Resolving all atoms of an alkali halide via nanomodulation of the thin NaCl film surface using the Au(111) reconstruction

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We investigated the local influence of the Au(111) herringbone reconstruction on the properties of thin adsorbed NaCl films using cryogenic scanning tunneling microscopy (STM) and spectroscopy. Depending on the local hcp versus fcc character of the reconstruction, NaCl adsorption gives rise to a different shift of the Au(111) surface state toward the Fermi level, in agreement with *ab initio* calculations. Such lateral modulation may allow for tunable nanostructuring of thin insulating films, which opens up new perspectives for molecular electronics applications. Furthermore, we demonstrate the simultaneous visualization of both the alkali and the halogen atoms in hcp regions of the NaCl/Au(111) surface using a functionalized STM tip. *Ab initio* calculations relate this simultaneous visualization to the larger electron density in the hcp regions.

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I. INTRODUCTION

Nanometer-scale patterned templates with tunable electronic properties are of prime importance in current state-of-the-art nanotechnologies. The adsorption and self-assembly of functional molecular systems on solid surfaces is a powerful tool to fabricate well-ordered structures that are suitable for future applications in molecular electronics or nanomechanics.¹ Studies of molecular self-assembly on metal surfaces have shown that such structures can be conveniently grown via self-organization by a proper choice of molecules and substrate.² A notable example is the self-assembly of the fullerene derivative phenyl-C61-butyric-acid-methyl-ester when grown on Au(111) surfaces, for which there is a preferential adsorption on the fcc areas of the known herringbone reconstruction of Au(111) surfaces, leading to the growth of molecular nanowires at low coverages.³

For the purpose of molecular electronics it is often required that the molecular assemblies are grown on a complementary insulating support rather than directly on a metal support. Thin alkali halide films are considered as an important candidate for this purpose. For example, it has been shown that thin NaCl films can effectively decouple molecules from the underlying metal support.⁴ Such NaCl layers have recently also been used successfully for various scanning probe microscopy studies,^{5–8} and self-assembly of adsorbates through intermolecular hydrogen interaction.⁹

Lateral modulation of the interaction between the alkali halide and the underlying metal support may allow for tunable nanostructuring of the thin films and opens up new perspectives for molecular electronics applications. This lateral modulation can be achieved by considering a metal support that exhibits a surface reconstruction. Previous studies are mainly limited to atomically flat supports that do not exhibit a surface reconstruction as for example Cu(111). The Au(111) surface is in contrast known for its characteristic herringbone surface reconstruction. In one-half of the reconstructed unit cell, the surface atoms occupy hcp sites, while in the adjacent half they occupy fcc sites.¹⁰ This reconstruction acts as a superlattice for the Au(111) Shockley surface

state (SS) electrons, thereby creating a modulation in its density.¹¹

In this paper we demonstrate that herringbone reconstructed Au(111) surfaces can be effectively exploited to modulate the surface properties of thin insulating NaCl films. Relying on scanning tunneling microscopy (STM) and spectroscopy (STS), we reveal that the adsorption of NaCl causes an upward shift of the Au(111) SS. This shift is shown to depend spatially on the local NaCl/Au(111) interaction, which is modulated by the hcp versus fcc character of the Au(111) reconstruction. Using a functionalized Cl[−] terminated STM tip we show that the enhanced electron density at the hcp regions of the modulated NaCl/Au(111) interface influence the tip-sample interactions, giving rise to the remarkable simultaneous visualization of both the atomic species of the thin alkali halide bilayer in maps of the local density of states (LDOS). By *ab initio* calculations we show that the site-specific behavior of the NaCl indeed stems from the underlying Au(111) herringbone reconstruction.

II. EXPERIMENT

A description of the STM setup and details on the preparation of the Au(111) surface and W tips are given elsewhere.¹² NaCl (99.999% purity, Alfa Aesar) is thermally evaporated at 800 K in a separate setup (pressure in the 10^{−9} mbar range) with the substrate kept at room temperature. The sample is transferred to the STM setup by means of an ultrahigh vacuum transport vessel (pressure in the 10^{−10} mbar range). All STM measurements are performed at 4.5 K. Image processing is performed by Nanotec WSxM.¹³

III. RESULTS AND DISCUSSION

A. NaCl/Au(111) interface state

When deposited on a clean Au(111) surface at room temperature, NaCl forms bilayered (100)-terminated islands with perfect nonpolar step edges.^{9,14} Figure 1(a) illustrates the carpetlike growth of NaCl islands over the steps of the

FIG. 1. (Color online) (a) $60 \times 60 \text{ nm}^2$ pseudo-three-dimensional (3D) topographical STM image of NaCl islands grown on Au(111) ($V = 1.0 \text{ V}$; $I = 0.1 \text{ nA}$). (b) $30 \times 4 \text{ nm}^2$ atomically resolved STM image of trilayer NaCl grown on Au(111) ($V = 600 \text{ mV}$; $I = 0.6 \text{ nA}$). (c) Atomically resolved 2D visualization of $(dI/dV)(V)$ spectra along the black line in (b). The color scale in the figure indicates the density of states; see inset in (e). (d) $1.6 \times 0.9 \text{ nm}^2$ atomic resolution closeup view of the trilayer NaCl island shown in (b). Protrusions correspond to the Cl⁻ ions. (e) $(dI/dV)(V)$ spectra taken on clean Au(111), and on trilayer NaCl on the hcp [diamond in (b)] and fcc [cross in (b)] region of the reconstructed Au(111).

Au(111) surface. The Au(111) herringbone reconstruction is not influenced by the NaCl islands and its corrugation is the same on NaCl/Au(111) as on the bare Au(111). Large patches of trilayer NaCl were obtained by postannealing to 460 K, which turns the NaCl from being predominantly bilayered to trilayered.¹⁵ Figures 1(b) and 1(d) present typical closeup views of the atomically resolved surface of NaCl(3 ML)/Au(111), where the bright protrusions correspond to Cl⁻.^{5,16}

In Fig. 1(c) we present an atomically resolved 2D visualization of $(dI/dV)(V)$ curves taken above trilayer NaCl along the black line indicated in Fig. 1(b). The increased intensity (electron density) around -250 meV stems from the onset of the newly formed two-dimensional interface state (IS) that originates from the Au(111) SS at the NaCl/Au(111) interface. Remarkably, the onset energy E_0 of the IS appears to be spatially dependent on the Au(111) herringbone reconstruction. From the spectra in Fig. 1(e) it can be seen that the IS is shifted by an extra 60 meV toward the Fermi level in the fcc region when compared to the hcp region. The ridges provide a smooth transition of the IS shift between the two regions of the reconstruction. A similar modulation of the IS by the Au(111) herringbone reconstruction is observed for bilayered NaCl. On pristine Au(111), however, the delocalized SS electrons respond to the reconstruction mainly by spatially transferring state density near E_0 of the SS around -480 meV , but there is no difference in the value of E_0 of the SS for the fcc and hcp regions.¹¹

To understand the origin of the observed shift and modulation of E_0 , we have performed *ab initio* calculations for the NaCl/Au(111) system. The complexity of the system, associated with (i) the long-range herringbone reconstruction and (ii) the incommensurate growth of the square NaCl lattice

on the hexagonal Au(111) surface, makes a full *ab initio* treatment of the system unfeasible. The IS shift analysis was therefore performed in three steps, here described briefly (see the Appendix for a more detailed description). First, the clean Au(111) surface is described using the “embedding method” approach to model the potential along the z coordinate normal to the surface.^{17,18} Key quantities such as the bulk band projected gap at $\bar{\Gamma}$, E_0 of the Au(111) SS, and the work function of the Au(111) surface are correctly described by this model. Second, the more attractive potential in the hcp region is modeled by considering the potential change induced in the surface region upon a 3% compression of the interatomic distances. To simulate this compression *ab initio* perturbing potentials are employed. A downward shift of 48 meV (i.e., 16 meV for each unit of percentage of compression) was found, which is consistent with the attractive potential of 25 meV for the hcp region estimated by Chen *et al.*¹¹ Third, the adsorbed NaCl bilayer is simulated by potential wells computed *ab initio* and fitted by an analytical model potential. The NaCl film causes the Au(111) SS to become an IS that is localized in the region between the metal and the NaCl film. Although the potential due to the overlayer is attractive, the ionic film acts as a repulsive potential for the SS, implying that the IS is less bound. This can be understood considering the potential barrier generated by the insulating gap. In some energy regions the electronic states cannot penetrate. Consequently, the potential well “felt” by the SS is narrower and the bound state shifts from -480 meV to $-220/-270 \text{ meV}$.

The model potentials of pristine Au(111) and of the NaCl/Au(111) system in the fcc region are presented in Fig. 2, together with the calculated square moduli of the SS and IS in the fcc region. By taking the potential of the adsorbed insulating layer explicitly into account, we find that the IS

FIG. 2. (Color online) Lower panel: model potentials for Au(111) (dashed line) and NaCl(2 ML)/Au(111) (solid line) in the fcc region. Upper panel: squared moduli of the wave functions for the Au(111) SS and NaCl/Au(111) IS in the fcc region.

wave function exhibits maxima at the positions of the two NaCl layers, unlike in earlier work where the NaCl is taken into account only via its static dielectric constant.⁵ The calculated values for E_0 of the IS in the different regions of the Au(111) reconstruction are listed in Table I. The good agreement between the theoretical and experimental values of E_0 in both the fcc and hcp regions demonstrates that the proposed model potential captures the physics involved in the IS shift. As the IS wave function is already damped after two NaCl layers, the calculated shift for the trilayer (see Table I) is essentially the same as for the bilayer, suggesting that the experimentally found small difference may be related to a difference in the structural parameters of bilayer and trilayer NaCl films.

B. Simultaneous imaging of the Na and Cl atoms

The above results clearly demonstrate that the reconstruction of the Au(111) surface gives rise to the spatially modulated electronic properties of the NaCl/Au(111). This modulation allows us to investigate the influence of the local electronic properties of the NaCl/Au(111) system on the site-specific interaction between the NaCl and an adsorbate. For this purpose, we investigated the local interaction between the alkali halide film and a Cl^- terminated STM tip. Such a tip was obtained simply by scanning the bilayer NaCl surface in close proximity until a change of the microscope tip apex

TABLE I. Theoretical and experimental values of the onset energy E_0 (in meV) of the NaCl/Au(111) IS for both fcc and hcp Au(111) reconstructed regions. Experimental values are determined from $(dI/dV)(V)$ curves following the geometrical procedure given in Ref. 19. The experimental E_0 of the pristine Au(111) SS is -480 ± 10 meV for both regions.

	Experimental		Theoretical	
	fcc	hcp	fcc	hcp
NaCl(2 ML)	-220 ± 20	-270 ± 20	-211	-267
NaCl(3 ML)	-230 ± 20	-290 ± 20	-211	-268

was observed.²⁰ Local variations of the interaction between tip and sample were measured by mapping the LDOS.²¹ Figures 3(a) and 3(b) present a topographical STM image and the corresponding LDOS map of a bilayer NaCl island recorded with a functionalized STM tip. In the topography image in Fig. 3(a) only one of the atomic species of NaCl is revealed. Remarkably, the LDOS map in Fig. 3(b) reveals a different resolution on the fcc and the hcp regions: whereas only one of the atomic species is observed in the fcc regions (similar to the topography image), both atomic species are visualized in the hcp regions (in contrast to the topography image). Both atoms are also resolved on the “ridges” of the herringbone reconstruction, which provide a transition region from the fcc to the hcp configuration. This is the first observation of both atomic species of an alkali halide in real space by scanning probe experiments. Previously, imaging of both ionic sublattices has been achieved on TiO_2 .²² Our result demonstrates that one can modulate the surface properties of an alkali halide by growing the alkali halide on a patterned support.

Now the question arises whether the observed simultaneous imaging of the Na and Cl atoms is related to the inherent LDOS of the NaCl/Au(111) system only or if specific tip-sample interactions play a prominent role as well? To answer this question, we calculated the electronic structure of the NaCl/Au(111) system with density functional theory (DFT) and simulated LDOS maps neglecting possible tip effects. If the observed simultaneous imaging would not be related to specific tip-sample chemical interactions, these simulated LDOS maps must be able to describe the images in Figs. 3(a) and 3(b).²³ If not, the simultaneous imaging is (at least partially) related to tip-sample interactions.²⁴

DFT calculations are performed with the exchange-correlation functional proposed by Perdew, Burke, and Ernzerhof.²⁵ We constructed a model of the system with a coincidence structure, obtained by superposing a (2×2) NaCl unit cell on a $\begin{pmatrix} 3 & 1 \\ 1 & 3 \end{pmatrix}$ superstructure of the Au(111) substrate. This coincidence structure presents a residual strain of about 5%, which is accommodated in the Au(111) substrate. Moreover, the angle of the substrate unit cell is changed from 82° to 90° to match the square symmetry of the NaCl film. We have chosen to accommodate the distortion on the metallic substrate and to keep the NaCl undistorted to avoid artificial rumpling in the deposited film, although we verified that the results obtained by deforming the NaCl are essentially the same. The metal surface is modeled by a five atomic layers thick slab. The atomic coordinates of the Au slab are relaxed in z direction in order to accommodate the above-mentioned strain and are then kept fixed for the NaCl/Au combined system. The NaCl coordinates are then relaxed in z direction and the NaCl in-plane lattice parameter is fixed at 3.91 Å, the average of the optimized lattice parameters of unsupported NaCl bilayer and trilayer.

We have included an estimate of the van der Waals interactions, not present in DFT theory, with the pair-wise force field as implemented in the DFT-D2 method of Grimme.²⁶ The model accounts for the experimentally measured work function reduction of 1.1 eV with respect to the Au(111) surface,²⁷ estimated from the energy shift of the $n = 2$

FIG. 3. (Color online) (a) $2 \times 13 \text{ nm}^2$ topographical STM image (after applying a Fourier filter) and (b) corresponding LDOS map (raw data) of NaCl(2 ML)/Au(111) ($V = 600 \text{ meV}$; $I = 0.4 \text{ nA}$). Whereas only the Cl atoms are resolved in the topographic image (a) as well as in the fcc region of the LDOS map (b), both the Na and the Cl atoms are visible in the hcp region of the LDOS map (b). A model of the NaCl lattice is added as a guide for the eye (Cl: large dots; Na: small dots). (c) and (d) Schematic representation of bilayer NaCl on fcc and hcp Au(111), respectively, that are imaged by a Cl terminated STM tip. Note that the bulk Au stacking remains intact, while only the stacking of the top atomic layer is different in the fcc and hcp regions. For clarity reasons the NaCl rumpling is not drawn to scale.

image state. The interface coincidence structure does not allow one to model the hcp region of the Au(111) by a compression of the interatomic distances. Instead, the Au(111) surface reconstruction is taken into account by considering an artificially reduced NaCl/Au(111) interface distance in the hcp region (by 0.02 nm), which gives rise to an enhanced electron density in this region, in agreement with the $(dI/dV)(V)$ curves in Fig. 1(e). Upon atomic relaxation we find a reduced NaCl rumpling in the hcp region (about 6.3 pm , with the Cl relaxing outward) compared to the fcc region (about 7.6 pm). This effect is schematically illustrated in Figs. 3(c) and 3(d). The computed STM images for both regions (fcc and hcp) always show the Cl atom only, in agreement with the experiments [Fig. 3(a)]. However, the simulated LDOS maps also show the Cl atom only and hence cannot account for the observed imaging of both types of atoms. It must be noted that Figs. 3(a) and 3(b) are recorded at the same feedback settings that enabled the STM tip to pick up a Cl atom, implying a small tip-sample distance. It is thus reasonable that the STM tip, neglected in the simulations, plays indeed a key role in the imaging.^{23,24}

Hence we verified the role of the functionalized STM tip (i.e., terminated by a Cl^- ion) for the visualization of both atomic species in the hcp regions of the NaCl surface in LDOS maps by electrostatically attracting the Na^+ ion above the surface. For this purpose, we calculated the energy cost of lifting a Na atom from the NaCl layer for both hcp and fcc NaCl/Au(111), which allows its detection in LDOS maps. We find that the average energy needed to lift a Na atom to the level of the mean Cl plane is 20% larger for the fcc region than for the hcp region (of the order of 5 meV). The (additional) rumpling of the NaCl surface induced by a negative ion on the STM tip apex²⁸ is schematically illustrated in Figs. 3(c) and 3(d) and can explain the enhanced Na signal at hcp regions in the experimental LDOS maps. Furthermore, our calculations show that the DOS at the Na (Cl) sites increases (decreases)

with increasing energy above the Fermi level. This implies that simultaneous visualization of both atomic species is most pronounced in LDOS maps [Fig. 3(b)], i.e., at positive bias voltages, while it is less pronounced or even not discernible in topography images [Fig. 3(a)].

IV. CONCLUSIONS

In summary, by growing NaCl on a Au(111) surface we are able to study the interaction between a stiff insulating material and a reconstructed surface. This interaction is found to modulate the newly formed IS that is confined by the NaCl potential barrier, which acts differently in the hcp and fcc regions of the Au(111) reconstruction. Using a functionalized STM tip, the enhanced electron density in the hcp regions allows us to resolve both species of the alkali halide. The NaCl/Au(111) system opens new perspectives for the templated growth of self-organized molecules.

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APPENDIX: THEORETICAL MODELING OF THE INTERFACE STATE MODULATION OF NaCl(2–3 ML)/Au(111)

The clean Au(111) surface and the NaCl film are described by a model potential depending on the z coordinate only,

FIG. 4. (Color online) Surface density of states for the Au(111) surface. DOS at $\bar{\Gamma}$ (solid line) and DOS integrated over the surface Brillouin zone (dashed line). The region considered for the spatial integration contains two gold layers plus the vacuum.

normal to the surface. We use a phenomenological potential¹⁸ to describe the clean Au(111) surface. *Ab initio* perturbing potentials were then employed to simulate the surface reconstruction and the NaCl adsorption. A similar model was used to describe the upward shift of the surface state in Ref. 29, although our model takes explicitly into account the potential of the insulating layer.

1. Clean Au(111)

The model potential describing the Au(111) surface has been proposed in literature some years ago by Chulkov *et al.*¹⁸ and is reported as dashed line in the lower panel of Fig. 2. This potential has been built in order to reproduce some experimental features which play a role in our experimental observations: the amplitude and energy position of the surface projected bulk band gap, the energy of the Shockley surface state, and the work function of the gold metal surface.

Following the embedding method proposed by Inglesfield,¹⁷ we use semi-infinite boundary conditions to solve the Schrödinger equation, obtaining results close to the experimental ones (see Table II).

In Fig. 4 the surface density of states (DOS) at $\bar{\Gamma}$ (solid line) for the Au(111) clean surface is presented. The surface projected bulk band occupies the higher binding energy part of the spectrum. The model potential is able to describe only the

TABLE II. Parameters for the Au(111) surface. Energies in eV with respect to the Fermi energy for all data, except for the image state which is given with respect to the vacuum.

	Experiment	Theory in Ref. 18	This work
Lower gap edge	-1.0	-1.0	-1.09
Upper gap edge	3.6	3.6	3.51
Shockley SS	-0.48 ^a	-0.47	-0.47
First image state	-0.6 ^b	-0.80	-1.01

^aSome other values are reported in literature: -0.50,³⁰ -0.35,³¹ -0.47,³² and -0.41.³³

^bAs taken from Ref. 30, but some other values are reported in literature: -0.42³⁴ and -0.8.³⁵

FIG. 5. (Color online) Potential induced by a 5% compression of the interatomic distance.

s-p-like band. The *d* band is absent, but this does not play any role for the experimental results considered here. In the gap, extending from -1.09 to 3.51 eV, the Shockley surface state at -0.468 eV is clearly visible. The upper gold bulk band starts at 3.51 eV and the image state series appears in this band near the vacuum level. The work function for this system is 5.55 eV. The dashed line in Fig. 4 represents the DOS integrated over the surface Brillouin zone. As expected for the surface state, the DOS shows a steplike behavior which can be probed by scanning tunneling spectroscopy.

2. Effects due to surface reconstruction

All the *ab initio* calculations were performed within the generalized gradient approximation of DFT as proposed by Perdew, Burke, and Ernzerhof (GGA-PBE).²⁵ A five layers Au slab was considered to determine the effective potential in the surface region. After a structural relaxation with the theoretical bulk lattice parameter (4.17 Å), the resulting structure has been scaled to the experimental one (4.08 Å).³⁶ The corresponding surface interatomic distance amounts to 2.88 Å. To address the influence of the altered in-plane bond length along the Au(111) reconstruction, simulations were also performed using shorter interatomic distances while keeping the perpendicular coordinates fixed. In Fig. 5 the lateral average of the potential induced in the surface region caused by a 5% compression of the interatomic distance is presented. More explicitly we present the quantity

$$\Delta V_{eff}(z) = \frac{1}{S} \int_S dx dy V_{eff}^{5\%}(x, y, z) - \frac{1}{S'} \int_{S'} dx dy V_{eff}^0(x, y, z), \quad (A1)$$

where S (S') is the surface unit cell and V_{eff} is the local part of the Kohn-Sham effective potential. We verified that $\Delta V_{eff}(z)$ depends linearly on the compression. By adding this quantity to our model potential for the Au(111) surface we are able to simulate in a very simple way different regions where the gold atoms arrange themselves according to a hcp or fcc stacking.

The induced potential is attractive and it should increase the binding energy of the surface state. In fact, we found a downward shift of 16 meV for each unit of percentage of

FIG. 6. (Color online) Lateral average of the *ab initio* effective potential for the NaCl bilayer.

compression. There is no experimental verification possible for this quantity, but as a first approximation it can be compared to the attractive potential of 25 meV for the hcp region proposed in Ref. 11.

3. Adsorption of NaCl

In order to simulate the adsorption of a bilayer of NaCl we added in front of the Au(111) surface a double well potential computed *ab initio* and fitted by an analytical model potential. In Fig. 6 we present the lateral average of the effective potential computed within DFT.

The interface distance has been arbitrarily fixed to 3.2 Å which is comparable to the sum of the covalent radius of Au

and the ionic radius of Cl^- . As will be discussed below, the results depend on this distance.

For the NaCl interlayer distance we take the computed equilibrium distance of the NaCl bilayer, i.e., 2.828 Å (2.815 Å is the experimental equilibrium distance for bulk NaCl). The model potential representing the NaCl bilayer adsorbed on Au(111) is presented as a solid line in the lower panel of Fig. 2. The presence of the NaCl bilayer causes an upward shift of the pristine Shockley state, which is now better described as an IS localized in the region between the metal and the NaCl film.

The IS is now 257 meV less bound, i.e., its energy is −211 meV. Also the phase shift model has been used by Repp *et al.* to understand this phenomenon.²⁹ In Ref. 29 the upward shift of the surface state is attributed to the weaker image potential due to the polarization of the adsorbed dielectric.

A comparison between the Shockley surface state and the IS is presented in the upper panel of Fig. 2. The narrower shape of the principal maximum of the IS indicates a stronger confinement of this state.

4. Effect on the interface state due to surface reconstruction

The effect of the compression of the Au(111) surface, simulating the hcp region, can be added to the previously calculated effective potential. With this additional attractive perturbation the IS is located at −0.267 meV, i.e., more bound by 56 meV for a compression of 3%. All the previously reported results are obtained for a fixed NaCl-Au(111) distance. Indeed, a variation of this distance modifies the binding energy of the IS: we estimate a downward shift by about 45 meV for an increase in distance of 0.1 Å. In a similar way, a rearrangement of the overlayer, i.e., a rumpling of the NaCl surface layer, can influence the results as well.

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