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Tun-Wen Pi
Iowa State University

A.-B. Yang
Iowa State University

C. G. Olson
Iowa State University

David W. Lynch
Iowa State University, dlynch@iastate.edu

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Abstract
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Keywords
Ames Laboratory, gold, rf-sputtered, adatoms

Disciplines
Atomic, Molecular and Optical Physics | Condensed Matter Physics | Physics

Comments
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Tun-Wen Pi, A.-B. Yang, C. G. Olson, and D. W. Lynch

Department of Physics and Ames Laboratory–Department of Energy, Iowa State University, Ames, Iowa 50011

(Received 26 April 1990)

We report a high-resolution photoemission study of Au evaporated on rf-sputtered a-Si:H at room temperature. Three regions of coverage can be classified according to the behavior of the valence-band and core-level spectra: an unreacted region with an equivalent thickness of 2 Å, followed by an intermixed Au/a-Si overlayer (~9 Å), and a dual-phase region at higher coverage. Au adatoms are dispersed in the unreacted region. They subsequently cluster in the intermixed region, where they attach to Si atoms that are not hydrogen bonded, suggesting that the intermixed Si is mainly from those that have dangling bonds. In the dual-phase region, two sets of Au 4f core levels evolve with higher binding energy, one from Au intermixed with Si, and the lower one exhibiting pure gold character. The interface eventually ends up with the sequence: a-Si:H(sub.)+(pure Au mixed with intermixed Au/Si)+(vac). This is unlike the case of Au on c-Si, which has a pure gold layer sandwiched by intermixed Au/Si complexes along the surface normal. Traces of silicon atoms on top of composite surfaces appear even at the highest coverage, 205 Å, of the gold deposit. The applicability of the four models previously used for the Au/c-Si interface is also briefly discussed.

INTRODUCTION

Comprehending completely the metal-semiconductor interface is a challenge, not only for academic reasons but for improved industrial application. Au/c-Si is a good example to demonstrate the complexity of the interface. This diffuse interface has stimulated a number of researchers to use assorted surface-sensitive techniques, e.g., ultraviolet photoemission spectroscopy (UPS), Auger-electron spectroscopy (AES), electron-energy-loss spectroscopy (EELS), low-energy electron diffraction (LEED), transmission electron microscopy (TEM), and MeV He⁺-ion scattering. The general picture of the growth of gold atoms on single-crystal Si at room temperature can be sketched as follows. From the onset of deposition, Au atoms grow randomly on the c-Si surface without interacting with the underlying Si. After a critical equivalent thickness is exceeded, Au commences to intermix with Si atoms. Because the lowest eutectic temperature of Au/Si is 370 °C, no equilibrium silicide phase can be formed at room temperature. As deposition of gold increases, the interface ends up with the sequence Si(sub.)–(Au/Si)–(pure Au)–(Au/Si)–(vac.), where (Au/Si) denotes intermixing. The thickness of the intermixed region in the vicinity of the vacuum is claimed to be <1 monolayer (ML) in Ref. 3, but to be 1.5 ML in Ref. 13, where a monolayer is defined as the atomic density of a Si(111)7×7 surface. The bonding environment of the intermixed Si atoms has been proven different from that of tetrahedrally bonded bulk Si. The substrate for the intermixed Au/Si on each side of the pure gold layer mean that their electronic properties and chemistry are not necessarily the same.

In this paper, we report a high-resolution photoemission study of the Au/a-Si:H interface using synchrotron radiation. Some differences are found from its crystalline counterpart. For instance, the presence of the Si 2p core level in each measurement suggests that the interface is intermixed all the way (after an inert thickness of 2 Å is deposited). That is to say, for Au/a-Si:H, there is no pure Au layer as in the case of Au on c-Si. Moreover, two components of the Au 4f levels develop. One of them evolves intermixed with silicon, while the other develops as pure gold.

We present the paper as follows. The experimental methods, including film preparation and data acquisition, are followed by a presentation of the results, which divide into four subsections according to interfacial behavior: null (0 Å), low (θ < 2 Å), intermediate (2 ≤ θ ≤ 9 Å), and high-coverage (θ > 9 Å) regions. Then a discussion leads to explaining the behavior in each region. Conclusions are drawn at the end of the paper.

EXPERIMENT

Hydrogenated amorphous-silicon substrates were prepared by rf sputtering. A polycrystalline silicon target was the upper electrode of the rf diode sputtering system. The single-crystal silicon substrate held at room temperature rested on a stainless-steel disc which, in turn, mounted on the lower electrode with the same diameter as the target. The electrodes were pulled 1 in. apart, offset to the thickness the stainless steel disc. The pressure was reduced to 2×10⁻⁷ Torr before sputtering. A mixture of argon, with a partial pressure of 25 mTorr, and hydrogen at 2 mTorr, was then allowed to flow kinetically into the chamber during deposition. The 13.56 MHz rf power was set at 500 W, giving a power density of 2.74 W/cm². The silicon deposition rate was 6.7 Å/s. The thickness of the product was measured to be 2.2 μm. A brief study was made on a “device quality” glow-discharge a-Si:H sample.
The surfaces of the \( a \)-Si:H films needed to be chemically clean before insertion into the UHV experimental chamber in order to reduce sputtering time. They were etched in HF and rinsed with distilled water. The cycle was repeated, if necessary, until water was able to wet the surface. Dry helium was used to blow off the liquid. The cleaned sample was then attached to an oxygen-free high-conductance (OFHC) copper rod screwed in the manipulator. An Ar-ion sputter gun was employed at normal incidence to remove residual contamination on the surface. Recently, Lu et al.\textsuperscript{15} reported a comparison of the oxidation kinetics of HF-etched \( a \)-Si:H, c-Si, and Ar-etched \( a \)-Si:H exposed to the ambient atmosphere. The results indicated a higher oxidation rate for the Ar-etched surface, signifying continuous production of free SiH\(_3\) radicals.\textsuperscript{15} Nevertheless, heat treatment should not be applied since large bubbles and holes might be formed on the heated sample.\textsuperscript{16}

The metal overlayers were obtained by evaporation onto the substrate kept at room temperature. The evaporation rate was 0.12 Å/min at low coverage. Well-outgassed Au was evaporated from a tungsten basket. The pressure during evaporation never exceeded \( 1 \times 10^{-10} \) Torr. The thickness of the deposits was monitored by a quartz crystal. Thicknesses reported are those of an equivalent uniform homogeneous \{111\} layer of Au, although the actual coverage may be inhomogeneous.

The experiment was performed at the Synchrotron Radiation Center, University of Wisconsin. Monochromatized radiation was incident from a Seya/ERG (extended-range grasshopper monochromator) beam line,\textsuperscript{17} scannable from 5 to over 1000 eV. Photoelectrons were collected via a double-pass cylindrical mirror analyzer in an UHV chamber with a base pressure of \( 5 \times 10^{-11} \) Torr. Photoelectron energy distribution curves (EDC's) were recorded at selected photon energies while the kinetic energy was swept.

The evolutions of the density of states of the valence band taken at photon energies of 40 and 140 eV are shown in Figs. 1 and 2, with Au coverage in angstroms indicated at the ends of the spectra, while information gained from scanning core levels is shown in Figs. 3–5. All spectra are normalized to the current from a nickel mesh placed in front of the sample. We use the Fermi energy, \( E_F \), of the copper sample holder as the zero of binding energy. However, when the semiconductor surfaces become metallic, their Fermi levels become the reference for the Au \( E_F \). The position of the top of the valence-band maximum (VBM) is evaluated conventionally as the intercept of the baseline and the line with steepest slope at the leading edge of the spectrum.

**RESULTS**

**The surfaces of \( a \)-Si:H**

In Figs. 1 and 2, the EDC's from a clean \( a \)-Si:H surface are characterized by the emission from Si 3p states, bonding states of Si 3p–H 1s, and Si 3s–H 1s orbitals. They are located at about 3, 6.5, and 10.5 eV below \( E_F \), respectively. An argon peak at 9 eV also appears in the spectrum taken at a photon energy of 25 eV (not shown), a residue of the sputter cleaning. Even though the Si 3p state appears as a featureless hump, its attenuation can tell us roughly the bonding status between Si and H. Since the formation of hydride bonds in \( a \)-Si appears as an intensity transfer from the upper portion of the valence band to the vicinity of the Si–H bonding states, a decrease in intensity of the Si 3p states indicates the fraction of Si atoms bound to hydrogen. Or, oppositely, when a depletion of H atoms occurs, the intensity of the Si 3p state increases. The intensity of the Si 3p state increased with sputter time, after the loss of contamination. This suggests that the surfaces have more Si–H bonds than the bulk does, in agreement with the study of Wagner et al.\textsuperscript{18} and Láznicka.\textsuperscript{19}

Band-bending effects on the \( a \)-Si:H surface have been studied by several groups. Goldstein and Szostak\textsuperscript{20} used the surface photovoltage (SPV) technique to study band bending and surface states on \( a \)-Si:H. They found that the energy required to empty a surface state is different from that required to refill it. They then concluded that the bands were bent upwards. An upward band bending was also reported by Clemens\textsuperscript{21} and Foller and co-

![FIG. 1. Valence-band spectra taken at \( h\nu = 40 \) eV to enhance the emission from Au 5d orbitals. All spectra are normalized to photon flux and then adjusted to the maximum magnitude at 205 Å. Note that the Au 5d-derived states have already dominated the EDC's at the onset of the deposition. The Fermi level appears at 2 Å. A \( d_0 \) peak bulges out at 9 Å of Au and the intensity increases as coverage increases.](https://example.com/fig1.png)
workers.\textsuperscript{22} On the contrary, Winer et al.\textsuperscript{23} used total-yield photoelectron spectroscopy to investigate a-Si:H, undoped and doped. They reported a difference of 0.3 eV in the activation energy and work function for undoped a-Si:H. Downward surface band bending was thus proposed. Schade and Pankove drew a similar conclusion.\textsuperscript{24}

In the present work, the position of the Si 2p\textsubscript{1/2} line implies the bands bend upward. Our fitted result, using the same schemes as in Ref. 21, to the Si 2p core level taken at \(h\nu=160\) eV shows the binding energy of \(\alpha\)-SiH\textsubscript{0}, Si 2p\textsubscript{1/2} without bonding with hydrogen, is at 99.43 eV with respect to \(E_F\) at the surface. The energy of the crystalline Si 2p\textsubscript{1/2} state has been reported to be 98.74 eV with respect to the VBM.\textsuperscript{25} However, the energy of \(\alpha\)-SiH\textsubscript{0} is 0.22 eV higher than that of c-Si, according to Ref. 26, using a bulk-sensitive scan. The energy of \(\alpha\)-SiH\textsubscript{0} in bulk is therefore 98.96 eV with respect to the VBM. Assuming that the VBM is below \(E_F\) by 0.87±0.05 eV (because for undoped material the Fermi level is pinned at midgap by ionized centers\textsuperscript{27}), the binding energy of \(\alpha\)-SiH\textsubscript{0} in bulk is then 99.83±0.05 eV. Thus, bands at the surface are bent 0.40±0.05 eV upward.

**Low-coverage region (\(\theta<2\) Å)**

In Fig. 1, the density of states of the valence band shows the evolution of the Au 5d spin-orbit-split states. At the lowest coverage, the binding energies of the two prominent spin-orbit-split Au 5d peaks are 6.53 and 5.03 eV. As coverage increases, they move oppositely, consequently increasing in separation. Further, the d-band width expands. However, the contribution from the a-Si:H substrate is seriously masked by the higher cross section of the d orbitals from the deposits. The valence-band spectra in Fig. 2 supply information complementary to that in Fig. 1. Looking at the spectra, we can easily realize that the emission from both Si 3p and Si 3s–H 1s bonding states shows no change in binding energy, but only an attenuation of intensity.

In Fig. 3, we present surface-sensitive data using a photon energy of 160 eV to detect the emission from the Au 4f and Si 2p core levels. As shown in Fig. 3, the Si 2p core level shifts to lower binding energy with increasing coverage, meaning the VBM continues to bend toward the Fermi level. The shift is 0.45 eV, at coverages from 0 to 1 Å, according to the fitted values. With \(E_F\) aligned across the interface, the shift is clearly within the band-

![Figure 2](image_url)

**FIG. 2.** Valence-band spectra taken at \(h\nu=140\) eV to enhance the contribution from the sp-electron-dominated substrate. Normalization scheme is the same as in Fig. 1. The bonding states due to Si 3s and H 1s orbitals are still visible at coverage over 9 Å, indicating the intermixed Si atoms with gold are those not bonded with H.

![Figure 3](image_url)

**FIG. 3.** Surface-sensitive core level EDC's taken at \(h\nu=160\) eV. The small bump on the high-binding-energy side of the Au 4f\textsubscript{5/2} state is due to Au NVV Auger emission. Development of two sets of Au 4f states are clearly seen. Si 2p spin-orbit splitting is easily differentiated at coverage over 9 Å of Au.
bending uncertainty given above. This indicates that the 0.40±0.05 eV band-bending value is reasonable. Also apparent in Fig. 3 is no appreciable line-shape change during the movement. The same features can also be appreciated in Fig. 4, where a bulk-sensitive scan with a photon energy of 110 eV was used. No lines due to chemical shifts appear, indicating that interaction between gold and a-Si:H in this region is weak. Furthermore, the intensity of the Si 2p states decreases as coverage increases. In the Au 4f core levels, a shift of 1.1 eV to higher binding energy at the lowest coverage is observed, with respect to the bulk value (83.9 eV). The shift is reduced to 0.9 eV at 1 Å of Au deposition.

In summary, we assign the initial state ( ≤ 1 Å) of gold evaporated onto a-Si:H surface as a band-bending region with no significant chemical reaction.

Intermediate region (2 ≤ θ ≤ 9 Å)

From Fig. 1 the presence of the Fermi level in the valence-band spectra at coverages above 2 Å means that the interface has become metallic. This is evidence that Au atoms have already clustered enough to show a Fermi level. A rapid movement of the Au 5d_{5/2}-derived state toward the Fermi level is noticed, whereas the Au 5d_{3/2}-derived state exhibits much less change. The centroid of the Au 5d band thus continues to shift toward the Fermi energy, and the bandwidth keeps increasing.

Figures 3 and 4 show a drastic change in the emission from the Au 4f and Si 2p core levels, both in line shape and binding energy. From Figs. 3 and 4 the energy of the Si 2p core lines shifts away from the trend of the band-bending region and moves from 99.13 eV at 1 Å to 99.60 eV at 3 Å. Likewise, the Au 4f lines shift in the same direction as the Si 2p lines to higher binding energy, from 84.8 eV at 1 Å to 84.9 eV at 3 Å. Most significant of all, however, is the altered line shape. The distinct feature is the moderate intrusion of the Si 2p_{1/2} peak. This suggests that an interaction between gold and silicon occurs in the interface. Specifically, Si atoms have been set free by absorbing energy released from clustering gold.

As gold clusters grow in size, when a Fermi level is detected they provoke a reaction with the underlying a-Si:H substrate. However, the reaction occurs at regions deficient in hydrogen. Referring further to Fig. 2, we observe that the peak due to the Si 3s–H 1s bonding state is still visible, but attenuated. On the contrary, the Si 3p state is completely gone. These suggest that the Au atoms forming clusters can be located “over” both Si–Si and Si–H bonds, but the reaction between Au and Si occurs at regions devoid of hydrogen. This is demonstrated by the reduced intensity of those Si atoms which do not bond with hydrogen and the altered line shape of the Si 2p levels. Another justification can be made by noticing that a shoulder appears on the low-binding-energy side of the Si 2p states (Figs. 3 and 4). This feature, at about the same energy as in the low-coverage region, corresponds to the Si atoms in Si–H bonding states. The a-Si:H IR spectrum shows vibrational frequencies due to the SiH stretching model (2100 cm⁻¹), wagging mode (638 cm⁻¹), and SiH₂ bending mode (897 cm⁻¹). Those SiH₃ radicals are typical in an a-Si:H sample fabricated at room temperature. Since the Si–Si bond energy is 2.35 eV while that of Si–H is 3.4 eV, it is easier to break Si–Si bonds or weaken the back bond of dangling bonds. Thus the clusters form primarily on regions of the surface deficient in hydrogen. On “device grade” a-Si:H, the Au coverage at this thickness has qualitatively the same effect: The Si-Si peak in the EDC is reduced more rapidly than the (weak) Si-H peak as Au is added.

High-coverage region (θ > 9 Å)

The evaporation rate was increased by 1 Å/min for coverages between 13 and 118 Å. As we will see, this region shows similarities to, as well as differences from, the work on c-Si. In what follows, coverages under discussion, unless stated otherwise, will be those below 118 Å.

In this region, the distinctive double peak of the Au 5d band does not vary dramatically in intensity, line shape, and energy position, as are seen in Figs. 1 and 2. However, in Fig. 1 a peak, labeled d₂, appears at the top of the Au 5d antibonding state. Its position, 2.75 eV below E_F,
is coverage independent, but the intensity increases as the amount of gold increases. The \(d_0\) peak, however, loses its prominence at higher photon energy. The growth of the \(d_0\) peak is the most pronounced change in the valence band over this region. Even so, the appearance of the valence band is far from that of bulk gold, even at the highest coverage.

A number of groups have studied the behavior of gold in the form of small particles. Pertinent in their work is the evolution of the \(d_0\) peak in the vicinity of the antibonding area. The development of the \(d_0\) peak has exhibited a strong dependence on the volume of a cluster. The larger the volume, the more prominent is the \(d_0\) peak. Furthermore, theoretical calculations have precluded an explanation of the two prominent peaks of the Au 5d band as simply due to spin-orbit splitting, but rather a strong crystal field effect comes into play.31

Spectra from both Au 4f and Si 2p core levels provide information that characterizes the region in a more sensible way. Observing the development of the Si 2p core lines as shown in Figs. 3 and 4, we have no trouble differentiating the spin-orbit-split peaks. Furthermore, it is interesting to note that the intensity of the Si 2p core lines exhibited in Fig. 3 remains quite the same regardless of coverage, except for the highest coverage. The binding energy of the Si 2p\(3/2\) line peaks at 99.83 eV at 13 Å of thickness, and then shifts gradually to lower values with increasing coverage.

In addition to the well-resolved Si 2p spin-orbit core levels in the high-coverage region, the most remarkable phenomenon is the development of two sets of Au 4f core levels. We call the higher-binding-energy peak in the vicinity of Au 4f\(7/2\) Au(1), and the lower-binding-energy 4f\(7/2\) peak Au(2), as shown in Fig. 3. Naturally, the same assignment can also be made for the Au 4f\(s/2\) lines. (The small hump at the high-binding-energy side of the Au 4f\(s/2\) peak is from Au NVV Auger electrons.)

In Fig. 3, the Au(1) line shows a monotonic decrease in binding energy as coverage increases. However, larger Au deposition does not cause Au(1) to grow in intensity. A closer examination of the line shape at 9 Å shows a barely perceptible asymmetry on the low-binding-energy side of Au(1). This is the position where Au(2) develops. At increased coverage, it becomes more and more evident. The steady growth of Au(2) makes it comparable to Au(1) at 65 Å, and larger for larger thickness. However, the binding energy of Au(2) is coverage independent and remains fixed at a value of 84.15 eV.32

In order to determine why the intensity of the Au(1) 4f or Si 2p core lines does not change, we used a different approach: increasing the evaporation rate to 4 Å/min and increasing the coverage to 205 Å in a single step. First of all, from Fig. 3 it is clearly seen that the intensities of the Si 2p and Au(1) lines drop simultaneously, while that of Au(2) keeps on growing. Secondly, a binding-energy shift of the Au(2) (83.98 eV) to the bulk gold value (83.9 eV) appears. At this point, we attribute the higher-binding-energy component [Au(1)] to intermixed Au and Si, and the lower-binding-energy set to pure gold alone. This assignment is indeed in agreement with the work of Ref. 13, whose core-level photoemission study of Au on c-Si indicated the presence of two Au 4f components. They assigned the higher-binding-energy component to Au silicide, and the lower to Au itself.

For coverage as high as 205 Å, the Si 2p peak is still present as shown in Fig. 3. The thickness far exceeds the escape length of the Au overlayer.26 If the interface were abrupt, we would anticipate seeing nothing originating from the a-Si:H substrate. One might argue that the surfaces are certainly rough from either the rf-sputtering sample fabrication or the Ar-etch cleaning treatment, and some clean Si remains in “shadows.” To this argument, our study of Ag on similar samples of a-Si:H,33 where no strong interactions occur, revealed no signals from the a-Si:H substrate above 65 Å of silver. Therefore, the continued presence of Si at the surfaces is due to Si outdiffusing through the Au film, consistent with expectations of a high diffusion coefficient for Si in Au.

**DISCUSSION**

We depict the behavior of the Au 5d band in Fig. 5 against coverage. Figure 5(a) plots the individual movement of the two peaks and Fig. 5(b) the energy separation between them. Also included in Fig. 5(a) is the centroid of the 5d band denoted by ○. Note that what is not shown in Fig. 5 is the \(d_0\) peak whose track would be a straight line located at 2.75 eV. In Fig. 5(b), the two peaks in the Au 5d band are separated by 1.5 eV, the atomic Au splitting,34 at the lowest coverage. This indi-

![Fig. 5](image-url)
PHOTOEMISSION STUDY OF Au ON a-Si:H

FIG. 6. Evolution of the binding energy of the Au 4f7/2 [○, Au(1); ●, Au(2)] and Si 2p3/2 (×) lines. The line drawn is a guide to the eye.

cates that the initial gold deposit is in a dispersed, atomic-like state. As coverage increases, Fig. 5(b) demonstrates a monotonic increase in separation at low coverages followed by a plateau starting at 9 Å. Needless to say, the shift of the centroid toward the Fermi level with increasing coverage is greatly assisted by the presence of the d0 peak. The evolution of the double-peak separation reflects a trend similar to that found for Au on Si(111) by Braicovich et al3 and on Si(100) by Carriere et al.4 However, the trend is unlike that in the work of Iwami et al. on Si(111)2×1,5 which shows a constant separation at low coverages.

We plot the development of the binding energy of the Au 4f7/2 and Si 2p3/2 core levels in Figs. 6 and 7, where the former tracks individual binding energies and the latter the energy separation between the Au4f7/2(1) and Si 2p3/2 core lines. The lines in Fig. 6 serve as a guide to the eye, and are not fitted curves. We simplify by omitting spin-orbit symbols hereafter.

Figure 6 reveals a monotonic decrease in binding energy for both the Au(1) and Si 2p lines at low coverages (the band-bending region), followed by an increase (the intermediate coverage region) and then a decrease (the high coverage region) in the binding energy. The Au(2) core level, however, remains at the same value independent of thickness. We can see that the binding energy of the Si 2p line changes more rapidly than that of the Au(1) line at thicknesses below 13 Å. Above 13 Å, the variation rate of Au(1) and Si 2p are basically the same. This implies that Si 2p orbitals seem to be more vulnerable to the chemical environment, particularly in the intermixing region where the interaction between the deposit and substrate commences. This strongly suggests that the local strain of the a-Si:H network is disturbed by clustered gold atoms. The disturbance, however, is slow enough that subsequently incoming gold atoms see a different unrelaxed substrate. The slow relaxation process can also explain a decrease in the Si 2p–Au(1) energy separation, for example by 0.2 eV at 9 Å, over 12 h later at the same coverage.33 The decrease resulted from an observation of a shift to lower binding energy in both core lines.33 Láznička19 has studied an ion-sputtered a-Si:H surface. He found that a dramatic increase in a hydrogen-bond-related Auger peak appeared after the surface had remained in situ in a vacuum chamber for 24 h. He claimed that hydrogen embedded in the bulk had diffused to the surface because of a concentration gradient at the surface induced by the argon-ion sputtering of H atoms.

FIG. 7. Energy separation between Au 4f7/2 and Si 2p3/2. ○, Au(1) and Si 2p; ●, Au(2) and Si 2p.
This implies that the dangling bonds on the surface disappear not only by reconstruction but also by bonding with H atoms diffused from the bulk. Carriere et al. have done a comparison study of the Au/c-Si interface using AES, with ordered Si(100), and disordered, ion-bombarded Si(100) substrates. They reported that gold was gittered by bulk defects under the amorphous surface. This mechanism constrained the Si diffusion coefficient and caused silicon to disappear at a thickness over 23 Å. This effect did not occur on ordered Si(100) substrates. More interestingly, diffusion of silicon is relatively slower in a disordered Si(100) substrate than in an ordered one, supported by detection of an increased silicon signal in the disordered substrate after 12 h. Their work and ours leads to the important point that an amorphous semiconductor surface takes time to relax fully after the surfaces have been sputtered. Metal deposits like gold do not assist the relaxation.

As displayed in Fig. 7, the energy separation between the Au(1) and Si 2p lines increases below 13 Å of Au followed by a plateau. At this point, regarding the features shown in Fig. 7, it is worth mentioning that at low coverages the Au/a-Si:H interface does not behave the same way as Au/c-Si does.3,5 Braicovich et al.,3 using a Si(111) substrate, did not observe an appreciable movement of the Si 2p core levels, and the Au 4f – Si 2p energy separation was basically constant at low coverages. Iwami et al.,3 who also explored Si(111)2×1, reported that the energy separation between Au 4f and Si 2p had a minimum at about one monolayer of gold coverage. They further showed that a Fano-like resonant emission of the Au 5d peak accompanied by the Si 2p core excitation took place at this coverage.6 On the contrary, our study clearly exhibits features with no similarity to the c-Si results in the initial low-coverge region. Moreover, the rigid Au(1)-Si energy separation and nearly constant intensity of Au(1) in the high-coverage region strongly indicate that the development of Au(1) is associated closely with Si.

In the case of the interface formed by Au on c-Si, there is a pure gold layer sandwiched by intermixed Au/Si at high coverage. In the Au/a-Si:H interface, we find no such layer. As a matter of fact, the two-component feature of the Au 4f core levels is always present in bulk-sensitive scan (not shown) with an escape depth of 25 Å. This, accompanied by uniminished emission from the Si 2p core level from Fig. 4, suggests the absence of a pure Au layer. In other words, the interface consists of the intermixed gold along with pure gold, regardless of coverage, after a certain critical thickness is exceeded.

Up to now, there have been four models proposed for the Au/c-Si interface. They are the interstitial model,37 the screening model,12,13 the thermodynamic model,38,39 and the chemical-bonding model.5 All these models emphasize particularly the effect of the gold atoms in the initial stage. We briefly describe the essence of each model. We will see later how applicable each model is to the current study. Tu's interstitial model17 predicts that Au atoms continuously exert stress on the Si lattice, thereby causing breakage of Si–Si bonds and resulting in a silicide-like compound. This occurs at the instant of arrival of the Au atoms. Hiraki's screening model,12 which was created to explain the existence of an unreacted thickness of Au, postulates the necessity of a critical thickness of Au to provide metallic electrons for electronic screening of the covalent bonding of Si. The effect of metallic screening is to weaken the Si–Si bond. The thermodynamic model59 explains a core binding-energy shift of the Si 2p level due to metal deposits from thermodynamic properties of the bulk constituents. Iwami's chemical-bonding model1 addresses the bonding between gold and silicon that occurs below 1 ML thickness, accomplished by a charge transfer between the Si surface state and Au 6s valence electrons.

Applying the four models used for the Au/c-Si interface to the current system, we find that none of them explain satisfactorily Au/a-Si:H. First of all, the existence of a nonreacted band-bending region precludes the interstitial model, an instantaneous stress of the substrate surface region by the metal deposit. Second, the nonreacted region of the interface, 1 Å, is not thick enough to justify the applicability of the screening model, where a minimum of about 5 ML is required.1 Moreover, one of the premises in the screening model is a substrate energy gap less than 2.2 eV and a static dielectric constant larger than 12.12 For a-Si:H sputtered at room temperature, the dielectric constant is about 7.40 Correspondingly, our system does not fit the criteria of the model. Third, the largest magnitude of the Si 2p 3/2 core level shift (0.3 eV at 13.3 Å) is smaller than the thermodynamic model would predict (0.6 eV at 50% of Si).59 Last, the absence of a nearly constant separation of the two main peaks of the Au 5d states as well as a minimum occurring in the Au 4f – Si 2p separation precludes the applicability of the chemical-bonding model. Note that surface states, a necessity in the chemical-bonding model, exist on the surface of the a-Si:H material.27

Tsai et al.41 have studied the Au/a-Si:H system but used other techniques. They reported that intrinsic differences exist between the interactions of Au with crystalline silicon and hydrogenated amorphous silicon. For example, a crystallization phenomenon occurred after a thin film of 80 Å of Au and 350 Å of a-Si:H was annealed at T > 150°C, well below the Au/Si eutectic temperature of 370°C. Therefore, we do not expect identical behavior of Au on a-Si:H and on c-Si. We believe the surface structure of a-Si:H is important to rationalize the behavior of the Au/a-Si:H interface. Roughness of the surfaces42,43 might also contribute, but a full understanding of the surfaces is more demanding. Due to a lack of knowledge, we cannot comment on the role that the surfaces of a-Si:H play.

**CONCLUSION**

Our study clearly demonstrates that three regions are identifiable in the Au/a-Si:H interface. From the outset of gold deposition, a band-bending region, at a coverage below 1 Å, exhibits no strong interactions between the deposit and the substrate. This appears as a monotonic shift of the Si 2p core level to higher kinetic energy without a change in line shape, as well as a continuous
decrease in intensity. As coverage increases from 1 to 9 Å, a simple-intermixing region appears. In this region, Si atoms not bonded to H leave the substrate and intermix with the gold thin film. Continued deposition leads us to the final region, the dual-phase region. The noticeable features in this region are development of a 2.75-eV peak in the valence band, well-resolved silicon 2p spin-orbit core levels, and two sets of Au 4f core levels with one set associated closely with Si, the other exhibiting the character of pure gold. The observation of a silicon signal and a shifted Au signal is understood by a high diffusion rate of Si through the Au film, giving rise to a surface layer of Si in Au. Instead of the sequence of Si(sub.)-(Au/Si)-(pure Au)-(Au/Si)-(vac.) at the Au/c-Si interface, the Au/a-Si:H interface exhibits a-Si:H(sub.)-(Au/a-Si+pure Au)-(vac.). Namely, a pure Au layer is not found in the Au/a-Si:H interface. The intermixed overlayer persists, once an unreacted thickness is exceeded. Whether or not Au forms a silicide with a-Si:H in the intermixed region is still unclear at this moment. This is also an unresolved point in the case of Au on c-Si.

ACKNOWLEDGMENTS

The Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-ENG-82. The Synchrotron Radiation Center is operated by the University of Wisconsin under National Science Foundation (NSF) Contract No. DMR-80-20164. We also thank Saibal Mitra for his assistance in making the a-Si:H samples.

32The binding energies cited for the two components of the Au 5f levels are determined from their individual positions in the spectra, not from a curve-fitting routine.
41C. C. Tsai, R. J. Nemanich, and M. J. Thompson, J. Vac. Sci.