Interfacially initiated crystallization in amorphous germanium films

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The amorphous to microcrystalline phase transition of Ge in Pb/Ge multilayers has been extensively studied. During crystallization, the x-ray diffraction peaks of the modulated structure disappear and the Pb texture improves. It is shown that the crystallization temperature decreases with decreasing amorphous Ge thickness and is strongly affected by the texture of the metallic component. These results imply that the crystallization is interfacially initiated.

The crystallization of amorphous semiconductors is a problem of considerable interest for the understanding of fundamental kinetic processes as well as in many applications, such as solar cells and multilayer mirrors, that are subject to thermal cycling. The precise mechanism for the nucleation and growth of a crystalline film starting from an amorphous layer is, however, not well understood.[1,2]

Earlier studies on the crystallization of amorphous Ge films have concentrated on (a) single films[3] ($d > 1000$ Å) for which crystallization has been found to occur in the range of 350–600 °C, (b) Ge films in contact with a variety of metals (mostly transition and noble)[4] which exhibit a eutectic equilibrium binary phase diagram. In this case, for a fixed film thickness, a correlation was found between the crystallization and eutectic temperatures, (c) Ge films in Ge/Pb multilayers which were prepared for the study of the melting behavior of Pb.[5] In this case it was noticed that the Ge crystallizes in the temperature range of 135–180 °C; however, no detailed studies were presented.

The study of the temperature stability of an amorphous semiconductor in contact with a metal 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 binary 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.[8]

We present here extensive measurements on the crystallization of amorphous Ge sandwiched between crystalline Pb, in a multilayer geometry. The results show that as the temperature increases the Ge layer crystallizes ($90\,°C < T_x < 180\,°C$) producing roughness at the interface and improved Pb texture. As a consequence, the layered structure disappears due to the massive transport of Ge and Pb atoms, initiated by the Ge crystallization. This is confirmed by the transmission electron microscopy (TEM) study in this system. The results show that the crystallization is interfacially initiated and it is strongly affected by the texture of the metallic component.

The Pb/Ge multilayers were prepared on liquid nitrogen cooled sapphire substrates in an ultrahigh vacuum molecular beam epitaxy (MBE) apparatus equipped with two electron beam gun evaporators. The evaporation rate was controlled to better then 5% accuracy with a time constant of 3 ms using a mass spectrometer in feedback mode.[9] The x-ray measurements were performed on a Rigaku DMax II diffractometer with a 2-kW Cu K_α x-ray gun equipped with a high-temperature stage capable of measurements up to 1500 °C and a control of better than 1 °C.

The high quality of the layered structure was confirmed by the existence of up to 13 low angle multilayer peaks, by the fact that the even order peaks were of lower intensity than the odd ones in equal layer thickness case (see Fig. 1) and the appearance of finite size limited secondary diffraction peaks. At high angles one peak accompanied by secondary fringes was observed given by the incoherent scattering from the finite size limited individual Pb layers. This also indicates that the thickness of the individual Pb layers is constant across the whole multilayer stack. The broadening

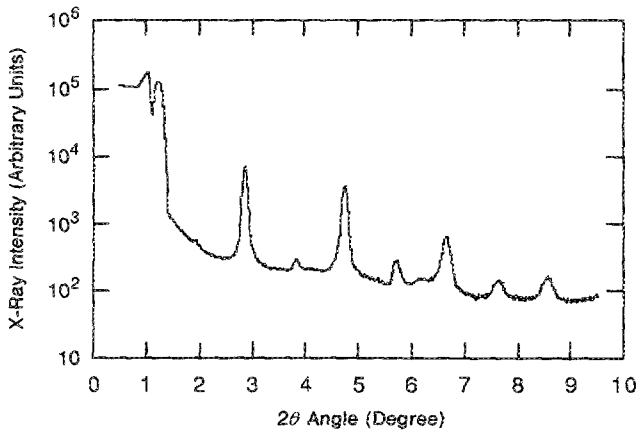

FIG. 1. Small angle x-ray diffraction from a Pb (50 Å)/Ge (50 Å) multilayer. The fact that the even order peaks are smaller in intensity than the odd order ones shows that the modulation is square with minimal interdiffusion.

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of the high angle multilayer peaks[10] has been earlier related to the thickness variation ("cumulative disorder") of the amorphous Ge layers.[11]

The Pb (111) texture is considerably affected by the thickness of the constituents. Figure 2 shows the Pb (111) mosaic-spread angle, $\Delta\omega$ (full width at half-maximum) as a function of d_{Pb} for $d_{Ge} = 50$ Å and as a function of d_{Ge} for $d_{Pb} = 50$ Å, respectively. As expected, the thicker the Pb film is (keeping the germanium thickness constant), the smaller $\Delta\omega$, i.e., the higher the texture (solid circles in Fig. 2). On the other hand, however, for fixed Pb thickness $\Delta\omega$ is almost constant showing that the Ge film does not strongly affect the texture of the Pb film. These results are very important for the present studies since they clearly show that the texture of the metallic component can be varied in a systematic, reproducible way by simply changing the layer thickness. As we shall show below, this has a drastic effect on the crystallization temperature.

The study of the crystallization has been performed by monitoring at the same time the Pb (111), the Ge (111), and the multilayer peaks as a function of temperature in a large number of samples. Figure 3 shows the intensity of the Pb (111), Ge (111), and the fourth order small angle peaks from a Pb (45 Å)/Ge (50 Å) multilayer as a function of temperature. Each one of the data points was measured after 5 min at the particular temperature. For this sample below 90 °C the Ge remains amorphous as indicated by the presence of a broad x-ray diffraction peak around the Ge (111) spacing. As the fourth order small angle peak is dropping in intensity, both the Pb (111) and the Ge (111) peaks are dramatically growing starting around 90 °C. This shows that as the Ge layer crystallizes, the Pb (111) texture improves and the layer structure is destroyed. The improvement in the Pb (111) texture might be expected if an epitaxial relationship exists at the interface, i.e., as the Ge crystallizes it acts as a "template" for the rearrangement of the Pb into a better texture. We confirmed that the appearance of the Ge (111) peak is always accompanied by an increase in the intensity of the Pb (111) peak and the disappearance of small angle

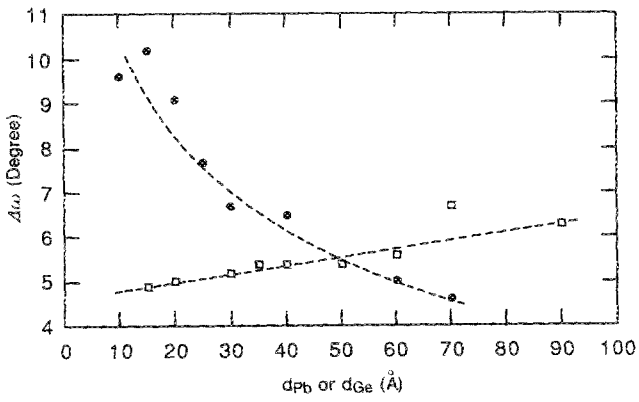

FIG. 2. Mosaic-spread angle $\Delta\omega$ for the Pb (111) peak as a function of (a) d_{Pb} with $d_{Ge} = 50$ Å (solid circles) and d_{Ge} with $d_{Pb} = 50$ Å (open squares).

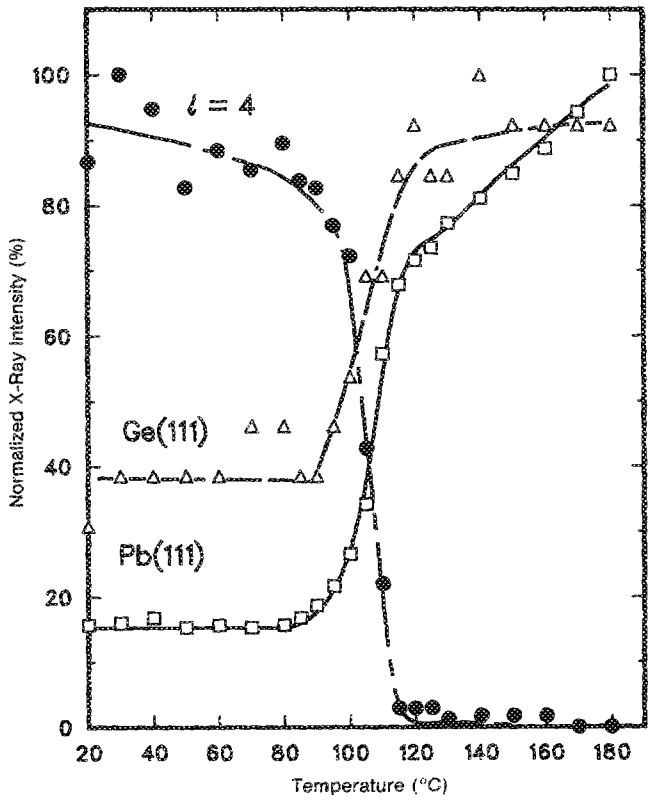

FIG. 3. X-ray intensity for the fourth order multilayer reflection ($l = 4$), the Pb (111) and the Ge (111) peaks in Pb (40 Å)/Ge (50 Å) superlattice. The lines are guides to the eye.

modulation peaks. These measurements and conclusions were also confirmed by independent transmission electron microscopy (TEM) and electron diffraction (ED) measurements. Details of these measurements will be the subject of a later publication.

In order to study the behavior of the crystallization temperature T_x (determined from the midpoint of the transition) as a function of layer thickness, we measured the Pb (111) peak for a series of Pb (50 Å)/Ge (variable thickness) and Pb (variable thickness)/Ge (50 Å) multilayers as a function of temperature. The Pb (111) diffraction peak was used to monitor the recrystallization phenomenon since it had a much higher intensity than the Ge (111) and therefore gave more accurate values of T_x. The change of crystallization temperature of the Ge keeping the Pb *texture* constant (by keeping the Pb *thickness* constant) is shown in Fig. 4. The increase of T_x with increasing Ge thickness is due to the fact that the "interface induced" crystallization is easier in thinner Ge layers. The change of T_x with changing Pb texture (i.e., $\Delta\omega$) is quite striking as shown in Fig. 5. T_x increases dramatically with increasing Pb (111) rocking curve width, i.e., the higher the texture is, the lower the crystallization temperature. This is exactly what one might expect if the crystallization is interfacially initiated. Since the Pb acts as a "template" for the Ge, an improved texture of the Pb facilitates the Ge crystallization and therefore lowers the crystallization temperature. At this stage, unfortunately,

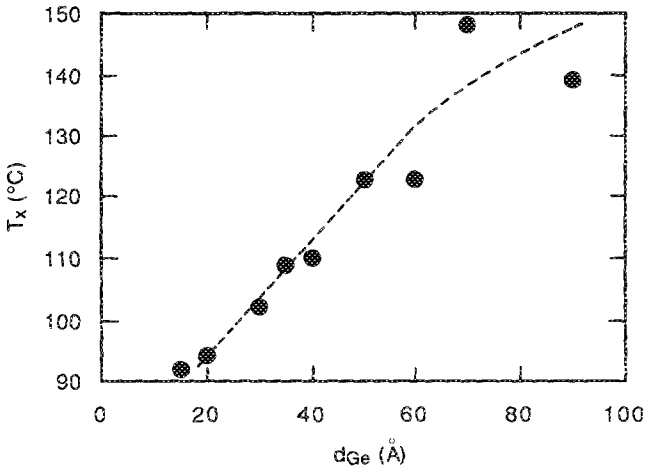

FIG. 4. Crystallization temperature T_x as a function of Ge thickness, d_{Ge} keeping $d_{Pb} = 50$ Å. Note that in this case the Pb (111) texture remains almost constant (see Fig. 2).

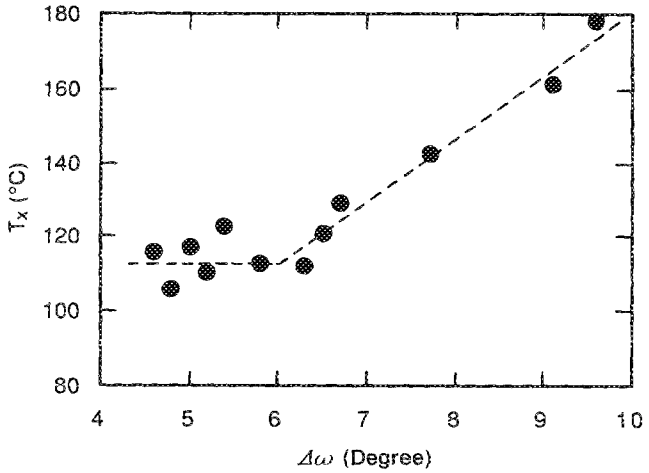

FIG. 5. Crystallization temperature T_x as a function of Pb (111) mosaic-spread angle $\Delta\omega$ for constant $d_{Ge} = 50$ Å.

it is impossible to uniquely ascertain whether the change in texture of the thickness of Pb is the main driving force. Further experiments, to change independently $\Delta\omega$ from d_{Pb}, perhaps by different growth conditions might clarify this issue. On the other hand, if the crystallization is interfacially initiated, clearly the change in texture is the relevant quantity, not the Pb thickness.

In summary, we have shown that the crystallization of a thin amorphous Ge film sandwiched between Pb layers depends on the thickness of the Ge and that the crystallinity or texture of the metal component strongly influences the crystallization temperature. These facts are consistent with the idea that the crystallization is interfacially initiated. It is reasonable to assume that these statements have a more general validity and they apply to many other crystalline-metal amorphous-semiconductor sandwiches.

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