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Glancing Angle X-ray Study of Crystallization of Amorphous Ge at the Ge-Al Interface

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ABSTRACT

The amorphous to crystalline transformation of Ge in Al/Ge thin film couples has been studied using glancing angle EXAFS, x-ray reflectivity and diffraction. It was found that crystallization occurs at a much lower temperature (118-150 °C) than for bulk Ge, and initiates at the Al/Ge interface. X-ray diffraction studies were made at 152 °C to study the kinetics of the reaction. After an initial period we find good agreement with a square root dependence of the time, characteristic of a diffusion limited reaction.

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INTRODUCTION

The crystallization of amorphous Ge and Si received considerable attention about 20 years ago when it was discovered that the crystallization temperature depended strongly on the contact metal[1-5]. In the absence of a metal contact amorphous Ge crystallizes at temperatures of at least 300 °C, while when in contact with, for example, Al the temperature is reduced to ~120 °C. When studies of a variety of metals were carried out, the crystallization temperature was found to be strongly correlated with the Ge-metal eutectic temperature[1, 2]. Crystallization occurred at a temperature of about 0.65 that of the eutectic temperature. Since bulk diffusion generally becomes significant at temperatures near 0.6-0.7 of melting the results are suggestive that interface diffusion is enhanced by the metal-Ge mixing, allowing sufficient mobility for crystallization. However, recent work on Pb-Ge multilayers[6] showed that the situation may be more complex. For this case the crystallization temperature also varied with the thickness of the Pb layers, and it was suggested that the metal layers are modifying the electronic nature of the a-Ge making it more metallic. The resultant weakening of the covalent bonding allows diffusion to take place at lower temperatures. In this picture, increasing the thickness of the metal layers increases the number of free electrons available for weakening the covalent bonds. Also of interest is recent work on a-Si which showed that the solubility of various metals is enhanced, and that the metal atoms concentrate ahead of the crystallization front analogous to zone refining at the solid liquid interface of growing crystals.[7]

In this paper we present some preliminary efforts at using glancing angle x-ray techniques to gain insight into this problem. The techniques used are glancing angle x-ray diffraction, reflectivity and EXAFS. Glancing angle diffraction has sufficient sensitivity to monitor the crystallization of thin layers in order to study the kinetics of the crystallization process, and we have also employed glancing angle x-ray reflectivity and EXAFS measurements[8,9] to look in detail at the initial stage of the crystallization process.

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EXPERIMENTAL

The samples were prepared by electron beam evaporation in a liquid-nitrogen-trapped diffusion-pumped system with a base pressure of 5×10^{-8} torr. Fused quartz substrates were used, and both the Ge and Al films were about 1000Å thick, with the Al on top. The reflectivity and EXAFS measurements were made at beamline X-11A at the National Synchrotron Light Source using a double crystal Si(111) monochrometer. Reflectivity measurements were made at energies of 300 eV above and below the Ge K-edge (11104 eV), and the EXAFS measurements were made at angles slightly above the Al critical angle to enhance the interface sensitivity. The diffraction measurements were made at beamline X-11B using a modified Phillips goniometer with a vacuum heating stage. The detector was an INEL 120° position sensitive detector which allowed a complete diffraction pattern to be acquired in about 15 min, even though the count rates in the strongest peaks were only a few counts/sec.

For the EXAFS and reflectivity measurements the samples were annealed at successively higher temperatures for 5 minutes, and the data taken at room temperature. Both measurements showed no change up to 110 °C, and significant reaction at 118 °C. A comparison of the unannealed and 118 °C annealed data is shown in figures 1 and 2. With annealing the reflectivity oscillations become less distinct, indicating that the interface is being disrupted. The EXAFS is sensitive to the crystallinity of Ge by changes in the amplitude of the second shell of atoms. Figure 2 shows the Fourier transformed EXAFS data. The peak near 3.5 Å is due to the second shell, and is seen to grow for the 118 °C annealed sample. For the EXAFS there is some distortion of the amplitude due to anomalous dispersion affects at glancing angles [7], but the qualitative features are preserved. EXAFS measurements were also made at larger angles (3 degrees) to probe the entire depth of the Ge layer. This data looked the same as the unannealed sample indicating only a thin layer (estimated to be ≤ 100Å) near the interface has crystallized. Subsequent

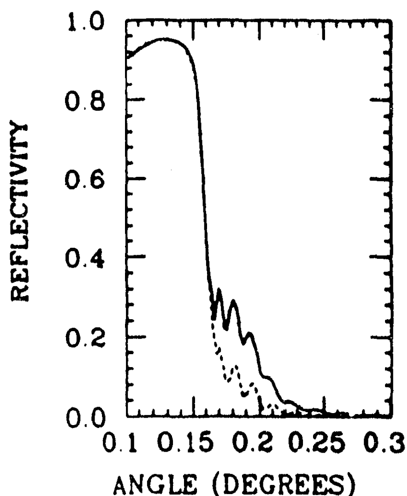

Figure 1
X-ray reflectivity for the unannealed (solid) and 118 °C annealed (dashed) samples.

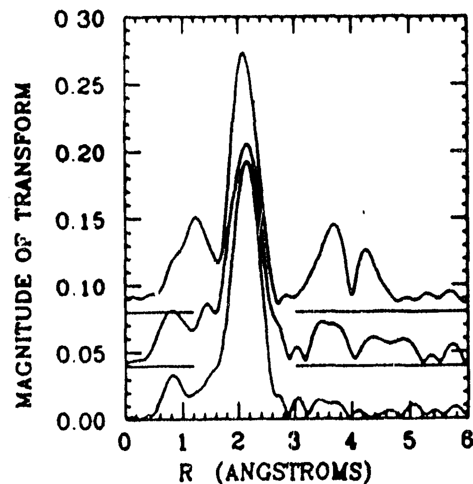

Figure 2
Fourier transformed EXAFS for the unannealed (bottom), and 118 °C annealed (middle) samples compared to crystalline Ge (top).

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x-ray diffraction measurements on this sample indicated only a small amount of crystallization, near the limit of our detection capability.

A second sample was used for time dependent studies of the x-ray diffraction. Unfortunately this sample crystallized at a higher temperature, and several anneals in the range 115-140 °C were made before the first signs of crystallization were observed at 146 °C. Figure 3 shows some examples of the x-ray diffraction patterns obtained for an incident angle of a few degrees after annealing for various times at 152 °C. For short annealing periods the sample was heated for the chosen time, and then cooled to 70 °C for measurement. For long times the sample was maintained at temperature and diffraction patterns were continuously taken. The time dependence of the Ge diffraction peaks is shown in Figure 4.

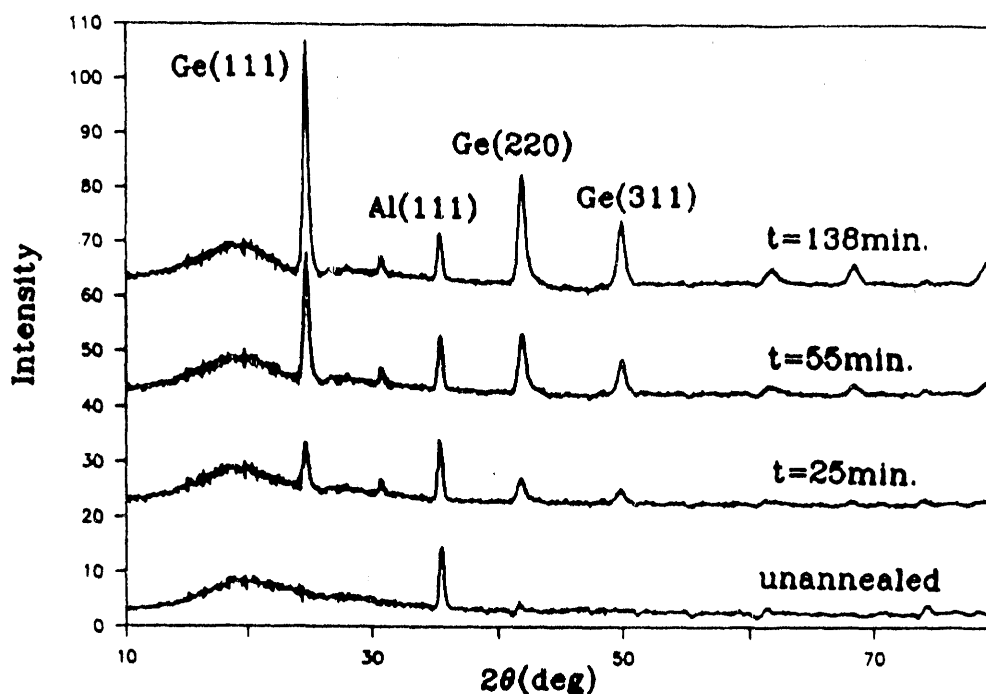

Figure 3

Some examples of x-ray diffraction patterns taken at 8 keV after annealing at 152 °C for the indicated times.

DISCUSSION AND CONCLUSIONS

At the present stage it is difficult to draw many firm conclusions regarding the meaning of the results, and more measurements are planned to further look at this problem. However, some points can be made. The EXAFS and reflectivity results clearly establish that the crystallization begins at the interface. This could only be inferred from previous studies. They also show that the crystallization process strongly disrupts the interface structure. The crystallization region is not a smooth layer, but likely grows irregularly from many nucleation sites. It has previously been observed that surface or interface imperfections can serve as nucleation sites for crystallization[4],

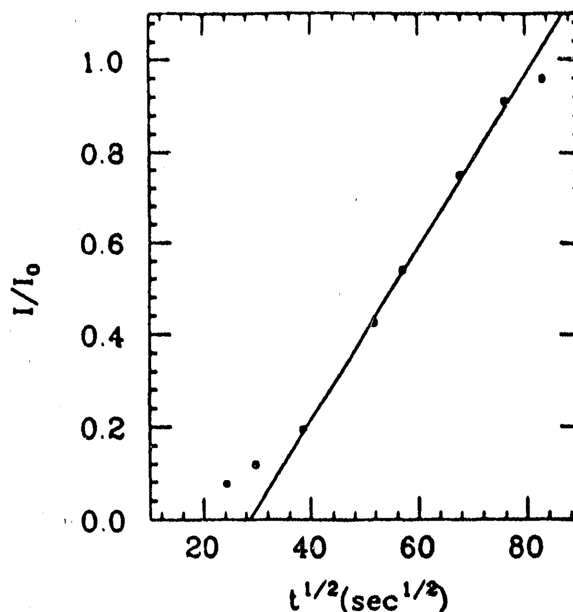

Figure 4

Intensity of the Ge (111) diffraction peak plotted versus $t^{1/2}$. I_0 is the fully annealed intensity.

and a multitude of nucleation sites would result in a rough reaction front. Analysis of the reflectivity to quantify the roughness of the reaction was hampered by the intrinsic roughness of the quartz substrates used. Further measurements are planned using more ideal float glass substrates. The results do show the sensitivity of the reflectivity and EXAFS measurements. Both clearly showed levels of crystallization which were difficult to observe by diffraction. Better substrates should make the measurements even more sensitive. The diffraction results in Fig. 4 are in reasonable agreement with a square root time dependence, which would indicate a diffusion limited process. There are some deviations at the extremes. For large times the curvature is almost certainly due to completion of the reaction. The origin of the delay at small times is less clear. Interpretation of this region is complicated by annealing carried at lower temperatures prior to the initiation of crystallization. However in view of the rough reaction front observed, the crystallization may be hindered at short time by a limited number of nucleation sites available.

The current results do not provide much clarification on the role of the metal layer in enhancing the crystallization. It seems that more direct studies of the fate of the metal is needed. This can be done using EXAFS to probe directly the environment of the metal atoms. It is likely that diffusion of the metal into the crystallizing region is needed to maintain crystallization after the reaction front has moved away from the interface. The depression of the crystallization temperature is so large that it difficult to explain if the Al interface is simply providing nucleation. Such metal diffusion could explain the diffusion limited behavior observed. Direct EXAFS studies of Al are difficult due to the low energy of the Al K-edge, and so we plan to extend our measurements to heavier metals such as Au which also cause a large suppression of the

crystallization temperature.

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