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Measuring the Au(1 1 1) surface state at the solid–liquid interface

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Abstract

We present the first direct observation of an occupied noble metal surface state at the metal/liquid interface. The Au(1 1 1) Shockley-like surface state was measured by scanning tunneling spectroscopy (STS) at the Au(1 1 1)/*n*-tetradecane interface. These results show that the surface state of gold survives in a liquid environment, and can be probed by STS. More generally it indicates that STS can be used to study electronic properties of surfaces at the solid/liquid interface, and that spectra can be directly compared to measurements and calculations of a surface's electronic structure in ultra-high vacuum.
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1. Introduction

The Scanning tunneling microscope [1] (STM) enables one to study surfaces and adsorbates in real space, and with atomical resolution. Scanning tunneling spectroscopy (STS) [2], makes it possible to probe the local electronic structure of a surface, and thus study electronic properties of real space features, such as defects and adsorbates. The combination of STM and STS has been very successful in the investigation of surfaces and adsorbates. Some important examples are: chemical identification of single atoms on the surface of an alloy [3]; inducing and monitoring all steps of a chemical reaction on a Cu(1 1 1) catalyst [4]; and revealing the first and second occupied and unoccupied molecular orbitals of molecules in an highly ordered organic thin film [5].

However, aforementioned studies were all carried out in ultra-high vacuum (UHV) conditions,

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or at low temperatures. These conditions are not realistic for many chemical and biological systems, which involve a liquid environment. Over the last decade, STM studies at this interface have been increasingly successful. Areas of research to which STM at the solid/liquid interface has been applied include: the investigation of molecular electronics by self-assembly from solution [6], the study of supramolecular self-assembly on surfaces [7], and the imaging and manipulation of highly ordered monolayers of large porphyrin complexes [8]. Surprisingly, while STM studies are abundant, there are notably few cases where STS has been performed at the solid/liquid interface. Reported results are, to the best knowledge of the authors, limited to the observation of current–voltage curves which indicate rectifier-like behaviour of molecules [9–14], and current–distance curves, at the metal/electrolyte interface, showing oscillations due to the ordering of water molecules in multilayers [15]. Until now, to the best of our knowledge, it has not been possible to assign discrete peaks in tunneling spectra, obtained at the solid/liquid interface, to known electronic states of the surface.

To demonstrate that also at the solid/liquid interface STS can be a powerful tool for electronic characterization, one has to obtain tunneling spectra with distinct peaks which can be directly related to peaks in the density of states of the surface. To do this, one needs a model system of known composition and with a distinct electronic signature. The Au(1 1 1)/*n*-tetradecane interface is such a system. The clean Au(1 1 1) surface has a distinct electronic structure due to a Shockley-like surface state, which has been investigated by STS in ultra-high vacuum [16]. Furthermore, the Au(1 1 1)/*n*-tetradecane interface has been studied by STM, and results indicate a clean interface with the typical $23 \times \sqrt{3}$ reconstruction intact [17]. The insulating liquid does not contribute to the electronic states in the region around the Fermi energy, and is therefore not expected to induce peaks in the tunneling spectra. The absence of accessible empty states in the solvent ensures that the surface state electrons will remain confined to the surface. Direct experimental evidence for the survival of the Au(1 1 1) surface state upon the

adsorption of *n*-tetradecane is not available, but it is known that the image states on Ag(1 1 1) are preserved upon coverage by multiple layers of *n*-alkanes [18]. Additionally it has been shown by electroreflectance spectroscopy measurements on Au and Ag electrodes in aqueous electrolytes that unoccupied surface and image states can be observed at the metal/electrolyte interface [19–21].

In this letter, we report the observation of a surface state at the solid/liquid interface (strictly speaking: a surface state derived interface state), by means of STS measurements at the Au(1 1 1)/*n*-tetradecane interface.

2. Experimental

Our experiments were performed with the home built *Nijmegen Liquid-Cell STM* and an Omicron SCALA SPM controller. Measurements were done on fresh Au(1 1 1) films mounted in a liquid cell filled with tetradecane. The complete STM was enclosed in a bell-jar with an argon atmosphere. The Au(1 1 1) films were prepared in an evaporator using 99.99% gold and freshly cleaved mica. The gold was grown epitaxially on the heated mica ($\sim$300 °C), at a pressure of 10^{-7} mbar, and annealed for 2 h at 300 °C, 10^{-8} mbar. The tetradecane (Aldrich, 99+%) was purified by distillation and degassed by bubbling with argon for several hours. STM tips were mechanically cut from platinum-iridium (80–20) wire. The films were quickly transferred from the evaporator to the cleaned tetradecane (within 60 s), and this was done in the nitrogen flow originating from the evaporator.

To estimate the contamination rate of a surface in our setup, we have performed finite element calculations taking into account diffusion and migration [22]. The concentrations of oxygen and other dissolved gases were deduced from the specified purity of the argon gas. The maximum ion concentrations were estimated by measuring the conductivity of the solvent with the STM itself. Results from these calculations indicate that *worst case* surface contamination by dissolved oxygen and ions are less than a monolayer per day, which is comparable to the contamination of a surface in ultrahigh vacuum by oxygen.

3. Results

Liquids of *n*-alkanes are known to have a layered ordering, with the main axis of the molecules parallel to the surface, at the interface with a flat solid. At the *n*-hexadecane/Au(001) interface (at 350 K) 3–4 such layers are present, with the first layer 3–4 Å above the gold (center to center) [23]. On a Au(111) surface, the layer at the interface forms a crystalline monolayer at a temperatures above the bulk melting temperature [17]. The bulk melting temperature of *n*-tetradecane is 5.89 °C which is too low to have a uniform crystalline monolayer on the Au(111) surface at room temperature. However, small domains of self-assembled tetradecane are formed, as can be seen in Fig. 1. The presence of these ordered layers reduces the diffusion constant perpendicular to the surface, which slows down possible contamination of the surface. Furthermore, the observation of such defect free domains of *n*-tetradecane proves that the Au(111) surface has a low amount of defects and adsorbed impurities.

Underneath the *n*-tetradecane, the $23 \times \sqrt{3}$ reconstruction of the gold is still present, as can be seen in Fig. 1, and more clearly in Fig. 2. The observed period, shape, and corrugation of this reconstruction are in agreement with values obtained by UHV-STM measurements [24]. We can conclude from these STM topography results, that our liquid-cell STM allows us to study a clean Au(111) surface, with the typical $23 \times \sqrt{3}$ reconstruction intact; i.e., the conditions are similar to those under which typical UHV-STM and -STS
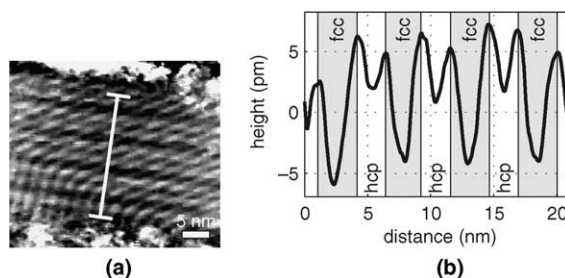

Fig. 2. (a) Constant current image of Au(111) ($I = 15$ pA, $V = -300$ mV) showing the typical Au(111) $23 \times \sqrt{3}$ reconstruction. (b) Cross-section along line in a. showing the typical reconstruction period and the alternating fcc/hcp domains.

measurements are carried out, with the notable difference: a liquid environment.

Subsequently spectroscopy measurements were performed. Normalized differential conductivity curves, i.e., $(\mathrm{d}I/\mathrm{d}V)/(I/V)$ curves, obtained from two separate experiments performed under identical conditions, are shown in Fig. 3. The spectroscopy curves were taken with the feedback off, and simultaneously with a STM constant current
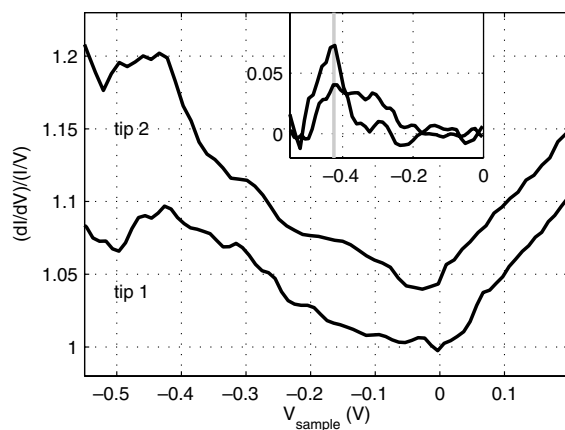

Fig. 3. $(\mathrm{d}I/\mathrm{d}V)/(I/V)$ spectroscopy curves, normalized differential conductance versus sample bias voltage. Spectra from two separate experiments are shown (tip 1, setpoint: 300 mV, 0.5 nA, sweep: 0.3 V → −0.7 V; tip 2, setpoint: 300 mV, 0.5 nA, sweep: −0.7 V → 0.3 V) which have been offset and scaled for comparison. The two curves are each averages of several hundreds of curves taken on a single terrace, and in a single measurement. Both curves show a peak in the differential conductivity at ∼−430 mV. The inset shows the same curves minus the exponential background, obtained by subtracting an exponential fit to the whole curve.

Fig. 1. Constant current image ($I = 10$ pA, $V = 300$ mV) of Au(111) with a self-assembled monolayer of *n*-tetradecane. Both the reconstruction of the gold and the individual $C_{14}H_{30}$ molecules are discernible. The inset shows a correlation averaged zoom-in, with some molecules drawn in to indicate the structure of the monolayer.

topography measurement. The experimental data so obtained consist of a topography image, with for each point of the topography a current–voltage, $I(V)$, curve. Both curves shown in Fig. 3 are the normalized derivatives of the average of several hundreds of $I(V)$ curves in an area on a single, large (>100 nm^2) terrace on the gold. All curves in the selected area were used to calculate the average, no selection criteria were used. The $(dI/dV)/(I/V)$ curves from both experiments have a single peak around −430 meV. The position of the peak falls well within the range of previously reported values for the surface state on Au(1 1 1) as measured by UHV-STS: −317 meV [25], −520 meV [26], and −400 meV [16]. The peak is rather sharply terminated at the left side, and falls of more slowly towards the Fermi level, this is due to the dispersion of the surface state electrons, and is in qualitative agreement with results from UHV-STS. We therefore contribute the peak around −430 meV to an interface state, derived from the Au(1 1 1) surface state.

In order to provide additional experimental evidence, we have studied the behavior of the interface state near, and on step edges. It is well known from UHV-STS measurements that a surface state is quenched near steps and impurities [25]. Fig. 4 shows spectroscopy curves from a single measurement which took approximately 30 min (one topography frame with simultaneous spectroscopy measurements). The black curve represents the normalized derivative of ∼100 curves taken in an area on a single terrace, the gray curve shows the normalized derivative of ∼100 curves taken in an area with a high step density (steps 1–3 nm apart). The black curve, obtained at a large terrace, has a distinct peak corresponding to the interface state, while the gray curve, taken at the steps, has no significant peak. Clearly the interface state is quenched in the vicinity of steps, which strongly supports our hypothesis that the interface state is indeed derived from the Au(1 1 1) surface state.

Tetradecane has a HOMO-LUMO gap of 14.5 V; therefore the bulk liquid, and also any absorbed crystalline layers, will have a large band gap; so any states observed around the Fermi energy will not be directly due to states of the
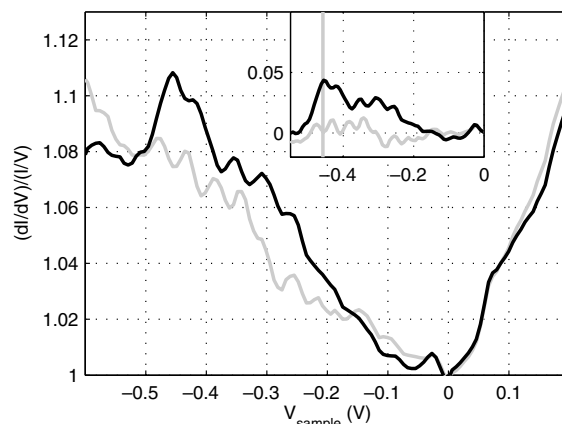

Fig. 4. $(dI/dV)/(I/V)$ spectroscopy curves (setpoint: 300 mV, 0.5 nA, sweep: −0.7 V → 0.3 V). The black curve is the average of ∼100 curves taken on a single flat terrace, the gray curve is the average of ∼100 curves taken on or in the vicinity of a step. All curves were taken from the same topography+spectroscopy measurement, which took 30 min to complete. The black curve contains a significant peak at ∼−440 mV, the gray curve does not. The inset shows the same curves minus the exponential background, obtained by subtracting an exponential fit to the whole curve.

tetradecane. However, it has been shown that at a metal/insulator interface the presence of the metal can induce states in the gap of the insulator; these metal induced gap states (MIGS) have been investigated by NEXAFS [27], EELS [28], and by STS [29]. MIGS originate from metal wave functions that penetrate into the insulator and induce the spilling over of states from the valence and conduction band of the insulator into the gap. Their energy should be close to the edges of either the valence or conduction band of the insulator. Due to the large band gap of the tetradecane, it is not expected that MIGS are present in the small energy range around the Fermi energy that we studied here. In the light of this and earlier presented arguments, we are confident to assign the observed peak to the Au(1 1 1) surface state, and not to a MIGS.

Although the spread in the literature values for the surface state binding energy is large, our results indicate that when the Au(1 1 1) surface is covered by *n*-tetradecane, the surface state survives and it's energy is not altered significantly (>100 meV) in comparison to the binding energy of the surface

state on clean Au. In order to get an estimate of the expected energy difference between the surface state at the Au(1 1 1)/vacuum and the Au(1 1 1)/*n*-tetradecane interface one can use the one-dimensional phase accumulation model combined with nearly free electron (NFE) theory [30]. In this model the barrier on the vacuum side is derived from the image potential. In the presence of an adsorbate the image potential will be modified due to dielectric screening. One can approximate the effect of the modified image potential on the surface state, by modeling the adsorbate as a dielectric slab, this is done in the so called dielectric continuum model [31]. However, it has been established that when layers of NaCl are grown on Cu(1 1 1), the wavefunction of the surface state does not change significantly due to the presence of the dielectric; this implies that one can use first order perturbation theory to determine the energy shift of the surface state [32]. This approximation is also valid for the Au(1 1 1)/*n*-tetradecane interface, as *n*-tetradecane has an even lower dielectric constant than NaCl (2.0 compared to 5.0). According to first order perturbation theory, the energy difference between the Au(1 1 1)/vacuum and the Au(1 1 1)/*n*-tetradecane interface will be: $\Delta E = \langle \Psi | \Delta V | \Psi \rangle$. The perturbation potential ΔV is the potential difference between the different interfaces. Because the wave function Ψ is located close to the surface ($\sim$1 Å) and decays exponentially outside the Au substrate, only the perturbation potential close to the Au substrate contributes significantly to ΔE. The potential change close to the surface is only due to the change in the image potential by dielectric screening, and is not influenced by the change of the workfunction. Applying this to the Au(1 1 1)/*n*-tetradecane interface we find a ΔE between 50 meV and 100 meV (a shift towards the Fermi level), depending on the choice for cut-off and origin of the image potential. This is in qualitative agreement with our results.

4. Conclusions

In summary, by performing STS at the solid/liquid interface, we observed an interface state at the Au(1 1 1)/*n*-tetradecane interface, which is de-

rived from the Au(1 1 1) Shockly like surface state. The observed energy of this interface state does not significantly shift (difference <100 meV) with respect to reported literature values for the energy of the surface state on clean Au. This is in agreement with first order perturbation calculations using the dielectric continuum model, which indicate only a small shift in energy for the Au(1 1 1)/*n*-tetradecane interface state with respect to the surface state on clean Au.

The presence of the liquid does not significantly alter the electronic structure of the surface, and STS results obtained at the interface with a chemically inert and low-polarizable liquid such as *n*-tetradecane can be compared directly to UHV STS measurements.

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