Nanostripe Pattern of NaCl Layers on Cu(110)

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A sodium chloride monolayer on a Cu(110) surface gives rise to a highly corrugated periodic nanostripe pattern of the (100) lattice as observed by scanning tunneling microscopy and low-energy electron diffraction. As revealed by density-functional calculations, this pattern is a consequence of the frustration of the overlayer-substrate chemical bonding produced by epitaxial mismatch. The coexistence of regions of strong Cu-Cl covalent and weak nonbonding interactions leads to a chemically induced topographic modulation here realized in a two-dimensional dielectric. The carpetlike growth of the NaCl layer across Cu step edges induces a distinct contrast inversion in the stripe pattern as a result of the change in epitaxial relationship due to the stacking sequence of the (110) Cu layers. It is demonstrated that the competition between local substrate-overlayer and intraoverlayer interactions can support a well-defined heteroepitaxial relationship of a ionic dielectric film and a metal surface, with important consequences for the nanoscale morphology and related properties.

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Thin films of dielectric materials are of interest in micro- and nanotechnological applications, such as electronic, magnetic, optic and spintronic devices, gas sensors, corrosion protection, or heterogeneous catalysis. Ultrathin dielectric layers grown on metal surfaces have been used successfully as support systems for individual atoms and molecules in studies related to monomolecular electronics [1], single-molecule synthesis [2], nanocatalysis [3–6], and atomic-scale technologies in general. The dielectric layer decouples the atomic-molecular species chemically and electronically from the metallic substrate and thereby allows the application of scanning probe microscopy techniques to image individual molecular orbitals [1,6–8]. The atomic-scale imaging of the metal-supported insulating layers in scanning tunneling microscopy (STM) is also possible, due to mixing of electronic states of the metal and insulating film for thicknesses $\leq 1$ nm. A suitable dielectric material for nanoscience purposes is NaCl [1,2,4,7,8], whose popularity is based on its ease of thin film deposition by vacuum sublimation of NaCl molecules from solid sodium chloride, and on the formation of well-defined one to three monolayer (ML) thick islands on low-index surfaces of noble [9–13] and simple metals [14], and semiconductors [15]. The NaCl layers grow in (100) orientation irrespective of the substrate orientation, and this is indicative of a weak overlayer-substrate coupling.

Whereas a NaCl ML on the Cu(100) and Cu(111) surfaces is thus only weakly adsorbed [9,10,12], the interaction with the more corrugated high-index Cu(311) [16,17] and Cu(211) [18] surfaces is much stronger. The Cu(110) surface is an intermediate case between compact and the highly stepped vicinal surfaces. This gives rise to a peculiar morphology of the NaCl ML in the form of a nano stripe pattern, which resembles a Moiré-type interference structure, but which, as we demonstrate, is based on strong geometry relaxations as a result of anisotropic bonding interactions. NaCl on Cu(110) is a prototypical example that reveals the capability of local chemical bonding in a ultrathin-dielectric on metal system to induce both overlayer epitaxy and nanoscopic anisotropic pattern formation in two dimensions, thus creating a novel type of templating substrate.

Moiré patterns of NaCl overlayers have been observed on Ag(100) [11], Cu(100) [12], and Cu(111) [19] surfaces, with the Moiré contrast in STM [11,20] typically interpreted as the superposition of two periodic lattices with a small lattice mismatch and corresponding modulations in charge density [21] and local surface potential [11,21]. In contrast, the stripe pattern observed in STM for NaCl on Cu(110), though related to the misfit between the NaCl(100) and Cu(110) lattices, is the result of site-specific Cu-Cl interactions and the associated strong substrate relaxation, as revealed by density-functional theory (DFT) calculations. The frustration of the Cu-Cl bonding due to the lattice mismatch leads to a compromise between Cl-Cu and Cl-Na interactions that gives rise to a nanoscopic stripe pattern. Moreover, the “carpetlike” growth [22] of the NaCl overlayer over Cu step edges induces an antiphase contrast alternation of the nanostripes running across a step, achieving a further anisotropic confinement along their main axis.

The growth and structure of NaCl overlayers on Cu(110) were studied experimentally using STM and LEED, and theoretically via DFT. The STM images were recorded in a 5 K STM instrument [23], the NaCl overlayers were prepared by thermal evaporation onto clean Cu(110) surfaces at substrate temperatures 300–400 K. Experimental and computational details are given in the Supplemental Material (SM) [24].
Figures 1(a)–1(c) show STM images of NaCl on Cu(110), from sub-ML (a),(b) up to one ML NaCl coverage (c). The monoatomic height NaCl islands nucleate initially at the step edges [Fig. 1(a)], but with increasing coverage the islands grow on both upper and lower terrace areas (b). The NaCl islands display a pattern of bright and dark stripes running perpendicular to the step edges, i.e., in the [110] direction. The step edges of the clean Cu(110) surface are typically wavy and appear fuzzy when imaged at 300 K [Fig. 1(a)], and are significantly modified by the NaCl overlayer growth: in Fig. 1(b), left-hand side, three topographic contrast levels of NaCl can be recognized, separated by a monoatomic Cu step height each. This is recognized from the STM line scan (1) in Fig. 1(e), where an apparent height difference of $-2.5 \text{ Å}$ is measured. Taking into account the corrugation across the stripe pattern of $\sim 1.2 \text{ Å}$ [line scan 2, Fig. 1(e)], this is consistent with a height difference of a monoatomic Cu step of $1.28 \text{ Å}$ between the NaCl stripe levels. Contrast boundaries are thus associated with monoatomic Cu step edges, which display an increased irregularity and occasionally sharp dendritic fingerlike features underneath the NaCl overlayer. This is most apparent in Fig. 1(c), where the Cu(110) surface is covered with a full ML of NaCl: the stripes show an irregular pattern of contrast level changes due to the Cu step edges underneath, which are indicated by the dotted lines; some of the nanostripes appear wavy [see center of Fig. 1(c)], which is presumably caused by local defects in the Cu substrate. Restructuring of Cu steps during NaCl overlayer growth is possible because of the high mobility of Cu surface atoms at temperatures $\geq 300 \text{ K}$ [18].

Figure 1(d) shows a monoatomic NaCl island bordering a Cu step edge. The STM line profiles 3 and 4 [Fig. 1(e)], taken from the bright and dark NaCl stripes to the Cu surface, of $2.1 \pm 0.05 \text{ Å}$ and $0.95 \pm 0.05 \text{ Å}$, respectively, are consistent with the corrugation of the stripe pattern of $\sim 1.2 \text{ Å}$ (line profile 2). Height line profiles 5 and 6 from the NaCl island to the lower Cu terrace of $3.3 \pm 0.05 \text{ Å}$ and $2.1 \pm 0.05 \text{ Å}$, respectively, are internally consistent, because they include the Cu step height of $1.28 \text{ Å}$. Additional characterization of the system work function

![Figure 1](https://example.com/figure1.png)
and field emission resonances as obtained via scanning tunneling spectroscopy can be found in the SM [24].

Significantly, the NaCl stripe pattern changes contrast at the Cu step edges [see Fig. 1(b)]: bright stripes at the upper terrace level become dark stripes at the lower terrace level and vice versa. This contrast inversion is characteristic of the presence of a Cu step edge underneath the NaCl layer (see below). The NaCl stripe pattern is periodic in [001] direction with a period of ~40 Å determined by autocorrelation analysis of STM images and by the spot splitting in the LEED pattern [inset of Fig. 1(c)] (see SM, Fig. S1 [24]).

Figure 2 shows STM images of the NaCl surface (a) and of a NaCl-Cu boundary region (b) with atomic resolution. The NaCl (100) surface orientation along the high symmetry directions of the substrate is indicated by the square unit cell stretched out by the Cl atoms, which are imaged bright [14]. Analysis of the lattice parameters reveals first-neighbor Cl-Cu distances of ~4 Å in [001] direction and 3.83 ± 0.05 Å in [110] direction to be compared with values of 3.96 Å for bulk NaCl and 3.56 Å for a free ML [15] (the interaction with the surface counteracts the shrinking due to reduced dimensionality [25]); this yields a [(3/2)a_{110} × (11/10)a_{001}] overlayer lattice in terms of the Cu(110) unit cell vectors. In Fig. 2(a) the NaCl overlayer “flows” over a Cu step edge—the position of the latter is approximately defined by the dashed line. The smooth contrast variation across the step edge (step down is left) confirms the “carpetlike” NaCl growth mode. The NaCl-Cu(110) boundary region imaged in STM with atomic resolution of both Cl and Cu atoms [Fig. 2(b)] shows that rows of Cl protrusion in the middle of the dark stripes are on-top of Cu [110] rows, whereas on the bright stripe Cl rows are in between Cu rows (see dashed lines). This is opposite to what should be expected on the basis of a (3 × 11) coincidence lattice, suggesting that this is not a simple Moiré-type structure, as confirmed by theoretical analysis.

A [(3/2) × (11/10)] structural model of a NaCl ML on the Cu(110) surface was constructed and locally optimized at the DFT level, with the relaxed unit cell shown in Fig. 3(a). The topmost Cu layer has three rows per unit cell running along the [001] direction, whose average distance from the Cu layer immediately underneath is shown in Fig. 3(b). Note that two Cu rows [Fig. 3(a)] are almost unaffected by the presence of NaCl, with an interlayer distance similar to that of a clean relaxed Cu(110) surface [dashed-dotted black line in Fig. 3(b)]. The Cu atoms in the row, instead, which have Cl atoms directly on top, interact strongly with them and are pulled outwards by about 0.2 Å. The shortest Cl-Cu distances range around 2.5 Å and are indicative of covalent bonding, as proven by charge density analysis in Figs. S3 and S4 (SM). Weak and strong covalent NaCl/Cu bonding thus coexist in this system and shape its structure. The relaxation of the two Cl rows in the [001] direction is shown in Fig. 3(c) and analogously exhibits a rumpling of about 0.9 Å. This modulation in height correspondingly produces an alternation of bright or dark stripes in the simulated STM image—Fig. 3(d)—in excellent agreement with the experimental stripe pattern in Fig. 1. Note that Cl atoms are imaged as bright protrusions [14]. To evaluate the lateral compression in the [110] and [001] directions, average Cl-Cu distances were calculated, projecting their coordinates onto the (x, y) plane, and obtaining 3.84 ± 0.1 Å and 3.98 ± 0.19 Å in the [110] and [001] directions, respectively, in excellent agreement with experiment.

To simulate a NaCl ML covering a step edge, a minimal model consisting of a replicated three-atom-wide step-terrace structure was considered; see Fig. 4(a). The four Cl rows in the unit cell are highlighted with different
colors and their heights along the [001] direction are plotted in Fig. 4(b). These plots clearly show that the corrugation of the Cl row on the upper terrace is shifted in anti-phase with respect to the Cl row on the lower terrace (with the other two rows exhibiting a less pronounced modulation). This is due to the geometrical mismatch of consecutive layers in (110) stacking in the Cu support, which shifts the position of Cl/Cu strong covalent

FIG. 3 (color online). (a) The unit cell of the [(11/10) × (3/2)] NaCl ML structure is illustrated as side views in the [110] and [001] directions. (b) Difference in height between Cu atoms in the second and third top layers as a function of the position along the [001] direction. The two curves correspond to the three distinct rows of Cu atoms and are as in (a). The dotted line shows the value of the top interlayer distance for a relaxed Cu(110) clean surface. (c) The height in the z direction is shown for the two rows of Cl atoms—as in (a)—with respect to the lowest Cl atom. (d) STM image of the ML structure simulated at −1.36 V bias together with its structural top view: the unit cell is highlighted with a dashed rectangle.

FIG. 4 (color online). (a) Structural model of the [(11/10) × (6/4)] structure with a step. (b) Heights of the Cl atoms in the rows along the [001] direction—as in (a). (c) STM image of the structure in (a) simulated at −1.36 V bias, together with (d) the corresponding experimental STM image. In both (c) and (d) the contrast inversion along the step-edge [110] direction is highlighted with a dotted ellipse and an arrow. The unit cell used for the calculation is enclosed by a dashed rectangle.
interactions in such a way that on-top sites on the upper terrace become bridge sites on the lower terrace. In Fig. 4(c), the simulated STM image is shown and the contrast inversion along the [110] direction is highlighted by a dotted ellipse, in good agreement with the experimental STM image in Fig. 4(d), therefore, strongly supporting this simple model of a step. Simulations on NaCl bilayers were also conducted, but found to be unable to rationalize the experimentally observed behavior. The interaction of the NaCl interfacial layer with a 2nd NaCl overlayer in the experimentally observed behavior. The interaction of the NaCl interfacial layer with a 2nd NaCl overlayer in fact competes with that with the metal support, reducing the NaCl interfacial layer with a 2nd NaCl overlayer in the experimentally observed behavior. The interaction of the NaCl interfacial layer with a 2nd NaCl overlayer in fact competes with that with the metal support, reducing substantially (from about 0.9 to 0.3 Å) the topographic corrugation in the [100] direction and the associated STM contrast (see the SM [24]). No indication of an antiphase behavior is found in this case, proving that contrast inversion cannot be due to changes in coverage.

In summary, using STM, scanning tunneling spectroscopy, and LEED characterization and DFT modeling we show that a NaCl ML on Cu(110) exhibits a strong geometrical rumpling of both the NaCl and the topmost Cu layers, due to strong Cl-Cu covalent interactions on selective epitaxial sites coexisting with weak nonbonding interactions, which produces a characteristic nanostripe pattern in both experimental and DFT-predicted STM images. When the NaCl ML carpet flows over a step edge of Cu(110), epitaxial constraints produce a contrast inversion of the stripe pattern, and an associated antiphase shift and longitudinal confinement of proximal stripe regions. This demonstrates that epitaxy of a dielectric film on a metal in the nanolayer limit can be supported in the presence of lattice mismatch and anisotropic overlayer-substrate interaction, which in turn induces nanoscopic pattern formation. The resulting system represents a novel template, which in perspective seems ideally suited for the growth of strongly anisotropic exotic superstructures, such as nanorod checkerboard patterns in combination with high-index vicinal surfaces.

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