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Imaging a buried interface by scanning tunneling spectroscopy of surface states in a metallic system

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We proposed a method based on scanning tunneling spectroscopy of the Shockley states in thin Ag films on Au(111) to get structural and chemical information and to image the buried stepped substrate. Using the thickness dependence of the energy of the Shockley surface state band, we have been able to determine the local thickness of the film over the surface and to derive the growth mode of this system. We also evidenced the alloying mechanism which occurs at the buried substrate step edges under annealing. Our method could in principle be applied to any epitaxial metallic systems having Shockley-type surface states.

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Scanning tunneling microscopy (STM) is recognized as a powerful surface technique which provides information about the topmost atomic layer of a crystal down to the picometer scale. Since its invention by Rohrer and Binnig,¹ it has been widely applied to elucidate surface structures, reactivity and dynamics.^{2,3} Within the most simple approach, the surface morphology is obtained by recording the tip displacement in the direction perpendicular to the surface, keeping constant the tunneling current, i.e., also the distance to the surface.⁴ In such a way, the tip exactly reproduces the surface corrugations but is almost insensitive to subsurface details.

For further understanding one must take into account that STM is actually sensitive to the local density of states (LDOS) in the vicinity of the surface. Therefore, constant current images may reveal spatial variations of the surface LDOS. Bulk electronic states as well as surface states can contribute to the surface LDOS but both are differently affected by surface and subsurface details. It has been demonstrated some time ago that the relief of a semiconductor surface buried under a thin metallic film can be imaged with STM by using electron interferometry.^{5–7} For metal/semiconductor systems, the surface LDOS is dominated by the evanescent part of transverse quantized states which develop in the metallic overlayer. As the energy of the bulk resonances depends on the local thickness of the film, spatial variations of the surface LDOS can be evidenced by imaging at a proper voltage and related to the buried relief. Originally the method was proposed by Kubby *et al.*⁵ to investigate the Ni/Si(111) interface and silicide formation by mapping the tunnel conductance which is almost proportional to the density of states at the surface. A few years later Altfeder *et al.* have been able to image the step edges of a Si(111) substrate buried under thick (~ 100 Å) Pb islands by simply recording constant current images at small gap voltage (few millivolts).⁶ Indeed, with such conditions the constant current images are strongly dependent of the density of states near the Fermi energy.⁴ In some cases the atomic resolution of the topmost substrate layer has been achieved.⁷ In these

original works, the electron interferometry was restricted to metallic films grown on semiconductor substrates having a forbidden energy gap, then allowing quantized state to develop. We want to show here that we can derive this method to surface states on full metallic systems to investigate a buried interface and to obtain information about the growth mode of the epitaxial overlayer.

Surface states arise from the breakdown of the translational symmetry at the surface of the crystals. This peculiar boundary condition allows electronic states to develop with energy in partial gap of the bulk band structure and with evanescent wave function inside the crystal. The associated electronic density is then highly localized right over the surface, making them very sensitive to the surface topology. For instance, during the last two decades, the interference pattern resulting from the Shockley surface states scattering in a variety of natural and artificial surface structures (step edges, point defects, quantum corals,...) on the (111) noble metal surfaces have been intensively investigated.^{8–11} In these systems, the interference pattern gives rise to spatial variations of the surface LDOS which can be evidenced at very low gap voltage in the constant current images or by recording the differential conductance dI/dV over the surface for different tip/sample bias.

We show in this report that the Shockley states are not only surface sensitive but can also be used as a probe of bulk like properties of a metallic interface. In particular we have applied scanning tunneling spectroscopy to obtain the local thickness of thin Ag films on Au(111) and a fingerprint of the interface, buried under a few Ag atomic layers.

We have prepared ultrathin films (1 to 10 ML) of Ag on Au(111) at room temperature by thermal evaporation from a Knudsen cell. The nominal thickness was determined by measuring the frequency shift of a quartz oscillator with a 12 digits frequency meter. The calibration of the frequency shift/thickness was obtained with the help of STM measurements on submonolayer Ag deposits on Au(111) or Cu(111). All STM and STS measurements were recorded at 60 K with an Omicron LT-STM. Differential conductance maps and

FIG. 1. (a) Sketch of the morphology of a 2.5 ML Ag film near a step edge of the Au(111) substrate. The $\bar{\Gamma}$ energy of the Shockley band is given, respectively, for 2 (-255 ± 5 meV) and 3 Ag ML (-190 ± 5 meV). (b) Differential conductance spectra recorded on a 2 ML (gray) and 3 ML (black) Ag film. (c) gray scale+3D view of the Ag film topography as revealed by constant current STM images (the position of the surface step edges are marked by the vertical arrows and the dotted line shows one underlying substrate step edge). (d) gray scale+3D view of the conductance map recorded simultaneously with the topography in (c); the constant current image and conductance map have been recorded with $I_t = 1$ nA and $U_{\text{sample}} = -210$ mV.

spectra was recorded with a lock-in (LI) detection by adding to V_{gap} a small sinusoidal component (30 mV pp) at the frequency of 650 Hz. This frequency was chosen in order to minimize the capacitive part of the detected current but keeping the time constant of the LI output low pass filter lower than 10 ms.

In Fig. 1(a) we sketch the situation for a fractional coverage of Ag (2.5 ML). For such a noninteger number of atomic layers, even assuming a perfect layer by layer growth, some regions must be covered with 2 ML of silver and some others with 3 ML; the boundary between them being aligned with the initial atomic step edges of the substrate [see Fig. 1(a)]. One must note, as the lattice parameter of Ag and Au are nearly the same, the surface on both regions appear at the same height [see Fig. 1(c)]. Here we do not expect any influence of the electronic properties on the constant current images which could permit to distinguish between 2 and 3 ML because of the rather large gap voltage used for scanning (>100 meV). Therefore the memory of the original atomic steps of the substrate is lost in the topographic STM images of the Ag films; only the surface atomic steps of the Ag over layer are identified [marked by vertical black arrows in Fig. 1(c)]. We want to show here that we can recover the trace of the substrate step edges and the local thickness of the film by using a spectroscopic mode of STM measurements.

As it has been reported for Ag/Cu(111) (Refs. 12 and 13)

and more recently for the Ag/Au(111) interface,^{14,15} a shift of the Shockley band toward the Fermi energy is observed when the Ag film is growing. This shift, induced by the change of the electronic potential at the interface, is a characteristic of the local thickness of the Ag film as far as the thickness does not exceed the penetration depth of the Shockley state wave function inside the crystal. The attenuation length in Ag/Cu(111) and Ag/Au(111) has been estimated from photoemission measurements to 5 ML and 3.6 ML respectively,^{13,16} leading to a significant penetration of the wave function of 12–15 ML.

The $\bar{\Gamma}$ energy of the Shockley state can be obtained by tunneling spectroscopy from the sharp increase in the differential conductance spectrum dI/dV as recorded versus sample voltage. In Fig. 1(b) we report two differential conductance spectra obtained on 2 and 3 ML Ag films. Both curves exhibit a step like shape but with an onset at different voltages. The measured positions of the edges give $E_{\bar{\Gamma}} = -255 \pm 5$ meV and $E_{\bar{\Gamma}} = -190 \pm 5$ meV for 2 and 3 ML, respectively. The accuracy in $E_{\bar{\Gamma}}$ determination is limited by the signal to noise ratio and the energy resolution which depends mainly at 5 K on the modulated voltage. The shift of 65 meV is in very good agreement with our ARPES data published in a separate paper.¹⁶ Therefore, by making a map of the differential conductance at $U_{\text{sample}} = U_{\text{map}} = -210$ mV on a 2.5 ML Ag film [presented Fig. 1(d)], we are able to identify the regions corresponding to 2 ML and those corresponding to 3 ML of Ag. Indeed, at such a voltage, the 2 ML regions give a significant contribution to the dI/dV signal (light gray) whereas the signal corresponding to 3 ML is very weak (dark gray). As a result, the position of the underlying substrate step edges can be revealed at the boundary between dark and bright areas on the dI/dV map. Therefore, a map of the differential conductance recorded at a proper voltage allows to evidence the local thickness of the film and recover the position of the buried original substrate step edges.

We have applied this method to study in detail the morphology of Ag films deposited on Au(111). In Fig. 2 (left), we show the typical morphology of the surface, as revealed by constant current topography with STM, for two deposits corresponding to nominal coverage of 3.5 and 4.5 ML on Au(111). For both samples, the STM images reveal perfectly flat terraces separated by height of $z = 2.34 \pm 0.02$ Å, corresponding to Ag monoatomic steps. The same morphology is obtained for 1 to 5 ML of Ag nominally deposited on the substrate. These results suggest that the growth of Ag/Au(111) interface proceeds by step flow in a perfect layer-by-layer mode. The conductance measurements do not confirm this assumption. Indeed, the maps of the differential conductance, presented in Fig. 2 (right-hand side) reveal at least three levels of gray, corresponding to three different values of the surface conductance. For both coverage presented here, each level can be assigned to a well-defined local thickness of the Ag film proving that more than two incomplete layers exist on the surface. Again, it allows to locate the position of the underlying step edges of the Au(111) substrate, even buried under five Ag atomic layers. This spectroscopic investigation of the films evidenced that the actual growth mode of this system is not a pure layer-by-

FIG. 2. (Left-hand side) Constant current STM images on 3.5 and 4.5 ML Ag deposits. The gray levels correspond to Ag terraces separated by monoatomic steps. (The position of the underlying substrate step edges are indicated by the thin dotted lines.) (Right-hand side) gray scale conductance maps recorded simultaneously with the topography. Topography and conductance maps have been recorded with $I_t = 1 \text{ nA}$ and $U_{\text{map}} = -160 \text{ mV}$ for 3.5 ML and $U_{\text{map}} = -130 \text{ mV}$ for 4.5 ML.

layer one but more likely multilayer one. Nevertheless the deviation from the perfect two-dimensional (2D) growth mode is only small and for a mean thickness, corresponding to an integer number N of monolayer deposited, the surface covered by $N-1$ and $N+1$ atomic layers is small. This growth mode is similar to that encountered for Ag film deposited on a stepped Cu(111) surface¹³ and can be explained by the fast surface diffusion of silver atoms at room temperature and the limited size of terraces ($\sim 300\text{--}500 \text{ \AA}$). Indeed as far as the diffusion length of Ag and ad-atoms is larger than the width of terraces, a step flow growth is favored. On large terraces one would expect a three-dimensional (3D) like growth of silver with more exposed Ag layer, as reported in Ref. 17.

Let us now return to the spectroscopy and explain how the local thickness can be identified. The maps of the differential conductance in Fig. 2 have been obtained at $U_{\text{map}} = -160 \text{ mV}$ and $U_{\text{map}} = -130 \text{ mV}$ for 3.5 and 4.5 ML, respectively. The resulting contrast can be explained from Fig. 3 where we displayed the conductance spectra recorded over the different local thickness for both deposits. As expected, for the two samples presented here, the onset of the curves is shifted to the right (toward the Fermi energy) as the thickness increases. On the two set of curves, we have indicated by a vertical dotted line (labelled U_{map}) the gap voltage set for mapping the differential conductance presented in Fig. 2. As we can see, for example, in the case of 3.5 ML, for

FIG. 3. Conductance spectra recorded over the different local thickness for a 3.5 (left) and 4.5 ML (right) nominal deposit. The vertical dotted lines indicate the sample voltage set to record the conductance maps presented in Fig. 2.

$U_{\text{sample}} = U_{\text{map}} = -160 \text{ mV}$ three typical values of the conductance are evidenced for 4 ML, 3 ML, and 2 ML, respectively, from the lowest to the highest. Therefore, in the corresponding conductance map of Fig. 2 (top), the lowest value of conductance (dark gray) is associated with a local thickness of 4 ML, the middle value (middle gray) with 3 ML and the highest one (light gray) with 2 ML. By comparing the conductance maps with the constant current STM images we can therefore recover the position of the underlying substrate step edges. On the same principle one can identify for the 4.5 ML deposit the region corresponding to 5 ML, 4 ML, and 3 ML (respectively, from dark to light gray).

With the help of the spectra of Fig. 3 it is easy to see that the contrast in the conductance map critically depends on the sample voltage. For example, for the 3.5 ML deposit the dI/dV signal is the same for 3 and 4 ML in the range from -320 mV to -250 mV . A conductance map recorded at any sample voltage in this range shall give rise to only two levels of signal and making impossible to distinguish between regions covered by 3 or 4 ML of Ag. At U_{sample} lower than -320 mV , the three curves collapse and a constant dI/dV map is expected. In the case of the 4.5 ML deposit, U_{map} has been set to -130 mV to optimize the contrast in the conductance map. For both deposits we have verified by sweeping U_{map} from -300 mV to -80 mV that never more than three levels was observed on the conductance maps.

In the last part of this paper we will show that our method based on the Shockley state tunneling spectroscopy can be applied to investigate the Ag-Au alloying mechanisms occurring when a thin Ag film is annealed at 475 K for 10 min . In Fig. 4 we present the conductance maps recorded on a 2.5 ML Ag film before (a) and after (b) annealing. On the film before annealing, two levels of the conductance are evidenced and, as explained before, can be associated to a thickness of two and three atomic planes of Ag. By comparing these images with the constant current topography recorded simultaneously (not shown here), one can identify the position of the underlying step edges of Au(111) substrate which separate domains of 2 and 3 ML of Ag. Before annealing, these boundaries appear fairly sharp. The transition from low to high level of conductance extends over a typical length of 3.5 nm as shown on the corresponding profile. On the other hand, after annealing, the boundary appears on the conductance map like a broad diffuse area, which extends

FIG. 4. (Top) Conductance maps recorded at $U_{\text{map}} = -220$ mV on a 2.5 ML deposit before (left-hand side) and after (right-hand side) annealing at 475 K during 10 min. (Bottom) Profile of the intensity of the conductance signal along a line crossing the boundary between areas thick of 2 and 3 ML.

over more than 20 nm (see profile). This result suggests that intermixing between Au and Ag starts from the buried Au step edges and is more likely activated in the plane of the

film rather than in the normal direction. It demonstrates that the in-plane diffusion at the Ag/Au(111) interface is faster than the interlayer mass transport. To go further in the alloying properties of this system, a systematic study of the shift of the Shockley band when crossing the domain boundary should permit to estimate the concentration profile around substrate step edges.

We have presented a detailed study of the local spectral properties of thin Ag films deposited on Au(111). We proposed a methodological approach based on the tunneling spectroscopy of Shockley surface states to get structural and chemical information about a buried metallic interface. In particular we were able to produce a mapping of the local thickness of the overlayer. It allowed a detailed study of the growth mode which has been found to differ from a perfect Frank Van der Merwe one. Finally the same method was applied to evidence the intermixing between Au and Ag which is favored under annealing at the buried step edge of the Au(111) substrate. This method provides a significant extension to the former approach restricted to quantum well state metal/semiconductor systems and could be applied to any systems presenting surface states as far as the thickness of the film do not exceed the penetration length of the surface state wave function.

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