PHYSICAL REVIEW B VOLUME 54, NUMBER 11 15 SEPTEMBER 1996-I

Initial growth of insulating overlayers of NaCl on Ge(100) observed by scanning tunneling microscopy with atomic resolution

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(Received 11 March 1996)

The epitaxial growth start of an insulating NaCl film on a Ge(100) surface was directly imaged by scanning tunneling microscopy. Atomic resolution was achieved for islands of the first NaCl double layer with upright-standing NaCl dipoles. The tunneling current is preferentially determined by occupied Ge states extending into the NaCl layer. The results corroborate and extend the earlier proposed ''carpetlike'' growth mode of the NaCl layer over monoatomic Ge steps, even for small NaCl islands submonolayer coverage. [S0163-1829(96)00635-2]

Very thin layers of insulating materials with wide band gaplike oxides or alkali halogenides on semiconductor or metal surfaces are in principle transparent to electron tunneling. Thus scanning tunneling microscopy (STM) should allow us to study their structural and electronic properties. This was demonstrated for a few examples, e.g., for various metal oxide films on metal surfaces.[1] Nevertheless, this possibility has not been exploited to a great extent up to now. Films of more ionic materials such as NaCl, KCl, or CaF_2, which can be epitaxially grown on Ge(100) (Refs. 2 and 3) and Si(111) surfaces,[4] respectively, have been subject to STM investigations only in very few cases, but no atomic resolution was achieved.[5] However, such investigations are currently of great interest for several reasons. First, they can help to gain further insight into the STM imaging process itself. Second, STM measurements can thus help to clarify the heteroepitaxial growth processes of wide-gap materials on conducting surfaces. This is especially important for the start of epitaxy, because other methods, for instance diffraction techniques, may not be appropriate if large enough periodic structures are not yet formed.

Thin NaCl films can be grown epitaxially on Ge(100) with high quality under appropriate conditions due to the small mismatch of only 0.5% of the NaCl (5.63 Å) and Ge (5.66 Å) lattice constants.[2] Up to now NaCl films of a few layers in thickness have mostly been studied by low-energy electron diffraction (LEED) by Henzler and co-workers[2,3] and Schwennike, Schimmelpfennig, and Pfnür.[6] The use of electrons as a probe is possible, as charging does not occur for thin insulating films due to rapid charge neutralization from the substrate by electron tunneling. This also made this system a promising candidate for our STM investigations.

In this work we report STM images for NaCl films up to a thickness of three atomic layers, and we demonstrate that even atomic resolution can be achieved for the initial double layer. In addition, our investigation clarifies two specific questions which have been discussed for this particular system but which are of quite general importance. First, the STM data give direct and additional information about the interesting growth start of NaCl on Ge, for which the formation of a double layer (DL) of upright-standing NaCl dipoles, followed by a layer of NaCl dipoles with their axes parallel to the surface, was suggested.[2] Second, STM allows us to study the behavior of the NaCl overlayer at monoatomic (1.42 Å high) Ge steps directly. A remarkable and unique growth mode (''carpet mode'') which is a consequence of the two different lattice types of Ge and NaCl (diamond/fcc) was derived from high-resolution LEED studies on NaCl films of 3–8-DL thickness.[6] The suggested mechanism is that the epitaxial NaCl layer remains in registry with the Ge substrate on terraces, but avoids strong Coulombic forces by a smooth elastic deformation in the regions near the steps, instead of forming a sharp step. Thus the NaCl layer covers the Ge steps like a ''carpet.'' In the present study we answer the open question of whether this growth mode can also be observed for the initial NaCl double layer or whether an alternative mechanism of strain relief occurs, e.g., a preferential nonwetting of the step sites.

All experiments were performed under UHV. STM scans were recorded in the constant current mode (I_T=0.7–1.8 nA) imaging occupied sample states with a Pt-Ir tip, using tip voltages of $U = 1.5 - 2.7$ V. Remarkably, we were not able to perform STM measurements on NaCl using other tip voltages.[7] Some of the scans were recorded using a 1/f filter (Fig. 2) but no further data processing was performed on the data reported here.

For the clean Ge(100) surface we observed a clear (2×1) LEED pattern typical of the $p(2\times1)$ reconstruction. Upon cooling the phase transition to the $c(2\times4)$ reconstruction was observed at about 200 K as expected.[8] Our STM measurements revealed large, nearly perfect terraces of 300–800-Å width, separated by mainly monoatomic steps. NaCl was evaporated onto the $c(4\times2)$ reconstructed surface at a substrate temperature of about 150 K. For the submonolayer films reported here, integral NaCl coverages of 0.1–0.3 DL were estimated from x-ray photoemission spectroscopy (XPS). For these coverages, LEED showed a (2×1) diffraction pattern in agreement with Ref. 9, and sharp LEED spots from the substrate. No changes of the LEED patterns were detected when the sample was warmed up to room temperature prior to the transfer into the STM chamber.

Figure 1 displays a typical large-area image showing NaCl islands of various sizes, between 30 and 320 Å in diameter, which are mostly one DL high (I_T = 0.7 nA). The island edges run predominantly along the [100] and the [110]

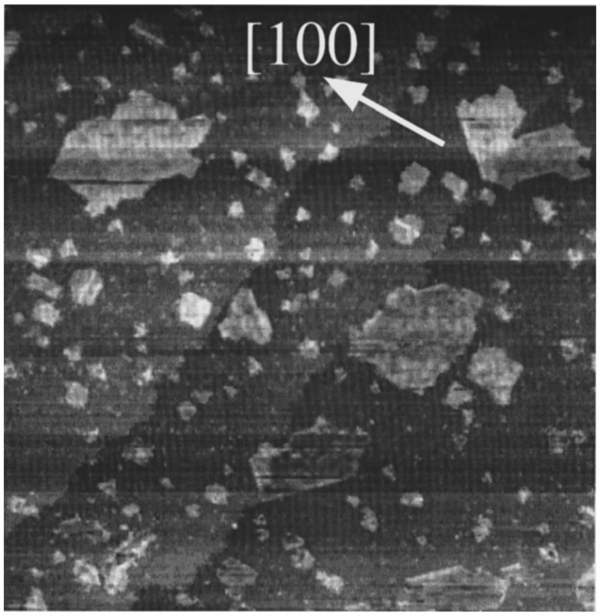

FIG. 1. Large-area STM scan (1130×1130 Å^2) of NaCl on Ge (100) (integral coverage about 0.15 DL). Nearly all NaCl islands have a height of one double layer ($U = 2.7$ V, $I_T = 0.7$ nA).

directions of the Ge substrate, yielding 90° and 135° island corners. We note that *no* preferential nucleation of islands at monoatomic steps is observed, and that some islands even extend across monoatomic Ge steps, for example, the big island in the upper right corner of Fig. 1.

Lateral atomic resolution was obtained for NaCl islands of one DL height for slightly enhanced tunneling currents (I_T=1.8 nA), which force the tip closer to the surface (Fig. 2). A well-resolved square lattice with a lattice constant of 4.0 Å is observed. From this lattice constant we conclude that only one type of ions (Na$^+$ or Ca$^-$) of the NaCl(100) plane is imaged as white protrusions. It is remarkable that the observed height corrugation of 0.5 Å is close to the one observed by atomic force microscopy AFM measurements on NaCl surfaces.[10] For NaCl layers of more than one DL thickness, we could not obtain lateral atomic resolution; vertical resolution was lost for NaCl films of more than two 2-DL thickness.

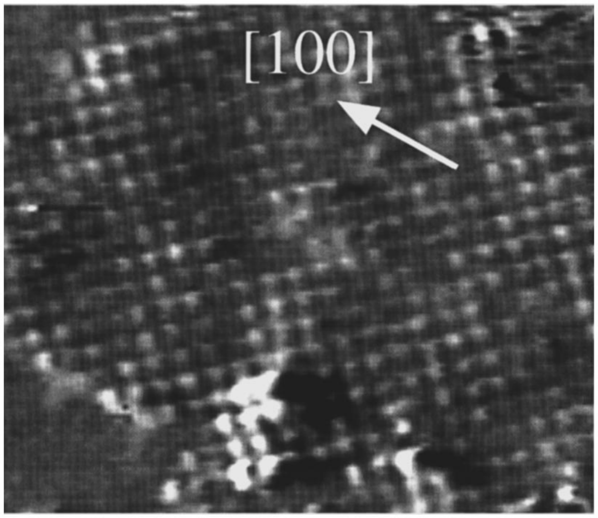

FIG. 2. STM image (98×81 Å^2) with atomic resolution of a NaCl layer of one double layer. The square lattice has a lattice constant of 4.0 Å, and is oriented along the [110] and [-110] directions of the underlying Ge (100) surface ($U = 2.7$ V, $I_T = 1.8$ nA, 1/f filter used).

A very interesting question is which kind of orbitals or states contributes to the tunneling process. We have evidence that the tunneling current is predominantly due to emission from Ge states through the NaCl layer. This evidence stems from UV photoelectron spectroscopy (UPS) investigations on NaCl layers on Ge,[3] and on NaCl crystals.[11] Remarkably, UPS data for one-DL thick NaCl films on Ge do already exhibit features which are characteristic of the two uppermost NaCl valence bands (Δ_1,Δ_5) of the NaCl bulk. This indicates that the band structure of the NaCl double layer, at least for **K** parallel to the surface, is already similar to that of the bulk. In Ref. 3 the NaCl valence-band maximum (VBM) was observed at about 4.2 eV below the Ge VBM, and, in particular, no evidence of the existence of NaCl-derived orbitals was found for lower binding energies. The occupied NaCl states are thus too far below the Fermi energy to contribute efficiently to the tunneling at or below 2.7 eV. Of course, these arguments have to be considered with some caution, since states contributing to the tunneling current and to photoemission, respectively, may differ due to tip-sample interaction and to final-state effects in the photoemission process. Nevertheless, we believe that our suggestion is essentially correct, as the energy difference of the above-mentioned states (1.5 eV) is relatively large. Thus we conclude that tunneling from Ge bulk and/or Ge(100) surface states[12] which extend into the tunneling barrier consisting of the NaCl double layer and vacuum is most likely responsible for the observed current. The contribution of a Ge surface state is also derived from scanning tunneling spectra performed on bare Ge(100). These spectra revealed a strong contribution of a surface state at about 2.6 eV tip voltage with a full width at half maximum of 1 eV,[13] which was assigned to back-bonded Ge orbitals of the topmost layer by comparison with theoretical calculations.[14] Since we used a tip voltage of 2.7 eV, a significant contribution of this state to the tunneling current appears very plausible.

Of course, there must be an additional mechanism which contributes to the lateral contrast in atomically resolved STM images. A resonant tunneling process via occupied NaCl states is very unlikely according to the arguments given above; resonant tunneling through unoccupied NaCl states can be excluded because of the large band gap (9 eV) of NaCl.[11] Also, tunneling via contaminants[3] or defects[2] can be excluded because this would not result in the observed periodicity, and because XPS and other surface techniques showed a clean and perfect NaCl overlayer. We thus suggest that the lateral contrast is due to a perturbation and interaction of the Ge wave function(s) by the NaCl layer, and to a lateral variation of the tunneling barrier, for instance, by a variation of the local work function due to the alternating Na$^+$ Ca$^-$ dipoles. In this case high tunneling probability, i.e., white protrusions in Fig. 2, would correspond to the positions of the Na$^+$ ions.[7] An additional contribution of electrostatic forces to the tunneling contrast, especially when an ‘‘active’’ microtip is formed by a Na$^+$ or Ca$^-$ ion, is also possible.

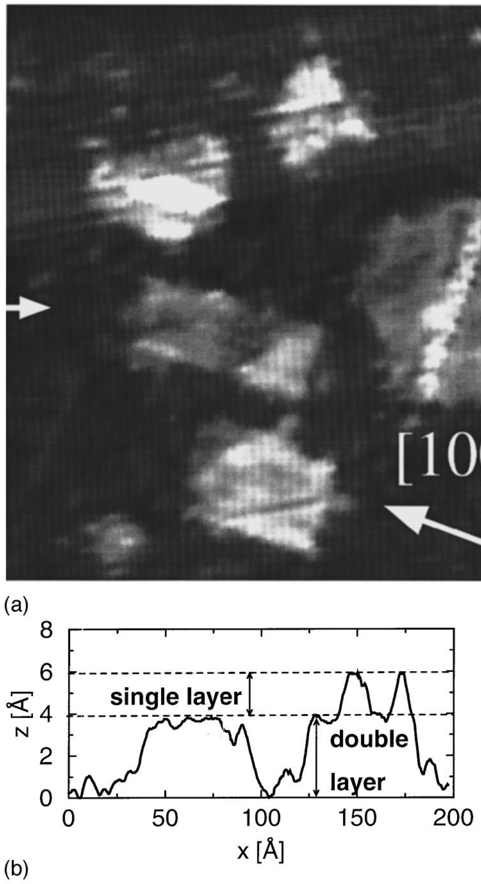

FIG. 3. (a) Close-up (200×200 Å^2) of an interesting area of Fig. 1, and (b) line scan from (a) extracted between the two arrows. For further details, see text.

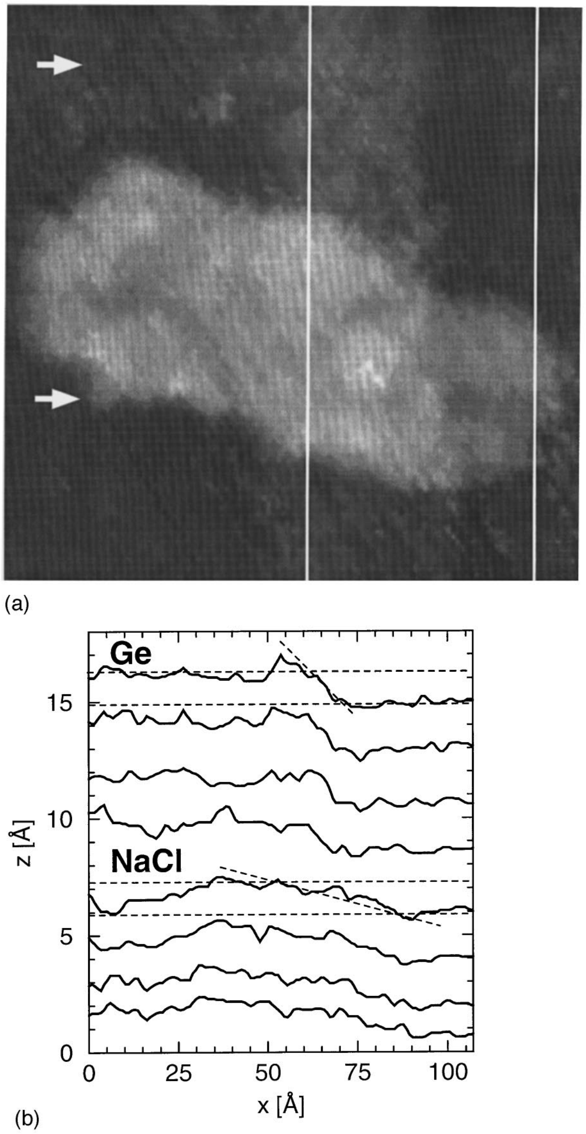

FIG. 4. (a) One NaCl island of double-layer height extending across a monoatomic Ge step (scan area 288 × 288 Å^2, U_T =1.5 V, and I_T =1.8 nA). The figure is rotated by 55° with respect to the original scan direction. (b) 2×4 line scans extracted from (a) between the two vertical white lines to compare the step profiles of the uncovered Ge step [four scans in the region of the upper arrow in (a)] with that of the NaCl overlayer (four scans in the region of the lower arrow).

We now return to further details of the growth process. On some NaCl islands of DL height we observed the nucleation of a second NaCl layer, although the first double layer was far from being complete (*Volmer-Weber*-type growth). This is demonstrated in Fig. 3. Surprisingly the NaCl of the second layer tends to form chainlike ensembles, which are oriented along the [100] or [010] directions [see Fig. 3(a)]. We suggest that these chains result from a growth process which favors the nucleation of antiferroelectrically ordered rows of *flat-lying* NaCl dipoles.[7] This model is supported by line scans like that in Fig. 3(b), from which *nominal* heights of 3.8 ± 0.3 and 2.0 ± 0.3 Å are derived for the first (double) and the second (single) NaCl layers, respectively. The value of 3.8 Å is well above that of 2.8 Å expected for a single NaCl monolayer, leading to the conclusion that the first NaCl layer indeed consists of upright standing NaCl dipoles. However, it is clearly below the ideal DL height of 5.6 Å. This is certainly due to the fact that the tunneling barrier is not only determined by the vacuum between tip and NaCl layer, but also by the NaCl layer itself, which does not provide the density of states between the Fermi energies of the tip and Ge substrate, as discussed above. Thus the tip must be closer to the outermost surface atoms on the NaCl islands by about 1.8 Å in order to keep the current constant. The same behavior is observed for the second NaCl layer, for which the nominal height is again about 0.8 Å smaller than the ideal value of 2.8 Å expected for a layer of flat-lying NaCl dipoles. We note that this observation is fully consistent with the above-suggested tunneling from Ge states, and with the failure of STM imaging of thicker layers. Moreover, we emphasize that the present STM results clearly confirm the double-single-layer growth model of Ref. 2, and exclude the triple-layer growth model of Ref. 9 with an initial layer thickness of about 8.3 Å for the preparation conditions used. Of course the latter suggestion may result from a different evaporation rate and/or a larger first evaporation step which was too large to observe the initial growth of islands of DL thickness. Indeed, our data reveal the onset of nucleation of the second layer before the first double layer is completed.

Finally we address the question of elastic deformation of the first NaCl double layer at Ge steps. For this purpose, we compare STM line scans, taken perpendicular to a monoatomic (1.42 Å) Ge step in a region of a bare Ge(100) surface and in a region where a NaCl island of DL height extends across the step [Fig. 4(a)]. Four line scans are shown in Fig. 4(b) for each case. As expected, the steps are 1.42 Å high in both sets of line scans, as indicated by the horizontal dashed lines. Under the reasonable assumption that the tip was in the same state in all cases, we can clearly derive a much smoother step profile (by about a factor of 5) on the NaCl island than on the bare Ge [Fig. 4(b)]. This smoother NaCl ''step profile'' across a Ge step can also be derived from a comparison with the much steeper step profile of the NaCl single or double layer in Fig. 3(b). From our STM data we thus derive the interesting result that the carpetlike deformation of the NaCl overlayer across the substrate steps is already present for small double-layer islands of NaCl. From energy considerations, the width (Λ) of the deformed (inclined) region is expected to be about proportional to the NaCl thickness.[6] From our experimental data [see, e.g., Fig. 4(b)] we estimate $\lambda \approx$ 25 Å, which would fit well into this trend, since values of $\Lambda = 80$ and 160 Å were derived for NaCl layers of three and eight DL's in thickness, respectively, by Schwennike, Schimmelpfennig, and Pfnür.[6] From this result we may expect that the ''carpet'' mode provides a very efficient mechanism for stress relief of overlayers across substrate inhomogeneities which can also be expected for other heteroepitaxial systems.

In summary, we have demonstrated that STM measurements can be performed on a ultrathin submonolayer film of insulating NaCl on a Ge surface, and that an even atomic resolution is obtained. We could confirm and extend the growth model found earlier with one double layer of upright-standing, alternating NaCl dipoles, and we could also directly observe the carpetlike behavior of the NaCl overlayer at step sites of the substrate. In addition, our experiments gave some insight into the tunneling process which occurs from Ge states through the energy gap of the NaCl interface. We believe that STM measurements like the one reported here can serve to clarify important details of the heteroepitaxial growth of many other wide-band-gap materials.

The authors wish to thank Professor H. Pfnür, Professor M. Henzler, and Professor U. Köhler for stimulating discussions. Financial support by the German government (BMBF Grant No. 01BM 250/2) is gratefully acknowledged. One of us (E. U.) would like to thank the Fond der Chemischen Industrie for financial support.

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