Resonant-photoemission study of the mechanism for room-temperature-alloyed interface formation of Au and Ag on Si(111)-(2 × 1)

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Room-temperature deposition of gold and silver on the Si(111)-(2 × 1) surface was studied by photoemission spectroscopy. We successfully observed, around the photon energy of the Si(2p) core excitation threshold ($\sim$ 100 eV), a resonancelike enhancement of the photoemission signal of Au(5d) at around monolayer coverage of Au, while no enhancement of the Ag(4d) signal was observed at around monolayer coverage of Ag. This result indicates the formation of a covalentlike bond between Au (deposited) and Si (substrate) atoms and not in Ag-Si, and the mechanism of room-temperature-alloyed interface formation at a metal-semiconductor interface can be described by the "chemical-bonding model" proposed before by the authors [M. Iwami, T. Terada, M. Kubota, H. Tochihara, and Y. Murata, Surf. Sci. **119**, 115 (1988)].

I. INTRODUCTION

Among many problems in metal-semiconductor contact systems,[1-4] the phenomenon of room-temperature-alloyed interface formation (RTAIF) at metal-semiconductor contact is one of the most important problems both in the field of electronic devices and in the field of pure science. In the Au (film)–Si (substrate) contact system, intermixing at the interface and oxidation on the specimen surface were first reported from Rutherford backscattering spectrometry[5] (RBS) and Au-Si alloy formation was confirmed by more microscopic Auger electron spectroscopy[6] (AES) followed by many works.[7] There have also been many studies[8] of the Ag (film)–Si (substrate) system, where the system is considered to be nonreacting in contrast to Au-Si, although there still are studies which claim alloy formation, or intermixing, at the Ag-Si contact. Among many experimental and theoretical works, several models have been proposed for the origin of RTAIF: (I) the "screening model,"[9,10] in which it is proposed that an intermixing reaction is induced through a screening effect of metallic electrons in an overlayer metal film formed by the deposition of metal atoms; (II) the "interstitial model,"[11-13] in which it is claimed that a silicidelike compound is formed, or that an intermixing occurs between metal and semiconductor atoms, immediately at the beginning stage of the metal-atom deposition at coverages much less than one monolayer, $\Theta(M) \ll 1$, where $\Theta(M) = 1$ means one monolayer (ML) coverage of metal atoms on a crystal substrate and is defined by $\sim 7.8 \times 10^{14}$ atoms cm^{-2} on a Si(111) surface; and (III) the "thermodynamical model," which classifies metal-semiconductor contact systems into reacting and nonreacting systems by using the quantity defined as the heat of reaction, ΔH_R.[2] As for the mechanism of RTAIF, we have recently proposed another one named

the "chemical-bonding model" from an experimental study of the Au/Si(111)-(2 × 1) system,[14] where it is claimed that the formation of a covalentlike bond between metal (M) and Si at $\Theta(M) \sim 1$ induces weakening of back bonds in the Si lattice which leads to M-Si alloy formation at higher metal coverage, $\Theta(M) \gtrsim 1$.

We have been studying M/Si(111)-(2 × 1) systems using synchrotron radiation. In the earlier photoemission study on Au/Si(111)-(2 × 1), it was shown that the formation of the chemical bond between Au and Si atoms plays an essential role,[14] but a more detailed investigation including studies on Ag/Si(111)-(2 × 1) has clearly followed into the explanation of RTAIF in terms of the chemical-bonding model. In Au($\Theta \sim 1$)/Si(111)-(2 × 1), a resonancelike enhancement of the Au(5d) signal was observed at incident photon energies of around 100 eV, i.e., the enhancement is accompanied by the Si(2p) core excitation. This result is a clear contrast to the fact that such an enhancement cannot be observed in Ag($\Theta \sim 1$)/Si(111)-(2 × 1). On the basis of these experimental observations, it will be shown that a covalentlike chemical-bond formation at $\Theta(M) \lesssim 1$ is important for RTAIF in M/Si(111) systems at $\Theta(M) \gtrsim 1$.

II. EXPERIMENT

The present study was carried out in the BL-2 system of the SOR Ring in the Synchrotron Radiation Laboratory of the Institute for Solid State Physics at the University of Tokyo. Analyzing and sample-preparation chambers were constructed by a stainless-steel ultrahigh-vacuum (UHV) system consisting of conventional ion and titanium sublimation pumps; $\sim 3 \times 10^{-9}$ Pa in the analyzing chamber and low-10^{-8}-Pa range in the sample-preparation chamber. A spectrometer used for electron energy analysis was a double-pass cylindrical-mirror analyzer (CMA) with a retarding grid at the entrance.

Photoemission spectra were taken under angle-integrated conditions, where the incident photon beam was 47.7° to the specimen surface and 90° to the CMA axis. The total energy resolution was 0.7 eV or better. The Si(111)-(2×1) cleaved surface was prepared in the sample-preparation chamber. Au- and Ag-atom deposition was performed by using W baskets. Thickness of Au and Ag layers was estimated by using a quartz thickness monitor. Details of experimental conditions are given elsewhere.[14]

III. RESULTS AND DISCUSSIONS

A. Comparison between Au and Ag on Si(111)-(2×1)

In order to clarify the difference between Au and Ag deposition on Si(111)-(2×1) at room temperature, we describe briefly the results observed in Au/Si(111)-(2×1).[14,15] The binding energies for Si(2p), $E_b[Si(2p)]$, and Au(4f), $E_b[Au(4f)]$, show a clear change at $\Theta(Au) \sim 1$; i.e., $E_b[Si(2p)]$ slightly decreases and $E_b[Au(4f)]$ increases until $\Theta(Au) \sim 1$, while both show opposite changes above $\Theta(Au) \sim 1$. The value $\Delta E[Au(5d)]$, the energy difference in the double peak of the Au(5d)-related valence-band spectrum, shows a slight decrease until $\Theta(Au) \sim 1$ and a clear increase above $\Theta(Au) \sim 1$. The saturation values of $E_b[Au(4f)]$ and $\Delta E[Au(5d)]$ are quite different from those of pure Au. These results indicate that a Au-Si alloy is formed on the Si(111) surface. In a low-energy electron diffraction (LEED) pattern, the Si(111)-(2×1) structure disappeared at $\Theta(Au) \sim 1$ and no special structure, except for a (1×1) pattern corresponding to the bulk Si(111) at high incident electron energy, was observed at $\Theta(Au) \gtrsim 1$.

We observed the Ag-coverage dependence of the valence-band spectrum of Ag/Si(111)-(2×1) deposited at room temperature. An important feature of the results is the fact that the saturation values of both the full width at half maximum (FWHM) of the Ag(4d) signal, $E_w[Ag(4d)]$, and $\Delta E[Ag(4d)]$, the energy difference between $E_b[Ag(4d_{5/2})]$ and $E_b[Ag(4d_{3/2})]$, are exactly the same as those of pure Ag. The value of $E_b[Si(2p)]$ is nearly constant over a wide Ag-coverage region. An experimental result of the LEED study on Ag/Si(111)-(2×1) is shown in Table I. The results tell us that Ag atoms disperse almost uniformly on the Si(111) surface without making islands until $\Theta(Ag) \sim 0.7$. Ag atoms form a two-dimensional layer up to $\Theta(Ag) \sim 0.7$ and grow as islands above $\Theta(Ag) \sim 0.7$, i.e., Ag atoms deposited on the Si(111)-(2×1) surface grow in the Stranski-Krastanov mode, as is the case in Ag/Si(111)-(7×7).[8(a)]

From these comparisons, we can tentatively deduce the

following conclusions: A room-temperature deposition of Ag on Si(111)-(2×1) does not induce RTAIF, while the Au deposition on Si(111)-(2×1) does. Namely, Ag islands grow on the surface without inducing any alloying due to the deposition of Ag atoms on the Si(111)-(2×1) surface, which is consistent with the previous report on Ag/Si(111)-(7×7).[8(a)]

B. Resonant photoemission

We have succeeded in observing an enhancement in the valence-band photoemission spectrum mainly contributed from Au(5d) electrons of Au(Θ~1)/Si(111)-(2×1) at the incident photon energies of ~100 eV, where the threshold energy of the Si(2p) core excitation is 99.5 eV. The experimental data given in Fig. 1 clearly show the following facts. (a) No special change appears in valence-band spectra at $h\nu < 99$ eV. (b) At incident photon energies above the threshold, $h\nu = 99.5$ eV, the photoemission spectra from the valence band at $E_b \sim 7$ eV
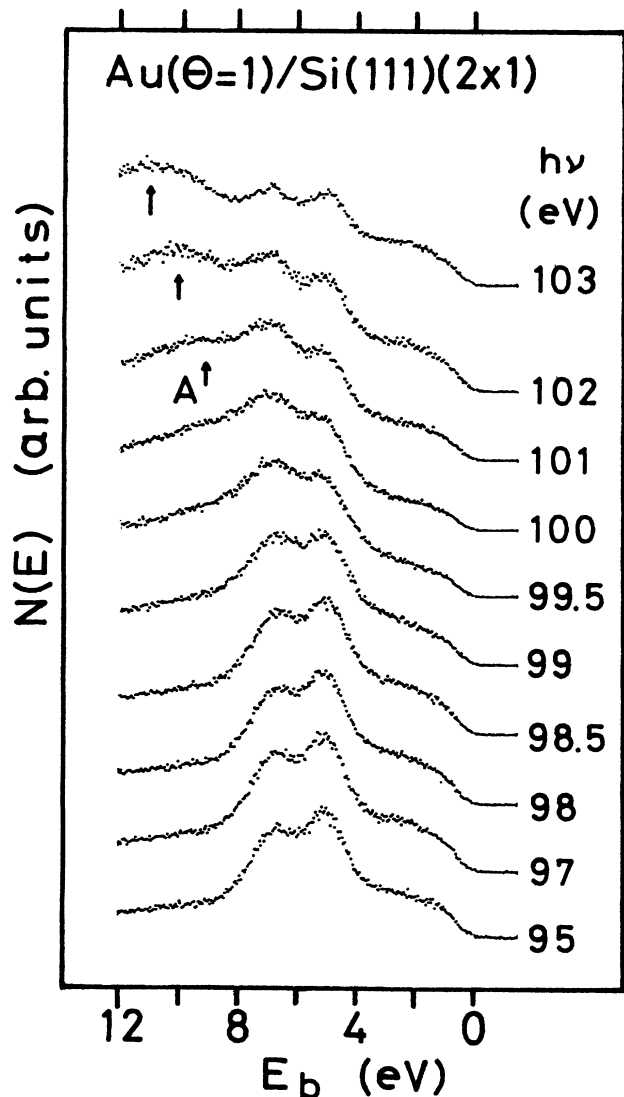
TABLE I. Ag-coveraged (Θ) dependence of the LEED pattern: Ag/Si(111)-(2×1).

Θ (Ag)	LEED pattern
0	Si(111)-(2×1)
0.6	Si(111)-(2×1)
1.0	Si(111)-(2×1) and Ag(111)-(1×1)
1.5	Si(111)-(2×1) and Ag(111)-(1×1)
2.5	Si(111)-(1×1) and Ag(111)-(1×1)
7	Si(111)-(1×1) and Ag(111)-(1×1)
14	Si(111)-(1×1) and Ag(111)-(1×1)

FIG. 1. Valence-band photoemission spectra of Au(Θ~1)/Si(111)-(2×1) at photon energies around the threshold of the Si(2p) core excitation: $h\nu = 99.5$ eV.
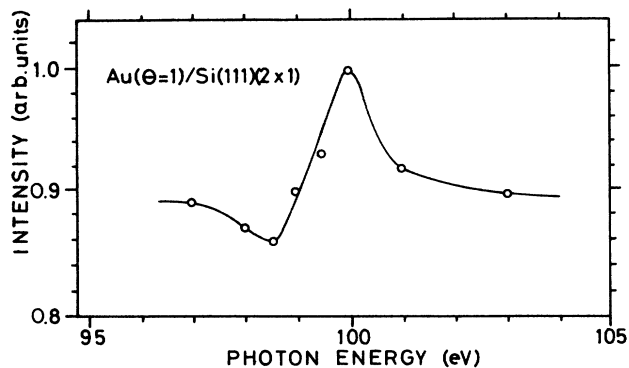
FIG. 2. Plot of the photoemission intensity at $E_b = 7$ eV from Fig. 1 against the incident photon energy. The effect of Si(LVV) Auger electron emission has been subtracted. The intensity is normalized by the photoemission intensity at $E_b = 5$ eV of $h\nu = 100$ eV.

show an enhancement in their intensity. Such an enhancement cannot be seen in the Au(5d) signal of pure Au.[15] It should be noted, in this photon energy region, that another structure indicated by an arrow A appears, which is due to Si(LVV) Auger electron excitation. Considering the fact that there is an enhancement of the valence-band spectrum of pure Si including that due to the Auger electron excitation,[16] background signals in the spectra are carefully subtracted. In the background subtraction, the existence of Au atoms by an amount of $\Theta(\text{Au}) \sim 1$ is, of course, taken into account. Normalized intensity of the valence-band signal at $E_b \sim 7$ eV, $I(7$ eV), is shown in Fig. 2 as a function of the incident photon energy. The normalization is performed by using the intensity of the valence-band photoemission from $E_b \sim 5$ eV at $h\nu = 100$ eV. One can clearly see a Fano-type resonance in Fig. 2.[17] The preferential enhancement of $I(7$ eV) is consistent with the experimental result that the photoemission peak at $E_b \sim 7$ eV has a slight dispersion in
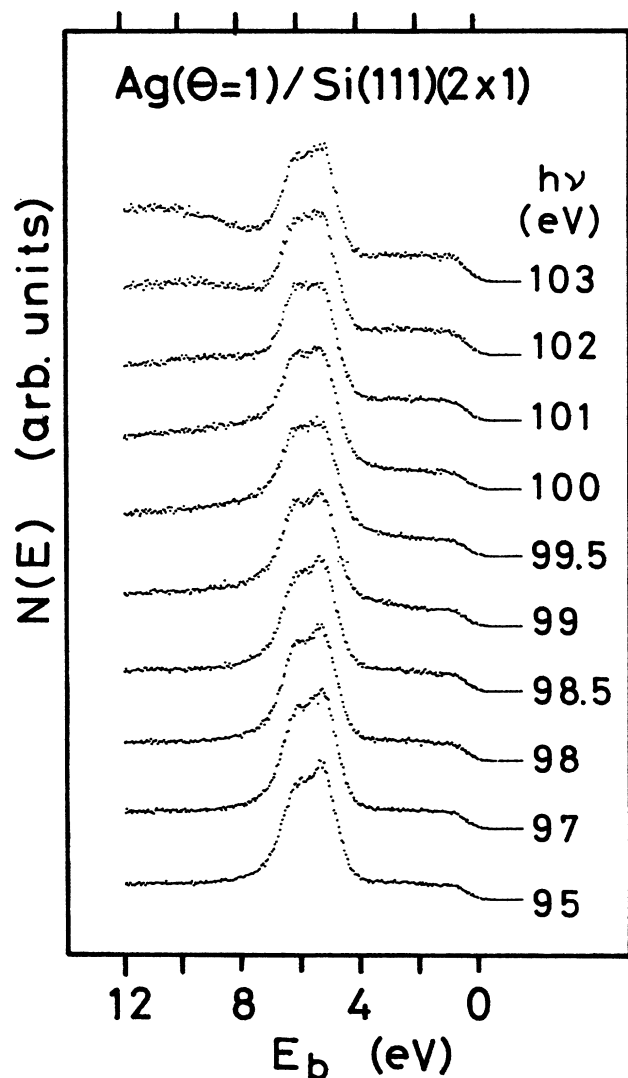

FIG. 3. Valence-band photoemission spectra of Ag($\Theta \sim 1$)/Si(111)-(2×1) at photon energies around the threshold of the Si(2p) core excitation; 99.5 eV.

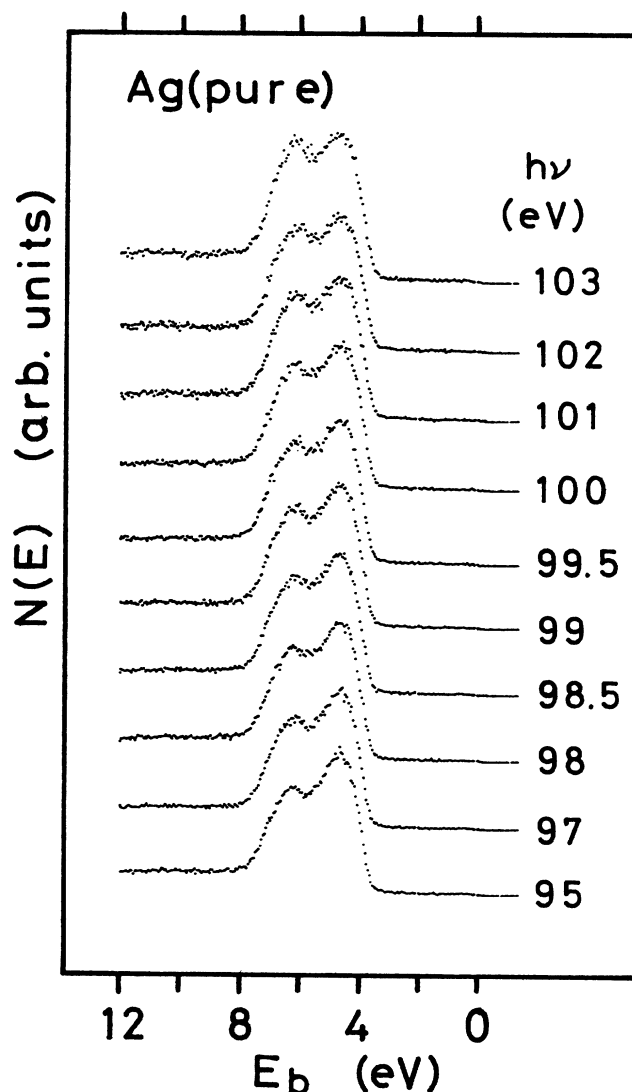FIG. 4. Valence-band photoemission spectra of pure Ag at photon energies corresponding to those of Fig. 3.

Au/Si(111).[18] In the previous paper,[14] we assigned the doublet peak of Au(5d) at Θ(Au) < 1 as the one due to the spin-orbit splitting. However, the peak at $E_b \sim 7$ eV must correspond to the bonding state of Au(5d) with Si(3s,3p). This resonancelike enhancement clearly shows the intermixing of valence electrons between Au and Si atoms in Au/Si(111)-(2×1) at Θ(Au) ~ 1, i.e., Au and Si atoms make a covalentlike bond. A similar resonancelike enhancement has been reported for the Al-GaAs system.[19]

The situation is quite different in Ag/Si(111)-(2×1). Photoemission spectra of Ag(Θ ~ 1)/Si(111)-(2×1) corresponding to those of Fig. 1 are shown in Fig. 3. From this experimental result, it can be deduced that there is no special enhancement of the Ag(4d) signal. Though a slight enhancement of I(6 eV) relative to I(5.5 eV) is seen at photon energies above 99.5 eV in Fig. 3, a similar enhancement can be observed in pure Ag, as shown in Fig. 4. Therefore, this enhancement is explained by the band (formation) effect in Ag. In other words, the bulklike Ag islands are formed at Θ(Ag) ~ 1. This observation is consistent with the above result that the island formation starts at Θ(Ag) ~ 0.7. Hence, it can be concluded that no strong chemical bond is formed between Ag and Si atoms at the stage of Θ(Ag) ~ 1.

It can be said from the results shown in Figs. 1, 2, and 3 that the formation of a covalentlike bond between M and Si atoms at the beginning stage of the M-atom deposition takes an important role in inducing RTAIF. In Au/Si(111)-(2×1), the covalentlike bond is formed between Au and Si atoms at Θ(Au) ~ 1, which is confirmed by the observation of the existence of a resonancelike enhancement of the Au(5d)-related photoemission signal at $h\nu$ ~ 100 eV. A metallic Au-Si alloy formed above Θ(Au) ~ 1 on the Si(111) surface changes its composition during the course of the Au deposition between Θ(Au) ~ 1 and Θ(Au) ~ 10 in such a way that the concentration of Au becomes rich. On the other hand, in Ag/Si(111)-(2×1) there is no strong chemical bond, as is

clarified by several experimental observations. This is the reason the Ag-atom deposition does not induce a Ag-Si alloy formation, i.e., RTAIF, on the Si(111)-(2×1) surface. Indeed, pure Ag islands grow epitaxially on the Si(111) surface.

From the discussion given above, it can be concluded that the covalentlike chemical-bond formation at the initial stage of metal-atom deposition, $\Theta(M) \lesssim 1$, plays an important role in the course of the alloyed interface formation in metal-semiconductor contact systems at room temperature. It is concluded that the covalentlike-bond formation between M and Si atoms induces a weakening of the back bond of surface Si atoms. Then, the further deposition of metal atoms above $\Theta(M) \sim 1$ enhances the weakening of the back bond of substrate Si atoms to result in a metallic M-Si alloy formation. It can be said that the chemical-bonding model works very well in order to explain RTAIF in the Au/Si(111)-(2×1) system.

IV. CONCLUSIONS

A resonancelike enhancement of a Au valence-band photoemission signal at $E_b \sim 7$ eV is observed in Au(Θ ~ 1)/Si(111)-(2×1) accompanied by the Si(2p) core excitation. This result shows the covalentlike-bond formation between Au and Si atoms. On the other hand, it is not the case for the Ag-Si system. The covalentlike-bond formation at $\Theta(M) \lesssim 1$ is essentially important for RTAIF. As for the mechanism of RTAIF, the chemical-bonding model is most promising among the proposed models.

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