Ionic Films on Vicinal Metal Surfaces: Enhanced Binding due to Charge Modulation

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NaCl films on Cu(311) exhibit a remarkably strong and localized binding between adlayer and substrate. The binding sites of the ions in the NaCl film with respect to the Cu surface are determined from atomically resolved scanning tunneling microscopy images. A new model is proposed in which the binding mechanism is controlled by the charge modulation of a regularly stepped surface due to the Smoluchowski effect. This model can be extended to explain the growth of ionic adlayers on regularly stepped and kinked metal surfaces in general.

There is a long standing interest in the growth of ultrathin insulating films on conductive substrates due to their importance in catalysis and device applications. Additionally, the use of thin films circumvents the problem of surface charging and thereby allows one to investigate insulator surfaces by standard surface analysis techniques. To grow thin insulating films different techniques have been developed, depending on the selected substrate and deposit. In the important field of metal oxides, for example, both components of the film are introduced separately and the film can be grown either by metal deposition and subsequent oxidation, or by simultaneous oxidation during growth [1,2]. In the case of alkali halides the film is grown by direct deposition of the complete alkali halide molecule. While the chemical reactivity of insulators varies, a common feature is their polar nature. In the case of nonreactive alkali halides surface binding is dominated by Coulomb interactions between ionic and/or image charges [3]. Therefore, substrates with polar character will have a strong influence on the growth characteristics. In this respect vicinal surfaces are of utmost interest [4] since charge smoothing at step edges due to the Smoluchowski effect and the resulting electrostatic dipole at steps produces a charge-modulated surface [5]. Since regularly stepped or regularly kinked surfaces can be prepared in multiple orientations, the lateral periodicity of this kind of charge modulation can be varied with great flexibility.

In this Letter, we show that the concept of the charge-modulated substrate surface is a powerful tool to control epitaxial 2D growth of ionic insulator films with high perfection. As an exemplary case, we have studied the epitaxial growth of NaCl on Cu(311) by low temperature scanning tunneling microscopy (LT-STM). From a series of detailed STM experiments we determine the location of the chlorine ions to be on top of the intrinsic step edges of the Cu(311) surface. This observation can be explained by a very general model, which takes into account the charge modulation of a stepped surface due to the Smoluchowski effect. The model can be also extended to the growth be-

havior observed on regularly kinked surfaces as shown in the case of Cu(531).

Our experiments were performed with a LT-STM [6] operated at 13 K. We used a chemomechanically polished Cu(311) single crystal which was cleaned by Ne$^+$ sputtering and annealing at 750 K. Bias voltages refer to the sample voltage with respect to the tip. As STM tips we used electrochemically etched tungsten wire. NaCl was evaporated thermally and the deposition/annealing temperature was varied in the range of 400–570 K. In this temperature range Cu surface atoms are mobile. The STM images were taken at 13 K. The Cu(311) substrate consists of alternating monatomic (111) and (100) nanofacets as shown in Fig. 1. The resulting intrinsic steps are aligned with the $[01\bar{1}]$ direction and are separated by 4.23 Å. Along the intrinsic steps the nearest neighbor distance is $a_1 = 2.55$ Å and between neighboring intrinsic steps the atoms are shifted by $a_1/2$ along the step direction.

In a previous study [7] we have shown that the growth of NaCl on Cu(211) induces a dramatic faceting effect of
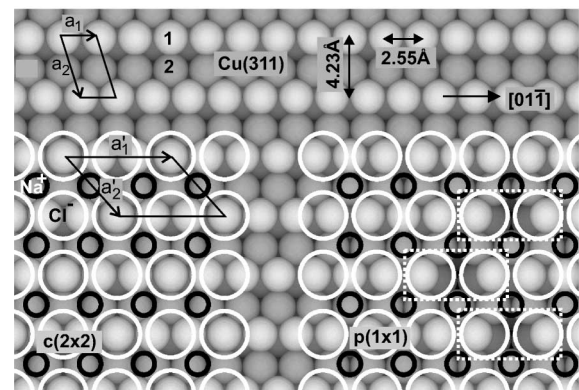

FIG. 1. Sphere model illustrating the Cu(311) surface with alternating monatomic (111) and (100) nanofacets. The (100)-terminated NaCl adlayer is indicated by white circles (Cl) and black circles (Na). The arrangement with respect to the substrate (as deduced from the STM data, cf. Fig. 2) leads to a $c(2 \times 2)$ and $p(1 \times 1)$ superstructure.

the substrate surface. In this case, a periodic array of (111) and (311) facets is formed with NaCl growing selectively on the (311) facets only. So far, the driving force for this restructuring process has remained unclear. To resolve this problem we investigated the growth of NaCl directly on the Cu(311) surface at growth temperatures above 400 K. For coverages below 1 monolayer (ML) flat (100)-oriented NaCl islands of monatomic height could be observed. After increasing the coverage to 1 ML, NaCl islands of up to several hundreds of nanometers width were formed. As a first indication of a strong substrate-adsorbate interaction we find that the second layer growth of NaCl starts only after the first layer is completed. For higher coverages the growth slightly deviates from perfect layer by layer growth and the third and fourth layer grow before the second layer is completed. While NaCl islands in the second or higher layers always have nonpolar edges, the shape of islands in the first layer is determined by defect steps of the substrate showing both nonpolar and polar edges. The STM measurements further indicate that NaCl grows pseudomorphic with its polar $\langle 110 \rangle$ direction parallel to the intrinsic Cu steps. Perpendicular to the intrinsic steps the lattice constant of the NaCl adlayer is adapted to that of the substrate which leads to a stretching of more than 6% with respect to the bulk value of $a_0/\sqrt{2} = 4.0$ Å.

To get further insight into the underlying growth mechanism we will determine in the following the exact lateral position of the NaCl layer relative to the underlying Cu(311) surface. This can be achieved by using atomically resolved STM images of the NaCl film and additional information extracted from single point defects in the film and in the underlying substrate surface. Atomically resolved images were taken at bias voltages between -1.5 V and $+45$ mV while the current was set to values from 5×10^{-11} A up to 2×10^{-8} A. As reported in previous studies on NaCl layers only one of the two ions is observed in the STM images [7,8]. First principles calculations performed for NaCl on Al showed that the observed species is the Cl ion [8]. To begin with the determination of the NaCl/Cu(311) interface geometry the STM image in Fig. 2a is analyzed, which shows a 40×18 Å surface area in the submonolayer regime. To visualize both the corrugation of the uncovered Cu(311) substrate (left) and the 2D NaCl deposit (right) two separate gray scales have been used. As evident, the dashed line which marks columns of Cl ions coincides with the position of intrinsic Cu(311) steps on the left-hand side (the intrinsic steps show up as a faint corrugation and run along the horizontal direction). We hence conclude that the Cl ions are located above the intrinsic steps of the Cu(311) surface while the Na ions are located between the steps. In order to prove experimentally that also in our case the Cl ions are imaged as protrusions, we have performed electron-stimulated desorption experiments with the STM. If we retract the tip by more than 10 Å from the surface and apply a positive sample voltage
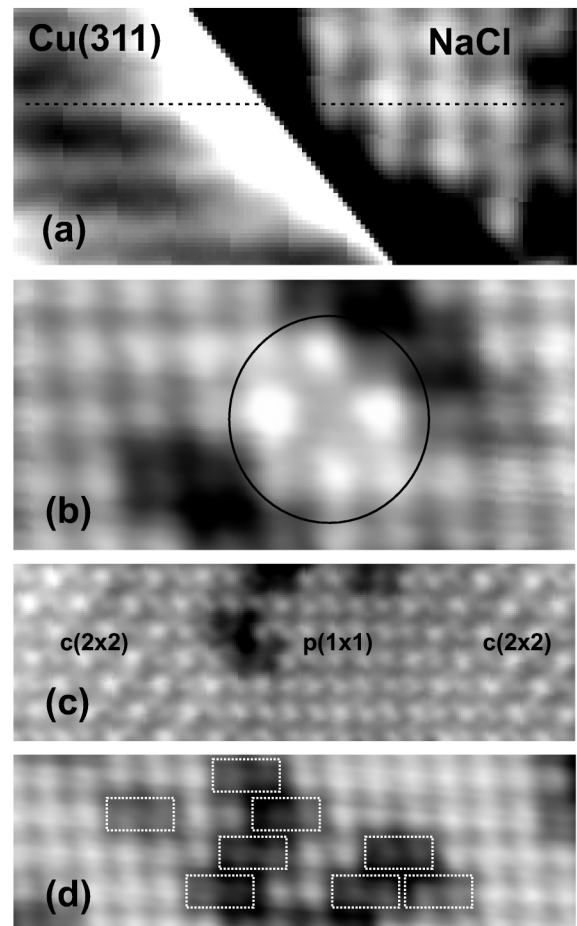

FIG. 2. (a) The Cl ions of a NaCl island (appearing as protrusions, right) are located above the intrinsic steps of the substrate surface (left) as indicated by the dashed line; image size 40×18 Å. (b) Electron bombardment creates single Cl vacancies (circle); size 38×18 Å. (c) A single layer of NaCl shows alternatingly a $c(2 \times 2)$ and a $p(1 \times 1)$ structure; size 88×27 Å. (d) Defects are observed (dotted lines), which consist of two neighboring Cl ions that appear darker due to a missing Cu atom underneath; size 62×19 Å.

>7 V we can desorb single Cl ions from the surface. Electron-stimulated halogen desorption is well known from experiments where electron bombardment creates F centers [9,10]. After extended periods of electron bombardment also metallic Na was observed in the present case. An example of a single Cl vacancy site created by electron bombardment is shown in Fig. 2b, indicated by the circle. As can be seen, this defect appears in the STM image as a missing protrusion which is identified as a missing Cl ion. The neighboring Cl ions appear slightly elevated (note that the other defects appearing as depletions were already present before bombardment and will be discussed later). Hence, our desorption experiments reveal that Cl ions are imaged as protrusions, in agreement with the calculations in Ref. [8].

Next, the position of the NaCl adlayer parallel to the intrinsic steps is determined. We observe two different

reconstructions with a $c(2 \times 2)$ and a $p(1 \times 1)$ unit cell with respect to the NaCl layer, respectively (cf. Fig. 2c). For coverages <1 ML areas with $c(2 \times 2)$ superstructure alternate periodically with areas of $p(1 \times 1)$ structure (Fig. 2c). Between neighboring $c(2 \times 2)$ structures we find a shift of half a unit cell. This indicates a remaining misfit deviation from a 3/2 distance ratio between the Cu-Cu and the Cl-Cl spacing, corresponding to a compression of 2.5% with respect to the bulk value of NaCl. To determine the exact position of the NaCl layer we use single vacancies in the underlying substrate surface (cf. Fig. 2d) which show up as two Cl ions that appear darker than others. These defects occur primarily in areas with $p(1 \times 1)$ symmetry and are always located on the lattice points of a $c(2 \times 2)$ lattice. Again this $c(2 \times 2)$ lattice is shifted by half a unit cell between adjacent $p(1 \times 1)$ domains. This indicates that the defect under consideration is located in the substrate surface layer. The only explanation that meets both the symmetry of the defect itself as well as the symmetry of its lateral position is that a Cu atom is missing, which is illustrated in the right part of Fig. 1: in areas with $p(1 \times 1)$ structure, Cu vacancies are located symmetrically with respect to two Cl ions. It is thus deduced that with respect to the Cu(311) surface the arrangement of the $c(2 \times 2)$ structure is characterized by a mirror plane located at the Cl ions, while for the $p(1 \times 1)$ structure the mirror plane is located at the Na ions. Hence, with respect to the underlying substrate the unit cell of both structures can be written in matrix notation as $\begin{pmatrix} 3 & 0 \\ 1 & 1 \end{pmatrix}$ with a mutual shift of $a_1/4$ parallel to the intrinsic steps. The frequent occurrence of this defect is reasonable since Cu surface atoms are mobile at the growth temperatures employed and Cu mass transport is likely to occur to flatten the interface between the NaCl overlayer and the Cu template.

The above discussed growth characteristics indicate a remarkably strong and localized binding between NaCl and the underlying Cu surface. Previous investigations on the growth of ionic layers on flat metal surfaces [8,11,12] show that the here-observed behavior is unique. Hebenstreit *et al.,* for instance, investigated the room temperature growth of NaCl on Al(111) and Al(100) [the misfit between Al(100) and NaCl is <2%]. In contrast to our observations they reported that NaCl islands could be moved easily on the surface by the STM tip showing that the interaction between NaCl and the Al substrate is weak. In addition the (100)-terminated NaCl islands showed no orientational influence of the substrate and second layer formation took place well before the first layer was completed.

A convincing model of the binding mechanism relevant to our observations has to take into account the inherent properties of a regularly stepped metal surface and the characteristics of an ionic layer which is—in the case of alkali halides—chemically inert. This model has to explain (1) the binding sites of NaCl with respect to the Cu(311) surface, (2) the difference in binding strength for NaCl on Cu(311) and on flat metal surfaces [8,11,12], and (3) the comparably large misfit of 6% perpendicular to the Cu rows—common models as the picture of image charges fail to explain these features without further complicated assumptions. We therefore propose a new model which is based on an inherent attribute of regularly stepped metal surfaces, namely charge modulation due to the Smoluchowski effect. In his pioneering work [5] Smoluchowski discussed two effects responsible for the charge distribution $\rho(\vec{r})$ at metal surfaces. The first effect is the relatively slow drop of negative charge density perpendicular to the surface. The second effect, the so-called smoothing, implies that conduction electrons do not follow entirely the short range corrugation of the surface. While Smoluchowski discussed the influence of surface corrugation on the work function, we will now focus on the lateral charge differences and the corresponding potential differences near the surface. At the highly corrugated Cu(311) surface one expects a positive charge along the intrinsic steps and a negative charge between the steps. The lateral charge modulation thus corresponds to alternating stripes of positive and negative charge with a periodic length given by the intrinsic step separation. The exceptional stability of a NaCl/Cu(311) interface becomes immediately apparent (cf. Fig. 3): columns of Cl (Na) ions align with stripes of opposite charge located at steps (troughs), resulting in a strong electrostatic interaction between NaCl adlayer and Cu(311) substrate. Apparently, the interaction is strong enough to stabilize a stretching of over 6% perpendicular to the Cu rows. We conclude from our model that an energetically favorable interface matching is achieved for a regularly stepped surface with a suitable geometry, if the polar columns of the ionic layer fit with the intrinsic steps of the metal substrate. This directly explains the driving force for the NaCl-induced reorganization effect of Cu(211) reported previously [7].

While detailed theoretical calculations would be necessary to completely understand the binding mechanism, we can roughly estimate the binding energy contribution due to the Smoluchowski smoothing effect. We apply the Coulomb potential as calculated in Ref. [5]: to a first approximation, the unidirectional corrugation of a stepped surface like the fcc (311) surface can be described by a triangle function. Taking further into account surface relaxation [13], we get for reasonable distances of 2–4 Å
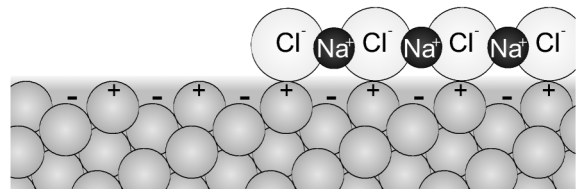

FIG. 3. Basic model of the binding geometry: The Smoluchowski smoothing effect leads to a charge corrugated surface, forming a strong bond with NaCl.
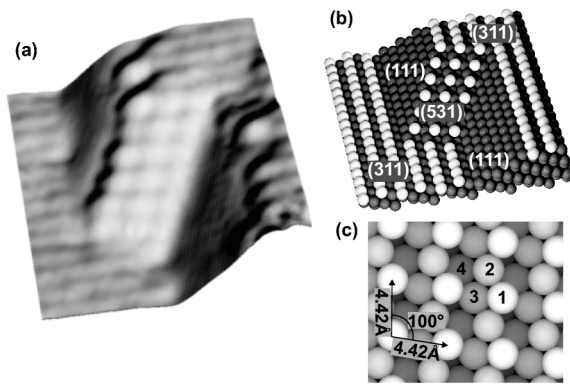
FIG. 4. (a) STM image of a NaCl-covered Cu(531) facet beside NaCl-covered (311) and uncovered (111) facets after evaporation of NaCl on Cu(211). (b) Sphere model of the underlying Cu substrate with the kink atoms of the (531) facet and the intrinsic step atoms of the (311) facets shown in white. (c) Detailed sphere model of the Cu(531) surface.

between the topmost Cu and the NaCl layer a binding energy in the range of a few tenths of eV, which is comparable with the surface energy of a NaCl(100) surface (0.22 eV per ion pair [14]). The essential difference in ionic layer growth on a flat metal surface or on a corrugated surface can now be described as follows: On a flat surface image charges that are responsible for the binding [3] cannot develop in full magnitude because a strong localization of the electrons causes an increase of their kinetic energy $\sim [\nabla \rho(\vec{r})]^2$. On a highly corrugated surface like Cu(311) it is the other way around—by developing image charges the conducting electrons can even decrease their kinetic energy due to a stronger smoothing.

We finally show that the above discussed growth model for ionic layers on regularly stepped metal surfaces can also be applied to understand the growth on regularly kinked surfaces. As we have shown previously [7], NaCl growth on Cu(211) results in substrate surface faceting into (111) and selectively overgrown (311) facets. Important for the following is that additionally a small fraction of the surface is reorganized into NaCl covered (531) facets [15]. Figure 4a shows a representative area of the surface with a small (531) facet. A corresponding model of the (531) facet is shown in Figs. 4b and 4c. From the STM images we see, that the unit cell of the NaCl lattice is identical in size and shape to that of the underlying (531) surface. This results in a strain of more than 10% in both directions. Furthermore, the rows of Cl ions are located on top of the rows of kink atoms. Therefore we propose a structure where each Cl ion is located on top of a kink site atom. Taking into account the large strain in the film, we again need a strong interaction of the film with the underlying substrate. We can explain this effect with the same

model as we have discussed above, if we take into account that similarly to step edge atoms, kink atoms will carry a positive charge due to the Smoluchowski smoothing effect.

To conclude, we have discussed a new binding mechanism for ionic thin films on vicinal metal surfaces. The STM data presented indicate an exceptionally strong interaction between a NaCl film and a Cu(311) surface. From registry information we deduce that the Cl ions are located on top of intrinsic Cu step edges. Taking into account the positive charge accumulation on top of the step edges due to the Smoluchowski smoothing effect, we have developed a general model explaining this newly observed growth behavior. We could also successfully apply this model to the growth of NaCl on the regularly kinked Cu(531) surface. Since the model is based on a very basic phenomenon inherent to stepped and kinked metal surfaces, it will be applicable also to the growth of ionic films on vicinal metal surfaces in general. In particular, it points out the important role of vicinal metal surfaces for the growth of ionic thin films in the future and provides conveniently applicable criteria for the proper choice of substrate/film combinations.

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