/50Å) multilayer heated in air is shown in Fig. 5. Additional Debye-Scherrer powder diffraction experiments on samples scraped off the substrate clearly showed that Pb

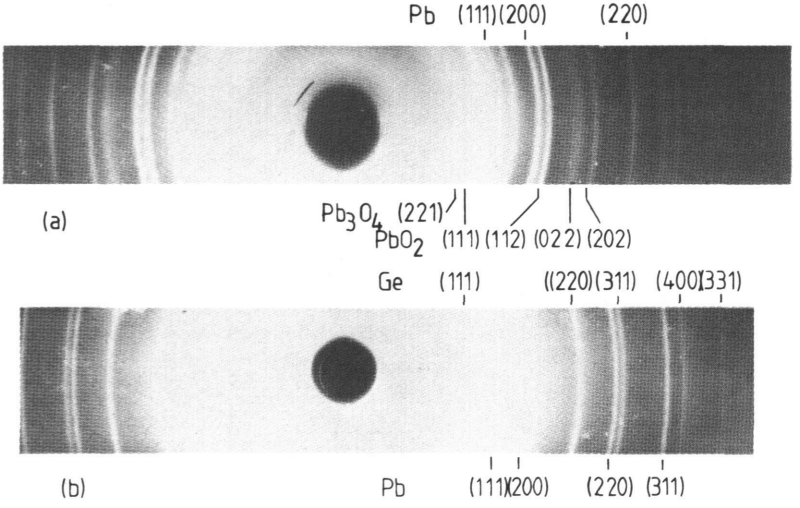

Figure 6: Debye-Scherrer powder diffraction pattern of a Pb/Ge multilayer heated in a) air; the Pb-oxides are clearly visible. b) vacuum; no oxides are visible.

oxidizes when the multilayer is heated in air (Fig. 6a), whereas only pure Pb and Ge was found when heated in vacuum (Fig. 6b).

Destruction of the multilayered structure due to crystallization does not occur in Pb/C multilayers. Partly due to the very large difference of the melting temperature of Pb and the sublimation temperature of C the quality of the Pb/C multilayers was not as good as that of the Pb/Ge multilayers. Nevertheless, very interesting results were obtained. Whereas in Pb/Ge multilayers the layers were destroyed far below the melting temperature of Pb they clearly survived in the Pb/C multilayers even far beyond the melting temperature of Pb. In Fig. 7 the intensity of the Pb (111) as well as the second and third order (l=2, 3) multilayer diffraction peaks versus temperature is shown for a Pb/C (25Å/46Å) multilayer. Again a sharp transition in the Pb (111) intensity is noticed at 328 °C, indicating the absence of two-dimensional melting

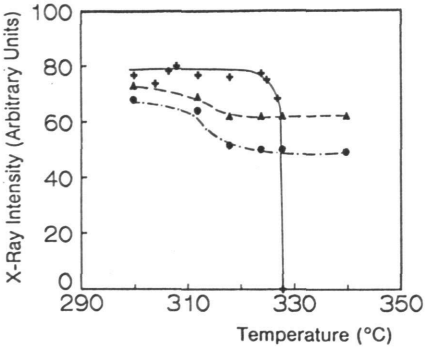

Figure 7: Evolution of the intensity of the Pb (111) and the second and third order small angle diffraction peaks (+ Pb(111), △ l2, • l3) as a function of the temperature.

effects. This is in accordance with the experiment of Frenken and VanderVeen [6,9]. However, after the Pb was melted the second and third order multilayer peaks only dropped to 60 % of its initial value, indicating that the liquid Pb and solid C is still stacked in layers, even up to 340 °C. To our knowledge, this has never been observed before. Moreover, when the multilayer was cooled to room temperature its intensity recovered to $\simeq$ 80% of its initial value.

4 Conclusions

The amorphous to crystalline phase transition of Ge in Pb/Ge multilayers was extensively studied. It is shown that the crystallization temperature decreases with decreasing amorphous Ge thickness and increases with decreasing thickness of the metallic component. Due to the broken up structure of the Pb/Ge multilayers at T > 200°C, no two-dimensional melting was observed. The layered structure survived in Pb/C multilayers far beyond the melting temperature of Pb. The sharp transition in the Pb(111) intensity at 328 °C indicates the absence of two-dimensional melting effects down to Pb thicknesses of 20Å.

Acknowledgements

This work was supported by the Office of Naval Research contract number N00014-83-F-0031, the U.S. Departement of Energy, under contract number W-31-109-ENG-38 (at ANL), and DE-FG03-87ER45332 (at UCSD), and the Inter-University Institute for Nuclear Sciences (I.I.K.W.). International travel was provided by NATO grant number RG85-0695. H. Vanderstraeten and J.P. Locquet are Research Fellows of the I.I.K.W.

References

[1] For a recent review see Synthetic Modulated Structures, edited by L.L. Chang and B.C. Giessen (Academic Press, New York, 1985)

[2] D. Allenda, J. Bray and J. Bardeen, Phys. Rev. B **7**, 1020 (1973)

[3] J.M. Kosterlitz and D.J. Thouless, J. Phys. C **6**, 118 (1973), J. Phys. C **7**, 1046 (1974)

[4] R.H. Willens, A. Kornblit, L.R. Testardi and S. Nakahara, Phys. Rev. B **25**, 290 (1982)

[5] G. Devaud and R.H. Willens, Phys. Rev. Lett. **57**, 2683 (1986)

[6] J.W.M. Frenken and J.F. van der Veen, Phys. Rev. Lett. **54**, 134 (1985)

[7] T. Oki, Y. Ogawa and Y. Tujiki, Japan. J. Appl. Phys. **8**,1056 (1969)

[8] S.R. Herd, P. Chaudhari and M.H. Brodsky, J. Non-Cryst. Solids **7**, 309 (1972)

[9] J.W.M. Frenken, P.M.J. Marée and J.F. van der Veen, Phys. Rev. B **3**, 7506 (1986)

[10] J.F. van der Veen, Proc. of the 18th CMD of the EPS, Pisa (1987)

[11] W. Sevenhans, J.P. Locquet and Y. Bruynseraede, Rev. Sci. Instrum. **57**, 937 (1986)

[12] W. Sevenhans, M. Gijs, Y. Bruynseraede, H. Homma and I.K. Schuller, Phys. Rev. B **34**, 5955 (1986)

[13] H. Homma, I.K. Schuller, W. Sevenhans and Y. Bruynseraede, Appl. Phys. Lett. **50**, 594 (1987)

[14] W. Sevenhans, J.P. Locquet, Y. Bruynseraede, H. Homma and I.K. Schuller, to be published

[15] M. Hansen, Constitution of Binary Alloys, (McGraw-Hill, New York, 1958) and supplements