Interfacial Reaction in a-Si/Au and a-Si/Cu Thin Film Bilayers

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We have studied the interdiffusion and compound formation at the a-Si/Au and a-Si/Cu thin film interfaces using x-ray reflectivity and grazing incidence EXAFS techniques. In the 0 °C as-deposited samples, reaction between Si and Au is minimal, but reaction between Si and Cu is significant. Upon annealing for ten minutes in argon, the a-Si crystallized and reacted quite extensively with Au at 160 °C. Further reaction between Si and Cu proceeded at 130 °C. The compounds formed appear to be metal-rich silicides in both the Si/Au and Si/Cu systems. For Au/Si the silicide is likely stabilized on the surface of the newly formed crystallites.

Keywords: Interface reactions, amorphous semiconductors, EXAFS, Si, Au, Cu, x-ray reflectivity

1. INTRODUCTION

Studies of interface structure, interdiffusion and compound formation at metal-semiconductor interfaces has been of great interest. Reaction at the interface can occur at quite low temperatures and the metal contact often induces low temperature crystallization of amorphous semiconductors.¹⁾ The compound formation at interfaces often differs from bulk reactions and the current understanding of metal-induced Si and Ge crystallization is quite incomplete. We have chosen to study the crystallization process and compound formation in a number of metal-amorphous germanium (a-Ge) and metal-amorphous silicon (a-Si) systems, including Al-Ge,²⁾ Au-Ge,³⁾ Au-Si and Cu-Si. In Al-Ge and Au-Ge bilayers, we found that the Ge crystallizes at 120 and 170 °C respectively, much lower than the normal crystallization temperature of about 400 °C. The crystallization is accompanied by both metal and Ge diffusion across the interface. However, detailed EXAFS measurements of the Au-Ge bonding was complicated by the strong Ge absorption. To further determine the role of the metal in the low-temperature crystallization, we studied co-deposited $a\text{-Ge}_{1-x}\text{Au}_x$ films and found that the film crystallizes at temperatures as low as 130 °C, for Au concentrations of about 22%. Low concentrations of about 4% Au had much effects on the crystallization temperature. In the amorphous films, Au-Ge bonds are formed, but Au atoms tend to precipitate upon Ge crystallization and compound formation is insignificant. Our results suggested that for metals that do not form compounds with Si or Ge, metastable M-Si or M-Ge bonds form at the interface and the metastability of the bonds play a crucial role in inducing the

low-temperature crystallization.

We report in this paper our results on the Au-Si and Cu-Si systems and concentrate on the compound formation at the interface. Au-Si should be similar to Au-Ge, and the lower absorption of the Si allows a more detailed study of the fate of the Au. Cu-Si presents a different case where several equilibrium compounds are known to exist.

2. EXPERIMENTS AND DATA ANALYSIS

The a-Si/Au and a-Si/Cu bilayers were deposited by evaporation in a UHV chamber on 1x2 inch float glass held near 0 °C. The pressure was 1.2×10^{-9} torr before evaporation and remained below 5×10^{-8} Torr during deposition. High purity Au and Cu were evaporated from resistively-heated alumina crucibles, and Si deposition is done using an 3 kW electron-beam evaporator. Thickness and deposition rate were measured using a crystal monitor. Deposition rates were about 1-2 Å/s. The thickness of metal underlayers were chosen to be thick enough to avoid the effect of the metal-substrate interface on the Si-metal reaction, but thin enough for the film surface to essentially replicate the substrate smoothness. The silicon top layer thickness ($\approx 750 \text{ Å}$) was kept thin enough to allow easy penetration of the x-rays to the interface.

X-ray reflectivity and glancing angle EXAFS data were measured using a two-circle Huber goniometer on beamline X-11A at the National Synchrotron Light Source (NSLS). The Si(111) double crystal monochromator was detuned 20% to reduce harmonics. Incident and reflected beams were defined by a set of $0.2 \times 8 \text{ mm}^2$ slits. The incident, reflected and fluorescence signals were measured using gas ionization

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chambers. X-ray reflectivity data were taken at energies 300 eV below and above the metal absorption edge. Simultaneous analysis of data taken two energies constrains the reflectivity fitting, and enhances the sensitivity to metal diffusion into the Si layer. EXAFS spectra were collected at incidence angles below the critical angle of the metal to selectively probe a thin layer (20-50 Å) near the interface, and at large angles to measure the bulk of the film. The as-deposited samples were measured to obtain reflectivity and EXAFS data, annealed in a static argon atmosphere for 10 min., and remeasured at room temperature after each anneal at increasing temperatures.

The reflectivity data are fit using procedures described previously.⁴⁾ The sample is modeled by a number of layers, each with a uniform composition and thickness. The reflection and refraction at the interface between layers are described by Fresnel's law with an additional factor accounting for the effect of the interface roughness, which is treated with a Gaussian model in the present analysis. The EXAFS data were analyzed by the standard Fourier-filtering and non-linear least square fitting procedure. Data from gold and copper metal were used as standards for the EXAFS amplitude and phase of Au-Au and Cu-Cu pairs, respectively, while theoretically calculated (FEFF program)⁵⁾ values were used for Au-Si and Cu-Si pairs. The results of the fitting analysis are listed in table I. We have

corrected the EXAFS data, according to a procedure described before⁶⁾, for distortion due to anomalous dispersion in the real and imaginary parts of the optical constant. This was done only when a good fit to the reflectivity data was obtained, and results in table I are from corrected EXAFS data only.

3. RESULTS AND DISCUSSION

Figure 1 presents the reflectivity at 11619 eV (300 eV below the Au L₃ edge) for the as-deposited and annealed 755 Å Si/300 Å Au bilayer sample. The reflectivity exhibits strong oscillations in the region above the Si critical angles (0.12°) and below the Au critical angle, where the x-rays penetrate through the Si layer and are totally reflected at the Si/Au interface. These oscillations are the result of interference between the x-rays reflected at the Si surface and at the Si/Au interface, and the Si thickness determines the oscillation frequency. The reflectivity fitting results indicate that in the as deposited sample the Si-Au interface is sharp and there is very little interdiffusion. The Si layer thickness determined from fitting is 755 Å. Upon annealing at 130 °C, the reflectivity actually sharpens slightly (near the Si and Au critical angles), and the shift in the oscillations indicates the Si thickness has decreased by about 10 Å. The interface remains sharp and interdiffusion is negligible. The

Table I. Structural parameters obtained from fitting the Au and Cu EXAFS data for the Si/Au and Si/Cu samples. The σ^2 values are relative to the room temperature standards for the metal-metal bonds and relative to the theory for the metal-Si bonds.

sample	bond	R (Å)	N	σ^2 (Å ²)
<u>750 Å Si/300 Å Au</u>				
160 °C anneal, 0.12°	Au-Si	2.44(2)	2.3(6)	0.011(2)
	Au-Au	2.84 (2)	4.7(1.0)	0.001(1)
160 °C anneal, 0.282°	Au-Si	2.44(2)	2.3(5)	0.0014(2)
	Au-Au	2.84(2)	5.5(1.0)	0.000(1)
160 °C anneal, 2.0°	Au-Si	2.46(2)	1.5(0.5)	0.012(2)
	Au-Au	2.86(2)	8.1(2.0)	0.002(1)
<u>750 Å Si/750 Å Cu</u>				
as-deposited, 0.216°	Cu-Si	2.29(2)	1.9(0.4)	0.000(4)
	Cu-Cu	2.62(2)	2.0(0.6)	-0.005(4)
as-deposited, 0.244°	Cu-Si	2.29(2)	0.8(0.4)	0.000(5)
	Cu-Cu	2.57(2)	4.6(1.0)	0.001(3)
130 °C anneal, 0.214°	Cu-Si	2.31(2)	2.9(0.8)	0.020(5)
	Cu-Cu	2.57(2)	3.2(1.0)	0.001(3)
130 °C anneal, 0.240°	Cu-Si	2.32(2)	1.0(0.4)	0.001(3)
	Cu-Cu	2.59(2)	2.9(1.0)	-0.007(5)

Fig. 1. Reflectivity data for the Si/Au bilayer at 11619 eV.

reflectivity dramatically changes upon annealing at 160 °C, and only one critical angle can be identified. Fitting the reflectivity data suggest that Au diffused throughout the Si layer and the average Au concentration is 27 at.%.

The EXAFS data corroborate the reflectivity data and provide bonding information. Figure 2 displays selected Au L_3 EXAFS data and their Fourier transforms for the Si/Au sample. In the as-deposited form, the local structure around Au atoms in the interface region (0.16°) is nearly identical to that in the bulk of the film, showing that there is essentially no reaction during deposition and storage at room temperature. This is in accordance with the reflectivity result that interdiffusion in the as-deposited sample is insignificant. A non-linear least squared fitting analysis confirms that the bulk Au layer is in the fcc elemental form. No indication of Au-Si bonding is observed at 130 °C annealing either. We note that alloying has been observed upon initial deposition of Au on silicon single crystal surfaces⁷⁾. The finite penetration of the x-rays into the Au layer does not allow the detection of a single layer of bonds, but a definite Au-Si signal would be observed if several layers were involved.

Extensive reaction occurs at 160 °C accompanied by crystallization of the Si layer. The Au spectra from selected regions throughout the film all differ from that of fcc gold, as is clearly shown in fig. 2(b) where the 0.12° spectrum is from the near surface region and the 2.0° spectrum is from the whole film. The fitting analysis was done for the main peak (0.8-3.4 Å) and the result is listed in Table I. The Au-Si distance is 2.44 Å and remains the same for the 0.12°, 0.282° and 2.0°, i.e., constant throughout the whole film. The average Au-Au varies from 2.84 Å at the near surface

Fig. 2. Au L_3 EXAFS data for the Si/Au sample before anomalous dispersion correction. Top: k -weighted EXAFS. Bottom: Fourier transform magnitude.

region to 2.86 Å for the bulk. The systematic variation of the distance in the average Au-Au bond length and the variation of the number of Si neighbors versus the number of Au neighbors convinced us that the reacted film consists of a gold silicide and unreacted Au particles. The short Au-Au distance (2.84 Å) comes from a Au silicide, and the longer distance (2.86 Å) arises from the average of the Au-Au bonds in the silicide and unreacted Au metal ($R_1=2.88$ Å). The presence of a large number of Au neighbors at a short distance of 2.84 Å suggests that the silicide is rich in gold.

Fig. 3. Reflectivity data for the Si/Cu sample at 8680 eV.

Since Au and Si do not form any equilibrium compounds, there is no structural data to compare with our results. Photoemission measurements for Au on Si(111), however, indicate that a reacted phase with approximate composition Au_3Si is stabilized at the interface⁷⁾. Rapid Au transport throughout the film is required to promote the low temperature crystallization, and it is reasonable to assume that after crystallization the interfacial compound seen by photoemission can also form on the surface of the newly crystallized grains. This is consistent with the observation that only a small fraction of the Si atoms can be in the Au rich silicide since the average Au concentration is only 27%, and a substantial portion of the Au is in the normal metallic phase.

Figure 3 presents the reflectivity data for the 750 Å Si/750 Å Cu sample. Strong oscillations are also observed in the reflectivity data. Fitting results indicate that the Si/Cu interface is fairly sharp for the as-deposited sample. However, EXAFS data show that alloying occurred at the interface. Upon annealing at 130 °C and 150 °C, the underlayer critical angle decreases gradually, suggesting further reaction between Cu and Si and an alloy layer forming between the Si top layer and the unreacted copper layer. The Si critical angle remains unchanged, indicating that a layer of Si is preserved while the interface alloying proceeds. The overall reflectivity is dramatically reduced in the annealed samples, especially at 150 °C. This is probably due to a roughened surface and is not related to the reaction at the buried interface. Visually, we found that the color of the sample surface has changed and is not uniform.

Figure 4 (a) and (b) show the Cu K-edge EXAFS data and the Fourier transform spectra for the Si/Cu sample. The

Fig. 4. Cu K-edge data for the Si/Cu sample before anomalous dispersion correction. Top: k^2 -weighted EXAFS. Bottom: Fourier transform magnitude.

angle 0.216° is at the first peak in the reflectivity at 9280 eV, and at this angle the x rays only penetrate a thin layer (50 Å) near the interface, therefore the interface region is selectively probed. The spectrum for the bulk of the film measured at 5° (dashed line in Fig.4) is identical to that of copper metal. For the as-deposited sample, the EXAFS spectrum from the interface region is clearly different from that of the bulk film, revealing reaction between Si and Cu during deposition or storage at room temperature. In this regard, Cu is more reactive with Si than Au, since no significant alloying was detectable at the Si/Au interface at

room temperature. In addition, we found that the original Si surface of a Si/Cu film became reddish after a few months of storage at room temperature, probably because the reaction proceeded from the interface to the surface.

For the as-deposited and 130 °C annealed samples, the Cu-Si distance is about 2.30 Å. The Cu-Cu distance ranges from 2.57 to 2.62 Å (Table I). Contributions from unreacted copper alone cannot account for these bonds since the Cu-Cu distance in the metal is only 2.56 Å. Thus a significant part of the observed Cu-Cu bonds must arise from one or more Cu-Si alloys. The presence of these long Cu-Cu bonds indicates that the alloy is rich in Cu. The phase diagram for Cu-Si shows a number of complicated compounds, all of which are Cu-rich. We estimate that the total number of Si and Cu neighbors in the first shell to be about four to six. However, the present data is not sufficient to identify the stoichiometry of the alloy.

4. SUMMARY

In summary, we have studied the reaction at buried a-Si/Au and a-Si/Cu interfaces using x-ray reflectivity and glancing angle EXAFS methods. For the Si/Au interface, no significant alloying occurs at the interface at room temperature. At 160 °C crystallization is accompanied by extensive reaction forming a Au-rich silicide. The reaction extends throughout the whole film suggesting rapid Au diffusion, probably along the newly formed grain boundaries. Since there are no equilibrium Au-Si phases, the reaction may be related to Au-rich compounds observed to form upon deposition of Au onto single crystal Si surfaces. In the present case grain boundaries may play the same role as the surface in stabilizing the compound formation.

Si and Cu react at room temperature in a thin layer at the interface forming a Cu-rich silicide. Further alloying proceeds at 130 °C and higher temperatures. The reaction seem to occur in a more planar fashion and is more confined to the interface region as compared to the Si/Au materials. It should be interesting as a future study to examine the relationship between the compound formation and Si crystallization in the Si/Au and Si/Cu interface systems.

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