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Preferred orientations in the Ge/SiO_2 interface

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The study of preferred orientations in the Ge/SiO_2 interface was measured by observing the development and re-orientation of single crystal Ge spheres on amorphous SiO_2 substrates. The annealing temperatures ranged from 53 to 98 per cent of the melting temperature of Ge. At low annealing temperatures the Ge orientation distribution revealed three cusps in the interfacial energy versus misorientation curve corresponding to (1 1 1), (2 2 0) and (3 1 1) planes. For higher annealing temperatures one additional cusp in the interfacial energy versus misorientation curve for (4 0 0) planes is observed. The results are discussed in terms of interfacial entropy, atomic packing and electronic effects.

1. Introduction

Previous studies of solid state crystalline/amorphous interfaces have mostly been concerned with the creation and interpretation of models derived from the study of solid/liquid interfaces [1–6]. To give a few examples, in one approach Jackson's nearest neighbour bond model was used to predict faceting for atomically smooth interfaces or non-faceting for atomically rough interfaces [1]. Monte-Carlo simulations were created to study and predict the atomic structure at different distances from the interface [2–4]. Also, Cahn [5, 6] presented the concept of the "diffuse interface" when qualifying interfaces as either sharp (smooth) or diffuse (rough) in order to explain the gradient in the thermodynamic properties across the solid/liquid interface and that the transition from liquid to solid takes place over a number of atomic layers.

With respect to the orientation dependence of liquid/solid interfacial energies, from previous studies, it is known that the liquid/solid fcc metal system having the (1 1 1) or (1 0 0) planes parallel to the interface is of somewhat lower energy than interfaces having other crystal faces parallel to the interface [7]. In these liquid/solid cubic metal systems, interfacial anisotropies up to 20% have been reported with the interfaces of low energies being the two close packed planes parallel to the interface [8–10]. In other studies involving the faceting behaviour of liquid inclusions entrained in a solid matrix, anisotropies of up to 100% were measured for liquid/solid hexagonal metal systems. Unfortunately however, there are few studies known which have concentrated on observing the orientation dependence of the amorphous/crystalline interfacial energy in systems for which the amorphous phase is a solid. Similarly, little data is available from studies in which thin crystalline metal films are deposited onto glass, where some of the observed preferred orientations are due to low interfacial energy [11–18]. Furthermore, in order to resolve issues such as, for example, preferred orientations in thin film studies which can be the result of anisotropy in either the film nucleation and growth rates or the interfacial energy between the substrate and film, there is a need for future work on solid/solid interfaces of this type.

When comparing the above results for crystalline/amorphous interfaces, structural studies of solid state crystalline/crystalline interfaces and epitaxy studies, the latter are far more frequently reported in the research literature. In general, the majority of models concerning structure which are reported in these studies address the geometric nature of the crystalline/crystalline interface and completely ignore, for example, electronic effects. The same holds true for models of the structure of grain boundaries. Contrary to this point of view, however, some experimental observations suggest that electronic effects may be more important than once thought for controlling structure at the boundary [19–21]. This notion at least has a theoretical basis as calculated by Seeger and Schottky [22] using methods taken from the electron theory of metals. Essentially, Seeger and Bross [23] assumed in their study of grain boundaries that if the packing density is lower than in perfect crystals, this would impose a larger distance between atoms along grain boundaries, the obvious effect of separating atoms would then displace the positive charge of the atom cores, which must be screened by a redistribution of the conduction electrons. Furthermore, it was predicted that because the excess boundary volume is related to the boundary energy, an energy cusp would exist for boundaries of small excess volume [24]. However, analysis of the depth, the position and the width of the energy cusp are not possible without further knowledge of the boundary volume.

It is known that Ge and compound Ge_xSi_{1-x} thin films are of interest to SiGe based device technologies [25, 26]. For example they have been considered as

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a prospective buffer layer on silicon substrates for optoelectronic integrated circuits. Previous studies have addressed certain issues concerning the stability of GeSi films on SiO_2 and the solid phase epitaxial growth of GeSi on insulator layers [27, 28], but not the preferred orientations of such an interface system. In this work we present data on the preferred orientations in the Ge/SiO_2 interface using a well established technique which has been used for over 20 years to detect interfaces of low interfacial energy.

2. Experimental procedure

The modified sphere–plate technique was utilized in this study to explore the preferred orientations of Ge in contact with fused silica. This technique has successfully been used to detect interfaces of low interfacial energy, the details of which are found elsewhere [15–17]. The main characteristic of the technique is the sintering at sufficiently high temperatures of a large number (up to 10^7 cm^{-2}) of single crystal spheres (diameter 0.05–1.5 μm) on a substrate which forms the second phase of the interface. During the sintering stage if low energy orientations exist between the two phases of the sphere and plate material, then all of the spheres in originally high energy orientations will rotate into orientations of low energy.

For the preparation of the sphere–plate samples, thin amorphous Ge film (100 nm in thickness) were grown on clean fused silica (amorphous SiO_2) substrates at a deposition rate of 0.7 nm s^{-1} using e-beam heating. The purity of the germanium was 99.999 wt % and it was deposited from a graphite boat at a vacuum base pressure of 0.1 mPa in a Leybold L560 boxcoater. The sintering of these film/plate samples was performed at temperatures of 500, 817 and 921 °C in a clean quartz glass tube furnace continuously supplied with a dry argon atmosphere. These sintering temperatures correspond to 53, 87 and 98% of the melting temperature of germanium and in the latter case provided for fully oriented sphere–plate arrangements. The annealing treatments were carried out in each case for a period of 1 h.

Sphere–plate samples before and after sintering were analysed by X-ray diffraction (XRD). The XRD was performed on a Philips PW1700 automated diffractometer with a monochromator and spinner. The diffraction data and patterns were generated on a vertical goniometer attached to a broad focus X-ray tube with a copper target operating at 45 kV and 30 mA. This analysis was computer assisted so that the interplanar spacing values can be corrected for the instrument error function by analysing a silicon standard and subsequent quantitative analysis performed by matching the X-ray pattern of the sample with a data base of reference patterns [29].

The average single crystal size of the Ge spheres was calculated using the Scherrer formula, which required measuring the peak width at half maximum on reflections from the line broadening profiles of the expanded XRD patterns [30].

3. Results and discussion

To provide some idea of the microstructure of the sphere–plate samples, they were viewed under the scanning electron microscope (SEM) after annealing. All images showed rounded germanium particles at 500 °C and then the development into spheres of varied size up to about 1 μm in diameter at the higher temperatures. Since these images can be found elsewhere in many previous publications, see for example references [15–17], it was felt that some new data regarding the mean crystallite size should be reported on the microstructure instead. From the XRD line broadening profiles of the (1 1 1) reflections, the mean crystallite size after each annealing treatment is given in Table I. These data indicate that a fine grain size (22.33 nm) exists during the early stages as the film breaks up at an annealing temperature of 500 °C. As the spheres begin to form and surface diffusional forces increase, the mean crystallite size grows to 68.20 nm. This mean crystallite size does not change very much on final annealing close to the Ge melting point since the spheres are mainly crystallographically re-orienting into their low-energy orientations.

From the X-ray diffraction data and patterns (Fig. 1) obtained from the sphere–plate samples, the normalized intensities of the (1 1 1), (2 2 0), (3 1 1) and (4 0 0) Ge reflections are listed in Table II. Comparing these intensities for Ge spheres to that for randomly oriented Ge powder patterns, all spheres showed a [1 1 1] preferred orientation (or texture) at each annealing temperature [29]. The samples annealed at the lowest temperature (500 °C, $T_{mp} = 53\%$) initially had the strongest preferred orientation with $I_{111}/I_{220} = (100/33) = 3.03$ or an increase of 72.7% above the intensity reported for a random Ge powder pattern (see Table III) [31]. However, higher annealing temperatures caused a slight reduction in the intensity of the (1 1 1) reflection but it is still a strong preferred orientation. At 817 °C ($T_{mp} = 87\%$) the ratio (I_{111}/I_{220}) = 2.86 decreases to 61.6% above random and at the highest annealing temperature (921 °C, $T_{mp} = 98\%$) it drops to 2.38 or 36.7% above random. At the same time the intensity ratios I_{311}/I_{220} and I_{400}/I_{220} show some increase for increasing annealing temperatures. The (3 1 1) and (4 0 0) reflections have higher intensities than that reported for random Ge powder patterns and therefore both reflections become preferred orientations at 817 °C ($T_{mp} = 87\%$) and at 921 °C ($T_{mp} = 98\%$).

The intensity values indicate that the (1 1 1) reflection is strongly preferred at 500 °C and the (4 0 0) reflection is strongly preferred at both 817 and 921 °C. This means that as the Ge film breaks up into particles

TABLE I Crystallite size analysis after annealing

	Annealing temperature of the Ge phase		
	500 °C	817 °C	921 °C
Mean crystallite size (nm)	22.33	68.20	79.87

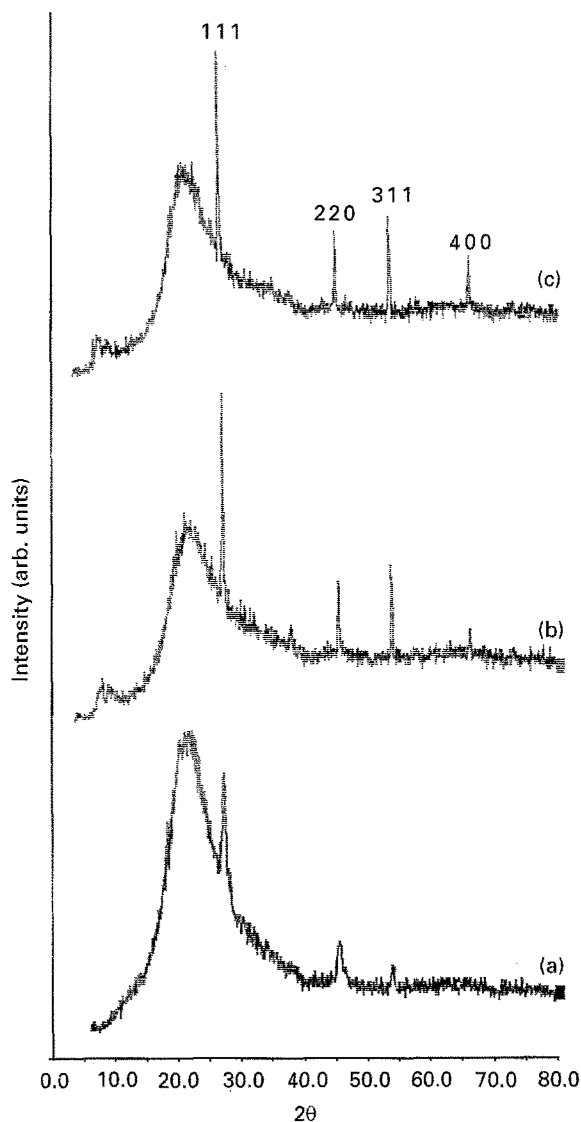

Figure 1 CuK_{α} X-ray diffraction patterns of Ge/silica sphere–plate samples annealed at (a) 500 °C, (b) 817 °C and (c) 921 °C.

TABLE II X-ray diffraction intensity results for Ge spheres

Intensity (reflection)	Random Ge powder	Intensity for a given annealing temperature		
		500 °C	817 °C	921 °C
I_{111}	100	100	100	100
I_{220}	57	33	35	42
I_{311}	39	20	45	48
I_{400}	7	0	16	27

TABLE III X-ray diffraction intensity ratios for (1 1 1) Ge reflections

Intensity ratio	Random Ge powder	Intensity ratios for a given annealing temperature		
		500 °C	817 °C	921 °C
I_{111}/I_{220}	1.75	3.03[a]	2.86[a]	2.38[a]
I_{311}/I_{220}	0.68	0.61	1.29[a]	1.14[a]
I_{400}/I_{220}	0.12	–	0.46[a]	0.64[a]

[a] Denotes a preferred orientation for reflections relative to (2 2 0) and the intensity of a random Ge powder pattern.

and spheres more (1 1 1) Ge planes are aligned parallel to the substrate surface at 500 °C after annealing. Upon annealing at 817 °C the Ge phase further develops into spheres and rearranges some of its (3 1 1) and (4 0 0) planes parallel to the substrate surface. Further annealing up to 921 °C rearranges crystallite planes into their lowest-energy configurations with (1 1 1), (3 1 1) and (4 0 0) planes being preferred and the (4 0 0) plane the most preferred orientation.

These results appear consistent with recent findings from electron microscopy studies of thin Ge films [32, 33]. In these studies fringes associated with (1 1 1), (3 1 1) and (4 0 0) planes were observed by high resolution electron microscopy for (1 1 1) and (2 2 0) oriented crystalline Ge islands embedded in amorphous Ge thin films. The fringes are the result of microtwins formed during growth. In the sphere–plate samples these planes would be undetected at the film growth stage and possibly at low temperature thermal treatments because the X-ray technique is insensitive to defects of such limited size and quantity. However, upon annealing at higher temperatures they are free to form annealing twins which can play a role in preferred orientation development during sphere formation. In a separate study, the crystallization of amorphous Ge films was observed by *in situ* transmission electron microscopy after annealing between 150 and 500 °C. Dendritic structures of Ge were observed in the bright field images and from the selected area diffraction patterns (1 1 1), (2 2 0) and (3 1 1) orientations had developed from the Ge microcrystallites [27].

What this means in terms of the science behind Ge–SiO_2 interfaces of the solid–solid, crystalline (cubic)–amorphous type is that there are several cusps in the interfacial energy versus misorientation curve after annealing at 500 °C which correspond to (1 1 1), (2 2 0) and (3 1 1) planes and at higher temperatures an additional cusp for (4 0 0) planes. This result is not surprising since it has been previously shown that different annealing temperatures lead to different orientation relationships due to interfacial entropy [34, 35]. For face centred cubic (fcc) systems of Ag and Cu on SiO_2 it was found that the number of cusps in the free energy versus misorientation curve for grain boundaries decreases from two ((1 1 1) and (1 0 0)), to one (1 1 1) with increasing temperature [17]. It is also possible that the appearance of (4 0 0) planes in Ge sphere–plate samples at higher temperatures (817 and 921 °C) may have gone undetected at a lower temperature (500 °C) if it was due to the development of microtwins during film growth but we were unable to prove it. Other results have shown that fcc Ni recorded a strong (1 0 0) and weak (1 1 1) orientation for Ni/SiO_2 sphere–plate samples annealed at $T_{mp} = 68\%$ [17]. An observation which is opposite of the behaviour of fcc Ag, Au and Cu on the same substrate material where (1 1 1) has been found to be the orientation of lowest energy. This causes some concern for the geometric arguments which try to explain cubic system results in terms of atomic packing factors playing a role in crystal grain boundary orientation and growth. What appears obvious is that geometric criteria alone cannot explain these results and that other

factors such as the boundary free volume and electronic effects across boundaries may provide an answer if it were practical to measure boundary volumes and boundary electronic properties.

For the case of metal/non-metal interphase boundaries, the electronic contribution involves a non-metal phase in contact with a metal which contains localized electrons. Therefore any charge in the metal phase or on the surface of the non-metal will be opposed by a subsurface space charge within the non-metal phase. Also, the density of states across the boundary is likely to be quite different to that for either bulk crystal phase, a condition which would be general to semiconductor/amorphous non-metal interfaces like Ge/SiO_2. At least for certain materials, such as silver halides and silver bromides, the existence of space charges has been confirmed experimentally [36–38]. What seems to be lacking is a more detailed description of the interface to allow for calculation and measurement of interfacial energies which up to now have remained a largely unsolved problem. This detailed description requires a larger body of applied research data such as from crystalline/amorphous interfaces in which the crystalline solid may be a metal or non-metal.

4. Conclusions

1. A strong preferred orientation exists for (1 1 1) Ge planes parallel to the silica substrate surface at intermediate annealing temperatures of about one half of the Ge melting point ($T_{mp} = 53\%$), while (3 1 1) and (4 0 0) planes become strongly preferred at higher annealing temperatures approaching the melting point of Ge ($T_{mp} = 87$ to 97%).

2. The effect of temperature is seen here to contribute one additional cusp in the interfacial energy curve for (4 0 0) planes at temperatures between 87 and 98% of the Ge melting point.

3. Effects other than the closeness of packing are involved in controlling the behaviour of low-energy orientations in Ge/SiO_2 interfaces.

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References

1. K. A. JACKSON, "Liquid Metals and Solidification" (ASM, Cleveland, 1958) p. 174.
2. F. F. ABRAHAM, *J. Chem. Phys.* **68** (1978) 3713.
3. A. BONISSENT and B. MUTAFTSCHIEV, *CRC Crit. Rev. Solid State Mater. Sci.* **14** (1981) 297.
4. A. BONISSENT, E. GAUTHIER and J. L. FINNEY, *Phil. Mag.* **B39** (1979) 49.
5. J. W. CAHN, *Acta Metall.* **8** (1960) 554.
6. J. W. CAHN, W. B. HILLIG and G. W. SEARS, *ibid.* **12** (1964) 1421.
7. J. BASTERFIELD, W. A. MILLER and G. C. WEATHERLEY, *Can. Met. Q.* **8** (1970) 131.
8. P. A. THACKERY and R. S. NELSON, *Phil. Mag.* **A19** (1969) 169.
9. M. MCLEAN, *ibid.* **A27** (1973) 1253.
10. N. EUSTATHOPOULOS and J. C. JOUD, in "Current Topics in Materials Science", Vol. 4, edited by E. Kaldis (North-Holland, Amsterdam, 1980) p. 4.
11. V. S. POSTNIKOV, V. M. IYEVLEV and A. D. POVALYAYEV, *Fiz. Metal. Metalloved.* **42** (1976) 208.
12. A. GITTIS and D. DOBREV, *Thin Solid Films* **130** (1985) 335.
13. D. DOBREV, V. GADJOKOV, V. VELUV and A. GITTIS, *Phys. Status Solidi (a)* **95** (1986) 93.
14. S. ROBERTS and P. J. DOBSON, *Thin Solid Films* **135** (1986) 137.
15. J. SHIROKOFF and U. ERB, *ibid.* **151** (1987) 65.
16. J. SHIROKOFF, J. W. SPRENGER and U. ERB, *Proc. Metall. Soc.* **9** (1988) 251.
17. J. W. SPRENGER, J. SHIROKOFF and U. ERB, *Scripta Metall.* **23** (1989) 1531.
18. K. MCCAFFERTY, A. SOPER, C. CHEUNG, J. SHIROKOFF and U. ERB, *ibid.* **26** (1992) 1215.
19. G. HERRMAN, H. GLEITER and G. BÄRO, *Acta Metall.* **24** (1976) 353.
20. H. SAUTTER, H. GLEITER and G. BÄRO, *ibid.* **25** (1977) 464.
21. R. MAURER, "Textures and Microstructures", Vols **8/9** (Gordon and Breach, UK, 1988) p. 509.
22. A. SEEGER and G. SCHOTTKY, *Acta. Metall.* **24** (1959) 353.
23. A. SEEGER and H. BROSS, *Z. Physik* **145** (1956) 161.
24. H. GLEITER and B. CHALMERS, in "High-Angle Grain Boundaries", in the series, Progress in Materials Science, Vol. 16, edited by B. Chalmers, J. W. Christian and T. B. Massalski (Pergamon Press, Oxford, 1972) p. 1, p. 34.
25. Y. M. MO and M. G. LAGALLY, *Mater. Sci. Eng.* **B14** (1992) 311.
26. EMRS 1992 Spring Symp. A: SiGe Technologies, *Thin Solid Films* **222** (1–2) (1992).
27. F. EDELMAN, Y. KOMEM, B. BENDAYAN and R. BESERMAN, *J. Appl. Phys.* **72** (1992) 5153.
28. F. EDELMAN, Y. KOMEN, S. S. IYER, J. HEYDENREICH and D. BAITHER, *Thin Solid Films* **222** (1992) 57.
29. Joint Committee on Powder Diffraction Standards (JCPDS), (Database of Inorganic Compounds, International Center for Diffraction Data, Swarthmore, PA, 1986).
30. B. D. CULLITY, "Elements of X-Ray Diffraction", 2nd Edn (Addison-Wesley Publ., Reading, MA, 1978) p. 102.
31. Powder diffraction file 5-545 from Swanson and Tatge, JC. Fel. Reports, NBS (1951) JCPDS, ICDD in reference 29.
32. H. HOFMEISTER, A. F. BARDAMID, T. JUNGHANNS and S. A. NEPIJKO, *Thin Solid Films* **205** (1991) 20.
33. P. H. GASKELL and A. SAEED, *J. Non-crystalline Solids* **106** (1988) 250.
34. U. ERB and H. GLEITER, *Scripta Mettall.* **13** (1979) 61.
35. G. HERRMAN, H. SAUTTER, G. BÄRO and H. GLEITER, in Proceedings of the 4th Bolton Landing Conference, June 1974, edited by J. L. Walter, J. H. Westbrook and D. A. Woodford (Claitor's Publ. Div., Baton Rouge, Louisiana, 1975) p. 43.
36. L. SLIFKIN, *Mater. Sci. Forum* **1** (1984) 75.
37. *Idem. Phys. Bull.* **39** (1988) 274.
38. *Idem. Mater. Res. Bull.* **14** (1988) 36.

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