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Formation of nickel nanoparticles on amorphous silicon thin film and its effect on crystallization

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Using in situ high-resolution transmission electron microscopy, we observe that, while annealed at 550 °C in the TEM, a Ni-deposited amorphous silicon thin film is crystallized, which is preceded by the formation of NiSi2 precipitates. In addition to the NiSi2 precipitates, nanometer-sized Ni particles, single crystalline or multiply twinned, form. Their unusual formation is attributed to beam heating effect by beam irradiation during the observations. Unlike the NiSi2 precipitates, no crystallization occurs around the Ni nanoparticles. © 2006 American Vacuum Society.

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I. INTRODUCTION

Bulk amorphous silicon (a-Si) crystallizes at about 600–700 °C (e.g., Ref. 1) and this intrinsic crystallization temperature is lowered by addition of metal impurities, such as Au,2 Al,3 and Sb,4 which form eutectics with Si, and Ni,5–7 which forms various silicides with Si. For the eutectic-forming metals, Radnoczi et al. suggested that Au, Sb, and Al dissolved in the a-Si film may loosen the covalent bonding in the a-Si and make the a-Si even unstable, enhancing crystallization.3

Unlike eutectic-forming metals, for the silicide-forming metal, such as Ni, silicides are reported to mediate crystallization.5–7 Hazelden and co-workers5,6 observed that after NiSi2 precipitates with CaF2 structure, which has a close lattice match to Si crystallization occurs around the Ni nanoparticles. Single crystalline or multiply twinned, form. Their unusual formation is attributed to beam heating effect by beam irradiation during the observations. Unlike the NiSi2 precipitates, no crystallization occurs around the Ni nanoparticles. © 2006 American Vacuum Society.

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II. EXPERIMENTAL PROCEDURE

A Ni-deposited a-Si thin film was made in the following way: On Corning 1737 glass, thin 80 nm a-Si was deposited by plasma-enhanced chemical vapor deposition (PECVD) at 280 °C using SiH4 and H2 as source gases. A thin 2 nm Ni layer was deposited on the a-Si layer on the glass by dc sputtering. Disks of 3 mm in diameter were cut from the wafer using a disk cutter for TEM specimen preparation. The disks were mechanically back thinned to a thickness of about 20 μm and then ion milled on the glass substrate side at an accelerating voltage of 4 kV using a precision ion polishing system (PIPS, Gatan Inc.). In situ observations were made in plan view at a temperature of 550 °C, using the Jeol JEM-ARM1250 at the Max-Planck-Institut für Metallforschung (Stuttgart, Germany) and the Jeol JEM-ARM1300S at the Korea Basic Science Institute (Daejon, Korea), both of which are operated at 1.25 MeV (0.12 nm point-to-point resolution) and equipped with a side-entry heating stage. The base pressure in the specimen chamber is in the range of (2–3) × 10−6 Pa. The heating rate was 20 °C/min. Electron current densities at the specimens were in the range of 15–20 A/cm² during the observations.

III. RESULTS

Figure 1(a), taken after annealing for 124 min, shows a high-resolution image of a (111)-oriented NiSi2 (or Si). Lattice images of Si and NiSi2 are not distinguished from each other.
other in the plan-view observation, because the silicide with CaF$_2$ structure has a close lattice match to Si (−0.4%). The measured spacings of three sets of planes are nearly identical to the {220} spacings (1.920 Å) of Si (cubic, $a=5.430$ Å) or the {220} spacings (1.911 Å) of NiSi$_2$ (cubic, $a=5.406$ Å). It is understood in Fig. 1(a) that at this annealing stage (i.e., after annealing for 124 min) the surface Ni layer reacts with the underlying $a$-Si to form NiSi$_2$, as for Ni-deposited $c$-Si. It cannot be excluded in Fig. 1(a) that a very thin layer $c$-Si forms below the NiSi$_2$ layer. After a prolonged annealing (e.g., for 252 min), in all {111} high-resolution images [e.g., Fig. 1(b)], the measured spacings of three sets of planes are revealed to become larger than in Fig. 1(a). Such spacings are not produced by the Si{220} reflections corresponding to the spacings of 1.920 Å but seem to arise from the forbidden 1/3 {422} reflections of Si corresponding to the spacings of 3.327 Å. The forbidden reflections are attributed to {111} twins and stacking faults of $c$-Si. Thus, Fig. 1(b) clearly implies that $a$-Si crystallizes below the NiSi$_2$ layer and, with the increase of annealing time, will be thickened and that we are observing the plan view of the overlap of the NiSi$_2$ and $c$-Si{111} layers.

Figure 2 shows another area, which was taken when annealed for 167 min. The measured interplanar spacings correspond to those of the NiSi$_2${111} (3.121 Å) or the Si{111} (3.136 Å) with the {110} zone axis parallel to the beam direction. In the {110} surface orientations, zigzagged surface defects are found. If only a disilicide layer forms, such defects would not exist, and thus, these defects are likely to arise from an overlap of the NiSi$_2$ and $c$-Si layers Tung et al. show that the interface between the NiSi$_2$ and the Si{110} ([110] interface) is faceted into {111} interfaces (interfaces between NiSi$_2${111} and Si{111}), and on the inclined {111} interface facets, the 1/2 {110}-type dislocations are observed. When NiSi$_2$ grows on Si{111} epitaxially, misfit edge dislocations with a Burgers vector $b$ of $1/2$ {110} are found, while edge dislocations with $b=1/6$ {112} form in the twin boundary between the NiSi$_2$ and the Si. Based on the previous result, the HRTEM image of Fig. 2 is likely to be a two-dimensional projection to the {110} surface of dislocations forming on the inclined {111} facets. Figure 3 is a schematic diagram showing the geometrical relationship between the {110} interface and the {111} interface facets. The {110} interface plane and one of the {111} facet planes form an angle of 35.26°. In the {110} zone axis, the dislocation line runs long along [001] and short along [110] at an angle

![Fig. 1.](image1)  
![Fig. 2.](image2)  
![Fig. 3.](image3)

**Fig. 1.** (a) High-resolution TEM image showing the {111} surface of NiSi$_2$ taken after annealing at 550 °C for 124 min. (b) Plan-view HRTEM image of the NiSi$_2$/c-Si{111} interface taken after annealing for 252 min.

**Fig. 2.** Plan-view HRTEM image of misfit dislocation networks in the NiSi$_2$/c-Si{110} interface taken after annealing for 167 min.

**Fig. 3.** Geometry of the {110} interface plane and the {111} interface facet planes viewed along [110].
of 90° with the long components. The shear displacement occurs along the short dislocation line in the (110) surface, which is represented by a vector of 1/2 [\(\bar{1}10\)] (whose magnitude is marked by a scale bar with a notation of \([b]\), as shown in Fig. 2), and this direction can appear also on the (111) interface facet plane [as exhibited in Fig. 3, the \([\bar{1}10]\) direction is common to both the (110) and (111) surfaces.], indicating that the displacement along the short dislocation line is associated with a screw dislocation with \(b=1/2 [\bar{1}10]\). It is thus accepted that the long dislocation line corresponds to the edge dislocation with the same Burgers vector. The dislocation line of the edge dislocation with the Burgers vector should have the [\(\bar{1}12\)] direction on the (111) interface, and as shown in Fig. 3, its two-dimensional projection to the (110) surface should be the [001] direction, in agreement with the present observation shown in Fig. 2. Because the 1/6 \(\langle 112\rangle\)-type screw dislocation in the \{111\} surface will produce a very small displacement, it cannot explain the observed displacement projected to the (110) interface in Fig. 2. In addition to the edge and screw dislocations, a mixed dislocation appears, whose dislocation line runs along \([\bar{1}12]\) in the projection of (110), which corresponds to [010] in the (111) interface facet. The observed dislocation line facets imply the dislocation line energy anisotropy, of which a theoretical analysis is in progress. The presence of the 1/2 \(\langle 1\bar{1}0\rangle\)-type dislocations in the NiSi\(_2\)/c-Si interface indicates the epitaxial relationship between the c-Si and the NiSi\(_2\).

In addition to the NiSi\(_2\), nanometer-sized Ni particles [cubic, Ni with 0–18 at. % Si, \(a=3.525–3.515\) Å (Ref. 16)] are observed, as shown in Fig. 4, during the \textit{in situ} examination at 550 °C. Figures 4(a) and 4(b) were taken from different particles after annealing for 26 and 206 min, respectively. The Ni particles seen in Figs. 4(a) and 4(b) are (110) oriented and the measured interplanar spacings indicated in Fig. 4 correspond to the \{111\} spacings (2.035 Å) of Ni. Their sizes are in the range of 3–4 nm in equivalent-square diameter. Some particles are single crystals revealing \{111\} and \{100\} surface facets arising from truncated octahedral shape, as shown in Fig. 4(a), and the others are observed to contain more than one twin boundaries (multiply twinned), as represented in Fig. 4(b). The particle in Fig. 4(b) also reveals flat \{111\} surfaces, but faceting is not so distinct as compared with Fig. 4(a). It is well known that small nanoparticles of fcc metals take a structure of the decahedral or icosahedral multiply twinned particles (MTPs).\(^{17–19}\) Figure 4(b) represents a decahedral MTP viewed along the fivefold axis in the \([\bar{1}10]\) direction. Unlike the NiSi\(_2\), crystallization does not occur around the Ni particles.

### IV. DISCUSSION

The dislocation lines shown in Fig. 2 are interpreted as forming at the interface between NiSi\(_2\) and c-Si, as observed by Tung et al.\(^{13}\) This finding indicates that the surface formation of the NiSi\(_2\) layer is followed by the crystallization of the a-Si below.

Below the eutectic temperature of 993 °C, NiSi\(_2\) is in equilibrium with Si,\(^{20}\) and actually, it is reported to exist at the Ni/c-Si interface.\(^{10–15}\) The Ni nanoparticles formed during the present observations by the high-voltage TEM (HVTEM) such as ARM have not been reported in studies using different methods. Their formation in the present study may be attributed to heat evolution effect by the high-energy electron beam during the observations. Because of the poor thermal conductivity of the a-Si layer and the glass substrate, the heat generated by electron beam is not expected to be efficiently dissipated. In this situation, the formation of NiSi\(_2\) will be prevented, because it is an exothermic reaction.\(^{21}\)

Nickel is observed to be the dominant diffusing species in the formation of NiSi\(_2\),\(^{22}\) and in a Ni/a-Si interface, Ni atoms will diffuse into the a-Si layer to form NiSi\(_2\). During the formation of NiSi\(_2\), a small amount of Ni atoms may not be incorporated into the formed NiSi\(_2\). As in the case of the eutectic-forming metals suggested by Radnoczi et al.,\(^{3}\) such free Ni atoms can diffuse into the a-Si layer, contributing to crystallization. Such a possibility can be found in the observation of Mohadjeri et al.,\(^{8}\) which shows that Ni diffuses through the a-Si layer toward a-Si/c-Si interface and the
V. CONCLUDING REMARKS

We have shown through in situ HRTEM that the NiSi$_2$ and Ni particles form during annealing at 550 °C in the TEM. The Ni particles are single crystalline or multiply twinned. The formation of the Ni particles is due to beam heating effect by the high-energy electron beam irradiation during the in situ observation by the HVTEM. Crystallization occurs with the formation of the NiSi$_2$ precipitates but is forbidden around the Ni particles. Around the NiSi$_2$, Ni solutes are expected to be dissolved in the amorphous silicon (α-Si) matrix. However, the presence of the Ni nanoparticles suggests that Ni solutes cannot diffuse into the α-Si matrix. The formation of the Ni nanoparticles could not be observed in the normal heat treatment without the electron beam irradiation, but the inhibition of crystallization around the Ni particles suggests that Ni solutes enhance crystallization.

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