VOLUME 70, NUMBER 24 PHYSICAL REVIEW LETTERS 14 JUNE 1993

Growth of the Room Temperature Au/Si(111)-(7 × 7) Interface

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(Received 12 January 1993)

Synchrotron radiation photoemission spectroscopy suggests that the room temperature grown Au/Si(111) interface is an abrupt interface with the contact made by metallic Au and bulk Si. Si $2p$ core level spectra show no sign of an interface component, but only the surface reacted and bulk Si components during the growth of the interface. A surface Au-Si alloy film is first formed for Au coverages below 3 monolayers. The alloy is then stabilized into an Au_3Si-like film and detached from the Si substrate when metallic Au starts nucleation in between.

PACS numbers: 68.55.Jk, 33.60.Cv, 68.35.Fx

The interest in studying Au/Si interfaces can be traced back two decades due to its possible application as a metal/Si contact in integrated circuit devices. Although the Au/Si contact has been found to be unsuitable for this purpose because Au atoms diffuse extremely fast and serve as deep-trap centers in Si, this interface is still of interest to scientists for many fundamental reasons. Au is a very stable, nonreactive noble metal, and yet it has been reported to be very reactive on a Si surface even when deposited at room temperature (RT). An intermixed Au/Si interface model, first proposed in 1973 [1], has apparently been supported by many experiments [2]. Several groups also support this model but with a critical coverage below which the RT Au/Si interface is abrupt [3]. Theoretically, an intermixed interfacial region between two adjoining phases can minimize the interfacial energy [4] and the RT Au/Si interface appears to fit into such a theory. Even though some doubt has been cast on this model by an Auger electron spectroscopy (AES) experiment [5] and transmission electron microscopy studies [6], the overwhelming support for the intermixed model still makes it the primary model in studying this interface [7] and related properties like Schottky barrier heights (SBH) or ballistic electron emission microscopy (BEEM) of the Au/Si(111) interface [8].

We investigated this controversial issue with synchrotron radiation photoemission spectroscopy (PES) with different photoelectron escape depths, and hence different surface sensitivities, in order to distinguish the surface and bulk Si components at the RT grown Au/Si(111)-(7×7) interface. We find that the RT growth of the Au/Si(111) interface is similar to the Ag/Si(111) interface where no interdiffused interface Si component exists at the metal-Si interface [9]. *In other words, we claim the RT Au/Si(111)-(7×7) surface is an abrupt interface.* As will be seen later, the previously proposed intermixed model is a consequence of energy and/or depth resolutions that were not able to resolve the signals of a surface segregated layer from the substrate.

The experiment was performed at beam line I-1 of Stanford Synchrotron Radiation Laboratory during a dedicated run with 3 GeV beam energy and about 50 mA beam current. The Si(111)-(7 × 7) surface was prepared using a cleaved n-type Si(111) crystal resistively heated at 700 °C for 5 min. Au films up to 20 monolayer (ML) coverage (1 ML $\equiv 7.8 \times 10^{14}$ atoms/cm^2), as measured by a quartz crystal monitor, were then evaporated onto this surface from a well-outgassed Au bead on a Mo filament. Ultrahigh vacuum (base pressure 3×10^{-11} torr) was maintained during sample preparation and data acquisition processes. The pressure during Au evaporation and resistive heatings was about 1.4×10^{-10} torr. Angle integrated photoemission spectra were taken with a double pass cylindrical mirror analyzer (CMA). Photon energies of 110 eV and 150 eV were used to probe the Si $2p$ core level with resolutions of 0.40 eV and 0.45 eV, respectively. A photon energy of 170 eV was used to probe the Au $4f$ core level to obtain the optimum signal-to-noise ratio on this particular beam line.

The Si $2p$ core level spectra are shown in Fig. 1. For Au coverages $\theta \geq 1$, these spectra can be decomposed into two Si doublets having opposite Au coverage dependent shifts from each other. Since the shifts of both peaks in the 110 eV spectra are the same as those in the 150 eV spectra, we know the two components probed at 110 eV photon energy are the two probed at 150 eV. Previous work [10] suggests that the 110 eV spectra with Si $2p$ electron kinetic energy of about 10 eV are more bulk sensitive than the 150 eV spectra. The shaded doublet is therefore identified as a surface component that is shifted to higher binding energies (BE) due to chemical reaction with Au atoms. The other doublet is the Si substrate peak shifting to lower BE due to band bending. Their intensities as a function of Au coverages are shown in Fig. 2. The smooth evolution in both Si $2p$ spectra with increasing coverages suggests that the reaction between Au and the Si surface is a continuing process, not an abrupt process with a critical coverage [11]. The growth of Au overlayers on the Si(111) surface can be divided into two stages at $\theta = 4$ ML according to the changes of

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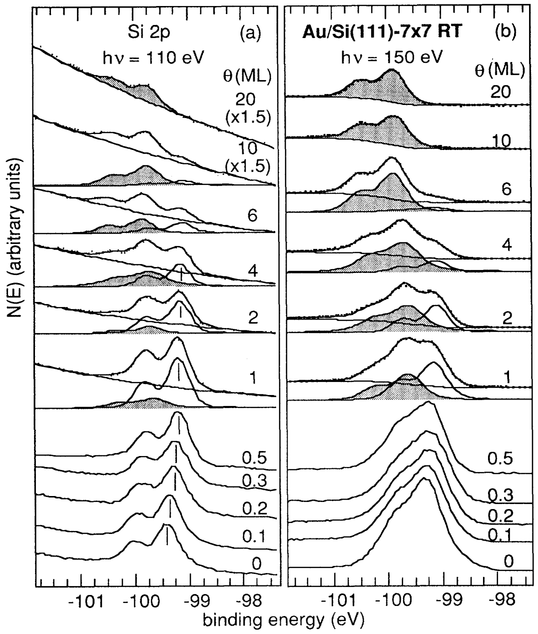

FIG. 1. The Si $2p$ core level spectra taken at 110 eV (a) and 150 eV photon energies (b). For $\theta \geq 1$ ML, the Si $2p$ core levels can be fitted with two components. The shaded component is the Si atoms reacted with Au atoms.

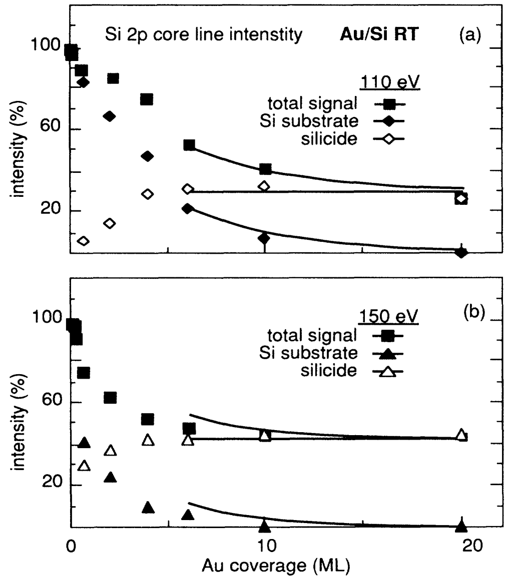

FIG. 2. The Si $2p$ core line intensities as a function of Au coverages at 110 eV (a) and 150 eV photon energies (b). The solid lines are estimates from a simple two-layer model (see text).

the Si $2p$ and Au $4f$ peaks. For $\theta \leq 0.5$, the most noticeable change is the band-bending effect; see Fig. 1(a). The Si $2p$ peaks cannot be resolved unambiguously into surface and chemical shifts as they can for $\theta \geq 1$ ML. X-ray standing wave measurements showed that most Au atoms are located in the 3-hollow sites between the surface Si double layer at this coverage [12]. At $\theta = 1$ ML, it has been reported [13] that the Si $2p$ core level and valence band line shapes of this surface are almost identical to those of an annealed $(\sqrt{3} \times \sqrt{3})$ surface. The similarity of the electronic structure for these two surfaces indicates that the surface reacted Si atoms have the same type of Au coordination as the $(\sqrt{3} \times \sqrt{3})$ surface, i.e., the RT deposited Au atoms also trimerize in the same manner as those on the ordered surface [14] and this surface geometry is likely to serve as a precursor for the $(\sqrt{3} \times \sqrt{3})$ reconstruction. At $\theta = 4$ ML, the growth of the reacted Si peak saturates (Fig. 2), suggesting that the Si surface is passivated against further Au-Si reaction after this stage. The changing chemical shift indicates that the reacted Au-Si film is an alloy, not a stoichiometric compound.

For $\theta \geq 6$ ML, the changes in both Si $2p$ spectra become just the attenuation of the substrate peak while the reacted peak remains constant. At $\theta = 20$ ML, the reacted peak is the only component on the surface. The presence of such reacted Si atoms on the surface of the Au overlayer has long been recognized for Au on Si with very high coverages (up to several hundred ML's) [5, 7, 15–17]. The film has been determined [7, 18] to be 1–1.5 ML of reacted Si with a composition of about Au:Si ~ 3:1. It has not been realized, however, that the growth of this silicidelike layer is already stablized at such a low coverage (6 ML). Since the stoichiometry of this film is constant after $\theta = 6$ ML, it is a stable compound which can be designated as a Au_3Si-like film. This surface film may not be identical to the Au_3Si silicide because the local atomic configuration can be different from the bulk phase as it is only 1–1.5 ML thick and resides on the surface.

A consistent view on the growth of the surface silicidelike layer can be obtained from the Au $4f$ core level spectra (Fig. 3). The Au $4f$ peak becomes broader with increasing Au coverages as an extra doublet is emerging at the right-hand side of the original peak for $\theta \geq 4$ ML. Our resolution is not sufficient to resolve the two peaks as well as in the Si $2p$ spectra. Thus we must rely on curve fitting, a procedure which only is unique for $\theta \geq 6$ ML. We can identify the shaded peak as the reacted Au atoms in the silicidelike film because this peak diminishes when the $\theta = 20$ ML surface is exposed to 10^{-3} torr O_2 for 1000 sec. The other peak is the metallic Au. Figure 4 shows that the growth of the reacted Au $4f$ peak is already saturated at $\theta = 6$ ML. Since the silicidelike layer has a composition of Au_3Si, we would expect only 3–4 ML Au atoms near the surface to be reacted and that they stay on top of the rest of the unreacted Au atoms (2–3 ML). The fact that the total Au signal increases with increasing Au coverages and yet the reacted Au $4f$ peak intensity saturates at 6 ML suggests that the growth of a metallic Au layer is underneath the surface silicidelike layer and not above.

PES is not an ideal tool in studying surface morphol-

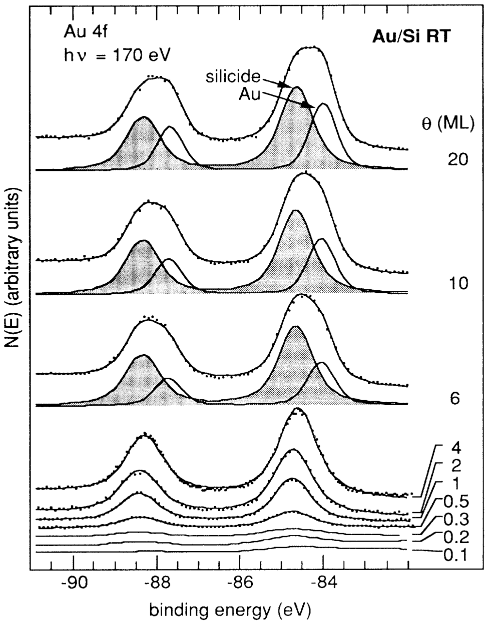

FIG. 3. The Au $4f$ spectra taken at 170 eV. The reacted (shaded) and metallic Au components can be separated by curve fitting for Au coverages higher than 6 ML.

ogy of an interface because intensity attenuation analysis commonly used in PES is only suitable for uniform overlayers with an ideal surface. Nonetheless, we find that growth of the Au/Si interface for $\theta \geq 6$ ML is consistent with a simple two-layer model where a metallic Au interlayer grows in between the Si substrate and a surface Au_3Si-like layer containing 1.8 Å (1.1 ML) Si and 4.2 Å (3.2 ML) Au. Assuming that the photoelectron intensity decays at a rate of $e^{-d/\ell}$ for an atomic layer d Å away from the surface and that $\ell = \lambda \cos\theta$ is the effective electron escape depth (with λ being the photoelectron's inelastic mean free path and θ the CMA's average acceptance angle, 43.2° [19]), the estimated relative intensities of various Si and Au components are shown as solid lines in Figs. 2 and 4. The corresponding escape depths are 5 Å (7 Å) and 3.2 Å (5 Å) for ~10 eV and ~50 eV electrons in the Si (Au) layers, respectively. In Au ℓ is 4 Å for ~85 eV electrons. These electron escape depths are chosen to give consistent estimates for different photon energies for $\theta \geq 6$ ML (to within 5% of the measured relative intensities). The trend of the λ for electrons in Si is consistent with an estimated value of intermediate kinetic energy (3.9 Å for ~20 eV electrons [10]). The fit to the layer growth model indicates that the growth of the Au overlayer on Si for $\theta \geq 6$ ML, though not epitaxial, is a rather uniform layer growth. This is consistent with the observation by scanning tunneling microscopy on a 150 Å Au covered Si surface where only about 10% roughness was found [8]. For $1 \leq \theta \leq 4$ ML, deviations from what the simple two-layer model predicts occur. Either the layer growth model is not applicable or a different scattering mechanism may be in place in this range. Better understanding of the local atomic structure for $1 \leq \theta \leq 4$ ML will require other techniques like surface extended x-ray fine structure (SEXAFS) studies.

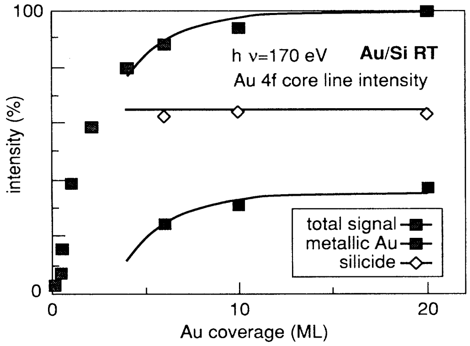

FIG. 4. The Au $4f$ core line intensities as a function of Au coverages. Solid lines are estimates from a simple two-layer model (see text).

Being able to distinguish the surface silicidelike component from the substrate in the Si $2p$ spectra is the critical step in our investigation of the RT Au/Si interface growth. In Figs. 1(a) and 1(b), with two different probe depths (5 Å and 3.2 Å), the Au covered Si surface shows only two Si components at $\theta = 6$ ML. At $\theta = 10$ ML, the Si substrate peak, which is buried under a 3–4 ML thick Au_3Si-like film and a 6–7 ML thick metallic Au layer, is not observable in the 150 eV spectrum but still observable in the 110 eV spectrum. Since we know that between these two components one is the surface component in the surface silicidelike layer and the other is the substrate component underneath the metallic Au interlayer for $\theta \geq 6$ ML, there are no other Si components that we can assign as "interface" components, which should exist for an intermixed interface, that make contact to the Si substrate. Consequently, the contact layer to the Si substrate must be the metallic Au interlayer itself. Previous experiments (PES, AES, or electron energy loss spectroscopy) [2] were not able to resolve the silicidelike peak on the surface from the substrate peak, and the transition of the Si spectra from the bulk to the silicidelike phases was taken as evidence for an intermixed model. As shown in Fig. 1 this transition can take 10–20 ML Au deposition to complete depending on the surface sensitivity. Although Molodtsov *et al.* [7] were able to resolve these two components, they only studied the surface and assumed that the interface will change in the same way. Therefore they came to the same conclusion as previous investigators.

Based on this analysis and existing data from the literature (when the resolution is not of critical importance), we can propose a growth model that summarizes our findings and previous work for the RT deposited Au/Si(111)-(7 × 7) interface. For $\theta < 1$ ML, most Au atoms are in the 3-hollow sites with some surface ordering [12]. When θ increases towards 1 ML, the Au atoms trimerize like those of a ($\sqrt{3} \times \sqrt{3}$) Au/Si surface [13, 14]. For $\theta >$

1 ML, deposited Au atoms continue to react with the surface Si atoms forming an Au-Si alloy until a layer of stable Au_3Si-like film is completed at $\theta = 3$–4 ML. Metallic Au starts nucleation underneath this silicidelike layer. When ∼1 ML metallic Au layer is completed at $\theta = 4$–5 ML, this layer then breaks the bonding between the surface silicidelike layer and the Si substrate. Once detached from the substrate, Si atoms in the silicidelike layer are displaced from the original bulk positions and that could account for the sudden increase of displaced Si atoms observed in the ion channeling experiments [11]. When more Au atoms are deposited onto the surface, these atoms penetrate through the surface silicidelike layer and nucleate with the underneath lying metallic Au. This process continues for thicker metallic Au growth. The final structure of a RT deposited Au/Si(111)-(7 × 7) surface is therefore composed of a 1–1.5 ML Au_3Si-like surface layer and a sandwiched Au layer with an atomically abrupt interface to the Si substrate.

We can infer the bonding strengths between various types of bonds at this interface from our model. On a bare (7 × 7) surface, metallic Au-Au bonding is surpassed by the bonding between Au and surface Si atoms until all surface Si atoms are reacted to form a Au_3Si-like phase. The fact that Au nucleation is underneath the surface layer and not above suggests that additional Au atoms favor the interaction with the bulk Si substrate over Au_3Si. The interaction, however, is not able to break the bulk Si bonds to form a second Au_3Si-like layer. Au atoms then start forming metallic bonding in between. The difference in reactivity between surface and bulk Si atoms to Au atoms is probably due to the disruption of the covalent sp^3 bonds on the surface Si atoms.

In conclusion, we find that the RT Au/Si(111)-(7 × 7) interface is an abrupt interface. The PES data suggest that 1–1.5 ML of surface Si atoms react with 3–4 ML Au atoms and this passivates further Au-Si reaction. Au then starts nucleate between the surface silicidelike layer and the substrate. There is no reacted Si component at the metallic Au and the bulk Si interface. The RT Au/Si interface is thus similar to that of a Ag/Si interface except with a surface segregated silicidelike layer. The SBH and BEEM properties of the RT Au/Si(111)-(7 × 7) interface are therefore determined by the metallic Au, not Au-Si alloys or other types of Au silicides. The interfacial free energy at the RT Au/Si(111)-(7 × 7) surface appears not to be controlled by the composition gradient [4], which favors the existence of an intermixed interface, but by the cohesive energy of metallic Au.

This work was originally funded by the Office of Naval Research under Grant No. N00014-86-K-0736. The Stanford Synchrotron Radiation Laboratory is supported by the Department of Energy, Office of Basic Energy Sciences, and the National Science Foundation, Division of Materials Research.

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