ARPES and STS investigation of Shockley states in thin metallic films and periodic nanostructures

D Malterre, B Kierren, Y Fagot-Revurat, S Pons, A Tejeda, C Didiot, H Cercellier and A Bendounan

1 Laboratoire de Physique des Matériaux, CNRS, Nancy Université, B.P. 239, F-54506 Vandœuvre-lès-Nancy, France
2 Matériaux et Phénomènes Quantiques, CNRS, Université Denis Diderot, B.P. 7021, 75205 Paris, France
E-mail: malterre@lpm.u-nancy.fr

New Journal of Physics 9 (2007) 391
Received 15 May 2007
Published 31 October 2007
Online at http://www.njp.org/
doi:10.1088/1367-2630/9/10/391

Abstract. Due to their extreme surface sensitivity, the Shockley states of (111) noble metal surfaces can be used to study the modifications of atomic and electronic properties of epitaxial ultra thin films and self-organized nanostructures. In metallic interfaces, the different parameters of the Shockley surface state bands (energy, effective mass and eventually spin–orbit splitting) have been shown to be strongly thickness dependent. It was also possible by scanning tunneling spectroscopy to evidence a spectroscopic signature of buried interfaces. Moreover, superperiodic surface structures like the reconstruction on Au(111) vicinal surfaces or self-organized nanodots, lead to spectacular spectroscopic effects. In the vicinal Au(23 23 21) surface, the opening of tiny energy gaps associated with the reconstruction potential of such surfaces has been evidenced. Peculiar growth on these Au vicinal surfaces allows us to obtain high quality self-assembled metallic nanostructures which exhibit homogeneous electronic properties on a large spatial scale resulting from a coherent scattering of the Shockley states.
1. Introduction

The electronic properties of (111) surfaces of noble metals are characterized by the existence of surface states with a nearly free electron (NFE) like behavior (Shockley state). Such electronic surface states survive to the presence of structural defects (vacancies or steps) and deposition of atoms (islands or thin films). Shockley states scatter at adatoms and steps. However in epitaxial films and in ordered lattices of steps, coherent Shockley states still exist with a well-defined wavevector due to the translation symmetry. But their energy and effective mass can be modified with respect to the bare and perfect surface. The symmetry and more explicitly the superperiodicity of the surface yields Bragg diffraction of the surface electron and then to band folding associated with the Brillouin supercell.

In this paper, we will present the modification of electronic properties of Shockley states induced by the presence of epitaxial thin films or nanostructuration of the surface in one dimension (vicinal surfaces) or two dimensions (self-organized nanostructures). For thin films, we will show that the spectroscopic properties investigated by angle-resolved-photoemission-spectroscopy (ARPES) and scanning tunneling spectroscopy (STS) of Shockley states are very sensitive to the atomic structure and thickness of the film. We also show that the thickness dependence of the surface state energy can be used in STM to study buried interfaces. Finally, we show that nanostructuration of the surface can induce interesting spectroscopic effects due to the scattering of surface states. The control of the surface nanostructuration could result in a fine-tuning of the surface electron density.

Experimental details are given in section 2. In section 3, we present the surface state parameters (energy, effective mass and spin–orbit splitting) in Ag/Cu(111) and Ag/Au(111) interfaces. Section 4 is devoted to the study of spectral signatures induced by the nanostructuration of the surface. We show that the Shockley state directly reflects the superperiodicity of the surface by electronic confinement or band folding.
2. Experimental details

The measurements were carried out in an ultra high vacuum (UHV) set-up composed of a molecular beam epitaxy chamber for the growth and characterization of the surfaces, a STM chamber equipped with a low temperature (low-T) (5 K) Omicron STM and a photoemission chamber with a high resolution Scienta SES 200 analyzer. The photoemission experiments can be carried out between 20 K and room temperature (RT). The He-I ($h\nu = 21.2$ eV) or Ar-I ($h\nu = 11.82$ and 11.62 eV) radiation is provided by a high intensity UVS-300 SPECS discharge lamp operating at a pressure of $10^{-5}$ mbar in the ionization chamber. The energy resolution is better than 5 meV and angular resolution better than 0.3°. The photoemission experiments presented in this paper were carried out at liquid nitrogen temperature. In STM, the bias voltage $U_S$ is related to the sample potential with respect to the grounded tip. Most of the $dI/dV$ maps were recorded at 5 K in the open or closed feedback loop mode using the lock-in technique with a bias modulation of 10 meV at 700 Hz. For STS measurements, we paid attention to tip cleanness. Before all sets of measurements, we checked the spectroscopic properties of the tip by recording $dI/dV$ curve on a well known surface (Cu(111) surface [1]), the tip was treated with argon sputtering, high temperature annealing and by field effect until a step-like curve was obtained. Samples were cleaned by several cycles of Ar⁺ etching and annealing at 500°C and they were characterized by STM and Auger electron spectroscopy (AES). Ag, Co and Cu atoms were evaporated from a Knudsen cell to the substrate held at temperatures between 130 K and RT.

3. Thin films

3.1. Band evolution with thickness of the film

For many years it has been known that thin epitaxial layers on noble metals can affect the Shockley surface state band. For instance, a shift of the band minimum has been shown for a variety of overlayers like noble gases [2, 3], alkali [4, 5], transition metals [6, 7] or insulating layers [8]. Noble metal epitaxial films are of special interest because of the simplicity of their electronic structure, and similarities between substrates and overlayers. A substantial shift of the minimum of the band was noticed by Shapiro et al [9] in the case of Ag/Au(111) thin films. Since these prior experiments, more detailed studies were achieved on this system [10]. Here, we will focus on a fine investigation of the thickness dependence of the surface state band in thin Ag films epitaxially grown on Au(111) and Cu(111) substrates and we propose a simple model to quantitatively describe the variations of the surface state parameters.

3.1.1. Band energy minimum and effective mass. In figure 1, we present the photoemission intensity maps giving the surface state dispersions for some coverages of silver films deposited on Au(111) held at RT. For such deposition conditions, the growth mode is nearly layer by layer [10]–[12]. On the bare Au(111) surface, the Shockley surface state is characterized by a $k$-split free electron-like band due to the significant spin–orbit interaction (see section 3.2). As the free electron-like character is preserved in the interfaces, obvious changes of the band are revealed, i.e. a shift of the band minimum toward the Fermi energy, increase in the effective mass and a smearing out of the spin/orbit splitting with increasing thickness. In the submonolayer case (0.5 ML), two dispersive bands are evidenced. These two bands arise from the two kinds of surface terminations (bare or Ag covered). Indeed, for a submonolayer coverage, we know...
Figure 1. He-II ARPES intensity map $I(E, k)$ recorded on Ag overlayers deposited on Au(111) at RT.

Figure 2. (a) Local tunneling spectroscopy $dI/dV$ on bare (solid line) and 1 ML Ag covered (dotted) Cu(111) and Au(111) surfaces. Normal EDCs recorded on Ag overlayers deposited on Au(111) (b) and Cu(111) (c).

from STM investigations [10] that the surface consists of large monatomic Ag islands, usually connected to step edges and separated by bare substrate areas. Therefore two surface states with different band minima can develop in the two corresponding areas. This is confirmed by local tunneling spectroscopy performed over Ag covered and uncovered regions. The resulting $dI/dV$ spectra are displayed in figure 2(a) for 0.5 ML Ag/Au(111) and 0.4 ML Ag/Cu(111). The latter interface also shows a nearly layer-by-layer growth for RT-deposition. In the figure 2(a), all the spectra show a step-like shape but with different onsets. The onset is known to correspond to the band minimum of the Shockley surface state [1]. For both systems, we found an onset shifted toward the Fermi energy for the spectra recorded over the Ag island with respect to the bare part.
Table 1. Coverage dependence of the band minimum and effective mass for both interfaces Ag/Au(111) and Ag/Cu(111). Band minima derived from ARPES and STS experiments are compared with pseudo potential calculations (see section 3.1.2).

| Coverage (ML) | $E_{0}^{\text{ARPES}}$ (eV) | $E_{0}^{\text{STS}}$ (eV) | $E_{0}^{\text{calc.}}$ (eV) | $m^*/m_e$ (eV) | $E_{0}^{\text{ARPES}}$ (eV) | $E_{0}^{\text{calc.}}$ (eV) |
|--------------|----------------------------|--------------------------|----------------------------|----------------|----------------------------|--------------------------|
| 0            | −0.475                     | −0.485                   | −0.485                     | 0.265          | −0.390                     | −0.400                   |
| 1            | −0.304                     | −0.320                   | −0.308                     | 0.329          | −0.290$^a$                 | −0.286                   |
| 2            | −0.237                     | −0.245                   | −0.235                     | 0.343          | −0.190$^b$                 | −                       |
| 3            | −0.168                     | −0.180                   | −0.158                     | 0.378          | −0.119                     | −0.090                   |
| 4            | −0.125                     | −0.135                   | −0.113                     | 0.404          | −                       | −                       |
| 5            | −0.93                      | −0.105                   | −0.090                     | 0.408          | −0.086                     | −0.0675                  |
| 10           | −0.59                      | −0.62                    | −0.065                     | 0.400          | −0.065                     | −0.065                   |
| 20           | −0.58                      | −0.63                    | −0.063                     | 0.406          | −0.059                     | −0.060                   |

$^a$Moiré structure.
$^b$Dislocation loop structure.

of the surface. We estimated the shift as $\Delta E = 200$ meV for Ag/Cu(111) and $\Delta E = 165$ meV for Ag/Au(111). These values are in very good agreement with the values derived from the band minima measured by ARPES. Therefore, in the ARPES dispersion of figure 1 recorded on 0.5 ML, we can assign the lowest band to the Au(111) surface states and the upper band to the Shockley surface state developing in the silver covered regions.

The shift of the band toward the Fermi energy is also revealed by the electron distribution curves (EDC) recorded at normal emission and presented in figures 2(b) and (c) as a comparison between Ag/Au(111) and Ag/Cu(111). In this figure, we have also reported normal emission spectra for coverages corresponding to fractional numbers of deposited Ag layers. Like for submonolayer coverage, two components are resolved but with separation decreasing with increasing thickness (see for e.g. 0.4 and 2.7 ML in figure 2(b)). One can conclude that the two peaks correspond to the band minima for regions covered by $n$ and $n + 1$ Ag atomic planes. Finally in figure 2(c), we show a set of EDCs for several Ag film thicknesses on Cu(111) at RT. The behavior is qualitatively the same as for Ag/Au(111) with one surface state band for integer numbers of Ag atomic layers and two contributions for fractional coverages. Only the energy position with respect to the film thickness is different. From all these results, we can conclude that a sp type Shockley surface state is preserved in the Ag terminated part of the surface, with band minimum (and effective mass) depending on the number of Ag atomic planes.

From a fitting procedure of the ARPES data, we were able to derive the numerical values of band minimum and effective mass for both cases (Ag/Au(111) and Ag/Cu(111)) as functions of the thickness of the film. The detailed analysis of the spin–orbit interaction will be presented in section 3.2. Numerical values of band minima and effective masses are summarized in table 1 and reveal a thickness dependence up to about 10 ML. The evolution of the effective mass with
Figure 3. (a) 1D pseudo potential model used in calculations (see text) for a 3 ML Ag film on Cu(111) and corresponding electron density; (b) thickness dependence of the calculated electron density at the Ag/Au(111) interface.

3.1.2. Pseudo potential model. To describe the shift of the surface state band, we have adapted a simple model first proposed by Chulkov et al [13] to predict surface state and image state eigenenergies on metallic surfaces. The semi-infinite crystal is described by a 1D pseudo potential in the direction perpendicular to the surface. The potential can be divided in a bulk contribution which is simply taken as a one Fourier component potential and a surface/vacuum potential based on Coulomb-like image charge potential. A numerical solution of the Schrödinger equation with this potential gives rise to surface (and image) states energies and wavefunctions. In our case, as the electronic structure of the overlayer and substrate are qualitatively the same (sp-like bands), one can simply built a one-dimensional (1D) potential of the interface by concatenation of the substrate and overlayer potentials. At the interface, the two potentials are fitted together by fixing the amplitude in the first overlayer atomic plane to the average value (see figure 3(a)). The adjustable parameters of the model ($A_{10}$, $A_{1}$, $A_{2}$ and $\beta$ parameters as defined in [13]), have been first determined for clean Au(111), Cu(111) and Ag(111) to obtain (i) the right bulk band gap amplitude and gap edges; (ii) the surface state band minimum. The best values of the parameters have been found to be very close to those published by Chulkov et al [13].

Then, by keeping fixed the surface/vacuum potential parameter $\beta_{Ag}(111)$, we solved this model for different thicknesses of Ag overlayer. One example of the solution is given with the corresponding potential in figure 3(a) for the 3 ML Ag/Cu(111) case and the thickness dependence of the wavefunction modulus is reported in figure 3(b) for the Ag/Au(111) interface. Calculated eigenenergies are given in table 1 and compared with the experimental ones. Like experiments, the numerical simulations show a monotonous shift of the band minimum toward the Fermi energy. Calculated values are in fairly good agreement with the experimental ones. The surface state wavefunction is found to be continuously pushed away from the interface region as the film grows. The evolution of the band is therefore observed as far as the wavefunction has significant weight inside the substrate. For thicknesses larger than
the penetration length of the Shockley state inside the crystal, the surface state only probes the Ag layer and the band parameters of the Ag(111) single crystal are restored. Note that for the Ag/Cu(111) interface, two values are given for 1 ML. They correspond to the two different possible structures: moiré structure for films prepared at low-T (150 K) and the triangular structure for preparation at RT. This latter structure is associated with a network of dislocations at the interface. The calculated value is in good agreement with the experimental value observed in the moiré structure, the triangular structure leading to a larger shift of the band minimum (see section 3.3.2).

3.2. Evolution of the spin–orbit splitting on Ag–Au interfaces

The recent improvement of energy and angular resolution \cite{14, 15} together with the emergence of spin resolution \cite{16, 17} these last 10 years in ARPES has allowed to fully characterize the relativistic spin-splitting evidenced for the first time on an Au(111) Shockley state in 1996 \cite{18}. We present in this section, the evolution of this spin–orbit splitting in thin Ag films on Au(111) and Ag–Au alloys. The ARPES experimental data presented in this section have been measured at 80 K with Ar-I radiation to magnify this spin-splitting by increasing the \( k_\parallel \) resolution up to better than 0.01 Å\(^{-1}\). The second derivative of ARPES intensity \( I(E, \theta) \) measured on the bare Au(111) surface is presented in figure 4 (a replica shifted by 0.20 eV is observed due to the Ar-I line doublet). Two well-defined angle \( k \)-split surface bands with parabolic dispersion are clearly evidenced collapsing into a single state at the center of the Brillouin zone (BZ). This \( k \)-splitting has been attributed to the breakdown of the inversion symmetry at the surface restoring the possible effect of spin–orbit interaction \cite{18}. In the NFE theory first developed to describe spin-splitting of quantum well states in semiconductors \cite{19}, the relativistic
surface-like Rashba spin Hamiltonian has been derived:

\[ H_R = \alpha_R (\hat{\sigma}_z \times \hat{\mathbf{k}}_\parallel) \cdot \hat{\sigma}, \]  

(1)

\( \hat{\sigma} \) is the spin operator and \( \alpha_R \), the Rashba parameter, is proportional to the surface potential gradient \( \frac{d\psi}{dz} \) governing the strength of the interaction. Therefore, the spin degeneracy is left and the new spin-dependent dispersion relations can be expressed as

\[ E_\pm(k_\parallel, \sigma^\pm) = E_0 + \frac{\hbar^2 k_\parallel^2}{2m^*} \pm \alpha_R k_\parallel \]  

(2)

\( \pm \) defining the two spin-polarizations in the in-plane direction perpendicular to the wavevector. Then, from a technical point of view, the Rashba coupling \( \alpha_R \) can be expressed as:

\[ 2\alpha_R = \hbar^2 \Delta k_\parallel(E_F)/m^* = \Delta E(k_F)/k_F, \]  

(3)

\( \Delta k_\parallel(E = E_F) \) and \( \Delta E(k = k_F) \) can be obtained from the momentum dispersion curve (MDC) at the Fermi energy and the energy dispersion curve (EDC) at the Fermi wavevector, respectively as shown in figure 4. From the surface state energy \( E_0 = -475 \) meV, the effective mass \( m^* = 0.26m_0 \), and the energy splitting at \( k_F \) (or the \( k \)-splitting at \( E_F \)), we have deduced a Rashba coupling \( 2\alpha_R = 0.66 \pm 0.08 \) eV Å\(^{-1} \) for the Au(111) Shockley state in agreement with previous estimations [14, 18]. Nevertheless, this value has been pointed out to be the sixth order of magnitude higher than the predicted value for the NFE model. A more realistic tight-binding description yields a spin-splitting proportional to the atomic spin–orbit parameter and to the surface potential gradient [20] in agreement with relativistic ab initio calculations [15, 21]. Then a smaller effect should be observed with lighter atoms explaining why the spin–orbit coupling has been shown to be negligible for the Ag(111) Shockley state.

We have recently made a quantitative systematic study of the reduction of the Rashba coupling upon Ag deposition and of its increase in the Ag–Au surface alloy [10, 22, 23]. The layer-by-layer growth of Ag ultrathin films on Au(111) at RT is easily achieved. The second derivative of the \( I(E, k_\parallel) \) intensity maps measured for Au(111) substrate and for 1 and 2 stacked Ag layers are presented in figure 4(a). In addition to the reduction of the binding energy already discussed in the previous section, the spin–orbit splitting is shown to be continuously reduced (0.39 for 1 ML and 0.29 for 2 ML). The observed two well separated features reflect the persistence of an explicit spin–orbit splitting. For higher coverage, the two peaks collapse into one broad feature whose line width is continuously reduced with increasing coverage up to 20 Ag layers (not shown here). A fit of the EDCs with two Lorentzians allows us to extract the coverage dependence of \( \Delta E(k_F) \) and the corresponding values of \( 2\alpha_R \) in the abrupt Ag/Au(111) interface (figure 6). Firstly, in the abrupt Ag/Au(111) interface, the Rashba coupling is shown to have an exponential decay as a function of the Ag thickness which scales the decay of the binding energy (inset of figure 6(a)). In addition, we have shown that its evolution does not scale the evolution of the work function of the interface [10].

The annealing of the Ag–Au interface above RT yields the formation of a chemically disordered alloy whose composition has been shown to depend on the number of stacked Ag layers, on the annealing temperature (\( T_A \)) and on the annealing duration (\( t \)). Indeed, the migration of Au atoms in the Ag layers is easily evidenced by monitoring the low-energy (69 eV) Au NVV AES transition upon temperature (not presented here). In the figure 5(a), the \( I(E, k_\parallel) \) intensity map measured for 2 Ag layers deposited on Au(111) is compared with the one obtained after an annealing at 510 K during 1 min. It is remarkable that despite the chemical disorder introduced by the alloy formation, the Shockley state remains very well defined without any
enhancement of its intrinsic line width at the band minimum. Nevertheless, a strong increase in the Rashba coupling is induced as shown by the comparison with the EDC ($k = k_F$) before and after annealing the interface (figure 5(b)). An overview of the behavior of the Rashba parameter in the Ag–Au interface is summarized in figure 6. A quantitative analysis of its increase as a function of the alloy composition in the case of 3 ML Ag film annealed up to 570 K is presented in figure 6(b). Again the Rashba parameter scales the binding energy and the increase in the
Auger NVV Au peak (not presented here). Starting from the pseudo-potential approach used to describe the coverage dependence of the surface state binding energies both in Ag/Cu(111) and Ag/Au(111), we have derived a model which describes the experimental variation of the Rashba coupling observed in the Ag–Au interface. An effective Rashba parameter $\alpha_R(T, \theta)$ is introduced as an average of the Rashba parameters associated with the Au ($\alpha_{Au}$) and Ag ($\alpha_{Ag}$) single crystal weighted by the proportion of Au ($p_{Au}$) and Ag ($1-p_{Au}$) atoms probed by the surface state electron density:

$$\alpha_R(T, \theta) = p_{Au}\alpha_{Au} + (1-p_{Au})\alpha_{Ag}. \quad (4)$$

Then, the proportion of Au atoms probed by the surface state wavefunction is obtained from the decay of the surface state electron density corresponding to each coverage $\theta$ or each annealing temperature $T_A$. For non-diffusive interfaces, it is straightforward to extract $\alpha_R$ as function of the Ag film thickness from the calculated wavefunctions. These calculations satisfactorily match the coverage dependence of the Rashba coupling in the abrupt Ag–Au (111) interface as demonstrated in figure 6(a). In the case of the diffusive interfaces, the number of Au atoms probed by the surface state depends on the Ag–Au alloy composition. We have first calculated the Au concentration profile in the framework of a simple 1D diffusion model which reproduces the variation of the Auger intensity observed for 3 ML of Ag annealed up to 570 K [10]. Then, a virtual crystal pseudo-potential was built for the alloys as the sum of the known Au and Ag potential weighted by the relative amount of each element in each atomic layer [10]. The wavefunction is calculated for each annealing temperature and its energy is shown to reproduce the experimental data (figure 6(c)). Then, the $T_A$-dependent proportion of Au atoms $p_{Au}(T_A)$ is simply obtained from the extension of the wavefunction and the composition profile. Figure 6 shows that the variation of the experimental Rashba coupling in the alloys is in good agreement with the calculated one in our 1D pseudo-potential-based calculations.

Our results strongly suggest that the amplitude of the Rashba (spin–orbit) parameter is mainly determined by the amount of ‘heavy’ atoms probed by the Shockley surface states. This has been experimentally evidenced here by changing the number of heavy atoms located in the vicinity of the surface either by adjusting the number of stacked Ag layers or by adjusting the concentration of Au atoms in the Ag–Au alloy. This strong dependence of the spin–orbit coupling on the local nature of the elements near the surface shows that the atomic potential gradient is the main factor that determines the amplitude of the Rashba parameter. It has been shown very recently that the deposition of 1/3 of Pb on an Ag(111) substrate leads to a giant spin–orbit splitting on hybridized Pb–Ag $p$ states (at least 10 times larger than in Au(111)) [24]. In this case, the atomic potential gradient experienced by surface electrons is probably exalted due to their extreme vicinity of the surface. Finally, we have shown here that the Ag–Au alloy formation gives the opportunity to continuously tune the spin-splitting.

3.3. Shockley state spectroscopy on buried interfaces

Shockley surface states are known to be very sensitive to surface defects [25]–[27] like adsorbates (atoms, molecules, clusters, . . . ) or step edges. In this section, we want to emphasize that the Shockley states can be sensitive to structural properties of interfaces buried below several layers. We will first show that STS investigations of the Ag/Au(111) interface allows to map the local thickness of the Ag film and to visualize the position of substrate step edges buried under several atomic planes. Then we will turn to the Ag/Cu(111) interface with an ARPES study of a sub surface structural transition occurring with temperature.
3.3.1. Buried step edges in Ag/Au(111). We have shown in the section 3.1 that the band minimum is a signature of the thickness of the deposited film. Therefore, by mapping the differential conductance at a chosen voltage, one may reveal the areas of the sample covered with different thicknesses. The method is sketched in figure 7(a) for the case of a 2.5 ML of silver. For such fractional coverage, even with a perfect layer-by-layer growth mode, the interface can be divided in two kinds of areas: areas covered by 2 ML and by 3 ML of Ag. The case of the vicinity of a buried substrate step edge is of particular interest since on the same terrace at the surface, two different local thicknesses can coexist. On the right-hand side of the buried step of figure 7(a), we have a 2 ML film and on the left-hand side a 3 ML one. Therefore, both sides are characterized by two different values of the band minimum: $E_{2 ML}^0 = -255$ meV and $E_{3 ML}^0 = -190$ meV, respectively for 2 and 3 ML. Then, mapping the $dI/dV$ signal at a sample bias $U_S = -210$ mV should give rise to areas of high intensity associated with the 2 ML thickness and areas of low intensity corresponding to 3 ML thickness since the onset of the band is higher than the mapping energy $e\cdot U_S$. The $dI/dV$ map recorded at $U_S = -210$ mV is reported in figure 7(c). The two expected levels of conductance are evidenced on terraces, revealing the two different thicknesses and the buried step edges of the substrate. The positions of the substrate step edges are pointed by the dotted lines in figure 7(b). This method has been applied on Ag films with a larger nominal coverage. In figures 8(b), (d) and (e) we report the conductance maps for two sets of experiments on a 3.5 ML Ag film. On images recorded at $U_S = -160$ mV (b) and $U_S = -350$ mV (d), three levels of the tunnel conductance appear from dark to light tones. The three values of the $dI/dV$ signal are obviously associated with three different numbers of Ag atomic layers due to a small deviation from a perfect layer-by-layer growth. The corresponding local thickness can be identified from the onset of the STS curves displayed for both cases and recorded at the cross positions in figures 8(b) and (d). In the case of figure 8(b), the lightest color corresponds to 2 ML, the darkest one to 4 ML and the medium one to 3 ML local thickness. By contrast, with $U_S = -350$ mV the situation is exactly reversed (figure 8(d)) with the lightest tone corresponding to 4 ML and the darkest
Figure 8. Comparison between two sets of tunnel conductance recorded on Ag film of 3.5 ML as nominal coverage. $dI/dV$ curves (a) and (c) and conductance maps (b), (d) and (e) recorded under closed feedback loop conditions at $I_t = 0.95$ nA and the following bias voltage: $U_S = -160$ mV (b), $U_S = -350$ mV (d) and $U_S = -200$ mV (e). The crosses on the conductance maps locate the position of the recorded spectra and the numbers indicate the local thickness.

One to 2 ML. In order to explain this tone inversion in the $dI/dV$ map, we have to analyze the STS curves and to consider the mapping voltage. For the map of figure 8(b), the mapping energy, $e \cdot U_S = -160$ meV is chosen between the onset of the surface state bands of 3 and 4 ML. Therefore, the different amplitudes of the $dI/dV$ signal yield the contrast observed in the conductance map of figure 8(b). One has to point out that if the mapping voltage was $U_S = -350$ mV, the $dI/dV$ signal would be the same for all the three regions giving rise to any contrast on the conductance map. In the case of figure 8(d), one has chosen a mapping energy $e \cdot U_S = -350$ meV but the STS curves show different background amplitudes at this energy for the different thicknesses. The background signal which now gives a significant conductance at energy lower than the onset of surface state, arises from the bulk electronic states and is known to depend on the tip electronic properties. Remarkably, the increase in the background level is perfectly correlated with increase in the surface state threshold. This behavior can be explained by a change in tip–sample distance between the different curves. Indeed, the vacuum gap is fixed by the tunneling set point, i.e. the tunneling current which integrates the density of states (DOS) from the set point voltage to the Fermi energy, with both bulk and surface state contributions. Therefore, the tip–sample distance depends on the set point and surface electronic properties. Here, as the surface state band is shifted toward the Fermi energy with increasing thickness, the Shockley state is depopulated. Assuming a constant bulk state contribution, the tip–sample distance is reduced to keep constant tunneling current as the thickness increases and the surface electronic states decreases. This effect will be more or less pronounced depending on the bulk/surface state ratio in the tunneling current. Finally, we show in figure 8(e), the conductance map of the same regions as in (d) but scanned at a bias voltage $U_S = -200$ mV. One can see now that the areas of 4 and 3 ML are rendered with the same color as can be predicted from the corresponding STS curves having the same amplitude at $U_S = -200$ mV. These results show that the choice of the working voltage for conductance mapping is of critical importance to obtain information on buried interfaces and can lead to contrast inversion.
The method we described here, based on Shockley state tunneling spectroscopy is a novel approach derived from the bulk state electron interferometry proposed by Kubby and Greene [28] and Alfterder et al [29, 30]. In the two latter cases, the authors were able to image buried interfaces by mapping at the surface the bulk quantized states which develop in the thickness of a metallic overlayer grown on a semiconductor substrate. Here, we have extended the method to surface states in a completely metallic interface.

3.3.2. Sub-surface reconstruction in Ag/Cu(111) and Ag/Au(111). Another example of the sub-surface sensitivity of Shockley state spectroscopy is first described in the following on the basis of the structural transition in an Ag/Cu(111) interface. It is known that a single Ag monolayer deposited on Cu(111) leads to two different atomic orders at the interface depending on the substrate temperature during deposition. For silver deposition on a low-T substrate (150–200 K), a simple moiré structure is observed with Ag atoms in top positions being unfavorable due to the lattice mismatch between Ag and Cu. For deposition at RT or for a moderate annealing (400 K) of a low-T prepared sample, the interface reorganizes with the appearance of a dislocation network in the sub-surface plane, i.e. in the topmost Cu atomic plane [31, 32]. We have shown that these two atomic structures give rise to a surface state band with two different band minima [33]. For the dislocation network structure, we found a band minimum at $E_0 = -190 \text{ meV}$ corresponding to a shift of $\Delta E \approx 200 \text{ meV}$ with respect to the band minimum of Cu(111). For the moiré structure the shift is reduced to $\Delta E \approx 100 \text{ meV}$ giving rise to a band minimum at $E_0 = -290 \text{ meV}$. Therefore, the two atomic orders can unambiguously be distinguished by ARPES measurement of the Shockley surface state band. When the first Ag layer is covered by a second one, the resulting energy of the Shockley state depends on the atomic structure (moire or dislocation network) of the first layer. This property has allowed us to find that the interface cannot reorganize under soft annealing if the first layer deposited at low-T is covered by a second one. This is demonstrated from the photoemission measurements on a 1.6 ML deposit reported in figure 9. In this figure, we compare the normal emission spectra recorded (a) on the low-T deposited film, (b) on the low-T deposition followed by annealing at 400 K and (c) on a RT deposit. A schematic view of the interface is proposed on the upper part of the figure. On the low-T deposited film, two peaks separated by $\Delta E = 120 \text{ meV}$ are identified. They correspond to the band minimum for the 1 ML ($E_0(S_{LT}^1) = -290 \text{ meV}$) and 2 ML ($E_0(S_{LT}^2) = -170 \text{ meV}$) on a topmost Cu atomic plane without dislocation network. After annealing, the two spectral lines collapse into a single broad peak (see figure 9(b)). This peak can be deconvoluted in two contributions. The low energy one corresponds to the Shockley state on the part of the surface covered by 1 ML which has been shifted from $E_0 = -290 \text{ meV}$ to $E_0 = -190 \text{ meV}$ due to the appearance of the dislocation network in the sub-surface Cu atomic plane. The high-energy peak is found at $E_0(S_{2}^2) = -160 \text{ meV}$, i.e. very close to the position of the $S_{2}^2$ line measured on the low-T deposited film. By contrast, on the spectrum corresponding to the 1.6 ML deposited at RT, again two contributions are resolved. The low energy one is at the same position as for the annealed interface and also corresponds to the surface state of the 1 ML on the dislocation network, but the high energy line ($S_{2}^{RT}$) is at a significantly larger energy ($E_0(S_{2}^{RT}) = -130 \text{ meV}$) than for the annealed interface. From the above results, we can conclude that the structure of the surface covered by a 2 ML Ag film is not significantly affected by a soft annealing following a low-T deposition. We suggest that the energy of Cu vacancy creation, necessary to develop the dislocation network is too large when 2 Ag atomic planes are deposited on the Cu topmost layer.
Figure 9. Normal emission spectra recorded on a 1.6 ML Ag film on Cu(111) at low-T (a), at low-T and then followed by annealing at 400 K (b) and at RT (c). In the upper part of the figure, the model for each set of preparation parameters is proposed.

Sub-surface reconstructions can also be investigated in real space by STS experiments. We have shown on the Au(111) surface that the well-known herringbone reconstruction has some influence on the growth of the first Ag atomic layer when deposited at RT \cite{10}. In particular, a limited interdiffusion occurs between Ag and Au atoms resulting in a chemical reconstruction at the interface. We have shown from atomic scale STM measurements that the Au surface concentration in the first Ag layer depends on the underlaying Au stacking and differs between fcc and hcp domains of the gold reconstruction. This leads to a modulated Ag–Au surface alloy (chemical superlattice (CS)) in the first Ag layer with a stripe pattern exhibiting the same period as the gold reconstruction (about 6.3 nm). The Au concentration has been found to be lower than 5%. We show here that Shockley state spectroscopy is able to reveal this stripe pattern even when buried under few atomic planes. In figure 10, we compare the STM topography (a) and two dI/dV maps (b) and (d) recorded at two different sample biases for a 2.5 ML Ag film. On the conductance maps, one can see two levels of the dI/dV signal related to the 2 ML and 3 ML local thicknesses as explained in section 3.2.1. Although on the STM topography, uncorrugated Ag terraces are revealed, a stripe pattern is evidenced on the conductance map recorded at $U_S = -150$ mV. This pattern develops near the buried substrate step edges in the regions corresponding to the 3 ML parts of the Ag film. It results from the scattering of the Shockley state by the buried CS in the first Ag layer. Indeed at the mapping energy of figure 10(b) ($U_S = -150$) the wavevector $k(E) = 0.05 \, \text{Å}^{-1}$ matches with the CS BZ boundary. Therefore the Bragg condition is satisfied and a gap can open, leading to a standing wave pattern with a period identical to the period of the (6.3 nm). In figure 10(c), the profile taken along the stripe region on the dI/dV map in (b) shows the typical distance between maxima ($d = 66$ Å).
very close to the superlattice period. For a mapping of the conductance at a significantly larger energy \( E = -200 \, \text{meV} \) (see figure 10(d)) the standing wave pattern is no longer revealed but one can observe embedded single impurities as high intensity spots. These sub-surface impurities are usually not revealed on the topography but their effect on the scattering of the Shockley state has been already described by Crampin [34] in the case of Cu(111).

In conclusion of this section, we have shown that Shockley state spectroscopy (ARPES and/or STS) can be applied to probe structural properties of thin metallic films with a depth sensitivity corresponding to the penetration length of the surface state wavefunction inside the crystal.

### 4. Periodic nanostructured surfaces

As discussed above, the Shockley states are very sensitive to structural and chemical modification of the surface. For example, surface reconstructions or the growth of periodic nanostructures which yield a new surface periodicity, should affect the surface state bands. As Shockley states are NFE-like states, they should be essentially modified in the vicinity of the 2D-BZ boundaries corresponding to the superperiodicity. In this section, we shall present a study of the spectroscopic properties induced by the surface superperiodicity associated with vicinal surfaces or self-organized nanostructured surfaces.

#### 4.1. Au vicinal surfaces

**4.1.1. Step periodicity.** Vicinal surfaces provide interesting surface periodicities (in the direction perpendicular to step edges). Such surfaces are obtained by cutting a crystal a
few degrees away from a given direction (the [111] direction for the Au substrate we are considering). This can lead to a periodic 1D array of monatomic steps separated by (111)‐oriented terraces. In the last few years, many ARPES [35]–[39] and STM [40, 41] studies have been devoted to the investigation of the Shockley state modifications due to such 1D arrays. The main consequence of the step array is a very strong anisotropy of the Shockley states [37]: electrons moving with a wavevector parallel to step edges, are not affected by the step array whereas electrons moving in the perpendicular direction are scattered by the step potential. The strength of the step barrier can be obtained from a fit of a surface state band by using a 1D Krönig–Penney model with a simple periodic array of delta functions. Systematic studies on Cu and Au vicinal surfaces led Ortega and co-workers [37, 39] to the conclusion that two extreme behaviors can be observed according to this step barrier strength. For small miscut angles and then large terrace widths, the surface states are confined in the (111)‐terraces leading to a quasi‐1D behavior characterized by quantum well states in the perpendicular direction. Therefore in this case, the strength of the step barrier is large. In contrast, for small terrace widths, the surface states exhibit propagation across the steps. The barrier potential is then small and thus preserves the 2D electronic behavior.

The Au(23 23 21) vicinal surface belongs to the confinement regime. ARPES data exhibit below the Fermi energy ($E_F$) three weakly dispersive bands at $E_F - 430$ meV, $E_F - 270$ meV and $E_F - 60$ meV [37] on a parabolic background. An averaging effect due to the terrace width distribution was proposed to explain this background [42]. Such a confinement effect is corroborated by our scanning tunneling experiments. In figure 11(b), we present a differential conductance map representing the $dI/dV$ spectra for 64 points along a line perpendicular to the step edges. As we shall see below, there is a reconstruction on the terraces and then the spectra are averaged over one unit cell of the reconstruction. This image shows that the local DOS (LDOS) is modulated and exhibits the different modes of the quantum well associated with the
step edge potential. The fundamental mode is characterized by a broad lobe in the middle of the terrace, the first excited state by two lobes and so on. Such images have been previously observed in isolated Ag terraces and interpreted in the framework of an electronic Fabry–Pérot interferometer [43]. Figure 11(c) presents the 1D spatial Fourier transform of this conductance map. It shows that, for the different modes of the interferometer, relatively well-defined values of the wavevector are obtained. They can be interpreted as the Fourier components of the electron states and then they represent the dispersion in the direction perpendicular to step edges ($E(k_{\perp})$). This kind of information can be compared with the direct determination obtained by ARPES. Comparison with the second derivative ARPES data of Mugarza et al [36] reported in figure 11(d) shows that electron dispersion estimated from STS is in quantitative agreement with the dispersion directly measured in ARPES.

4.1.2. Parallel direction. Although many studies have been devoted to the effect of step edges on the perpendicular electron dispersion (in particular by Ortega’s group), the effect of the reconstruction-induced nanostructuration on the parallel dispersion has not been extensively investigated in ARPES. Figure 11(a) presents a STM image of the Au(23 23 21) vicinal surface showing the surface reconstruction. This reconstruction, reminiscent of the herringbone one of flat Au(111), results from a uniaxial compression of the topmost atomic layer along the (110) direction [44]. In contrast to Au(111) reconstruction, the ridges are not parallel and are nearly perpendicular to steps as previously reported [45]. Moreover, the superperiodic cell ($L_{sp} = 66$ Å) is slightly larger than in flat Au(111) (63 Å). Diffraction patterns in LEED reveal this superperiodicity by the presence of satellite structures (not shown in this paper). Therefore, the Shockley states should be sensitive to the reconstruction which should induce Bragg diffraction and band folding in the direction parallel to the steps.

In figure 12(a), we present the energy distribution curves of the Shockley bands of the Au(23 23 21) vicinal surface obtained by high resolution ARPES. The two spin–orbit bands are clearly resolved with a Rashba parameter which is very similar to the value obtained for the flat Au(111) surface (section 3.2). However, deviations with respect to a pure parabolic behavior are

Figure 12. (a) Energy distribution curves of the surface state bands for several emission angles. The dashed line spectra correspond to BZ boundaries. (b) Same data presented as an intensity map. The 1D integrated signal (white line) reveals a loss of intensity at $E = 40$ and 145 meV revealing two energy gaps. The dotted lines represent parabolas centered at different reciprocal space vectors ($G_1 = 2\pi/L_{sp}$ and $G_2 = 4\pi/L_{sp}$).
observed. These deviations occur at wavevectors which are multiples of half the first reciprocal space vector associated with the reconstruction cell \((G_1 = 2\pi/L_{sp})\). Such a behavior is also seen in the intensity map of figure 12(b). The low intensity regions at \(E_1 \approx 40\,\text{meV}\) and \(E_2 \approx 145\,\text{meV}\) are found at the intersections of parabolas centered on the reciprocal vectors associated with the reconstruction cell (white dashed lines in figure 12). This suggests that it can be interpreted as the opening of reconstruction-induced gaps due to the superperiodic potential. This figure shows that although there is a gap corresponding to the first and second reciprocal vectors, no gap is observed for the third one. The gap opening is corroborated by the 1D angle integrated photoemission spectra (white line in figure 12(b)) which exhibits the characteristic shape of a 1D free electron DOS with two depletions at \(E_1 \approx 40\,\text{meV}\) and \(E_2 \approx 145\,\text{meV}\). A similar effect has been previously observed in the \(k\)-integrated spectrum of Au(111) surface [46]. But due to the three equivalent reconstruction domains in Au(111), the decrease in the DOS at the gap energies is very small (see figure 4 in [46]). Folding of bands are expected near band gaps due to the Bragg mechanism, but we would like to point out that there is no sizeable intensity in the folded bands [47]. The spectral weight is mainly localized along the parabolas centered at \(\Gamma\). The reconstruction effects are then subtle effects and a high energy and momentum resolution is needed to evidence them.

### 4.1.3. Spectral distribution.

In band theories, the energy is periodic in the reciprocal space but not the spectral weight. To understand this property, the simple model of NFEs can be considered. Group theory of periodic solid states shows that a Bloch wave is characterized by a wavevector which is defined modulo a reciprocal space vector. As a consequence, a Bloch state considered. Group theory of periodic solid states shows that a Bloch wave is characterized by a wavevector \(\mathbf{k}\) and \((\mathbf{k}+\mathbf{G})\) so that the two Bloch states \(|\Psi^{(\pm)}_k\rangle\), one below and one above the energy gap, can be written:

\[
|\Psi^{(\pm)}_k\rangle = C^{(\pm)}_k |\mathbf{k}\rangle + C^{(\pm)}_{k+\mathbf{G}} |\mathbf{k}+\mathbf{G}\rangle,
\]

where \(\mathbf{G}\) is a reciprocal vector associated with the reconstruction periodicity. The gap magnitude reflects the Fourier component \(V_{\mathbf{G}}\) of the potential which induces the Bragg diffraction. For a given wavevector \(\mathbf{k}\), one obtains two states whose energies are given by:

\[
E^{(\pm)}_k = \frac{1}{2}(E^0_k + E^0_{k+\mathbf{G}}) \pm \frac{1}{2} \sqrt{(E^0_k - E^0_{k+\mathbf{G}})^2 + 4|V_{\mathbf{G}}|^2},
\]

so that the energy gap is: \(E^+_{G/2} - E^-_{G/2} = 2|V_{\mathbf{G}}|\). The corresponding states are characterized by the \(C^{(\pm)}_k\) and \(C^{(\pm)}_{k+\mathbf{G}}\) coefficients which are related to the Fourier component of the potential:

\[
\frac{C^{(\pm)}_k}{C^{(\pm)}_{k+\mathbf{G}}} = \frac{-2V_{\mathbf{G}}}{(E^0_k - E^0_{k+\mathbf{G}}) \pm \sqrt{(E^0_k - E^0_{k+\mathbf{G}})^2 + 4|V_{\mathbf{G}}|^2}}.
\]

New Journal of Physics 9 (2007) 391 (http://www.njp.org/)
Figure 13. (Left) Schematic picture illustrating the conservation of wavevector in the photoemission process. Two different emission angles can be found, one in the first BZ, corresponding to $\vec{k}$, and the other one in the second BZ corresponding to $\vec{k} + \vec{G}$. (Right) Calculated spectral weight distribution for different values of the potential. With increasing the potential, the gap magnitude and the spectral weight of the folded bands increase.

From these coefficients, it is possible to deduce the spectral weight of the original and folded bands. Due to the conservation rule in the photoemission process, the photoelectron wavevector component parallel to the surface ( $\vec{K}_\parallel$ ) can be either $\vec{k}$ or $\vec{k} + \vec{G}$ (figure 13(a)). As a consequence, the spectral weight can be found in two BZ corresponding to these wavevectors ($\vec{k}$ and $\vec{k} + \vec{G}$) with intensity proportional to $|C_{\vec{k}}|^2$ and $|C_{\vec{k}+\vec{G}}|^2$, respectively. The spectral weight is then directly related to the magnitude of the potential. We illustrate this behavior in figure 13, where we report the calculated spectral weight for several $V_G$ values in this simple two-band approach. For small potential strength ($V_G = 0.2$), the spectral intensity is essentially found along the original free electron parabola. Therefore, the spectral weight is localized in the first BZ below the gap ($k < \pi/L_{sp}$) and in the second BZ above the gap ($k > \pi/L_{sp}$). Therefore, the spectral weight of the folded bands is very weak. With increasing $V_G$, the gap magnitude and the spectral weight of the folded band increase. This potential dependence of the spectral weight in the framework of the NFE picture is very similar to the results recently obtained in the tight binding approach [48, 49].

To take into account the spin–orbit interaction of the Au(23 23 21) Shockley state, two $k$-split bands have to be considered leading to the same gap opening at the same energies for the two spin polarized bands. This is illustrated in figure 14(a), where we report the calculated dispersion of the two spin–orbit surface bands of Au(23 23 21) in the framework of the nearly free electron model with an effective mass of $m^* = 0.26 m_e$, and gap values of 38 and 50 meV using equations (1) and (2) (these values have been chosen to be in agreement with the experimental data). The calculated spectral weight is reflected in the map by the intensity of the dispersion lines. This calculation disregards the spectral linewidth due to energy and angular resolution and intrinsic lifetime. The experimental EDC for several wavevectors are reported in figure 14(b). The evolution of the experimental EDC in figures 12(a) and (b) can be qualitatively explained with our simulation which also takes into account the experimental broadening. The nearly dispersionless feature near the band minimum ($E \approx 10$ meV) is associated with the two unresolved spin–orbit bands below the first gap. With increasing wavevector, this structure vanishes, whereas two additional features successively appear at $E \simeq 55$ meV and shift with different dispersions to high energy before reaching the second gap. These two structures
correspond to the two spin–orbit bands above the first gap. A similar behavior occurs for the second gap and due to the larger curvature of the dispersion, four contributions can be experimentally found for \( k \) values close to this second gap.

It is possible to obtain quantitative information from a careful analysis of the EDC presented in figure 12(a). This figure shows that the shape of the EDCs is complex especially in the wavevector range corresponding to the energy gaps. Indeed, there are several contributions originating from the two bands due to Bragg scattering for both spin–orbit branches. This behavior is illustrated in figure 14(b), where we report several EDCs in the three BZs, where the occupied Shockley states are found. These EDCs have been fitted by several contributions of Lorentzian shape whose positions and intensities give the band energies and their spectral weights. The Lorentzian linewidth is not a free parameter and their evolution as a function of energy which reflects the intrinsic lifetime and angular resolution due to band curvature, can be independently measured on flat Au(111). Let us discuss some characteristic EDCs. At low wavevector (spectrum 2 in figure 14(b)), the observed peak corresponds to two unresolved spectral features with similar intensities corresponding to the two spin-split bands. By increasing the wavevector, an additional shoulder appears at higher energy which corresponds to the folded band above the first gap (spectrum 3). At the limit of the first BZ (spectrum 4), only two contributions are observed as expected in the simulated dispersion (figure 14(a)). In the middle of the second BZ (spectrum 6) the EDC is composed of three structures: a shoulder at low energy corresponding to a folded band below the gap and two intense peaks associated with the two spin–orbit bands above the first gap. Just below the second gap (spectrum 8), a complex line shape is shown with four contributions corresponding to the main and folded bands. Finally above the second gap (spectrum 11), the spectrum is dominated by two contributions corresponding to the two dispersive spin–orbit bands. In figure 14(a), the open circles represent the result of the EDCs analysis (their size reflects the intensity of the corresponding contribution in the EDC). A satisfactory agreement is then obtained with the simple NFE approach. This

Figure 14. (a) Comparison between simulated and experimental Shockley band dispersions. The spectral weight calculated in the framework of a NFE model is represented by the intensity of the lines. The symbols represent the results of the fit of the experimental spectra. The size of the symbols reflects the experimental intensity of the corresponding spectral feature. (b) Experimental EDC spectra (solid lines) and spectral contributions as explained in text (dotted lines) for several wavevectors indicated by numbers.
Figure 15. (a) $dI/dV$ map obtained by measuring 64 $dI/dV$ spectra along a profile line in the middle of the terrace. The curve above the map represents the constant current topographic line-scan along the profile line. (b) $dI/dV$ recorded just below, in the middle and above the first (bottom curves) and the second gap (top curves). (c) $dI/dV$ spectra recorded in the three different domains (hcp in black, fcc in red and sf in green). Stabilization parameters $U_S = -0.65 \text{ V}$, $I_t = 0.6 \text{ nA}$.

analysis allows us to estimate the energy gaps: $\Delta E_{g1} = 38 \pm 5 \text{ meV}$ for the first one and $\Delta E_{g2} = 50 \pm 5 \text{ meV}$ for the second one.

4.2. STS on Au(23 23 21)

STS measurements can provide complementary information about the electronic properties of the surface. The curve on the top of figure 15(a) represents a constant current line scan in the middle of a terrace. It shows that the hcp region appears slightly higher than the fcc one and both domains are lower than the ridges. The same behavior has been observed in the herringbone reconstruction of Au(111) and was interpreted as an electronic effect due to a weakly attractive potential in the hcp regions compared with the fcc ones [50, 51]. The differential conductance map of figure 15(a) represents the $dI/dV$ spectra for 64 points recorded in an open feedback loop along a profile line in the middle of the terrace for an energy range containing the two gaps appearing in photoemission. This image shows that the LDOS is modulated in the reconstruction cell and changes with energy. Close to the energy onset of the surface state, the electronic density is mainly located in the ridges and hcp domains. Above the first gap energy ($E = 40 \text{ meV}$), a sudden change is observed and the LDOS is found in the ridges and fcc regions. As expected in the simple nearly free electron model, a phase shift of $\pi$ in the LDOS is observed below and above the energy gap. A similar behavior is observed in the energy range corresponding to the second band ($50 \text{ meV} \leq E \leq 150 \text{ meV}$). Although the LDOS is localized in the ridges and fcc regions just above the first gap (40 meV), a progressive evolution of the localization of the density occurs with increasing energy and at $E \simeq 130 \text{ meV}$, nearly all intensity is localized in the ridges. Around $E = 150 \text{ meV}$, the LDOS strongly decreases and a sudden change of localization from the ridges to the hcp and fcc regions is observed. This dephasing behavior of the LDOS reflects the opening of a second energy gap and then corroborates the photoemission results.
Figure 16. (a) Reconstruction potential used in the calculation. (b) Experimental (top) and calculated (bottom) maps of the electronic density just below and above the first ($E_1$) and second ($E_2$) gap energy exhibiting the dephasing behavior of the electron density.

We would also like to point out that some spectral intensity remains in the ridges through the first gap. This behavior was previously reported for the gap induced by a moiré structure of NaCl/Cu(111) [8] and can be attributed to bulk states.

Figure 15(c) presents conductance spectra recorded over the three (hcp, fcc and sf ) domains. The presence of the two gaps is directly reflected in the sf-spectrum by the two depletions appearing at $E \approx 40$ meV and $E \approx 145$ meV like in the integrated photoemission data (figure 12(b)). The spectroscopic signatures of these two gaps in the hcp- and fcc-spectra are much more subtle. The first gap corresponds to a pronounced decrease in the hcp-intensity and to an increase in the fcc-intensity. As shown in the conductance map (figure 15(a)), there is a transfer of electron density between these two regions at the first gap energy. The second gap is revealed by a sudden intensity increase in both the hcp and fcc regions since the conductance map indicates a transfer from the sf-line into the hcp and fcc domains.

Let us focus on the changes around the two gaps. Figure 15(b) represents the spectra recorded along the scan line below, above and in the gaps. It clearly reveals the phase shift across the gaps. Moreover, it indicates that a modulated spectral intensity with maxima on the sf domains is observed for the first gap. This phase shift is directly confirmed by 2D-differential conductance images of terraces recorded for energies just below ($E = 20$ meV) and above ($E = 70$ meV) the first gap as illustrated in figure 16. These two $dI/dV$ images clearly show a complete balance of spectral weight in the reconstruction cell from the hcp to the fcc domains.

Gap amplitudes and localization of the electron density are related to the Fourier components of the surface potential. Therefore by combining ARPES and STS data, it is possible to figure out the electron potential associated with the reconstruction. To take into account the electronic confinement in the perpendicular direction demonstrated by Mugarza et al [36], an infinite potential has been chosen for step edges. From the gap magnitudes determined in photoemission, it is possible to deduce the absolute value of the Fourier components. Indeed, in the first order of the perturbation theory, the gap is proportional to the magnitude of the corresponding Fourier component of the potential but is not sensitive to its sign (equation (1)). As only two gaps are observed, we can conclude that only the two first Fourier components are important. Moreover, the sign of these Fourier components can be obtained from the phase of the electronic density observed in STS. These measurements show that the Fourier components are both positive. The analysis of the spectroscopic data leads to a 1D-potential composed of two components with minima on the ridges ($E_{\text{sf}}$) and maxima...
on the fcc and hcp domains ($E_{\text{fcc}} - E_{\text{sf}} = 100 \text{ meV}$ and $E_{\text{hcp}} - E_{\text{sf}} = 35 \text{ meV}$, respectively) as illustrated in figure 16(a). This shape is reminiscent of the 1D potential determined on flat Au(111) from a linear response analysis of the total electron density measured by STM [51]. Nevertheless, we have to point out that the strength of the potential we found in the Au(23 23 21) surface is significantly larger than the potential deduced on flat Au(111). This suggests that the surface reconstructions in Au(111) and vicinal Au(23 23 21) surfaces are different. A similar conclusion has been obtained from STS spectra for adsorbed rare-gas layers on Au(111) [2]. In such systems, the comparison with bare Au(111) shows that a strong peak at the onset of the surface state is observed in the hcp domains. This behavior was analyzed in terms of a larger reconstruction induced potential for a rare-gas covered Au(111) surface. A similar increase in the hcp regions is observed in the Au(23 23 21) surface as shown in figure 15(c) corroborating our conclusion that the potential is larger in the vicinal surface than in Au(111).

From the reconstruction potential we found, it is easy to calculate the electronic band structure of the Shockley state for the vicinal surface by numerically solving the corresponding Schrödinger equation. We obviously reproduce the existence of only two gaps with the correct position $E_1 = 40 \text{ meV}$ and $E_2 = 145 \text{ meV}$ and amplitude 38 and 50 meV, respectively. We also calculated the LDOS at $E = 20$ and 70 meV, i.e. on each side of the first gap (figure 16(b)) which are found to be in good agreement with the experimental conductance maps and then confirm that the Shockley state is localized in the hcp and sf domains below the first gap energy and in the fcc and sf domains above. A similar dephasing behavior is observed for the second gap.

4.3. Surface state confinement in self-organized nanostructures obtained on Au(111) vicinal surfaces

The purpose of this section is to discuss how the self-organized growth of Ag, Cu and Co nanostructures on Au(23 23 21) modify the surface potential experienced by surface electrons. Local spectroscopic measurements are very useful to study the electronic properties, the surface state energies and also their possible confinement in and/or between the nanostructures. From the growth point of view, the herringbone-like reconstruction of Au(111) discovered in the 1990s [44, 52, 53] is well known to strongly influence the epitaxial growth of metallic islands. Indeed, preferential nucleation sites at the elbows of the reconstruction or in the fcc domains for various species such as transition metals [54]–[56], noble metals [10, 57] or supramolecular complexes [58, 59]. On vicinal surfaces, well-ordered step edges strongly modify the growth mode leading to very different types of self-organization depending on the adsorbates, on the size of the terraces and on the preparation conditions [60]. Indeed, self-organized growth of isotropic Co islands has been obtained on Au(788) [44, 61], whereas Fe adatoms have been shown to decorate the step edges to form 1D Fe wires on the same substrate [62]. One of the most striking examples of self-organization is obtained by growing Ag islands on a Au(788) substrate as we have shown recently [63, 64]. Growth mechanisms are not the same in the different systems.

The typical growth of Co islands on Au(23 23 21) is illustrated in the STM topographic image presented in figure 17(a). Islands are essentially of bilayer height but monolayer islands can nevertheless also be distinguished. Since the initial stage of growth occurs at the crossing of sf lines and step edges (inset of figure 17(a)) as already reported for the growth of Co/Au(788), the two possible nucleation sites per unit cell lead to a broadening of the distribution of island–island distances [65] and two neighboring islands can sometimes
collapse. As a consequence, the long-range ordering of Co islands is distorted. Nevertheless, for adequate growth conditions, a sharp distribution of Co island size has been obtained on Au(788) surfaces [44, 61, 65]. The growth of 0.22 ML of Cu, 0.34 ML of Ag deposited on Au(23 23 21) and 0.21 ML of Ag deposited on Au(788) is presented in figures 17(b)–(d) respectively. Ag and Cu islands grow exclusively in the fcc domains (see inset figure 17(c)) leading to only one adsorption site per unit cell of the reconstructed substrate. Therefore, highly ordered self-organized islands over a macroscopic scale are obtained. For Cu adatoms, mainly isotropic bilayer islands are observed. Nevertheless, anisotropic monolayer islands still exist and the presence of Cu islands strongly modifies the terrace morphology leading to arcade-like step edges. For Ag adatoms, we have observed exclusively monolayer islands with a well-defined triangular shape (figures 17(c) and (d)). Co, Cu or Ag islands define a rectangular unit cell whose size is related to the reconstruction periodicity and the terrace width: (7.2 × 3.8) nm² on Au(788) and (6.5 × 5.6) nm² on Au(23 23 21). Such a quasi-perfect periodicity of the surface structure should be also reflected in the surface potential experienced by the surface electronic states as is the case for some self-organized or self-assembled systems exhibiting interplay between structural and electronic properties [66]–[68].

The Au(23 23 21) surface state described in previous sections should be influenced by the ordered islands appearing at small coverages. New surface states should appear inside nano-islands with energy related to the nanoscopic size of the islands. Differential conductivity spectra obtained at the center of a typical unit cell defined by four Ag, Cu and Co islands are presented in figure 18(d). These spectra are characterized by a pronounced maximum suggesting a partial confinement of the electron density in the supercells. The LDOS maps of several unit cells at the energy corresponding to the maximum in the dI/dV STS spectra are presented in figures 18(a)–(c) for the different systems. As expected, no LDOS intensity is observed at these energies inside nano-islands. This localized mode appearing at the center of each quantum box extends over a large-scale revealing the long-range coherence of this surface electronic state. This fundamental mode is found to be systematically higher than the band minimum of the vicinal surface and its energy depends on the atomic nature of the deposit and on the island size. This behavior indicates an additional confinement of surface electrons induced by the nanodots: Ag and Cu islands are shown to only slightly increase the surface state binding energy from −475 to −467 and −457 meV respectively, whereas a stronger confinement effect is obtained for Co islands ($E_0 = −426$ meV).

Figure 17. Topographic STM images of 0.36 ML of Co (a), 0.22 ML of Cu (b) and 0.34 ML of Ag deposited on clean Au(23 23 21) substrate (d); 0.21 ML of Ag deposited on Au(788) (d); nucleation sites for Co islands (inset in a) and for Ag/Cu islands (inset in c).
Figure 18. (a) and (b) open feedback loop conductance maps recorded with stabilization parameters: $I_t = 0.4 \text{nA}$ $U_S = 0.5 \text{V}$ (for 0.2 ML of Ag (a)) and $U_S = 0.54 \text{V}$ (for 0.2 ML of Cu (b)). (c) Closed feedback loop conductance with the stabilization parameter : $I_t = 0.8 \text{nA}$. (d) Corresponding STS spectra obtained at the center, one unit cell.

Figure 19. Closed feedback loop conductance maps of the standing wave pattern for 0.4 ML of Co deposited on Au(23 23 21) for several energies ($I_t = 0.5 \text{nA}$).

The energy dependence of the conductance maps obtained with Co islands deposited on Au(23 23 21) is presented in figure 19. The standing wave pattern evolves continuously from a single fundamental mode (figure 19(a)) at the center of each unit cell to a more complex pattern (figure 19(c)) probably determined by the 2D shape of the potential induced by Co islands coupled to step edges (figure 19(c)). Indeed, as the energy increases, the LDOS is reduced at the center of each box and is transferred to the other domains (figure 19(b)) as expected in a simple quantum well model. Moreover, the second mode induced by the perpendicular confinement appears leading to this peculiar ring-shape at $-340 \text{meV}$. For $E = -260 \text{meV}$ (figure 19(c)), four maxima appear inside the rectangular box suggesting another well-defined...
Figure 20. (a) and (b) open feedback loop conductance with stabilization parameters $U_S = 0.540 \, \text{V}$, $I_t = 0.4 \, \text{nA}$ and $U_S = 1.50 \, \text{V}$, $I_t = 0.6 \, \text{nA}$ respectively. (c) STS signal in Cu and Ag islands.

mode. Finally, for energies far above the Fermi energy (figure 19(d)), the conductance map exhibits high intensity lines parallel to step edges indicating that the influence of Co islands becomes negligible at this energy whereas a strong perpendicular confinement due to steps still persists. In addition, we would like to point out that no well-defined states have been identified inside Co islands up to 400 meV.

From previous work, we expect new surface states inside Ag (Cu) islands resulting from the Au surface state being modified by the overlayer. For one Ag layer deposited on a flat Au(111) surface, its energy should be around $-300$ meV [10]. Nevertheless, we have shown recently that for 0.21 ML of Ag deposited on Au(788), the small size of the Ag island shifts the surface state band toward the Fermi energy [65]. The same behavior is observed here on the LDOS mapping of isotropic Cu bilayer islands with a diameter of 3 nm (figure 20(a)). The LDOS map obtained at $E = -100$ meV evidences a complex standing wave pattern on the Au terraces but with no spectral weight inside Cu islands. In this system, the first quantum mode, revealed by a strong maximum at the center of the Cu island, is observed for $E = +400$ meV well above the Fermi energy. By changing the vicinality, i.e. the terrace size and the Ag coverage, larger Ag islands can be obtained on Au(23 23 21) so that we can tune the surface state energy such as retrieving the Ag island quantum mode in the occupied part of the spectra as shown in figure 20(b). The fundamental mode localized in the center of the Ag triangles, appears now at $-290$ meV. At higher energies, a second mode appears with three maxima localized near the corners of the triangular Ag islands. STS spectra taken both in Cu and Ag islands are compared in figure 20(c). The fundamental and the first excited modes are clearly identified at $-290$ and $-120$ meV in the case of Ag, whereas only one mode is reached at $E = +400$ meV in the case of Cu. This suggests a stronger confinement effect in Cu due to a larger potential probably induced by the bilayer character of the islands.

To summarize, the standing wave pattern, in particular the LDOS maxima can be controlled by adjusting the adatom species, the deposition rate and/or the size of the terraces. A long-range ordering of electronic properties is reached which allows to obtain a macroscopic set of nano-islands characterized by nearly-identical electronic states over a macroscopic scale.
5. Conclusion

In conclusion, we have shown that, due to their extreme surface localization, the Shockley states of noble metals are sensitive to any surface (structural or chemical) modification. In particular in noble metal/noble metal interfaces, the surface state parameters (energy, effective mass and spin–orbit Rashba parameter for Au) strongly depend on the thickness of the overlayer. We have shown for Ag/Cu(111) which exhibits different surface reconstructions, that the surface state spectroscopy is sensitive to the atomic structure. Due to their high surface sensitivity, Shockley states can be used as a tool to study the atomic structure of ultra thin films. The best illustration maybe the possibility to study buried interfaces by local spectroscopy (STS).

Shockley states properties are also modified by surface nanostructuration. In vicinal surfaces, the surface states become very anisotropic and electron confinement can be observed in terraces. In Au(23 23 21), we have evidenced by ARPES and STS the effects of the reconstruction on the surface band structure by the existence of two very small gaps associated with the reconstruction potential. By combining ARPES, which gives the gap magnitude, and STS which gives the phase, we were able to build the reconstruction potential. The photoemission spectral weight essentially remains in the non-reconstructed BZs with a negligible intensity in the folded bands. Finally, the peculiar growth properties of the Au vicinal surfaces led us to elaborate artificial superperiodic surfaces formed of metallic nanodots. Owing to the quality of the self-organized array, electronic properties are homogeneous on a large-scale leading the observation of coherent electronic effects.

Acknowledgments

We would like to thank Professor Friedel Reinert for helpful discussions and collaboration about the evolution of spin–orbit splitting in the Ag/Au(111) interface and Christophe Chatelain for calculation of STS images.

References

[1] Crommie M F, Lutz C P and Eigler D M 1993 Nature 363 524
[2] Andreev T, Barke I and Hovel H 2004 Phys. Rev. B 70 205426
[3] Forster F, Nicholai G, Reinert F, Ehlm D, Schmidt S and Hüfner S 2003 Surf. Sci. 532–35 160
[4] Dudde R, Johansson L and Reihl B 1991 Phys. Rev. B 44 1198
[5] Kliewer J and Berndt R 2001 Phys. Rev. B 65 035412
[6] Pons S, Mallet P and Veuillen J Y 2001 Phys. Rev. B 64 193408
[7] Dikhöner L, Schneider A M, Baranov A N, Stepanyuck V S, Bruno P and Kern K 2003 Phys. Rev. Lett. 90 236801
[8] Repp J, Meyer G and Rieder K H 2004 Phys. Rev. Lett. 92 36803
[9] Shapiro A P, Wachs L and Chiang T C 1986 Solid State Commun. 58 121
[10] Cercellier H, Didiot C, Fagot Revurat Y, Kierren B, Moreau L, Malterre D and Reinert F 2006 Phys. Rev. B 73 195413
[11] Didiot C, Vedeneev A, Fagot Revurat Y, Kierren B and Malterre D 2004 Phys. Rev. B 72 233408
[12] Chiang T C 2000 Surf. Sci. Rep. 39 181
[13] Chulkov E V, Silkin V M and Echenique P M 1999 Surf. Sci. 437 330
[14] Nicolay G, Reinert F, Hüfner S and Blaha P 2001 Phys. Rev. B 65 033407
[15] Reinert F 2003 J. Phys.: Condens. Matter 15 S693

New Journal of Physics 9 (2007) 391 (http://www.njp.org/)
[58] Boringer M, Morgenstern K, Schneider W D, Berndt R, Mauri F, De Vito A and Car E R 1999 Phys. Rev. Lett. 83 324
[59] Clair S, Pons S, Brune H, Fabris S, Baroni R, Kern K and Barth J V 2006 J. Phys. Chem. B 110 5627
[60] Néel N, Kröger J and Berndt R 2006 Adv. Mater. 18 174
[61] Repain V, Baudot G, Ellmer H and Rousset S 2002 Europhys. Lett. 58 730
[62] Shiraki S, Fujisawa H, Nantoh M and Kawai M 2004 Phys. Rev. Lett. 92 096102
[63] Didiot C, Fagot-Revurat Y, Pons S, Kierren B, Chatelain C and Malterre D 2006 Proc. ECS-24 Conf. (4–8 September, Paris)
[64] Didiot C, Pons S, Fagot-Revurat Y, Kierren B and Malterre D 2006 Surf. Sci. 600 3917
[65] Didiot C, Pons S, Fagot-Revurat Y, Kierren B, Malterre D, Tejeda A and Rousset S 2007 Proc. ECSFS-13 Conf. (6–10 November, Bariloche) Appl. Surf. Sci. to appear
[66] Ternes M, Weber C, Pivetta M, Patthey F, Pelz J P, Giamarchi T, Mila F and Schneider W-D 2004 Phys. Rev. Lett. 93 146805
[67] Schiller F, Cordón J, Vyalikh D, Rubio A and Ortega J E 2005 Phys. Rev. Lett. 94 16103
[68] Bendounan A, Forster F, Reinert F, Kierren B, Fagot-Revurat Y and Malterre D 2006 Phys. Rev. Lett. 96 29701