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NaCl multi-layer islands grown on Au(111)-(22 × √3) probed by scanning tunneling microscopy

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Abstract
The growth of multi-layer NaCl islands on Au(111)-(22 × √3) surfaces was investigated using scanning tunneling microscopy (STM). We observed that the aspect of the NaCl islands drastically differs depending on the tunneling conditions. It is therefore possible to observe the layers forming an NaCl island or to image the gold reconstruction below the first NaCl layer. Atomically resolved STM images obtained on the first NaCl layer demonstrate that NaCl grows as an epitaxial crystalline film on Au(111)-(22 × √3). STM images also suggest that some NaCl layers can be non-crystalline.

(Some figures in this article are in colour only in the electronic version)
Polar surfaces usually exhibit surface reconstructions or charge reconstructions in order to minimize the charge distribution and the resulting dipole moment. In the case of NaCl, it has been experimentally shown that, depending on the growth conditions and charge distribution, (100) or (111) islands can be grown [27].

In this paper we report on the growth of NaCl islands on an Au(111) surface. We observed, using scanning tunneling microscopy (STM), that the variation of the tunneling parameters allows us to image different layers of the NaCl islands. STM images suggest that some NaCl layers are crystalline whereas the others are not.

The Au(111) substrates were prepared by sublimation of 99.99% gold (Umicore Materials AG) in a custom-built vacuum chamber having a base pressure of $10^{-7}$ Pa. A 250 nm thick gold film was grown on freshly cleaved mica sheets (Ted Pella, Inc.) held at 640 K. They were introduced into the ultrahigh vacuum (UHV) chamber of a scanning tunneling microscope (Omicron AFM-STM) operating at a pressure of $10^{-8}$ Pa, and repeatedly sputtered with argon ions (500 eV) and annealed at 500 °C typically for 45 min. The formation of a reconstructed Au(111)-(22 \times \sqrt{3}) surface was then checked by STM; see figure 1(b). The step height of a gold terrace was measured to amount to 2.35 Å, which corresponds to the gold plane separation in the [111] direction. Ideally, the Au(111) surface reconstructs into a herringbone pattern, but often this surface forms a complicated pattern of paired corrugation lines [28, 29]. These paired corrugation lines are aligned with the (112) gold direction and repeat periodically every 6.3 nm. NaCl was sublimated at 450 °C onto the gold substrate in the preparation chamber and then transferred to the STM chamber for imaging. Cut PtIr wire was used as the STM tip to obtain constant current images at room temperature with a bias voltage $V_e$ applied to the sample. The STM images were processed and analyzed with FabViewer [30].

Figures 1(c) and (d) show STM images of NaCl islands formed after deposition of NaCl on an Au(111)-(22 \times \sqrt{3}) surface at room temperature. These islands have almost straight step edges and the angle between the step edges is $\sim 90^\circ$. The small NaCl islands are mostly located on top of gold step edges. This suggests that gold step edges are preferential nucleation sites for NaCl islands; see figure 1(c). Further NaCl deposition leads to the growth of NaCl islands forming large domains; see figure 1(d). The STM images show that the second and third NaCl layer start to form on the first one before the latter completely covers the Au surface.

Figure 2 presents similar NaCl islands on Au(111) imaged by STM with two different tunneling conditions, namely $-0.3$ V @ 0.15 nA (a) and $-1.0$ V @ 0.7 nA (b). The gold step height of 2.3 Å was found independently of the tunneling conditions. NaCl multi-layer islands are clearly visible in figure 2(a), whereas only the first layer of same islands appears in (b). In figure 2(b) the Au(111)-(22 \times \sqrt{3}) reconstruction is clearly visible underneath the first NaCl layer. The height profiles extracted from the images in figures 2(a) and (b) are reported in figure 2(c) and show that the first NaCl layer (figure 2(a)) has an apparent height of $\sim 1.53$ Å, while the thickness of the second layer in the same image amounts to $\sim 0.7$ Å (curve A). The height profile corresponding to figure 2(b) gives instead an apparent height of the first NaCl layer of $\sim 0.9$ Å, and the second layer appears $\sim 1.1$ Å below the gold surface (figure 2(c), curve B). The tunneling parameters are hence strongly affecting the apparent height of the NaCl layers. Even the larger value for the height of the first NaCl layer is lower than its physical height (2.82 Å). The measured height of the additional NaCl layers is even smaller, and for islands composed of three and more layers the measured height of the NaCl multi-layer islands can appear below the gold surface. These observations are a perfect illustration of NaCl non-conducting...
The NaCl layers act as an insulating thin film, which perturb the tunneling between the STM tip and the gold substrate. The formation of thicker and thicker NaCl film on the gold substrate progressively insulates the gold metal surface.

Figure 3(a) shows atomically resolved NaCl islands. From the corresponding atomic corrugation reported in figure 3(b), one sees that the distance between two nearest bright spots in the NaCl layer is 4.0 ± 0.1 Å. This corresponds to the closest separation of one atomic species in the NaCl(001) surface. These bright spots in the NaCl island are attributed to Cl\(^{-}\) anions.\(^{25, 26, 31}\) The atomic corrugation is \(\sim 0.2\) Å. The atomic periodicity of NaCl is modulated by the large periodicity of the gold herringbone reconstruction, and figure 3(b) demonstrates that this reconstruction persists below the salt islands even after NaCl growth.

The STM images show that NaCl is growing as a (100) layer on the reconstructed (111) gold terraces. The square NaCl unit cell has been superimposed to each of the two NaCl layers in figure 3, as black and white squares. The two unit cells are rotated by 30° with respect to each other. The gold reconstruction visible underneath the NaCl layer shows that the NaCl unit cell is in both cases aligned with the \(\langle 1\bar{1}2 \rangle\) and the \(\langle 1\bar{1}0 \rangle\) gold directions (and equivalent directions). This indicates that NaCl grows preferentially as an epitaxial NaCl(100) film.

An NaCl monolayer will wet the Au surface if \(\gamma_{\text{Au}} > \gamma_{\text{NaCl}} + \gamma_i\), where \(\gamma_{\text{Au}}\) is the surface energy of the Au(111) substrate, \(\gamma_{\text{NaCl}}\) is the monolayer surface energy, and \(\gamma_i\) is the interface energy between the monolayer and the substrate. \(\gamma_{\text{Au}(111)} = 1.28 \text{ J m}^{-2}\) \(^{35}\) and \(\gamma_{\text{NaCl}(100)} = 0.16 \text{ J m}^{-2}\) \(^{36}\) are obtained from \textit{ab initio} and DFT calculations. Therefore the interface energy should be less than 1.12 J m\(^{-2}\).

Figure 4 illustrates details of a NaCl multi-layer island as imaged by STM. The first NaCl layer appears flat while the second NaCl layer has different aspects: the one labeled (b) in figure 4 resembles the first layer and seems flat as well; on the other hand, a complicated pattern is observed for the second NaCl layer labeled (a) in figure 4. We did
not succeed in finding tunneling parameters permitting us to record atomically resolved images of this layer. The STM image shows that the latter is formed by juxtaposed domains of stripes labeled A, B, and C in figure 4. The patterns in these domains do not have a high degree of symmetry and are oriented differently. They therefore cannot be attributed to a Moiré pattern [24, 32, 33]. However, this suggests that the second layer is not crystalline or that its crystallization is not fully completed at room temperature, despite the fact that its edges are almost straight and nearly perpendicular. These observations illustrate that the formation of the NaCl thin film growth seems strongly dependent on the growth conditions [34].

As shown by figure 2, the NaCl layers on Au(111) act as a insulating thin film. Figure 2 shows that increasing the NaCl thickness reduces the conductivity between the STM tip and the gold substrate. NaCl thin films are promising substrates to decouple supported nanostructures from a metal support. As was done by Qiu et al [2] using ultrathin Al2O3 films, insulating thin films can be used to decrease the coupling between the molecules and their metal support with the aim of observing the vibronic states of molecules using STM. It would be interesting to investigate the decoupling and charging effects of molecules on NaCl thin films as a function of NaCl thickness. This should be achievable using low-temperature scanning tunneling spectroscopy.

In this work we have studied NaCl multi-layer islands grown on Au(111)-(22 \times \sqrt{3}) using scanning tunneling microscopy. By changing the tunneling parameters we were able to selectively image the first NaCl layer of the islands or the other layers. Atomically resolved STM images of the first NaCl layer indicate that NaCl grows as an epitaxial (100) thin film on Au(111)-(22 \times \sqrt{3}). STM images of some NaCl layers show non-strictly-periodic stripes, which suggest that they can be non-crystalline or not perfectly crystallized.

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