ВІСНИК ЛЬВІВ. УН-ТУ *VISNYK LVIV UNIV.*
Серія фіз. 2009. Вип. 43. С. 249–254 *Ser. Physics. 2009. Is. 43. P. 249–254*

PACS number(s): 68.37.Ef, 68.37.Ps, 68.55.-a

STM AND AFM STUDY OF NaCl LAYERS ON Si(100) SURFACE

P. Mazur, S. Zuber

Institute of Experimental Physics, University of Wrocław
pl. M. Borna 9, 50-204 Wrocław, Poland
e-mail: stefan@ifd.uni.wroc.pl

NaCl thin layers were vapor deposited onto a single crystal of Si(100) and the morphology of the surface was investigated by scanning tunneling and atomic force microscopies under ultrahigh vacuum conditions. The imagings show a considerable influence of thermal processing onto the topography of the sample. Thin layers (less than 1ML) produce irregular clusters which, after annealing, get formed into small crystallites. The salt- and silicon-surface unit cells have the same orientation and the NaCl island borders are oriented along the <110>] and <101> directions, which results in nonpolar edges. After annealing, the sufficiently thick adlayers show their lattice constant such as the bulk material.

Key words: Scanning tunneling microscopy, atomic force microscopy, silicon, alkali halides.

There is a long-standing interest in the growth of ultrathin insulating films on conductive substrates due to their importance in catalysis and electronic device applications. Additionally, the use of thin films circumvents the problem of surface charging and thereby allows one to investigate insulator surfaces by the standard surface-analysis techniques. Very thin layers of insulating materials with wide band gap like oxides or alkali halides 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. Until now, several insulating materials were grown on metal and semiconductor substrates and studied by STM [1]. The misfit between an NaCl film and the unreconstructed Si(100) surface is 4,6%, which is not high enough to prevent epitaxy [2]. Epitaxy was found possible in the systems with even higher misfits (5,5% for BaF_2 on CdTe(100) [3]). Glöckler et al. [4] have observed the epitaxial growth of an NaCl film on a Ge(100) surface (misfit 0,5%) by scanning tunneling microscopy. So the NaCl epitaxy on Si(100) seems to remain an open question.

In this paper we discuss the formation of an interface of two model materials: the insulator NaCl and the semiconductor Si(100) as observed by the STM and AFM methods. We also discuss the thermal effect on the morphology of NaCl layers on the silicon substrate.

The samples were small pieces (7x2x0,4 mm^3 each) cut out from commercial p-type Si(100) wafers (0,01 Ωcm). After chemical cleaning (RCA procedure), the samples were transported to the UHV chamber (base pressure $1x10^{-8}$ Pa) through a load-lock. Atomically clean surfaces exposing a (2x1) pattern of Si(100) were prepared by repeated flashing to 1250°C after the samples had been outgassed at ~600°C for several hours. DC resistive heating was used to heat the samples and the temperature of the sample surface was measured by an optical pyrometer (Minolta Cyclops 153A). The samples were kept at the given heating temperature for 3 s in each case. The heating and cooling rates were due to the thermal inertia of sample.

Thin films of NaCl (of 99,9% purity, Fluka) were formed by vapor deposition from a tantalum crucible. The nominal film thickness was calibrated using a quartz microbalance by measuring the effective thickness by STM of submonolayer covered samples. The STM and AFM images were obtained using the Omicron variable-temperature STM/AFM apparatus. Electrochemically etched tungsten wire was used for the STM scanning tips. Bias voltages refer to the sample voltage with respect to the tip and all STM images were acquired in the constant current mode. The AFM contact mode images were generated with commercial silicon cantilevers (LFMR Nanosensors, force constant ~0,2 N/m). Film preparation and scanning were carried out at room temperature.

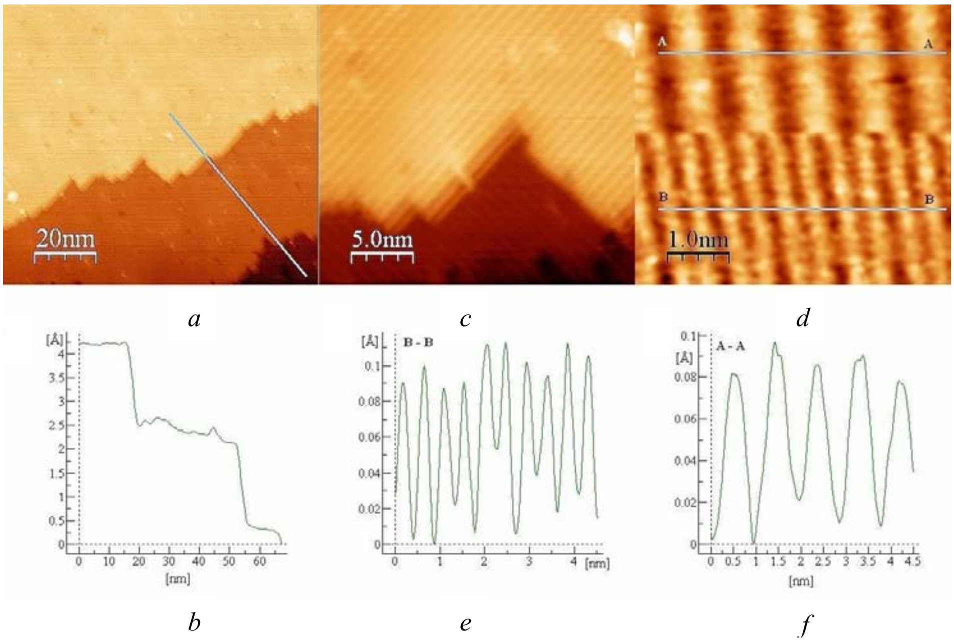
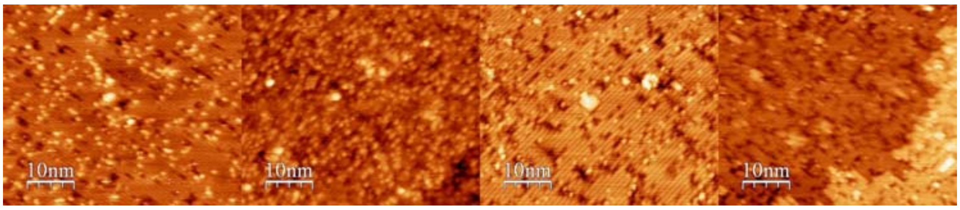


Fig. 1. (*a*) Large area STM scan of clean silicon Si(100) with two domains of 2x1 reconstruction (c) and close-up (*d*) images of filled (bias voltage –1,4 V, 0,1 nA tunneling current) and empty states (1,4 V, 0,1 nA) of the surface. Cross sections along the indicated lines are shown in (*b*), (*e*) and (*f*) respectively

Our STM measurements revealed large, nearly perfect terraces of several hundred Å width (fig. 1, *a*), separated by mainly monoatomic steps (fig. 1, *b*). On the terraces, we observed the typical 2x1 surface reconstruction. On the adjacent terraces separated by the monoatomic step the dimers are rotated by 90° (fig. 1, *c*). Tunneling microscope images of the occupied (sample bias –1,4 V) and unfilled states (sample bias 1,4 V) are shown on lower and upper parts of fig. 1, *d*, respectively. Cross-sectional profiles shown in fig. 1, *e* and 1f along the line A and B indicate that the spacings within a row and between the rows (along the <110> direction) are equal to 3,8 Å and 7,7 Å, respectively.



a *b* *c* *d*

Fig. 2. STM images of 0,2ML (*a*) and 0,8ML (*b*) thick NaCl layers deposited at room temperature and after annealing at 550K (*c*) and(*d*) respectively

Examples of topography images of the as-deposited NaCl layers of 0,2 ML and 0,8 ML thickness are shown in fig. 2, *a* and 2, *b*. For both coverages, isolated clusters are observed on the reconstructed surface (2x1) of the substrate. The clusters are approximately 2 Å high and have a size of about 25 Å^2, which corresponds to agglomerates composed of several molecules. The cluster size does not increase with layer thickness and the clusters still constitute a randomly oriented film. No preferential nucleation of islands at the monoatomic steps is observed, and some islands even extend across Si monoatomic steps. After a annealing at elevated temperature (about 550 K) the layers reveal changes in topography. NaCl clusters merge into large islands in the form of cubicoids with edges parallel to the direction <110>, to simultaneously uncover the substrate showing the (2x1) reconstruction (see fig. 2, *c*, *d*).

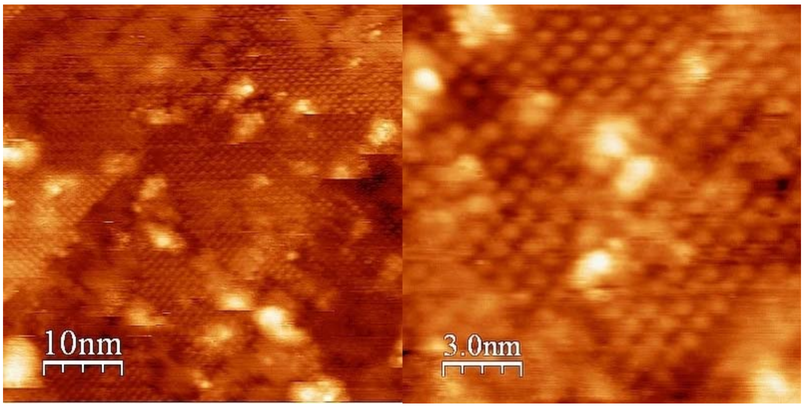
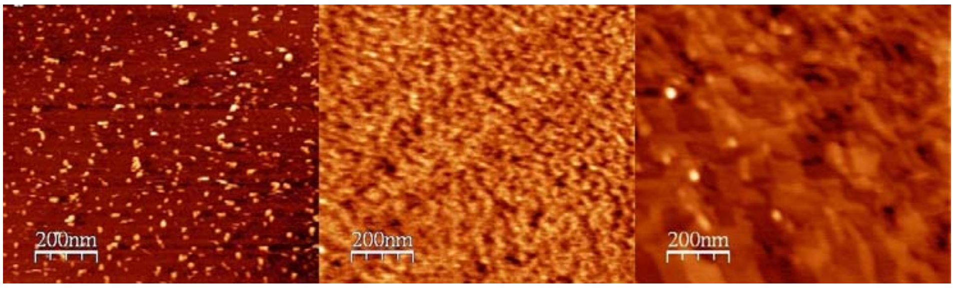


Fig. 3. Si(100)-(2x2) pseudo-reconstruction indced by NaCl layer annealed at about 700K

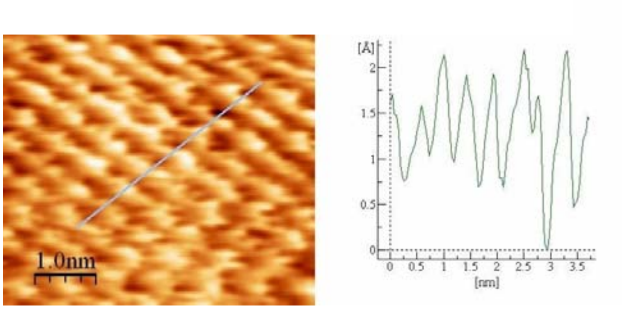
The NaCl islands, however, could not be imaged with the lateral resolution. Heating at about 700 K results in the appearance of (2x2) structures in the STM images (fig. 3) apart from small regions of the unchanged reconstruction (2x1). Also diffuse objects are seen, which likely come from imaging the three-dimensional (3D) islands of NaCl of fainting transparency. It is known [4] that only one type of the ions (Na or Cl) is responsible for the creation of the bright protrusions. This may account for the unexpected occurrence of the (2x2) pseudo-reconstruction. The minimum distance between neighboring bright protrusions is about 8 Å. Hence the distance between the adsorbed ions Na and Cl should be about 4 Å whereas the space in an NaCl molecule is lesser (about 2,86 Å). This means that the model of flat-lying NaCl admolecules on the Si(100) is doubtful. We believe that the initial phase of growth consists of upright standing NaCl dipoles. The electrostatic interaction makes the dipole moments of adjacent Si atoms have the opposite sense in the <100> direction (i.e. the outer Na and Cl ions are alternately arranged). The electric field due to the dipole moments interferes with the applied field of tip-sample. Sites of the algebraic sum of these field strengths are STM imaged as bright protrusions of the topography.



a *b* *c*

Fig. 4. Contact mode AFM images of 5ML (*a*) and 20ML (*b*) thick NaCl films. (*c*) image of layer (*b*) heated to 500K

For much thicker adlayers of several ML, it was not possible to obtain any STM images and the topographic measurement was carried out by AFM in the contact mode. Fig. 4, *a* shows an NaCl adlayer of the thickness 5 ML. Terraces of the substrate are not visible, the islands are uniformly distributed with their size ranging from 50 to 500 nm^2. Increasing the thickness to about 20 ML makes the substrate surface be completely covered with, however, neither clearly resolved islands of the adsorbate nor the crystalline structure of interest visible (fig. 4, *b*). Heating this adlayer at about 500 K leads to formation of NaCl crystallites (fig. 4, *c*).



a *b*

Fig. 5. AFM (*a*) and cross section (*b*) images of thick salt layer after annealing at 500K

Such prepared surface exhibits a quasi-atomic resolution (fig. 5, *a*). The atomic rows (fig. 5, *b*) are spaced by about 4 Å which is close to the Cl-interionic spacing in the direction [110] of NaCl crystal. This means that an adlayer of such a thickness has the structure typical of bulk material.

---

1. *PivettaM., Patthey F., Stengel M.* et al. Local work function Moiré pattern on ultrathin ionic films: NaCl on Ag(100) // Phys. Rev. B. 2005. Vol. 72. 115404 p.
2. *Hebenstreit W., Schmid M., RedingerJ.* et al. Bulk Terminated NaCl(111) on Aluminum: A Polar Surface of an Ionic Crystal? // Phys. Rev. Lett. 2000. Vol. 85. 5376 p.
3. *Repp J., Fölsch S., Meyer G.* et al. Ionic Films on Vicinal Metal Surfaces: Enhanced Binding due to Charge Modulation // Phys Rev. Lett. 2001. Vol. 86. 252 p.
4. *Hebenstreit W., Redinger J., Horozova Z.* et al. Atomic resolution by STM on ultra-thin films of alkali halides: experiment and local density calculations // Surf. Sci. 1999. Vol. 424. L321 p.
5. *Fölsch S., Helms A., Riemann A.* et al. Nanoscale surface patterning by adsorbate-induced faceting and selective growth: NaCl on Cu(211) // Surf. Sci. 2002. Vol. 497. 113 p.
6. *Saiki K.* Fabrication and characterization of epitaxial films of ionic materials // Appl. Surf. Sci. 1997. Vol. 9. P. 113–114.
7. *Farrow R.F.C., Sullivan P.W., Williams G.M.* et al. MBE-grown fluoride films: A new class of epitaxial dielectrics // J.Vac. Sci. Technol. 1981. Vol. 19. 415 p.
8. *Glöckler K., Sokolowski M., Soukopp A.* et al. Initial growth of insulating overlayers of NaCl on Ge(100) observed by scanning tunneling microscopy with atomic resolution // Phys.Rev. B. 1996. Vol. 54. 7705 p.

ДОСЛІДЖЕННЯ ШАРІВ NaCl НА ПОВЕРХНІ Si(100) МЕТОДАМИ STM ТА AFM

П. Мазур, С. Зубер

Інститут експериментальної фізики, Університет Вроцлава
пл. М. Борна 9, 50-204 Вроцлав, Республіка Польща

Досліджено морфологію поверхні тонких шарів NaCl, розміщених на монокристалі Si(100), методами сканувальної тунельної та атомно-силової мікроскопії в умовах надвисокого вакууму. Показано, що теплова обробка суттєво впливає на топографію зразків. Утворені кластерами тонкі шари після відпалу формуються в маленькі кристаліти. Після відпалу достатньо товсті шари NaCl характеризуються параметром комірки, властивим для об'ємних матеріалів.

Ключові слова: сканувальна тунельна мікроскопія, атомно-силова мікроскопія, кремній, лужні галогени.

ИССЛЕДОВАНИЕ СЛОЕВ NaCl НА ПОВЕРХНОСТИ Si(100) МЕТОДАМИ STM И AFM

П. Мазур, С. Зубер

Институт экспериментальной физики, Университет Вроцлава
пл. М. Борна 9, 50-204 Вроцлав, Республика Польша

Исследовано морфологию поверхности тонких слоев NaCl, размещенных на монокристалле Si(100), методами сканирующей туннельной и атомно-силовой микроскопии в условиях сверхвысокого вакуума. Показано, что тепловая обработка существенно влияет на топографию образцов. Образованные кластерами тонкие слои после отжига формируются в маленькие кристаллиты. После отжига достаточно толстые слои NaCl характеризуются параметром ячейки, который свойственен для объемных материалов.

Ключевые слова: сканирующая туннельная микроскопия, атомно-силовая микроскопия, кремний, щелочные галогены.

Стаття надійшла до редколегії 04.06.2008
Прийнята до друку 25.03.2009