Evolution of unoccupied resonance during the synthesis of a silver dimer on Ag(111)

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Abstract. Silver dimers were fabricated on Ag(111) by single-atom manipulation using the tip of a cryogenic scanning tunnelling microscope. An unoccupied electronic resonance was observed to shift toward the Fermi level with decreasing atom–atom distance as monitored by spatially resolved scanning tunnelling spectroscopy. Density functional calculations were used to analyse the experimental observations and revealed that the coupling between the adsorbed atoms is predominantly direct rather than indirect via the Ag(111) substrate. While the substrate influence is small owing to the surface-projected sp band gap, the direct interaction is most likely due to the large extension of the p wave functions at the adsorbate atoms contributing to the resonance.

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1. Introduction

The electronic structure of adsorbed atoms (adatoms) or clusters of atoms on surfaces determines the coupling between adsorbate and substrate [1]–[4], the mutual interaction between the adatoms [5], magnetic properties [6], as well as their catalytic activity and selectivity [7, 8]. The coupling between adatoms is particularly interesting since it plays a crucial role in nucleation and is thus at the base of the microscopic understanding of thin film growth on surfaces [9]–[11]. Typically, the mutual interaction comprises direct and indirect contributions. Direct interactions result from the overlap of atomic orbitals and are responsible for the bonding of dimers in vacuum. This type of interaction has been investigated for metal dimers in the gas phase and noble-gas matrices [12]–[14]. An exponential energy splitting of bonding and antibonding states with the atom–atom separation is characteristic for direct coupling. Indirect interactions may become important for adatoms on surfaces and they depend strongly on the electronic structure of the substrate. In particular, long-ranged and oscillatory coupling between two adatoms or adsorbed molecules is mediated by quasi-two-dimensional electronic states [15]–[22].

The evolution of the electronic structure of clusters on surfaces with cluster dimensions and geometric shapes has been analysed atom by atom. For example, results from artificial gold chains [23], quantum confinement of one-dimensional electronic states to chains of copper atoms [24], unoccupied electronic resonances of silver clusters with various sizes and shapes [25], and the evolution of the Kondo effect of a single magnetic atom with the number of adjacent non-magnetic atoms in vertical [26] and lateral [27] hybridization geometries have been reported. In a recent study of Au dimers on NiAl(110) a splitting of the Au monomer resonance into bonding and antibonding states was reported as a function of the Au–Au separation [5]. The emerging picture, which may be inferred from this work, is that substrate-mediated adsorbate–adsorbate interactions weaken the direct coupling between the adsorbates. In particular, it was found in [5] that the splitting between bonding and antibonding states varies linearly with the reciprocal mutual Au distance, rather than exponentially as would be expected from a direct coupling in vacuum.

Here, in a combined experimental and theoretical study, we investigated the evolution of a Ag monomer sp\(_z\) resonance, which shifts toward the Fermi level upon approaching a second Ag atom. Our theoretical analysis indicates that, at not too large adatom–adatom distances, the interaction between the sp\(_z\) electronic states on the surface is similar to the direct interaction between the two Ag p\(_z\) orbitals in vacuum.

2. Experiment

Measurements were performed with a custom-built scanning tunnelling microscope operated at 7 K and in ultrahigh vacuum with a base pressure of 10\(^{-9}\) Pa. The Ag(111) surface and chemically etched tungsten tips were cleaned by argon ion bombardment and annealing. Individual silver atoms were deposited onto the sample surface by controlled tip–surface contacts as previously described in [28]. Using the tip of the microscope, silver dimers were fabricated by atom manipulation. Spectra of the differential conductance (dI/dV) were acquired by superimposing a sinusoidal voltage signal (root-mean-square amplitude 5 mV, frequency 4.7 kHz) onto the tunnelling voltage and by measuring the current response with a lock-in amplifier. Prior to spectroscopy of monomers and dimers the tip status was monitored using...
spectra of the onset of the Ag(111) surface state band edge. To obtain sharp onsets of the surface state signal and to image single adatoms with nearly circular circumference the tip was controllably indented into the substrate. Due to this in vacuo treatment the tip apex was most likely covered with substrate material. All scanning tunnelling microscopy (STM) images were acquired in the constant current mode with the voltage applied to the sample. We divided the $dI/dV$ spectra by $I/V$ to reduce the influence of the voltage-dependent transmission of the tunnelling barrier [29].

3. Results and discussion

Figure 1(a) presents a sequence of constant-current STM images of a single Ag adatom (top) on Ag(111), two Ag adatoms (middle) with a distance of $\approx 0.58$ nm, and a silver dimer (bottom). Distances between adatoms of Ag–Ag assemblies were determined from maxima positions of cross-sectional profiles taken along the connecting line between the adatoms. Together with the orientation of the assembly with respect to high-symmetry directions of the Ag(111) substrate, which was determined from dislocation lines on the surface, the extracted adatom–adatom distances agree with lattice site separations on Ag(111). The Ag dimer appears as a single entity in STM images and we assigned the nearest-neighbour distance of Ag(111) to the adatom–adatom distance of Ag$_2$. Our calculations indicated a slight preference of the Ag adatom to occupy the face-centred cubic (fcc) adsorption site to occupation of the metastable hexagonal close-packed (hcp) adsorption site, which is of the order of the accuracy of the
Figure 2. (a) Energy of the unoccupied resonance as a function of the Ag adatom distance, $d_{\text{Ag–Ag}}$. For distances larger than 2 nm the spectra were acquired atop the individual Ag adatoms while for smaller distances spectroscopy was performed with the tip positioned above the centre of the assembly. The solid line is a fit to the calculated data in (b). (b) Logarithm of the calculated energy difference between monomer resonance (M) and bonding resonance (B) of an Ag–Ag assembly, $\ln(E_M - E_B)$, plotted versus $d_{\text{Ag–Ag}}$. The solid line is a linear fit to the data.

calculation. We experienced that in the course of fabricating silver dimers individual Ag adatoms were also found to occupy hcp adsorption sites (see the middle STM image in figure 1(a) and the corresponding sketch in figure 1(b)). Such assemblies occurred frequently for adatom distances smaller than 0.6 nm. In the following, these assemblies are referred to as quasi-dimers. The schematics in figure 1(b) illustrate adsorption sites of individual Ag adatoms (black circles) on the hosting Ag(111) lattice (grey dots) and the orientation of the quasi-dimer and the dimer with respect to the Ag(111) crystallographic directions. Figure 1(c) shows normalized d$I$/d$V$ spectra acquired on the centre of the single Ag adatom (top), of a quasi-dimer (middle), and of the dimer (bottom). A gradual shift of the monomer-related peak from $\approx 2.9$ eV via a resonance energy of $\approx 2.7$ eV observed for the quasi-dimer to $\approx 2.3$ eV for the dimer resonance binding energy was observed. The total shift of $\approx 0.6$ eV towards the Fermi level was not induced by the electric field of the tip. Although the tip–surface distances may have differed for the spectra shown in figure 1(c), it has been shown in [30, 31] that for shifts of the order of 10 meV the tip–surface distance had to be varied by several angstroms, which was not the case here.

Figure 2(a) summarizes the resonance energies measured for a variety of Ag adatom separations, $d_{\text{Ag–Ag}}$. For $d_{\text{Ag–Ag}} > 1$ nm the shift of the resonance energy is too small to be
resolved. For separations $d_{\text{Ag–Ag}} < 1$ nm a shift of the resonance energy is discernible and increases rapidly as $d_{\text{Ag–Ag}}$ approaches the nearest-neighbour distance of Ag(111). The solid line in figure 2(a) is a fit to calculated data (figure 2(b)), which has been extrapolated to larger Ag–Ag distances. The calculations are discussed below. For $d_{\text{Ag–Ag}} > 2$ nm, the spectra at the centre between two Ag adatoms were virtually identical with spectra of clean Ag(111) in the relevant voltage interval [25]. For this reason, the data points for $d_{\text{Ag–Ag}} > 2$ nm in figure 2 were acquired atop the individual adatoms.

Using density functional theory as implemented in the Vienna ab initio simulation package (VASP) [32]–[34] developed at the Institut für Materialphysik der Universität Wien, we determined the electronic structure of silver dimers adsorbed on Ag(111) with increasing adatom–adatom separation. The generalized gradient approximation (GGA) PW91 by Perdew and Wang [35] was applied to the exchange correlation functional. The electron–ion interaction was treated within the framework of Blöchl’s projector augmented wave (PAW) method [36]. The potentials for VASP were used from the database [37]. All configurations were modelled in a slab geometry comprising of 14 layers of Ag. Silver dimers with separations of 0.28, 0.44, 0.52 and 0.59 nm were modelled in a $(5 \times 4)$, $(6 \times 4)$, $(4 \times 4)$ and $(6 \times 4)$ surface unit cell, respectively. The surface Brillouin zone was sampled with 16, 9 and 6 $k$ points for the $(4 \times 4)$, $(5 \times 4)$ and $(6 \times 4)$ unit cells, respectively. The Kohn–Sham wave functions were expanded in a plane wave basis set with a 250 eV cutoff energy.

In order to identify the orbital composition of the experimentally observed unoccupied resonance, we have calculated the projected density of states (PDOS) with respect to atomic orbitals localized at the adatom sites. In the case of the silver dimer with both atoms at neighbouring fcc sites, the maximum of the resonance was found between 1.8 and 1.9 eV above the Fermi energy [25]. This resonance can clearly be observed in the $p_z$ PDOS (figure 3(a)), while it is absent in the $s$ PDOS (figure 3(b)). From this we conclude a dominant $p_z$ character, with some $s$ admixture, of this resonance.

By projecting onto bonding and antibonding combinations of $p_z$ orbitals located at the two Ag atoms of the dimer, we identified the centre of the bonding and antibonding $p_z$ resonance (figure 3(c)). From this we obtained the energy splitting between the bonding ($E_B$) and the antibonding ($E_A$) state, whose logarithm is plotted as a function of the mutual Ag atom distance in figure 3(d). The results shown in figure 3(d) are consistent with an exponential variation of $E_A - E_B$ within the calculated range of Ag adatom distances. In order to compare to experiment, we furthermore calculated the energy shift of the bonding resonance of the Ag adatom pair with respect to the energy of the monomer resonance ($E_M$) (figure 2(b)). We found that the energy splitting between the bonding resonance with respect to the monomer resonance, $E_M - E_B$, quite accurately coincides with half the energy shift between the bonding and the antibonding states, $(E_A - E_B)/2$. Thus, the splitting between bonding and antibonding states is approximately symmetric. The solid line in figure 2(a) represents a linear fit to $\ln(E_M - E_B)$ as a function of the Ag adatom separation $d_{\text{Ag–Ag}}$, which has been extrapolated to larger separations. We conclude that both experimental and theoretical data are consistent with an exponential variation of the energy splitting with $d_{\text{Ag–Ag}}$. However, due to computational limitations the range of Ag–Ag distances considered here for the two Ag adatoms on the Ag substrate is too narrow to reliably distinguish between an exponential and an algebraic $(1/d)$ [5] dependence of energy splitting on adatom separation.

For comparison we have calculated the energy splitting between the $5p_z$ bonding and antibonding orbitals of a Ag dimer in vacuum. The calculated splitting of the silver $5p_z$
bonding and antibonding orbitals varied exponentially with atom separation as expected [12, 14]. Surprisingly, as is evident from figure 3(d), the energy splitting between bonding and antibonding states for the dimer in vacuum is similar to the splitting of the dimer adsorbed on the surface for the Ag–Ag distances considered in the \textit{ab initio} calculations.

To further analyse the interaction between adatoms on a surface we resorted to a minimum tight-binding model, which is similar to the model reported in [38]. For simplicity, we did not consider a tight-binding model of the fcc crystal and its (111) surface, but we resorted to atoms
with a single s orbital forming a simple cubic lattice, and two adatoms adsorbed at on-top sites. We found a direct contribution, $2t$, to the energy splitting between bonding and antibonding states, which is due to direct adatom interaction. The parameter $t$ denotes the transfer integral for the two adatom states, and $2t$ is identical to the splitting occurring for the free dimer at the same adatom distance. Furthermore, there is a contribution to the splitting owing to the interaction via the substrate, $2 \text{Re}(G_{ab}) |v|^2$, where $v$ denotes the next-neighbour transfer integral and $G_{ab}$ the matrix element of the Green’s function of the substrate with respect to the adsorption sites. Calculations of such a matrix element of the Green’s function for two next-neighbour sites on the Ag(111) surface yielded values of $\text{Re}(G_{ab})(\varepsilon)$ varying between 0.05 and $0.15 \text{eV}^{-1}$ within the energy range of interest. For typical values of $|v|$ between 0.4 and 1 eV, the simple model also predicts that the interaction via the substrate is distinctly smaller than the observed splitting. At large adatom separations, we expect the substrate-mediated interaction to eventually dominate the direct interaction between the adatoms. In the case of Ag atom pairs on Ag(111) this appears to occur at a separation which is too large for the splitting to be resolved in experiment.

In a previous investigation of Au dimers on NiAl(110) the splitting of bonding and antibonding Au dimer states was reported for varying Au–Au distances [5]. Nilius et al [5] found that the variation of the splitting follows a $1/d_{\text{Au–Au}}$ rather than an exponential law. This observation was argued to be due to the influence of the substrate electronic structure, which reduces the direct overlap of Au orbitals. In the case of Ag–Ag assemblies on Ag(111), however, the interaction between the individual Ag adatoms is similar to the one in vacuum (figure 3(d)). A tentative explanation for this observation involves the electronic structures of the substrates. The Ag(111) surface exhibits an extended sp band gap of surface-projected bulk electronic states in the centre of the surface Brillouin zone [39], while NiAl(110) does not [40]–[42]. Since the resonance energy of the Ag–Ag assemblies falls into the surface-projected sp band gap it is likely that the Ag(111) substrate electronic structure plays a less important role in mediating the interaction between the Ag adatoms. As a consequence, the Ag adatom assemblies on Ag(111) are subject to a substrate influence to a lesser extent than the Au adatom assemblies on NiAl(110). We suggest that the large direct interaction in case of Ag dimers on Ag(111) is also caused by the large extension of the p wave function, which dominates the resonance. This results in a slow decay of the transfer integral as a function of Ag–Ag distance.

4. Conclusion

The interaction between two Ag adatoms on Ag(111) gives rise to a shift of a sp$_z$ resonance towards the Fermi level with decreasing mutual adatom distances. The shift was modelled by density functional calculations and is similar to the shift calculated for a Ag dimer in vacuum. This observation indicates a weak net influence of the substrate on the Ag–Ag interaction, which may originate from the surface-projected sp band gap of the substrate. We suggest that adatom–adatom interactions on surfaces with band gaps in the relevant energy interval exhibit similar behaviour. Moreover, the large extent of the p wave function favours a long range direct interaction.

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