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Bonding characteristics of the $\sqrt{3}\times\sqrt{3}$ Ag/Si interface identified by the energy dependence of the photoionization cross section

J.-J. Yeh, K. A. Bertness, R. Cao, J. Hwang, and I. Lindau
Stanford Electronics Laboratories, Stanford, California 94305

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Synchrotron-radiation photoemission of the metal-semiconductor interface has a unique advantage in identifying the bonding characteristics of the rehybridized orbitals between the metal and the semiconductor. By varying the photon energy and measuring the magnitude of the photoionization cross section, the bonding peak at the metal-semiconductor interface can be identified as being formed with or without hybridization with the metal's *d* orbitals. The latter case is clearly illustrated by the annealed Ag/Si(111) interface. A sharp structure at 3.8 eV below the Fermi level grows as a result of annealing of the Ag/Si(111) interface. This structure is also accompanied by the formation of the $\sqrt{3}\times\sqrt{3}(R\,30^\circ)$ low-energy electron diffraction pattern and the narrowing of the Ag 4*d* band signal. Since the so-called Cooper-minimum effect is not observed for this annealing-induced peak, it is concluded that the structure does not have 4*d*-orbital characteristics within the regime of the theory of linear combination of atomic orbitals. This is the direct evidence to show that the Ag 4*d* band does not hybridize with the substrate Si sp^3 orbitals in forming Ag—Si bonds after high-temperature annealing. Judging from the photoionization cross-section variation, it can instead be inferred that the sharp structure has mostly Ag 5*s* or 5*p* and Si *sp* characteristics. The methodology shown here can be extended to other metal-semiconductor interfaces and can provide information on the bonding formation of the metal atoms and the semiconductor substrate. This is important in discussing metal-semiconductor interfaces but difficult to obtain unambiguously with other techniques and in theoretical predictions.

I. INTRODUCTION

The bonding characteristics of the metal-semiconductor interface have always been an important factor in understanding the interface structure. This information, unfortunately, is difficult to obtain experimentally and one has to rely on theoretical calculations for the particular system[1] to interpret the valence-band structure. Partial photoionization cross-section (PPCS) measurements with synchrotron radiation in the soft-x-ray region, however, show the potential to distinguish the contribution of distinctive atomic orbitals to a particular structure[2] such as that formed at the interface when the metal interacts with the semiconductor. To separate contributions from the metal and the semiconductor, the Cooper-minimum[3] (CM) method is applied. Because of the destructive interference of the initial and the final state of the photoexcited electron, emissions from the *d* bands are strongly suppressed in the Cooper-minimum spectrum. Therefore, the otherwise small signals from the substrate are enhanced. Taking data at the metal valence electron's Cooper minimum makes it possible to see the contributions from the semiconductor substrate. It will be shown that the PPCS's of the 4*d* or 5*d* orbitals are quite different from those of the *sp* electrons, and this turns out to be a good fingerprint to distinguish the characteristics of the structures at metal-semiconductor interfaces. The interpretation of the data in this way does not require any specific theoretical calculation. The Ag/Si interface was used to demonstrate the methodology because Ag/Si forms a new structure at higher temperature which is not seen right after deposition at room temperature. This annealing-induced structure has a PPCS that resembles those of *sp* orbitals and not the *d* orbitals and it consequently implies that Ag *d* electrons do not participate in the bonding between the Ag/Si interface.

The details of the Ag/Si interface have been investigated for a long period with various techniques[4] and therefore are not discussed in this article. The experimental setup in measuring the PPCS's of the orbitals in the Ag/Si interface is described in the next section. Results are presented in Sec. III and followed by discussions and the conclusion in Secs. IV and V.

II. EXPERIMENTAL

The experiment was performed at beam line I-1 of the Stanford Synchrotron Radiation Laboratory during the dedicated run with 3 GeV and about 50 mA beam current. Photon energies between 70 and 140 eV were used to look at the valence-band energy distribution curves (EDC's) of the Ag/Si interface. Angle-integrated photoemission spectra were taken with a double-pass cylindrical mirror analyzer (CMA). The Si(111)-7×7 surface was produced using a cleaved *n*-type Si(111) crystal resistively heated at 700 °C for 5 min. Ag films, two monolayers (ML) thick (1 monolayer $= 7.8\times10^{14}$ atoms/cm^2), were then evaporated onto this surface from a well-outgased Ag bead on a Mo filament. The $\sqrt{3}\times\sqrt{3}(R\,30^\circ)$ Ag/Si surface was prepared also by resistive heating. The surface was annealed three times at 500 °C and then once at 600 °C. All heat treatments were 10 sec in duration. The temperature was monitored with an infrared pyrometer which was calibrated against a thermocouple (±25 °C). Ultrahigh vacuum (base pressure 3×10^{-11} Torr) was maintained during sample-preparation and data-acquisition processes. The pressure during evaporation was about 1.4×10^{-10} Torr. The same low pressure was also achieved when annealing the Si(111)-2×1 surface into a 7×7 surface reconstruction. The pressure during the other annealings were all below 7×10^{-11} Torr. The ultrahigh vacuum conditions reduced possible C or O contamination as checked by monitoring of the Si $2p$ core-level spectra. The valence-band spectra were taken around the maximum ($h\nu=70$ eV) and the minimum ($h\nu=140$ eV) of the Ag $4d$ PPCS. This changes the intensities of the valence-band Ag $4d$ and Si sp states and allows observation of the modification on the substrate electronic structure.

III. RESULTS

After normalization to the photon flux variation during the experiment, the valence-band spectra taken at different photon energies at various stages of annealing are shown in Fig. 1. Generally speaking, the 70-eV spectra of the Ag/Si interface are similar to other results using conventional uv photon sources since the high Ag $4d$ PPCS dominates the valence-band signal over this photon energy region. In contrast, the Cooper-minimum effect of the Ag $4d$ orbitals makes the 140-eV EDC quite different and the change of electronic structure of the Si substrate can be examined better. In the following paragraph, spectra taken at 70 eV and 140 eV after Ag deposition at various annealing stages will be compared.

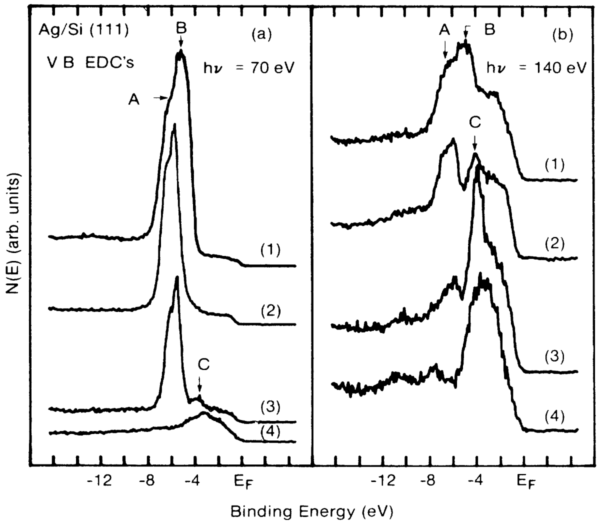

FIG. 1. The valence-band spectra referred to the Fermi level (E_F) of the Ag/Si interface as a function of annealing at two different photon energies are shown here. (a) is the 70-eV spectra and (b) is the 140-eV spectra. The 70-eV spectra show very strong Ag $4d$ signals and the 140-eV spectra (the Ag $4d$ Cooper minimum) show contributions from the substrate Si. Curves (1)—(3) in both (a) and (b) are as follows: curve (1), the valence-band EDC of 2 ML Ag deposited on Si at room temperature; (2), the system annealed at 500 °C for 10 sec, a new structure at 3.8-eV binding energy emerges and is denoted as C; (3), another annealing at 500 °C for 10 sec, one more annealing at same temperature gives same spectra indicating the existence of a metastable phase; (4), annealing at 600 °C for 10 sec. The surface is free of Ag after the last annealing. These spectra are exactly the same as the clean Si(111)-7×7 valence-band spectra.

After the Ag metal deposition, [curve (1)], the Ag $4d$-band signal dominates the valence band in the 70-eV spectra. The Ag d band is mainly composed of 2 structures at 6.2-eV (peak A) and 4.7-eV (peak B) binding energy below the Fermi level which is consistent with earlier reports.[5] The structures are less pronounced in the 140-eV spectra but the first peak of the Si valence band close to the Fermi edge—the most p-like peak can be clearly identified. After the first annealing at 500 °C [curve (2)], the surface displays a sharp $\sqrt{3}\times\sqrt{3}(R30°)$ low-energy electron diffraction (LEED) pattern. The 70-eV spectrum shows that the Ag $4d$ band shrinks from about 2.6 to 1.7 eV full width at half maximum (FWHM), and the centroid moves 0.4 eV from 5.7-eV to 6.1-eV binding energy, which is the same as that reported at 50 eV.[6] More changes can be seen in the 140-eV spectra: A new peak, noted as C in the figure, at 3.8-eV binding energy emerges and at the same time the emission at the previous B position disappears. This structure C is not observable in the 70-eV spectra at this stage because it is probably buried in

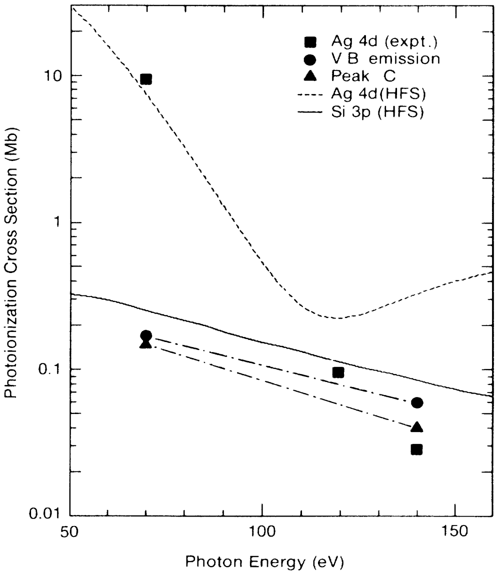

FIG. 2. Photoionization cross sections of the Ag $4d$, peak C and the emission close to the Fermi level together with theoretical calculations of the Ag $4d$ and Si $3p$ PPCS's (Ref. 14). The experimental PPCS's are normalized to the theoretical value at 70 eV, where the Ag $4d$ signal is the strongest. It is clear that the PPCS of peak C does not show the strong modulation from the Cooper-minimum effect where about a 2 order-of-magnitude change should be seen. This is used as the evidence that the bonding between Ag and Si has no Ag $4d$-orbital component but is instead composed of Ag $5s$ or $5p$ and Si sp orbitals.

the signal from the Ag 4*d* band. The total Ag signal decreases as is detected from the Ag 3*d* core-level spectra (not shown) taken with x rays. After the second annealing at 500 °C for 10 sec [curve (3)], the total Ag signals decrease again in both Ag 3*d* x-ray photoemission spectrum and valence-band 4*d* signal. A tiny shoulder now appears at the right hand side of the *d* band in the 70-eV spectrum. Besides these changes, the valence band at 70 eV looks more or less the same compared with the first annealing. The Cooper-minimum spectrum at 140 eV is quite different though. The 4*d* peak is almost absent and appears only as a small bump next to the new and sharp peak at 3.8-eV binding energy (*C* with FWHM about 1 eV). All spectra remain the same with further annealing at 500 °C indicating that a metastable phase exists at this temperature. In order to see any further reaction, the sample was heated to 600 °C for 10 sec [curve (4)], but it turned out that all of the remaining Ag was desorbed at this temperature and the spectra become those of clean Si. In order to compare the characteristics of these structures in the valence band, the PPCS of the Ag 4*d* orbitals (after the first annealing), the new peak *C*, and the emission (3-eV to 1-eV binding energy) close to the Fermi level (after the second annealing) together with theoretical calculations are plotted in Fig. 2. The PPCS's are measured by calculating the peak area and then normalizing to the ideal CMA transmission function,[7] the monochromator transmission function,[8] and the beam current decay. For small signals like peak *C* at 70 eV or Ag 4*d* at 140 eV, the PPCS is only correct to an order of magnitude, but this does not effect the main conclusion of the result.

IV. DISCUSSION

The details of the Ag/Si interface as a function of the annealing will be presented elsewhere since the purpose of this article is only to demonstrate the use of PPCS in identifying the characteristics of peaks formed at the metal-semiconductor interface. Comparisons with the other noble-metal—Si interface electronic structures (Cu/Si, Au/Si) are also left out for the same reason. Due to the variations of the PPCS's of different orbitals, it should be emphasized that the interface should be examined at different photon energies at the same time for a set of different coverages and annealing conditions. For instance, if one focuses on the evolution of the VB at the Ag 4*d* Cooper minimum as a function of annealing only, it can very easily lead to the impression that part of the Ag *d* band forms bonds with the Si atoms and appears as peak *C*; this peak obviously grows with further annealing when more Ag atoms bond to the Si substrate. On the other hand, the evolution of the Ag/Si interface at 70 eV shows no clear sign of Ag-Si interaction; the contraction of the Ag 4*d* band could also be explained in terms of removal or dissociation of the Ag clusters, the opposite of the Ag 4*d*-band formation during cluster formation. Peak *C* is not clearly observable at this photon energy (or lower) and it is too ambiguous for any interpretation. It could easily be neglected or mistaken for a Si(111)-7×7 structure.[6]

The new peak *C* provides clear and direct evidence that Ag bonds with Si when the Ag/Si interface is annealed into the $\sqrt{3}\times\sqrt{3}(R\,30^\circ)$ structure. The cohesive energy of this surface structure measured by isothermal desorption spectroscopy[9] is 65 kcal/mole. What remains unanswered is how Ag bonds with Si. Previous Auger line-shape analysis by Housley[5] suggested that the Ag 5*s* electrons bond with the Si 3*p* electrons when Ag was deposited on the Si surface at room temperature, in agreement with the prediction of a theoretical calculation.[10] On the other hand, based on the comparison with other *d*-metal—semiconductor photoemission spectra, Rossi[11] suggested that the Ag 4*d* band rehybridized with the Si sp^3 hybrid at the as-deposited Ag/Si interface. From angle-resolved photoelectron spectroscopy, Yokotsuka *et al.*[12] and Hansson *et al.*[13] mapped out the dispersion relations of the Ag-Si "bonding" peaks and the extrinsic surface states of an ordered $\sqrt{3}\times\sqrt{3}(R\,30^\circ)$ Ag/Si surface and mentioned that no Ag 4*d* and Si *sp* rehybridization occurred (though no experimental evidence was presented). Although the as-deposited Ag/Si interface may or may not have the same bonding scheme as the ordered $\sqrt{3}\times\sqrt{3}(R\,30^\circ)$ surface, all of the results obtained so far do not clarify whether the Ag 4*d* participates in the bonding with Si substrate. In other words, it is necessary to ask whether the peak *C* is from the rehybridization of Ag 4*d* or Ag 5*s*(5*p*) with the Si *sp* hybrids. Within the regime of the theory of linear combination of atomic orbitals (LCAO's), orbitals in the solid can be considered to keep the character of the atomic wave functions and therefore have similar energy dependence of the photoionization cross sections. Based on this guideline, one can assume that a new structure, like peak *C*, is unlikely to have a 4*d*-orbital component if peak *C* has quite a different PPCS energy dependence from that of 4*d* orbitals. For comparison, different PPCS's of the Ag 4*d* and Si 3*p* from Hartree-Fock-Slater (HFS) theoretical calculation[14] are also plotted in Fig. 2. Since the emissions close to the Fermi edge are mainly the hybridized Ag 5*s* or 5*p* and the Si *sp* orbitals, the PPCS of this portion does not show strong variation, in agreement with theory. On the other hand, the Ag 4*d* orbitals have very strong modulation of the PPCS over this short photon energy range due to the Cooper-minimum effect. By using these spectra as references, it is seen that the peak *C* has the same trend as the VB emission and shows no strong modulation between 70- and 140-eV photon energy. It is therefore concluded that the peak formed at the Ag/Si interface after annealing has very little Ag 4*d* character, if any. Instead, the trend of the PPCS of the peak *C* is similar to the PPCS of the *sp* orbitals. Assuming that the *d* orbital still keeps it PPCS behavior even if it hybridizes with Si *sp* orbitals, the observed behavior of peak *C* is the evidence that Ag 5*s* or 5*p* orbitals participate in forming the bond with Si and not Ag 4*d* orbitals. It is certainly not easy to justify experimentally or theoretically this assumption. However, this is generally true for other transition metal—semiconductor interfaces like Pd/Si, Pt/Si where the *d* band hybridizes with Si *sp* orbitals but the valence band spectra still shows very clear Cooper-minimum effect from the synchrotron radiation studies.[15,16]

V. CONCLUSION

The advantage of the synchrotron-radiation photoemission in identifying the bonding characteristics of the peaks formed in an interface has been illustrated by the Ag/Si system where the valence electrons of Ag and Si have significantly different PPCS's. Other examples[14] are the orbital pairs like 5*d* and *sp* or 4*d* and 3*d*, etc. where one of the orbitals has Cooper minimum (4*d*,5*d*) and one of them does not (*sp*,3*d*). Since the atomic subshell photoionization cross sections were calculated and plotted in the soft-x-ray to x-ray region for all elements $1 \leq Z \leq 103$,[14] the same approach can therefore be applied to other interfaces directly if no other interference of the PPCS exists (see example in Ref. 2). Based on the nature of the orbital's PPCS the metal—semiconductor bonding characteristics can be determined to some extent and these conditions are actually met for most transition metal—semiconductor and noble metal—semiconductor interfaces. From the measured PPCS's of different peaks in the valence band, it is possible to tell the atomic nature of those peaks within the regime of LCAO theory. In the case of the Ag/Si system, it was found that the Ag 4*d* electrons do not participate in forming the bonds with the Si atoms when the Ag/Si interface is annealed. The new peak which emerges after annealing at 500 °C shows no sign of the 4*d*-orbital's characteristics (the Cooper-minimum effect) and it is therefore concluded that this peak comes from the bonding of Ag 5*s* or 5*p* and Si *sp* orbitals.

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[1] See for example, J. E. Houston, C. H. F. Peden, P. J. Feibelman, and D. R. Hamann, Phys. Rev. Lett. **27**, 375 (1986).

[2] M. El-Batanouny, M. Strongin, and G. P. Williams, Phys. Rev. B **27**, 4580 (1983).

[3] J. W. Cooper, Phys. Rev. **128**, 681 (1962).

[4] See the review articles by C. Calandra, O. Bisi, and G. Ottaviani, Surf. Sci. Rep. **4**, 271 (1985); G. Le Lay, Surf. Sci. **132**, 169 (1983).

[5] M. Housley, R. Heckingbottom, and C. J. Todd, Surf Sci. **68**, 179 (1977).

[6] F. Houzay, G. M. Guichar, A. Cros, F. Salvan, R. Pinchaux, and J. Derrien, Surf. Sci **124**, L1 (1983).

[7] M. H. Hecht and I. Lindau, J. Electron Spectrosc. Relat. Phenom. **35**, 211 (1985).

[8] J. -J. Yeh, J. Nogami, D. J. Friedman, R. Cao, J. Hwang, A. Wahi, S. Koch, and I. Lindau, Nucl. Instrum. Methods **A246**, 286 (1986).

[9] G. Le Lay, M. Manneville, and R. Kern, Surf. Sci. **72**, 405 (1978).

[10] P. J. Feibelman, E. J. McGuire, and K. C. Pandey, Phys. Rev. Lett. **36**, 1154 (1976).

[11] G. Rossi, I. Abbati, I. Lindau, and W. E. Spicer, Appl. Surf. Sci. **11/12**, 348 (1982).

[12] T. Yokotsuka, S. Kono, S. Suzuki, and T. Sagawa, Surf. Sci. **127**, 35 (1983).

[13] G. V. Hansson, R. Z. Bachrach, R. S. Bauer, and P. Chiaradia, Phys. Rev. Lett. **46**, 1033 (1981); J. Vac. Sci. Technol. **18**, 550 (1981).

[14] J.-J. Yeh and I. Lindau, At. Data Nucl. Data Tables **32**, 1 (1985).

[15] G. Rossi, I. Lindau, L. Braicovich, and I. Abbati, Phys. Rev. B **28**, 3031 (1983).

[16] I. Abbati, G. Rossi, I. Lindau, and W. E. Spicer, J. Vac. Sci. Technol. **19**, 636 (1981).