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**In situ high-resolution transmission electron microscopy study of interfacial reactions of Cu thin films on amorphous silicon**

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Interfacial reactions of Cu with amorphous silicon (α-Si) in the Cu/α-Si/glass system are studied by in situ high-resolution transmission electron microscopy at 550 °C. Various Cu silicides, such as γ-Cu3Si, Cu13Si4, and Cu5Si, and Cu particles are observed. The formation of the Cu particles can be attributed to a heating effect from electron beam irradiation. Around the Cu silicides, crystallization of α-Si occurs. Around the Cu particles, however, crystallization does not occur. Crystallization appears to be enhanced by Cu dissolved in α-Si. © 2006 American Institute of Physics. [DOI: 10.1063/1.2179143]

Polycrystalline silicon (poly-Si) thin films and their processing are important for the fabrication of thin film transistors, flat-panel displays, and large-area electronic applications. Generally, poly-Si is made by annealing amorphous Si (α-Si) films which are deposited from the vapor phase and much research has been done on the crystallization mechanism of α-Si. The intrinsic crystallization temperature of α-Si (~600 °C) (Ref. 1) can be decreased by the addition of metal impurities, such as Au, Al, and Sb, which form eutectics with Si, and Pd (Ref. 5) and Ni, which form various silicides with Si. For the eutectic-forming metals, Radnoczi et al. suggested that Au, Sb, and Al dissolved in α-Si film may weaken the covalent bonding in the α-Si and make the α-Si even unstable thermodynamically, enhancing crystallization.

For the silicide-forming metals, the formation of silicides is reported to enhance crystallization. Lee et al. found in the system of Pd/α-Si that crystallization occurs at 500 °C. Considering that Pd reacts with Si to form Pd3Si even at room temperature, and that Pd3Si is hexagonal and its orientation relationship with Si is Pd3Si/Si(0001)//Si(111) and Pd3Si[2110]/Si[112]., they proposed that crystallization may occur at the Pd3Si/α-Si interface by the epitaxial growth of Si on Pd3Si. Also, in the case of the Ni/α-Si system, the formation of a silicide occurs prior to crystallization. NiSi2 precipitates with CaF2 structure are observed to form in α-Si in the shape of octahedra bounded by eight {111} faces at about 400 °C, and then at about 500 °C, the crystalline Si [c-Si, which is designated as opposed to amorphous Si (α-Si)] is epitaxially nucleated on one or more of the NiSi2 {111} surfaces. The NiSi2 precipitates are observed to migrate in α-Si films, leaving c-Si needles behind. Although Cu has the highest solubility and diffusivity as an interstitial diffuser in Si at elevated temperatures among all transition metals, the mechanism of crystallization by Cu has not been studied. It would be interesting to compare the effects of Cu on crystallization with those of other metal catalysts, both silicide and eutectic forming.

In this letter, we report how Cu reacts with α-Si and how such reactions affect crystallization of α-Si, using a Cu/α-Si/glass layered system. Rigorous study of Cu-mediated crystallization of α-Si requires real-time, atomic resolution observation, for which we have used in situ high-resolution transmission electron microscopy (HRTEM). We have found Cu particles, and various Cu silicides, such as γ-Cu3Si, Cu13Si4, and Cu5Si, during the annealing. The unusual formation of the Cu particles is explained by a heating effect from beam irradiation. Crystallization behaviors depend on the precipitate types (Cu particle or silicides), the reason for which is discussed.

Thin 80 nm α-Si was deposited directly on Corning 1737 glass by plasma-enhanced chemical vapor deposition at 280 °C using Si2H6 and H2 as source gases. The wafer was cut into 3 × 3 cm² square specimens and, subsequently, a thin 2 nm Cu layer was deposited on the α-Si layer by dc sputtering. Disks of 3 mm diameter were cut using an ultrasonic cutter for TEM specimen preparation. The disks were mechanically backthinned to a thickness of about 10 μm, and then ion milled on the glass substrate side at an accelerating voltage of 3.5 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 Stuttgart JEM-ARM1250 (JEOL Ltd., Japan) operated at 1.25 MeV (0.12 nm point-to-point resolution), which is equipped with a side-entry heating stage and whose specimen chamber base pressure is ~2 × 10⁻⁶ Pa. The heating rate was 20 °C/min. Electron current densities at the specimen were in the range of 15–20 A/cm² during the observation.

The TEM specimen was annealed at 550 °C in the TEM and observed in situ without tilting. Figure 1 reveals the formation of a large precipitate of ~40 nm in equivalent-sphere diameter [Fig. 1(a)]. Figure 1(b) shows an enlarged view of the upper part of Fig. 1(a), including a part of the large precipitate (shown at the bottom). The precipitate is γ-Cu3Si observed with a [111] orientation. The measured spacings of three sets of planes are nearly identical to the...
(110) spacing (2.02 Å) of η-Cu₃Si (rhombohedral, \(a=2.47\,Å, \alpha=109.74^\circ\)).\(^{10}\) Above the η-Cu₃Si in Fig. 1(b), c-Si exists, which is identified by Fourier transform of a selected area above the η-Cu₃Si (Fig. 1(c)). Two spots nearest to the center in the Fourier transform correspond to spacings of 1.93 and 1.62 Å, which are identical to the 220 (1.920 Å) and 113 (1.638 Å) spacings of Si. [Si also means crystalline Si (c-Si). Hereafter, it will be used when mentioning interplanar spacings.] Figure 1(d) shows an enlarged view of the left part of Fig. 1(a). The lattice fringes of the grain to the left of the η-Cu₃Si reveal the {200} spacings (1.800 Å) of Cu.

The upper part of Fig. 2 is c-Si and the bottom part is Cu₁₅Si₄. In this case, the c-Si is <111>-oriented. However, the spacings of a set of planes in the c-Si do not correspond to the Si{220} spacings (1.920 Å), but seem to arise from the forbidden 1/3{422} reflections corresponding to a spacing of 3.327 Å, which are attributed to {111} twins and stacking faults.\(^{11,12}\) The measured spacings and the angle in the lower part are consistent with the {510} spacings (1.890 Å) and the intersecting angle between them [e.g., (510) and (015)] (87.8°) of Cu₁₅Si₄ (cubic, \(a=9.615\,Å\)).\(^{13}\) As for Cu₁₅Si₄, c-Si is observed also around Cu₃Si, which is not presented here.

Additionally, Cu particles (cubic, 1.09–6.61–11.59 at. % Si, \(a=3.608–3.612–3.615\,Å\))\(^{14}\) are also observed, as shown in Fig. 3. The Cu particle is observed with a <110> orientation, and the measured interplanar spacings (2.08±0.05 Å) correspond to the {111} spacings (2.078 Å) of Cu. Its size is \(~9\,nm\) in equivalent-sphere diameter. The Cu particle reveals {111} and {100} surface facets. Such small, faceted Cu particles are frequently observed. Unlike the silicides, however, crystallization of a-Si does not occur around the Cu particles.

The metal-rich silicide Cu₃Si is in equilibrium with Si below the eutectic temperature of 802 °C (Ref. 15) and, actually, it has been reported that the Cu₃Si phase exists at the
Cu/Si interface.\textsuperscript{16,17} Ha et al.,\textsuperscript{18} however, observed the Cu$_3$Si$_4$ at the interface. In the present study, however, Cu particles are also observed, as seen in Fig. 3. This unusual effect may be due to electron beam heating. If generated heat by electron beam during the observation is not efficiently dissipated probably due to the poor thermal conductivity of the $a$-Si layer and the glass substrate, the exothermic silicide formation will be prevented, leading to the formation of the Cu particles. Although, presently, no experimental results are available on the wetting behavior of Cu on $a$-Si substrates, the formation of the very small Cu particles appears to imply that Cu tends to dewet, or partially wet on $a$-Si. The surface facets of the Cu particle indicated in Fig. 3 reveal the surface energy anisotropy of Cu.

Surprisingly, crystallization is prevented around the Cu particles as shown in Fig. 3 and it might appear that this is explained in terms of difference in lattice mismatch with Si between Cu particles and silicides. As for the Ni and Pd effects on crystallization of $a$-Si,$^5,6$ crystallization can be enhanced by the epitaxial growth of $c$-Si on silicides. However, the lattice mismatch between Cu and Si is reported to be reduced down to 6\% with the orientation relationship of Cu(100)/$\parallel$Si(100) and Cu[001]/$\parallel$Si[111],\textsuperscript{19} which is low compared to the $\sim$5\% for $\eta$-Cu$_3$Si with the orientation relationship of $\eta$-Cu$_3$Si/[111]/$\parallel$Si[111] and $\eta$-Cu$_3$Si[110]/$\parallel$Si[110].\textsuperscript{20} Therefore, the explanation by lattice mismatch can be excluded.

Copper is the dominant diffusing species in the formation of Cu$_3$Si (Ref. 21) and most likely of other Cu silicides, though not reported and, hence, when a Cu film contacts an $a$-Si layer, Cu atoms will diffuse into the $a$-Si layer, leading to the formation of Cu silicides. During that course, it may be that some Cu atoms are not incorporated in the silicides. They will continue to diffuse into the $a$-Si layer with a high mobility without forming silicides, because Cu has the highest mobility and solubility in Si among all transition metals.\textsuperscript{9} In contrast, the presence of the Cu particles, as seen in Fig. 3, implies that the diffusion of Cu into the $a$-Si is prevented around them. Therefore, we deduce that while the $a$-Si matrix around the Cu silicides obtains enough Cu solutes for crystallization, the matrix around the Cu particles undergoes the lack of Cu proving insufficient to induce crystallization. As mentioned before, Radnoczi et al.\textsuperscript{3} suggested that eutectic-forming metal impurities dissolved in an $a$-Si film may enhance crystallization by weakening the covalent bonding in the amorphous film. The same holds for Cu. Unlike other silicide-forming metals, such as Pd and Ni, Cu appears to enhance crystallization by being dissolved in and diffusing into the $a$-Si layer and making it unstable.

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