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Between Amorphous and Crystalline Cobalt Disilicide*

David A. Smith
IBM Research Division, Thomas J. Watson Research Center
P.O. Box 218, Yorktown Heights, NY 10598

and

Charles W. Allen
Materials Science Division
Argonne National Laboratory, Argonne, IL 60439

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Morphology and Motion of the Interface between Amorphous and Crystalline Cobalt Disilicide

David A. Smith

IBM Research Division, Thomas J. Watson Research Center
P.O. Box 218
Yorktown Heights, New York 10598

and

Charles W. Allen

Materials Science Division, Argonne National Laboratory
Argonne, Illinois 60439

Abstract: Amorphous CoSi_2 films were prepared by codeposition onto electron transparent silicon nitride window substrates. The deposits were crystallized in situ without further processing. Two sets of experiments were done: thermal crystallization and thermal crystallization with additional ion irradiation treatments before or during crystallisation. The interface between the amorphous and crystalline material is rough on the scale of 20nm with some tendency to facet. Irradiation by 1.5Mev Kr ions stimulates both nucleation and growth at room temperature. Prior ion irradiation followed by heating in the absence of an ion-flux also enhances the nucleation and growth kinetics relative to a purely thermal treatment.

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1. Introduction

Silicides are of both great technological importance and scientific interest. Their practical importance lies in applications as contacts and from the processing standpoint it is particularly attractive to find means to produce reactions at low temperatures. Thus it is desirable to find a way of forming a silicide by crystallization rather than through a metal-silicon reaction [1,2]. Again in the practical context of this work it is important to elucidate the effects of ion irradiation as an athermal processing technique. From the scientific point of view, in situ crystallization and irradiation provide a unique means of studying, separately, both the nucleation and the growth characteristics of a phase transformation. Many previous studies of the crystallisation of amorphous materials such as those in references [3,4] have relied mainly on indirect techniques, such as the study of electrical resistivity, differential scanning calorimetry or dilatometry; however all these methods have the disadvantage that the nucleation and the growth kinetics which are analysed according to the Johnson-Mehl-Avrami equation [5] are not separable. This paper is concerned with the morphology and kinetics of the motion of the interface between amorphous and crystalline regions of CoSi_2 in response to irradiation by 1.5 MeV krypton ions and heating. The thermal crystallization was carried out in a Philips EM430 operating at 300 kV. The in situ ion irradiations and ion assisted crystallization were carried out in the Kratos EM7 in Argonne's HVEM Tandem Facility operating at 130 kV.

2. Experimental Method

Cobalt and silicon were codeposited at ambient temperature in a dual e-beam system with a base pressure of 10^{-8} torr. The stoichiometry of the films was near to that of the compound CoSi_2 . The substrates were silicon nitride coated silicon

wafers in which windows had been opened up by anisotropic etching. The films were 40nm thick and according to electron diffraction invariably amorphous in the as deposited condition. The samples are suitable for examination in a transmission electron microscope without further specimen preparation. The stoichiometry of the deposited CoSi_x was checked by Rutherford back scattering; in the present work $1.85 < x < 2.3$; for fixed evaporation rates the film composition depends on the position of the substrate relative to the sources. The progress of the crystallization process was recorded on video tape and also on photographic plates. The heating holders are sufficiently stable that it is possible to select a field of view and continue to observe it throughout the crystallisation process. The energy of the ion beam was chosen so that the great approximately 99.9% of krypton ions were transmitted through the region of the film which is electron transparent; thus implantation and heating were both minimized. An electron microscope grid was placed on top of the sample so that certain regions of the specimen were masked from the effects of the ion beam. In this way it is possible to observe in one sample the effects of irradiation together with an untreated reference region of the sample, is a technique developed by Okamoto [6]. A typical field of view includes several hundred crystals; thus it is a relatively simple matter to obtain statistically significant measures of the nucleation kinetics and the interface velocity [7] both of which could be measured directly as a function of temperature, ion dose and ion flux. However the focus of this paper is on the microstructural aspects of interface motion.

3. Results

Figure 1 shows at low magnification a typical series of micrographs illustrating the morphology of the CoSi_2 crystals. The disc morphology which is maintained until impingement with neighboring crystals occurs and direct measurements in-

dicate an isotropic constant growth rate which is characteristic of an interface controlled process [7]. The crystallisation process is known from tilting experiments to be nucleated at the surfaces of the deposit. The nucleation kinetics are such that almost all the crystals grow to a size sufficiently large that the majority of the growth is *two dimensional* in the 40nm thick films used in this work. Although, averaged over time, after a crystal has penetrated both surfaces of the film the envelope of a growing particle is cylindrical, at high magnification it is clear that the interface between a crystalline island and the amorphous matrix is not an arc of a circle. This is illustrated in figure 2. There are two deviations from a disc-like morphology; one is a relatively weak tendency for the formation of facets, as shown in Fig. 2a, and the second is the formation of protruberances on the interface as illustrated in Fig. 2b. Facets are an expected aspect of the growth morphology of a particle although there are three possible mechanisms for this behavior. *Kinetic* factors result in a particle being bounded by slow growing surfaces [8]; alternately either a large entropy of crystallisation [9] or anisotropy of interfacial free energy [10] can provide a *thermodynamic* basis for faceting. The protruberances on the interface seem to be connected with deviations from stoichiometry.

The material shown in figure 2b is silicon rich according to RBS. It appears that CoSi_2 crystallizes and the excess silicon is distributed throughout the material as amorphous islands of which some are arrowed in Fig. 2b. It is not clear whether this phase separation occurs during deposition or the heating leading to crystallisation; the amorphous silicon islands are visible in both the crystallised and uncrystallised material. These amorphous islands scatter electrons less strongly than the CoSi_2 and thus appear lighter in the image. The amorphous silicon particles impede the motion of the interface between the crystalline and the amorphous material and a process analogous to Zener pinning occurs [11].

Evidently, the pinning force is insufficient to immobilize the interface and so the interface advances by bypassing the particles which become occluded by the advancing crystallisation front. Thus the waveform of the perturbations to the interface between amorphous and crystalline material is governed by the distribution of the amorphous silicon particles and the bowing of the interface during the bypassing process. Heat treatment for 30 minutes at 600°C crystallized the amorphous islands. The crystallised silicon precipitates as plates on the {111} planes of the CoSi_2 matrix.

Figure 3 illustrates the effect of ion irradiation without heating on a partially thermally crystallized specimen. Figures 3a and 3b are respectively micrographs recorded after irradiation by 1.5MeV Kr ions to a dose of 3.4×10^{14} and 6.8×10^{14} ions cm^{-2} at a flux of $3.4 \times 10^{11} \text{cm}^{-2}\text{s}^{-1}$. It is clear that ion irradiation causes previously nucleated crystals to grow and also stimulates copious nucleation of new crystals. The heating effect associated with the ion irradiation is thought not to exceed 15°K above ambient which is far too small to account for the observed enhancement of crystallisation. Pure thermal crystallisation occurs at significant rates only at temperatures in excess of about 150°C. Figure 4 illustrates the effect of ion irradiation on the subsequent thermal crystallization process of an as deposited sample. The as deposited sample was irradiated to a low dose at room temperature and then thermally crystallized. No change was observed in either the microstructure or the diffraction pattern after the irradiation and prior to the thermal treatment. The response of amorphous cobalt disilicide to rapid heating to 177°C followed by isothermal transformation is illustrated in the series of micrographs shown as figures 4a-d which were recorded at two minute intervals and show successive stages in the development of the microstructure for the case where the irradiated and nonirradiated material are visible together. The material in the lower part of each micrograph was ion irradiated to a dose of 3.4×10^{13}

Kr ions cm^{-2} at a flux of 3.4×10^{11} ions $\text{cm}^{-2} \text{s}^{-1}$. It is qualitatively clear that ion irradiation enhances both the nucleation and growth processes at 177°C ; direct measurements on the micrographs reveal that the ion irradiation treatment doubled the nucleation rate and increased the growth rate by about 50% at this temperature.

4. Discussion

One of the broader implications of the experimental program, described in part in this paper, is that the crystallisation reaction is representative of an interface controlled nucleation and growth transformation with the immense advantage that the nucleation and growth kinetics can be studied separately with the objective of gaining a deeper understanding of phase transformations in general. However this insight will only be of value if the experiments are not grossly perturbed by the conditions under which they are conducted. Electron displacement damage is certainly expected to occur at 300keV but comparison of irradiated and unirradiated regions shows that the transformation is unaffected except when the electron beam is incident on the thicker silicon at the edge of a nitride window, which evidently gives a local heating effect without any change in the morphological features of the transformation, or the electron beam is condensed for observations at magnifications exceeding 100KX for extended periods of the order 30 minutes or more which produces a shell of morphologically distinct material around an existing crystal. The crystallisation kinetics are determined at low magnifications, 5KX typically and the thermal crystallisation process is completed in less than 20 minutes at the lowest temperatures investigated. Electron irradiation enhanced transformation is characterised by copious nucleation, somewhat similar to that induced by ion irradiation and a character-

istic irregular crystal morphology. The experiments conducted in the HVEM were all done at sub-threshold accelerating voltages.

The morphology of interfaces between phases can be governed by either thermodynamic or kinetic factors. Minimisation of interfacial energy or kinetics resulting in the selection of slow growing boundary surfaces usually results in a faceted morphology. Close packing as in low index planes is correlated with both low energy and slow growth. In this respect the disk morphology observed at low magnifications and the protuberances seen at higher magnifications are both anomalous. Indeed CoSi_2 formed by reaction of a cobalt layer with a silicon wafer [12] or by precipitation from silicon amorphised by implantation with cobalt ions and then recrystallised [13], exhibits morphologies expected for an fcc material; reaction produces an interface faceted on $\{100\}$ and $\{111\}$ planes and recrystallisation produces octahedral precipitates bounded by $\{111\}$ planes. As figure 2b shows there is some tendency for facetting of the interface between amorphous and crystalline CoSi_2 but in general the interface is rough and perhaps aptly described as advancing in the manner of an amoeba by the formation of pseudopods which occlude silicon islands. The amplitude of this interfacial roughness and its wavelength are inconsistent with an entropically stabilised interface of the kind described by Jackson even though the entropy of crystallisation is estimated to be on the borderline between the values associated respectively with rough and faceted interfaces [9,14]. In materials science terms the interface advances despite a Zener pinning term; this pinning term, $3\sigma f/2r$ per unit area, where σ is the excess energy of the amorphous-crystalline interface, f is the volume fraction of amorphous silicon and r the particle spacing, is estimated as about four orders of magnitude less than the free energy of crystallisation. It may be anticipated that more ideal morphologies would be observed in stoichiometric material.

The basic atomic process in the nucleation and growth of a CoSi_2 crystal is a local reshuffle which may be thought of as a diffusive jump over a distance of the order of the near neighbor spacing. The enhancement of this process by a low ion dose is attributed to a transient increase in the concentration of point defects.

5. Conclusions

The rate determining process in the nucleation and growth of a CoSi_2 crystal is a local reshuffle which is speeded up by the transient increase in the concentration of point defects resulting from ion irradiation.

There is some tendency for facetting of the interface between amorphous and crystalline CoSi_2 but in general the interface is rough and occludes silicon islands as it advances. The amplitude of this interfacial roughness and its wavelength are governed by the particle distribution. The Zener pinning by the particles of amorphous silicon is estimated as about four orders of magnitude less than the free energy of crystallisation.

Electron displacement damage occurs at 300keV but comparison of irradiated and unirradiated regions shows that the transformation is unaffected except when the electron beam is incident on the thicker silicon at the edge of a nitride window or the electron beam is condensed for observations at high magnifications for times exceeding 30 minutes. Electron irradiation enhanced transformation is characterised by copious nucleation, somewhat similar to that induced by ion irradiation and a characteristic irregular crystal morphology.

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Figure captions

Figure 1 shows at low magnification a typical series of micrographs illustrating the growth sequence and disk morphology of the CoSi_2 crystals. The micrographs show the progress of the transformation in a particular area. The numbers in the upper right of each frame indicate the time elapsed, in minutes, at the isothermal transformation temperature of 154°C .

Figure 2 illustrates the deviations from a disc-like morphology which are visible at higher magnifications; Fig. 2a shows the rather weak tendency for formation of facets consistent with $\{111\}$ and $\{100\}$; the fringes are $\{200\}$.

Fig. 2b illustrates the formation of protruberances on the interface; these advance and occlude inclusions of second phases which in this case are silicon.

Figure 3 illustrates the effect of ion irradiation without heating on a partially thermally crystallized specimen. Figures 3a and 3b are respectively micrographs recorded after irradiation by 1.5MeV Kr ions to a dose of 3.4×10^{14} and 6.8×10^{14} ions cm^{-2} at a flux of 3.4×10^{11} ions $\text{cm}^{-2}\text{s}^{-1}$.

Figure 4 illustrates the effect of ion irradiation of an as deposited sample on the subsequent thermal crystallization process. The response of irradiated and unirradiated amorphous cobalt disilicide to rapid heating to 177°C followed by isothermal transformation is illustrated in the series of micrographs shown in figures 4a-d which were recorded at two minute intervals. The material below the line in of each micrograph was ion irradiated to a dose 3.4×10^{13} Kr ions cm^{-2} at a flux of 3.4×10^{11} ions $\text{cm}^{-2}\text{s}^{-1}$.

a

b

c

2 μm

d

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