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on Solid State Crystallization of Cobalt Disilicide Thin Films**

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**IN SITU STUDY OF EFFECTS OF ION-IRRADIATION ON SOLID
STATE CRYSTALLIZATION OF COBALT DISILICIDE THIN FILMS**

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Results of a continuing in situ study of the ion-irradiation-modified crystallization of amorphous CoSi₂ thin films are discussed. 1.5 MeV Kr ion irradiation is employed at 90 K to "mix" nominally amorphous, as-deposited material for subsequent epitaxial regrowth at 450 K. The ion irradiation also is employed at 300 K to produce ion-assisted crystallization. The average degree of transformation per ion is approximately 4×10^{-20} cm³ per ion. The resultant number density of crystals, however, depends sensitively on prior treatment of the film. For example, 300 kV electron irradiation at 300 K prior to ion irradiation may result in a large number density of crystal nuclei. Low dose Kr irradiation at 300 K may also cause a slight increase in the number density of crystals formed subsequently at 450 K, while larger Kr doses at 300 K ($> 3 \times 10^{14}$ cm⁻²) may double the subsequent thermal growth rate at 450 K. These results are discussed qualitatively in terms of nucleation and growth theory.

1. Introduction

The thermal crystallization of amorphous thin films of semiconductors has been extensively studied, because of the relevance of this phenomenon in microelectronic component systems which, for example, have suffered amorphization during ion implantation or rapid thermal processing. The phenomenon of ion irradiation assisted crystallization was reported in Ge under 40 kV self-ion irradiation in 1975 [1], since which time the ion assisted growth phenomenon has been extensively studied, especially in Si [e.g., 2]. Typically ion-enhanced crystallization occurs at temperatures as low as several hundred degrees Kelvin below those characteristic of thermal crystallization and thus is also of potential importance in microelectronic processing when thermal degradation would be a problem. In this paper results of a study of the ion irradiation-effected crystallization of amorphous CoSi_2 are presented and discussed in the context of nucleation and growth phenomena. The term 'irradiation-modified' is chosen to indicate that crystallization may be enhanced or suppressed, depending on the relative importance of nucleation and of growth in the particular crystallization scenario.

In addition to the potential for practical application, this particular crystallization process is a model phase transformation. The nucleation and growth kinetics of this polymorphic transformation can be studied directly in situ; in addition, the microstructure which develops by isotropic growth from random or controlled non-random nucleation events can be quantitatively modelled with the aid of a computer.

2. Experimental procedures

The irradiation experiments were performed employing the in situ ion beam capability of Argonne's HVEM-Tandem Facility. Thereby the response of an individual area of specimen is continuously observed during a given ion irradiation experiment. During the ion irradiations the high voltage electron microscope (HVEM) was operated at 130–144 kV, well below threshold for electron-induced displacement of Si or Co. For the ion irradiations 1.5 MeV Kr was employed at an incident flux of $(1.7 \text{ to } 3.4) \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$ to ensure that specimen heating associated with the ion beam was negligible. On the basis of TRIM 89 calculations [3] for the experimental conditions and an assumed displacement threshold of 18 eV which is a rather small value, an ion dose of 10^{14} cm^{-2} corresponds to approximately 1 displacement per atom (dpa). These

calculations also indicate that approximately one of every thousand Kr ions is implanted, which for the largest ion dose ($3 \times 10^{15} \text{ cm}^{-2}$) and the specimen thickness employed corresponds to approximately 0.5 atomic ppm. Both of these computed results are sensitive, of course, to the assumed displacement threshold, so that both the resultant displacement and implantation rates are expected to be overestimated by these values. The specimens were thin films $\sim 40 \text{ nm}$ thick, coevaporated at 300 K onto an amorphous 5 nm film of silicon nitride; this composite film covered $\sim 2.3 \times 10^{-4} \text{ cm}^2$ windows in thick Si substrates. Specimens from two nominally identical production lots have been employed, which were known to exhibit identical thermal crystallization behavior.

In several of the experiments to be discussed, the effects of ion irradiation and no ion irradiation are compared in a given micrograph of side-by-side areas of the specimen. In our present experimental setup the ion beam is apertured to a diameter of 2 mm prior to the specimen in the HVEM so that effectively the entire TEM specimen is irradiated by the ions. Nevertheless it is a fairly simple matter to have non-irradiated areas next to irradiated areas by placing a dense microscope grid over the specimen and making use of the shadow cast by a given grid bar during the ion irradiation [4]. This is illustrated in Figure 1. In the Argonne HVEM the ion beam is 33 deg from the electron beam, so that an adequate shadow is cast by such a grid when the specimen is tilted 15–20 deg toward the incident ion beam without compromising simultaneous imaging of the specimen. Furthermore if one wishes to compare several ion doses in the same specimen, sequential ion irradiations can be performed at different specimen tilt angles for which more or less extensive shadows are cast.

3. Experimental observations

The phenomenon of ion-assisted crystal growth at 300 K is illustrated in Fig. 2. The specimen had been thermally partially crystallized in situ in a 300 kV electron microscope prior to the ion irradiation. Fig. 2 shows the microstructure after $8.5 \times 10^{14} \text{ Kr}^+ \text{ cm}^{-2}$. The existing large crystals have grown and a profusion of small crystals has appeared. On average the increase in crystallized volume associated with this ion-assisted growth at 300 K is approximately $4 \times 10^{-20} \text{ cm}^3$ per ion for small, isolated crystals.

When an as-deposited film is subjected to ion irradiation to $3.4 \times 10^{14} \text{ Kr}^+ \text{ cm}^{-2}$ at 300 K and then thermally crystallized at 450 K, the sequence of thermal crystal formation is as shown in Fig. 3; the micrographs have been recorded at 2 min

intervals. The ion irradiated area is the lower third of each micrograph, in which the number density of crystals is about the same as that for the non-irradiated area. The crystal (thermal) growth rate in the prior-irradiated region is about twice that in the non-irradiated region. Both the observations of number density and growth rate are very different from those reported earlier for the same experiment involving one tenth the prior ion dose [5]. For an ion dose of $3.4 \times 10^{13} \text{ Kr}^+ \text{ cm}^{-2}$ at 300 K it was observed that the number density of crystals was increased by roughly 30 percent by the prior ion irradiation while the growth rates in the two regions were practically the same. The observation of increased number density for this smaller prior ion dose suggested that ion irradiation influences the nucleation of the CoSi_2 crystals. However, the results are just as well interpreted in terms of ion-assisted growth of preexisting embryos in the virgin films.

In order to determine if ion irradiation influences homogeneous nucleation or only heterogeneous nucleation in this material, several experiments have been performed in which a portion of each film is initially subjected to a substantial dose of ion irradiation ($3 \times 10^{15} \text{ cm}^{-2}$) at 80–90 K, where CoSi_2 is thoroughly amorphized. Following this treatment, the specimen was then heated to 450 K and thermal crystallization allowed to proceed. The results are illustrated in Fig. 4 which shows both the ion irradiated material on the left and the non-ion irradiated material on the right of both Figs. 4(a) and (b). In Fig. 4(a) the thin film has been annealed for 25 minutes and in Fig. 4(b), for 80 minutes. Even after 80 minutes at 450 K no nucleation of crystals is evident in the portions of the film which had been ion irradiated at 90 K. On the other hand growth of crystals is unimpeded as the amorphous/crystalline interface migrates into the ion irradiated region. In both regions the growth rate is $0.6\text{--}0.7 \text{ nm s}^{-1}$. Fig. 5 is an enlarged view of the growth zone in the prior ion irradiated material. The lower left of Fig. 5 shows a part of two large crystals, each containing a coarse subgrain structure, which have grown toward the upper right into the ion irradiated region, where the substructure has changed over a very short distance to a fine columnar structure. The diffraction patterns inset in Fig. 5 are from one of these crystals. The total range of misorientations for the columnar zone in the prior-irradiated area and for the large subgrain region in the non-irradiated region are comparable.

Several experiments to demonstrate ion-assisted crystallization at 300 K both in as-deposited films of CoSi_2 and in partially thermally crystallized films failed to yield the large number density of finely dispersed crystals shown in Fig. 2. However, when an as-deposited film is first subjected to sufficiently high energy electron irradiation, subsequent ion bombardment does yield such a result. This is illustrated in Fig. 6,

which shows an area of specimen which has been subjected to ion irradiation at 300 K to a dose of $1 \times 10^{15} \text{ cm}^{-2}$; before the ion irradiation, the region of specimen just off the bottom of the micrograph had been electron irradiated with 300 kV electrons at 300 K to a maximum dose of $3 \times 10^{22} \text{ cm}^{-2}$ and maximum electron flux of $0.8 \times 10^{19} \text{ cm}^{-2} \text{ s}^{-1}$. The electron beam profile is determined by means of a moveable Faraday cup which has replaced the beam stop in the viewing chamber of the HVEM. The gradient of particle number density in the lower portion of Fig. 6 is associated with the region of rapidly decreasing intensity at the edge of the electron irradiated region and the region at the top, to that with roughly two orders of magnitude less dose. It is likely that the fine dispersion of crystals shown in Fig. 2, which were produced during ion irradiation, were in fact nucleated by the incident 300 kV electron beam employed for observation during the prior thermal anneal.

4. Discussion

There are several aspects to the question of irradiation-effected crystallization which are revealed in the foregoing observations: the effect of electron irradiation on nucleation of crystallization, the effect of heavy ion irradiation on nucleation and the effect of ion irradiation on crystal growth. At this point only the last of these can we address with some confidence for silicide crystallization. The phenomenon of ion enhanced nucleation of crystallization has been studied, however, for the case of Si under 1.5 MeV Xe irradiation, for temperatures in the range 775–855 K, starting from amorphous material which had been well mixed by low temperature ion irradiation [6]. These nucleation studies were also performed *in situ* in the HVEM-Tandem Facility. In addition the phenomenon of ion beam induced epitaxial crystallization (IBIEC) of Si following ion implantation, for example, has been extensively studied [e.g., 2]. In the latter case the temperature range is 575–775 K and the analysis was performed by Rutherford backscattering rather than direct observation of microstructure evolution.

In the present study, the observation that ion beam mixing at low temperatures prior to thermal annealing suppresses nucleation suggests, as one might expect, that embryos of crystallization pre-exist in the as-deposited films, which are eliminated during the low temperature ion irradiation. It is clear from Fig. 4 that the ion-irradiated area has been thinned by sputtering and the supporting silicon nitride layer removed, causing the film to appear somewhat buckled. This buckling may be the origin of the refinement of substructure associated with crystal growth into the pre-irradiated

material. Another possibility, however, is the sweeping of "defects" into the subboundaries from the amorphous material as the crystal/glass interface migrates. The lack of nucleation in the ion beam mixed area over the 80 minute interval at 450 K indicates that homogeneous nucleation is very sluggish at the annealing temperature of 450 K. The observation by Smith, Tu and Weiss [7] that the thermal growth process for crystallization of these as-deposited silicide films may be described in terms of an activation energy of 1.09 eV suggests that the activation barrier for homogeneous nucleation may be significantly larger than the value of 1.27 eV determined from the thermal crystallization studies by Evans and Smith [8].

The observation that preirradiation of as-deposited material by 300 kV electrons results in formation of a profuse number of crystals during subsequent ion irradiation at 300 K indicates that the role of the electron irradiation is to increase the number density of crystal nuclei which are critical or supercritical in size with respect to ion-assisted growth. This interpretation is consistent with the microstructure developed on ion-irradiation at 300 K of a film which had been partially crystallized thermally during 300 kV electron irradiation in a medium voltage TEM. It is not clear at this point whether the electron irradiation simply assists growth of preexisting embryos to critical size with respect to ion-assisted growth or in addition promotes homogeneous formation of suitable nuclei. This latter ambiguity can be eliminated by comparing the ion-assisted crystallization of as-deposited material and of low temperature, ion beam mixed material, both of which are subjected to electron irradiation before the ion-assisted growth part of the experiment.

The observation that low dose ion irradiation ($3.4 \times 10^{13} \text{ cm}^{-2}$) at 300 K preceding thermal crystallization at 450 K enhances the subsequent apparent thermal nucleation rate at 450 K while an order of magnitude greater prior ion dose not is difficult to rationalize. These experiments have not yet been repeated, but nevertheless the side-by-side comparison of Fig. 3 is quite compelling. The thermal growth rate is evidently enhanced in the latter case by virtue of residual "defects" created in the amorphous material by the room temperature ion irradiation. But the results involving apparent nucleation suggest that the low dose ion irradiation causes growth of some preexisting crystallite embryos to critical or supercritical size with respect to thermal growth at 450 K but that the much larger ion dose wipes this tendency out by virtue of extensive cascade overlap. Perhaps any apparent increased thermal nucleation rate was the result of ion-assisted growth of embryos in the as-deposited material to critical size with respect to thermal growth at 450 K, which had been critical or supercritical in size initially with respect to ion-assisted growth.

For the case of amorphous Si (produced by ion implantation), thermal crystallization does not occur for temperatures much below 920 K, at least partly because of sluggish thermal nucleation kinetics. In the ion-assisted crystallization study of Im and Atwater [6] for 775–855 K, ion-assisted nucleation rates are reported to be six to seven orders of magnitude larger than the corresponding thermal nucleation rates. The apparent activation energy for ion-assisted nucleation is reported to be very large, however, 3.9 ± 0.75 eV, so that at lower temperatures nucleation—thermal or ion-assisted—is precluded and only epitaxial regrowth from existing crystalline Si occurs under ion bombardment down to temperatures of about 575 K [2]. Finally at still lower temperatures the disordering effects of ion damage become dominant. The present study of ion-modified crystallization of CoSi_2 is not complete; however, the following comparison with the results for Si seems worth pointing out. The range of temperatures over which the ion beam phenomena occur is considerably less in CoSi_2 than in Si, thermal crystallization occurring readily at 425 K, at least in material deposited at 300 K, and ion-induced amorphization of crystalline CoSi_2 , at 250 K. The thermal crystallization of CoSi_2 at 450 K, illustrated in Fig. 4, which may be termed thermal regrowth in the prior ion irradiated region, corresponds to the behavior of Si at 920 K.

The complexity of the observations in ion-affected nucleation and growth reported here are indicative of the subtle relaxation processes which may occur prior to crystallization and of the sensitivity of nucleation to stoichiometry. CoSi_2 is a line compound and the almost inevitable deviations from the intended composition are likely to result in heterogeneous nucleation on Si- or Co-rich clusters in the dense random network which may form at ambient temperature. In addition the role of such local compositional fluctuations on the local effect of high energy ion irradiation above the nominal amorphization temperature limit for a particular ion flux is not clear at this point.

5. Conclusions

A variety of effects of 1.5 MeV Kr irradiation on crystallization of CoSi_2 have been investigated, including the effects of low temperature bombardment on subsequent thermal crystallization and the effects of intermediate energy electron irradiation at ambient temperature on subsequent crystallization at the same temperature during Kr irradiation. The average volume transformed by 1.5 MeV Kr is approximately 4×10^{-20}

cm³ per ion. The creation of nuclei by electron irradiation, which are evidently of critical size with respect to ion-assisted growth, and the promotion or retardation of nucleation by high energy ion irradiation, depending on temperature and possibly on dose and ion flux, provide an arsenal of tools with which to probe both the nucleation and growth aspects of crystallization and the effective size of the ion damage zone in a nominally amorphous solid.

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Figure captions

Figure 1. Sketch illustrating use of a microscope grid to cast a shadow on a specimen during ion irradiation, so that comparison of irradiated and non-irradiated material may be directly made under otherwise identical conditions.

Figure 2. Ion irradiation assisted crystallization of CoSi_2 thin film at 300 K (fine dispersion of crystals), following partial thermal crystallization in a 300 kV TEM (massive crystals). Specimen has been irradiated with 1.5 MeV Kr to $8.5 \times 10^{14} \text{ cm}^{-2}$ at 300 K.

Figure 3. Thermal crystallization sequence at 2 minute intervals for a CoSi_2 film at 450 K. Lower third of region had been subjected 1.5 MeV Kr irradiation to $3.4 \times 10^{14} \text{ cm}^{-2}$ at 300 K.

Figure 4. CoSi_2 thin film, left hand portion of which has been irradiated with 1.5 MeV Kr to approximately $3 \times 10^{15} \text{ cm}^{-2}$ at 90 K. Thermal crystallization is produced subsequently at 450 K without additional ion irradiation. (a). Normal thermal crystallization occurs in the region shadowed during prior ion irradiation. 25 minutes at 450 K. (b). Crystals grow unimpeded into prior ion irradiated material, where no additional nucleation has occurred. 80 minutes at 450 K.

Figure 5. CoSi_2 thin film of Fig. 4. Fine columnar substructure of portions of two crystals which have grown into the prior ion irradiated region. Diffraction patterns are from one of these crystals in the non-irradiated and irradiated regions.

Figure 6. Transition zone in an as-deposited CoSi_2 film which has been subjected to uniform 1.5 MeV Kr irradiation at 300 K to a dose of $1 \times 10^{15} \text{ cm}^{-2}$. The region just off the bottom of the figure had been subjected to 300 kV electron irradiation at 300 K to $3 \times 10^{22} \text{ cm}^{-2}$.

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