Au/Si(111) and the Formation of Silicides at the Interface Examined by Spin-Resolved Photoemission

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Abstract. Au on Si(111) in the 1×1 structure for different coverages and in the $\sqrt{3} \times \sqrt{3}R30°$, and the 5×1 reconstructions has been studied by means of spin-, angle-, and energy-resolved photoemission. The photoemission studies were performed at normal incidence of the circularly polarized light and normal electron emission. In addition to Au- and Si-derived peaks other highly spin-polarized peaks are observed for a coverage of 8 Au layers grown at room temperature. In keeping with previous work these peaks are interpreted as silicide peaks. The spin polarization of these peaks gives clues concerning the levels involved in the silicide formation. For a coverage of 16 Au layers on Si(111) in the 1×1 structure the photoemission spectra are similar to the spectra of a Au(111) crystal, but also show a contribution of the silicide peaks. For lower coverages the spectra are nearly independent of the structure $(1 \times 1, \sqrt{3} \times \sqrt{3}R30°$ or $5 \times 1)$ and already show peaks other than the pure Au- and Si-derived peaks. The Auger signal, however, does not show contributions in addition to the pure Si signal.

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Au on Si(111) has been very intensively studied in the past with several techniques [1] and it is known from these studies that Au and Si form a chemical bond in the Au–Si alloy. For coverages above 5 layers all reports agree that silicide levels are formed for Au growth at room temperature [1, 2].

Differing statements can be found in the literature [2–6] concerning the growth of Au below 5 layers. Strong interaction and mixing is concluded by means of photoemission [3]. A Au–Si alloy in the range of Au_4–Si is proposed based on Auger electron spectroscopy (AES) and EELS [4] and photoemission yield spectroscopy [5]. The thickness at which the formation of silicide levels starts is the most important point of concern. In [6] it is claimed that formation begins above 5 layers. Silicide level formation below 5 layers is proposed in [2] based on AES studies.

Heating of a Au layer at a coverage below 0.5 layer, and at between 0.5 and 1 layer to a few hundred Kelvin above room temperature leads to a 5×1 and a $\sqrt{3} \times \sqrt{3}R30°$ LEED pattern [1], respectively. For these ordered surfaces, ordered Au layers are assumed in some studies [7, 8], while others [2] propose that a Au–Si reaction already occurs in the $\sqrt{3} \times \sqrt{3}R30°$ structure.

In the past, spin-polarized photoelectrons have been observed in the photoionisation of free molecules [9]. For $Cu_3Au(100)$ [10] and $Cu_3Au(001)$ [11] single crystals, a small intensity peak which was neither a pure Au nor a pure Cu peak was examined. The peak disappeared for disordered Cu_3Au and the corresponding photoelectrons have been measured to be spin-polarized to a degree of 10% [11]. The bandstructure of Cu_3Au helped to explain the existence of such a hybrid peak [11]. For molecular orbitals of adsorbates, spin-polarized photoelectrons have not been detected up to now. Spin-resolved photoemission has yet to be applied to $p - d$ orbitals. Orbitals of Au–Si should be able to eject spin-polarized photoelectrons, because the spin-orbit interaction in Au is very strong and spin-polarized photoelectrons have even been detected from Si [12].

As mentioned above, Au produces different LEED patterns at submono- and monolayer coverage which have been examined with a variety of methods [13–16]. It should also be of interest to examine the ordered structures of Au on Si(111) in order to establish whether hybrid peaks or their corresponding spin polarizations change or disappear. Spin-resolved photoemission should also distinguish between peaks which are superpositions of Au

and Si peaks and those which are derived from Au–Si levels: In the case of superposition, the Au and Si peaks remain separable by means of spin-resolved photoemission. For example for Ag on Pt(111) one intensity peak consisting of emission from Ag and Pt could be separated by means of spin-resolved photoemission because of the opposite sign of the spin-polarization corresponding to the Ag peak compared with the Pt peak [17]. For emission from Au, highly spin-polarized photoelectrons have been measured [18] and for emission from Si nearly unpolarized photoelectrons [12]. A double peak (unresolved in the intensity spectrum) can be separated by means of the spin polarization because of the different signs and magnitudes. Emission from a silicide level creates no double peak and thus no pronounced structure of the polarization in the spin-resolved spectrum.

1. Experimental

The experiments were performed at the 6.5 m normal incidence VUV-monochromator [19] at BESSY with circularly polarized off-plane radiation. The basic apparatus used for the measurements has been described elsewhere [20]. For the present work, an evaporator was added to the system.

All photoemission data were obtained for normal incidence of the circularly polarized radiation and normal emission of the photoelectrons. The photoelectrons were analyzed with respect to their kinetic energy and emission angle by an electron spectrometer [21]. The overall energy resolution (electrons plus photons) was better than 200 meV at an angular resolution of $\pm 3°$ (geometric resolution).

The surface normal of the Si(111) crystal coincided with the [111]-direction to within 0.5° and with the light direction to within 0.3°. A clean 7×7-surface was achieved by heating the crystal to 1200 K for a short time. The preparation of the surface was checked by Auger electron spectroscopy (AES) and LEED.

The evaporation was performed with the substrate at room temperature with a resistively heated Au evaporator. It was placed about 20 cm away from the target. The Au beam was collimated by a small tube. After an initial outgasing the evaporator could be operated without adversely affecting the UHV-conditions (base pressure in the 10^{-10} mbar range). It was used for short periods only, between which the surface was checked with LEED and AES.

2. Results and Discussion

The different structures of Au on Si(111) were prepared as reported in the literature [1]: a 1×1 surface for deposition at room temperature, a $\sqrt{3} \times \sqrt{3}R30°$ surface by heating one layer to about 900 K and a 5×1 surface by heating 0.5 layers to about 900 K. The coverage of one layer was determined by means of the saturation coverage of one $\sqrt{3} \times \sqrt{3}R30°$ layer. The Auger spectrum corresponding to the saturation coverage could be obtained by heating
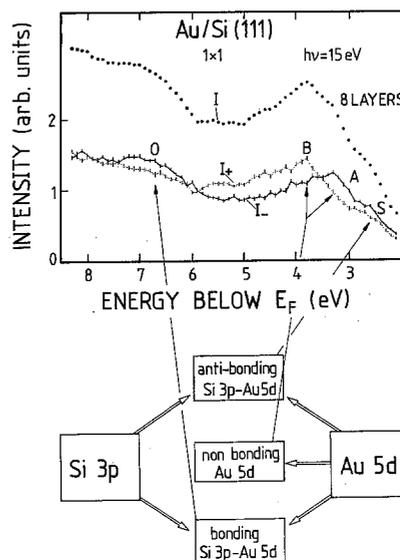

Fig. 1. Upper part: spin-resolved photoemission spectrum of Au/Si(111) in the 1×1 structure for a coverage of 8 layers and a photon energy of 15 eV. The total intensity I is shown as dotted curve. The dashed and solid curves denote the partial intensities I_+ and I_- with the electron spin polarization parallel or antiparallel to the photon spin, respectively. The vertical bars in the I_+ and I_- intensities represent the total experimental error containing the statistical error of the count rates and the uncertainties of the light polarization and the detector asymmetry function. Lower part: level scheme [22] for the levels involved in the silicide formation

thicker layers to 900 K, because the spectrum after the heating always had the same shape, independent of the former coverage due to the Stranski-Krastanov growth [1]. 900 K was chosen because, at this temperature, the 6×6 reconstruction, which occurs at lower temperatures and at coverages higher than one layer, is absent and the $\sqrt{3} \times \sqrt{3}R30°$ reconstruction is followed by three-dimensional growth after the completion of one layer [1].

Firstly an 8-layer adsorbate deposited at room temperature showing a 1×1 LEED pattern was examined. The Auger spectrum showed peaks at 90 and 95 eV, typical for silicide formation [22]. In this thickness range it is commonly assumed in the literature [1] that silicide orbitals are formed.

A spin-resolved photoelectron spectrum for a photon energy of 15 eV is shown in the upper part of Fig. 1. The total photoelectron intensity I (dotted curve) is separated into the partial intensity I_+ (dashed curve) and I_- (solid curve) by means of the measured spin polarization P according to

$$I_+ = \frac{I}{2}(1+P) \quad \text{and} \quad I_- = \frac{I}{2}(1-P).$$

Three peaks and a shoulder are visible in the spectrum in Fig. 1. Peak A and peak B agree in their energetic positions and spin polarization signs with two peaks for two dimensionally grown Au/Pt(111) [18] and a Au(111) single-crystal [23]. For a Au(111) crystal these peaks are due to transitions from the d-derived first $\Lambda_{4,5}^3$ and Λ_6^3 bands below E_F into the free-electron-like final band. For Au/Pt(111) and a Au(111) single crystal only two tran-

sitions are visible for our geometry at a photon energy of 15 eV [18, 23].

The existence of the additional structures can be understood by means of the scheme [22] in the lower part of Fig. 1. The principle silicide level formation for a reaction between the Si $3p$ levels and the metal $5d$ levels is shown. A bonding and an anti-bonding orbital are formed with energetic positions below and above the non-bonding $5d$ levels, respectively. Peaks A and B can be understood as non-bonding $5d$ levels, because of their similarities to the peaks of a Au(111) single crystal and Au/Pt(111). The shoulder S can be interpreted as corresponding to an anti-bonding orbital and peak O as corresponding to a bonding orbital. This interpretation is supported by the fact that both for Au [23] and for Si [24] electronic density exists in this energy range. For Au(111) a $\Lambda_{4,5}^3$ band lies 1.5 eV below the first levels corresponding to the peaks A and B. The spin polarization sign of the corresponding photoelectrons is negative [18]. This level could be involved in the silicide formation. This is supported by the spin-polarization sign of peak O and shoulder S which is also negative. The fact that the photoelectrons corresponding to the silicide orbitals and to pure Au levels have the same spin polarization signs suggests a dominant Au-level contribution to the silicide levels.

The broad shoulder between peaks B and O might also be explained by a further silicide level due to a Au level corresponding to the Λ_6^3 band of a Au(111) single crystal which is split from the Au band involved in the silicide formation by spin-orbit interaction. The spin polarization sign corresponding to the Λ_6^3 band is positive as for the broad structure. This and the opposite spin polarization sign of peak O and the broad structure suggest spin-orbit split silicide levels. A further analysis of the shoulder S reveals a shoulder in I_+ and I_-. This indicates spin-orbit split anti-bonding levels. The energetic ordering of the spin-polarization signs is $(-, +, +, -)$ analogous to the ordering of the spin-polarization signs corresponding to pure Au levels [18]. This indicates that the Au level symmetry dominates the silicide level symmetry.

The coverage dependence of the intensity spectra is presented in Figs. 2 and 3. In Fig. 2 spin-resolved intensities for a photon energy of 15 eV and coverages between 1 and 16 layers are displayed. The peaks A, B, O and the shoulder S are again visible as in Fig. 1. A comparison of the spectra for all coverages reveals that all spectra have the same peaks. A detailed comparison shows that peak O has the same binding energy in each spectrum, whereas the peaks A and B shift to lower binding energy and increase in intensity for higher coverages. This happens discontinuously at a coverage of 4 layers. Peak A increases more in intensity than peak B. For coverages higher than 4 layers, the shoulder S becomes clearly visible.

For a better understanding of this behaviour the energy dependence is examined for a coverage of 2 and 16 layers. The left part of Fig. 3 shows the spectra for 2 layers, and the right part the spectra for 16 layers. In the spectra for 2 layers the intensity peak at 4.5 eV below E_F, which consists of peaks A and B, does not show dispersion. This does not indicate three-dimensional growth. Peak O shows
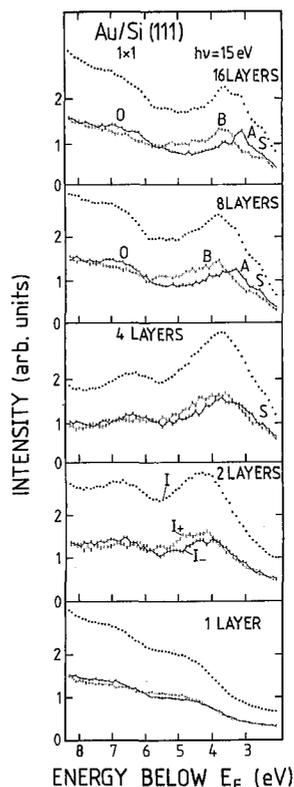

Fig. 2. Spin-resolved photoemission intensity spectra of Au/Si(111) in the 1 × 1 structure for photon energy of 15 eV and coverages of 1, 2, 4, 8, and 16 layers. I, I_+, and I_- as in Fig. 1
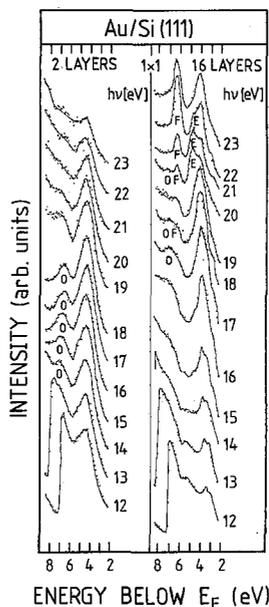

Fig. 3. Intensity spectra of Au/Si(111) in the 1 × 1 structure for photon energies between 12 and 23 eV and for a coverage of 2 layers (left part) and 16 layers (right part)

resonant behaviour for photon energies around 17 eV. In the spectra for 16 layers the intensity peak around 4 eV below E_F shows dispersion indicating three-dimensional Au growth. For photon energies above 20 eV peaks E and F occur in addition to the peaks A, B, O and the shoulder S. The spectra would only reveal the bulk transitions of a
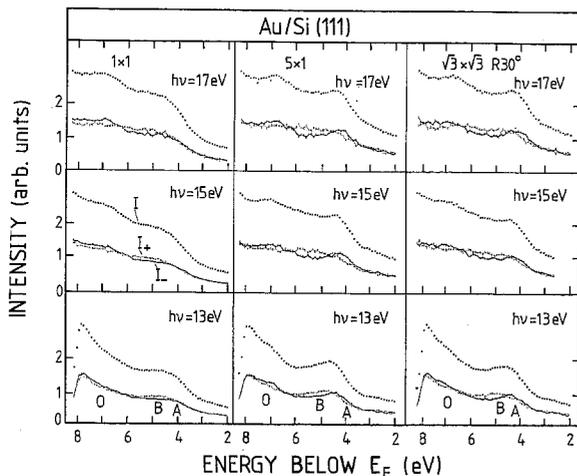
Fig. 4. Spin-resolved photoemission spectra of Au/Si(111) in the 1 × 1 (left part), the 5 × 1 (middle part) and the $\sqrt{3} \times \sqrt{3}$R30° (right part) structure for photon energies of 13, 15, and 17 eV. I, I_{+}, and I_{-} as in Fig. 1. The vertical error bars in this figure are nearly as small as the line thickness

Au(111) single-crystal [18, 23] if the energetically separated structures O and S were absent. Peaks E and F show resonant behaviour at about 20 eV as described in [18, 23]. But peak O is still present and behaves as for 2 layers, although it has decreased in intensity compared with the pure Au peaks. The spectra of a 16 layer Au adsorbate mainly show the bulk transitions of a Au(111) crystal (the first intensity peak below E_F consisting of peaks A and B and peaks E and F) and additionally the energetically separated structures O and S at higher and lower binding energy, respectively. The observed 1 × 1 LEED pattern at this coverage indicates an ordering of the adsorbate as for a Au(111) crystal. This is also the reason why an adsorbate thicker than 10 layers is often designated as an Au(111) crystal [1]. However, the existence of peak O and shoulder S shows that there must be silicide on the surface. The behaviour and the increasing intensity of the peaks A, B, E, and F show that the Au–Au interaction predominates over the Au–Si interaction with increasing coverage.

For 2 layers peak O is already present. For this low coverage the existence of this peak might be explained by Au clusters or Au atoms adsorbed in different sites. But as already discussed in detail for Ag/Si(111) $\sqrt{3} \times \sqrt{3}$R30° [25] these explanations are not probable. From pure Si levels highly spin-polarized electrons cannot be expected, because of the low charge number of Si. This suggests a Au–Si reaction even for 2 layers, in agreement with [2]. The Auger spectrum revealed mainly the Si peak at 92 eV. This demonstrates the sensitivity of spin-resolved photoemission to slicide level formation by detecting emission from the bonding orbital.

In addition to the studies of Au grown at room temperature on Si(111) we have also examined the 5 × 1 and $\sqrt{3} \times \sqrt{3}$R30° surface of Au/Si(111). For these structures the peak at 92 eV dominated the Auger spectrum. In Fig. 4 spectra of the 1 × 1, the 5 × 1 and $\sqrt{3} \times \sqrt{3}$R30° structures are displayed for comparison. The spectra are

very similar. The peaks A, B, and O are visible at the same energetic positions and with the same spin-polarization signs in all spectra for all structures. Peak intensities and shapes of the spectra agree well. Peak O increases in intensity from 13 eV to 17 eV photon energy and peak A and B do not show dispersion. The ordering of the surface has almost no influence on the electronic structure as probed by our experiments. These experimental results demonstrate that the Au–Si interaction strongly influences the photoemission in the ordered structures, an effect not seen in the Auger spectra [1, 2].

3. Conclusions

Au on Si(111) in the 1 × 1 structure for different coverages and in the $\sqrt{3} \times \sqrt{3}$R30° and the 5 × 1 structures has been studied by means of spin-resolved photoemission. Highly spin polarized peaks are observed for a coverage of 8 Au layers grown at room temperature and are interpreted as silicide peaks in keeping with previous work [1]. The spin polarization of these peaks indicates a spin-orbit splitting of bonding and antibonding levels. The symmetry of the silicide levels appears to be mainly the same as the symmetry of the Au levels involved in the silicide level formation. For a coverage of 16 layers Au on Si(111) a 1 × 1 LEED pattern was observed and the photoemission spectra are similar to the spectra of a Au(111) crystal, but they also show a contribution of the silicide peaks. For lower coverages in the monolayer regime the structure (1 × 1, $\sqrt{3} \times \sqrt{3}$R30° or 5 × 1) of the surface does not influence the spectra. Au–Si interaction is indicated by an additional photoemission peak as for 8 layers while the Auger signal does not show important additional contributions to the pure Si signal.

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