Stark Effect and Scanning Tunneling Spectroscopy of the Ag(111) Surface State

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Low-temperature scanning tunneling spectroscopy is used to study the Ag(111) surface state over an unprecedented range of junction resistances. The presence of the tip causes a shift of the surface state towards higher binding energies, increasingly stronger as the resistance decreases. A one-dimensional model calculation reproduces this observation and provides a connection to existing photoemission spectroscopy data. Implications of the effect on STS studies are discussed.

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1. Introduction

Since the early days of scanning tunneling microscopy (STM), it is known that the presence of an electric field between the surface and the tip of the microscope produces a displacement of the surface band structure. For example, in STM studies on semiconductors, where the electric field is only partially screened by the electrons, the electric field yields a drastic effect known as band bending [1]. This is not the case with metal surfaces where the electric field is efficiently screened out in the bulk. However it subsists outside of the bulk and consequently surface electrons, especially those with a large decay into vacuum — those states which are most easily probed by STM and by scanning tunneling spectroscopy (STS), are likely to be affected by a Stark effect. The archetype of such states are the field emission resonance states, which Becker et al. and Binnig et al. evidenced to exhibit a Stark effect in STS [2]. However, these states can only be probed in the field emission regime of an STM, i.e. at large tip-sample biases that exceed the tip and sample work functions ($\phi_{\text{tip}}, \phi_{\text{samp}} \lesssim V$).

Arises then the question whether the Stark effect is still sizeable enough to affect STS data even in the tunnelling regime where STS experiments are usually performed ($V \ll \phi_{\text{tip}}, \phi_{\text{sample}}$). To date, no study addressed this issue. We present here STS data on one of the long studied Shockley surface states [3, 4], the Ag(111) surface state, a quasi-two-dimensional electron gas trapped between the surface barrier potential and a band gap in the crystal, which enables us to answer this question. By varying the electric field of the junction over a large set of tip-sample separations, we establish, on an experimental basis, the existence of a tip-induced downward Stark shift of the Ag(111) surface-state spectrum. We also provide a one-dimensional model which disentangles the contributions to the experimental shift, namely the voltage bias of the junction, the multiple image potential and the contact potential, and which establishes a connection to existing angle-resolved photoemission spectroscopy (PES) data.

2. Experimental

A custom-built ultrahigh vacuum STM was used to perform all the measurements at a temperature of 4.6 K. The W tips were etched electrochemically *ex situ* and further treated *in situ* by indentations into the Ag(111) surface. Spectroscopy of the differential conductance (dI/dV) versus sample voltage V was performed by freezing the feedback loop always at the center of impurity- and step-free regions ($\geq 400 \text{ nm}^2$), a lock-in detection unit being used to record the dI/dV signal (the AC voltage was 1 mV rms in amplitude and $\approx 1\text{--}10 \text{ kHz}$ in frequency).

3. Results and discussion

A typical dI/dV of the Ag(111) surface state acquired at a tunneling resistance of $R = 2 \text{ G}\Omega$ is presented in Fig. 1. The conductance yields a sharp step-like onset at an energy E_0 which corresponds to the lower edge of the Ag(111) surface-

Fig. 1. dI/dV spectrum taken on Ag(111) ($T = 4.6 \text{ K}$). The feedback loop was opened at $I = 0 \text{ pA}$, $V = 100 \text{ mV}$ ($R = 2 \text{ G}\Omega$). A geometrical analysis is used to determine E_0 and the width Δ of the surface state [4].

-state band ($E(k_{\parallel}) - E_0 \propto k_{\parallel}^2$, see Fig. 2b) and is constant for $E > E_0$ as expected for a 2D electron gas. From the onset of Fig. 1 we determine $E_0 = -66.0(5)$ meV, typical of STS [4].

Figure 2 presents our essential experimental findings. As shown in Fig. 2a, the surface-state spectra undergo a negative shift when decreasing R , i.e. when decreasing tip-sample distance. No appreciable broadening is observed. When sweeping R from 2 G Ω to 20 k Ω , respectively the maximum and minimum resistances where we could perform reliable spectroscopy, a shift of ≈ -14 meV occurs for E_0 . This corresponds to a 20% lowering of the Ag(111) low band edge as depicted

Fig. 2. (a) Downward shift of E_0 when R is decreased. All spectra are averages of at least 5 single spectra from varying sample locations and tips; the spectra were renormalized to match the conductance of the 2 G Ω spectrum. (b) Schematic view of the Ag(111) surface state band shift when R is reduced.

in Fig. 2b. However, from Fig. 2a, it can be seen that in the k Ω -range the shift is more sensitive to small variations of R : when decreasing R from 50 k Ω to 20 k Ω the dI/dV is shifted by ≈ -10 meV, while when decreasing R over 5 orders of magnitude (from 2 G Ω to 50 k Ω) the spectrum is shifted by ≈ -4 meV.

Figure 3 is the quantitative evaluation of the band edge shift of all the recorded spectra: Fig. 3a is the dependency of E_0 on R and, similarly, Fig. 3b the dependency of E_0 on the tip displacement towards the Ag(111) surface, which we

Fig. 3. (a) E_0 versus R (log-scale for R). The arrow indicates the PES value of E_0 [8]. (b) E_0 versus tip displacement towards the surface. The solid line shows the calculated result for a tip work function $\phi_{\text{tip}} = 4.56$ eV (solid) and in absence of the tip (dash). Since experimentally we only probe a displacement of the tip towards the sample, the calculated curve was shifted horizontally to match the data.

will detail further below. The two distinct shift regimes mentioned above can be clearly seen in both figures. In order to ensure data quality, images of the surface and high- R spectra were systematically recorded prior and after the acquisition of each spectrum. Since no change was discernible in these images and in these spectra we conclude that neither a tip modification nor a tip-induced damage of the surface occurred when acquiring spectra in the 20 k Ω –2 G Ω range. A thorough testing of our experimental setup also ensured that artifacts likely to pollute the shift of the spectra are negligible (< 0.5 meV).

Finally, to gain a deeper insight on our data, we measured the evolution of R with tip–surface separation over a distance of ≈ 6 Å which covers the range of resistances of interest. This measurement enables us then to express the dependency of E_0 on tip displacement as shown in Fig. 3b and to link the data to our model calculation of the shift (presented below). Since, unfortunately, absolute tip–sample distances cannot be measured in STM, the origin of Fig. 3b is arbitrarily fixed to 2 G Ω . The dependency of R on tip displacement d also sheds light on the origin of the two regimes observed for the shift ($R \leq 50$ k Ω and $R > 50$ k Ω). Indeed, while for $R > 50$ k Ω we observe the usual tunneling behavior $R \propto \exp(1.025\sqrt{\phi}d)$, with an apparent barrier height of $\phi = 4.0(2)$ eV typical of noble metals [5], when $R \leq 50$ k Ω the resistance deviates from this exponential behavior, decreasing faster than expected. It is well known from break junctions [6] that this signals that the junction is no longer in a tunneling regime, rather in a contact regime where important modifications of the tip and the surface morphologies occur. As discussed later, this has strong implications on the surface-state shift.

In summary, our STS data underline the existence of a downward shift of the Ag(111) surface state which can be tuned by varying R , i.e. by increasing or decreasing the tip–sample distance. Since a variation in the tip–sample distance

implies also a variation in the amplitude of the electric field in the tunneling junction, we conclude that the shift is produced by a Stark effect acting on the energy levels of the surface state. In the following paragraph we develop this idea by proposing a model calculation which further comforts this conclusion. We first detail some aspects of the model and then discuss the calculation in the light of our data.

The Ag(111) surface-state electrons are modeled by using the one-dimensional potential proposed by Chulkov et al. [7]: it is periodic in the bulk ($z < 0$), has a potential well just outside the surface ($0 < z < z_1$), then decays exponentially towards the vacuum ($z_1 < z < z_{\text{im}}$) to finally cross over to a long-range image potential ($z > z_{\text{im}}$). The presence of the tip at $z \geq z_{\text{tip}}$ is then accounted for by adding to the potential the linear contribution of the voltage V between the tip and the sample, as well as the difference between the work functions of the tip (ϕ_{tip}) and the sample (ϕ_{samp}) to include the contact potential. Furthermore, the shape of the image potential is modified to account for multiple images in the tip and the sample. This yields

$$\begin{aligned} V(z) &= 2V_{111} \cos gz, \quad z < 0, & V(z) &= V_{20} + V_2 \cos \beta z, \quad 0 < z < z_1, \\ V(z) &= V_{\text{lin}}(z) + V_3 e^{-\alpha(z-z_1)}, \quad z_1 < z < z_{\text{im}}, \\ V(z) &= V_{\text{lin}}(z) - V_{\text{im}}(z), \quad z_{\text{im}} < z < z_{\text{tip}}, \end{aligned}$$

where

$$V_{\text{lin}}(z) = E_F + s(eV + \phi_{\text{tip}}) + (1-s)\phi_{\text{samp}},$$

where E_F is the sample Fermi energy, $s = (z - z_1)/(z_{\text{tip}} - z_1)$, and

$$V_{\text{im}}(z) = [1 - e^{-\lambda(z-z_{\text{im}})}] \frac{e^2 [2\Psi(1) - \Psi(\zeta) - \Psi(1-\zeta)]}{16\pi\epsilon_0(z_{\text{im}}^{\text{tip}} - z_{\text{im}})},$$

with $\zeta = (z - z_{\text{im}})/(z_{\text{im}}^{\text{tip}} - z_{\text{im}})$ and Ψ is the digamma function. The parameters V_{111} , g , V_{20} , V_2 , β , and $z_1 = 5\pi/(4\beta)$ describing the potential in the absence of the tip are fixed to their corresponding values of Ref. [7]. The remaining parameters V_3 , α , λ , and z_{im} and $z_{\text{im}}^{\text{tip}}$ that account for the tip contribution, were fixed by requiring the potential and its derivative to be continuous everywhere (except at $z = z_{\text{tip}}$ for the derivative). The energy of the surface state at a given tip-sample distance was calculated by searching for the corresponding maximum in the transmission probability for electrons tunneling from the tip to the sample. The solid line in Fig. 3b is the calculation performed using the Ag(111) work function $\phi_{\text{samp}} = \phi_{\text{tip}} = 4.56$ eV for both the tip and the sample. As shown, it reproduces the data down to resistances ≈ 50 k Ω , where a strong discrepancy occurs with the data.

We first focus on the $R \geq 50$ k Ω region where the model works. To probe the influence of the contact potential, we performed other calculations with different values for ϕ_{tip} . These failed to reproduce the data as well as the calculation with

$\phi_{\text{tip}} = 4.56$ eV, and therefore we conclude that for the tips used the contribution of the contact potential to the Stark shift is minor. We note also that since the data of Fig. 3b were obtained with a variety of tips, the highly reproducible shift observed indicates that our *in situ* tip preparation yields always a similar tip apex. In conclusion, on the basis of our model, the Stark shift is produced by the electric field stemming from the bias and the image potential, with, at these tip-sample distances, a 2 to 1 ratio in the contribution of the two.

We now discuss the asymptotic behavior of the Stark effect and its implications for STS. When the tip is retracted, the Stark effect progressively disappears and E_0 smoothly reaches its non-perturbed value. To evaluate this non-perturbed energy we simply suppress the presence of the tip in our model. We estimate then the non-perturbed energy to be -64 meV (dashed line in Fig. 3b), in agreement with the $-63(1)$ meV value reported from recent Ag(111) PES experiments where no electric field is present [8]. Unfortunately in real life, the highest tunneling resistances experimentally accessible in STS are typically in the $\text{G}\Omega$ -range, hence the Stark contribution cannot be eliminated, but only minimized. For Ag(111) the Stark contribution results then, at the best, in a $\approx 4\text{--}5\%$ error in the evaluation of E_0 .

Turning now to the $R < 50$ k Ω regime where our model calculation does no longer reproduce the experimental data, it can be seen that the comparison in Fig. 3b between data and theory indicates that the actual electric field in the junction is stronger than the one predicted in our model calculation. Since in the model the tip and the sample morphologies are assumed to be constant over the entire range of tunneling currents, we hint that in the $R \lesssim 50$ k Ω range, the tip and the sample deform to yield a stronger electric field. This picture agrees with calculations performed for Au(100) [5], which find that the tip and the surface stretch towards each other because of attractive adhesive forces acting at $R \lesssim 100$ k Ω . In particular, this is predicted to produce a deviation in tunneling behavior, such as we observe in our R versus displacement measurements when $R \lesssim 50$ k Ω .

4. Conclusions

To summarize, we evidenced the existence of a Stark effect for the Ag(111) Shockley surface state, which can be tuned by varying the tip-sample distance, but not suppressed. From a model calculation we extract a non-perturbed value of -64 meV for E_0 in agreement with PES data. Finally, for $R \lesssim 50$ k Ω , an enhanced shift is observed, which we assign to an elastic deformation of the tip and surface morphologies. The tip induced Stark shift of the Ag(111) surface state, supported by our recent observation of a similar shift in STS for other reference systems such as the Cu(111) and Au(111) surface states and the Ag/Ag(111) adatom [9], indicates that the Stark effect cannot be neglected in STS. Rather our data suggest that STS requires a thorough quantification of the Stark effect when striving for

high energy resolution, especially for states whose wave functions have large decay lengths into vacuum.

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