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To cite this version:
Igor Beinik, Clemens Barth, Margrit Hanbücken, Laurence Masson. KCl ultra-thin films with polar and non-polar surfaces grown on Si(111)7x7. Scientific Reports, 2015, 5 (8223), 10.1038/srep08223 . hal-01226812

HAL Id: hal-01226812
https://amu.hal.science/hal-01226812
Submitted on 10 Nov 2015

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KCl ultra-thin films with polar and non-polar surfaces grown on Si(111)7 × 7

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The growth of ultra-thin KCl films on the Si(111)7 × 7 reconstructed surface has been investigated as a function of KCl coverage and substrate temperature. The structure and morphology of the films were characterized by means of scanning tunneling microscopy (STM) under ultra-high vacuum (UHV) conditions. Detailed analysis of the atomically resolved STM images of islands grown at room and high temperatures (400 K–430 K) revealed the presence of KCl(001) and KCl(111) islands with the ratio between both structures depending on the growth temperature. At room temperature, the growth of the first layer, which covers the initial Si(111)7 × 7 surface, contains double/triple atomic layers of KCl(001) with a small fraction of KCl(111) islands. The high temperature growth promotes the appearance of large KCl(111) areas, which are built up by three atomic layers. At room and high temperatures, flat and atomically well-defined ultra-thin KCl films can be grown on the Si(111)7 × 7 substrate. The formation of the above mentioned (111) polar films is interpreted as a result of the thermally activated dissociative adsorption of KCl molecules on Si(111)7 × 7, which produces an excess of potassium on the Si surface.

The growth of thin alkali halide films on metals1–7 and, in a lesser extent, on semiconductor substrates8–10 has been the subject of many studies for the last two decades. Apart from a fundamental interest in such films, an emerging topic concerns the formation of supramolecular11,12,14 and covalent15 assemblies on such substrates for rising applications in organic electronics or molecule-based sensing devices since it has been recently shown that ultrathin NaCl layers grown on metal surfaces can be beneficially used for the efficient electronic decoupling of adsorbates from the conductive substrates16–18.

For this purpose, the formation of atomically well-defined flat layers with a low density of defects is of prime importance. In most of the cases, the initial growth stage of alkali-halide thin films begins with the nucleation of (001) islands with a non-polar surface termination (see Refs. 12 and 13 for a description of polar and non-polar surfaces of alkali halide crystals). In this respect it is interesting to consider the possibility to obtain a polar surface since this can be important for both technical applications and fundamental research. The polar surfaces, however, possess uncompensated net dipole moments perpendicular to the surface, which leads to an increase of the surface free energy making them unstable13,19. The vast majority of studies of alkali-halide thin films grown on metals20–27 and semiconductors8–10 confirms this fact. However, if some specific requirements are fulfilled, NaCl(111) islands with the uppermost layer corresponding to a polar surface can also be grown, like on Al(111) and Al(001)2. In particular, it has been shown that NaCl(111) islands can be grown by adsorption of Na and Cl on such substrates with an excess of Na at the interface2. To our knowledge, no other experiments about the formation of (111) alkali halide thin films have been reported so far.

In the present study, the growth of KCl thin films on Si(111)7 × 7 was studied by means of STM under UHV conditions. We demonstrate that the polar (111) surface can be obtained for the KCl films grown at 430 K. We suggest that the formation of the (111) areas occurs as a consequence of the thermally activated dissociation of KCl on Si(111)7 × 7, which produces an excess of potassium on the surface. Moreover, we show that flat and atomically well-defined ultra-thin KCl layers can be epitaxially grown on Si(111)7 × 7.

Results

In the early stages of KCl growth at RT, the formation of an almost complete amorphous adlayer with a corrugation of ~1 Å is observed, apart from small regions still showing the Si(111) substrate (see Fig. 1(a), (b) and Supplementary Fig. S1 online). The adlayer is similar to the one observed by Chung et al.10 for the NaCl/
Figure 1 | STM topography images of the Si(111) 7 × 7 surface in the early stages of KCl growth at room temperature: (a) growth of 2 ML(001) and 3 ML(001) square shaped KCl islands; (b) height profile along the transverse red line in (a). The red lower bar indicates the position of the silicon substrate.

Figure 2 | STM topography images of the Si(111) 7 × 7 surface after the deposition of KCl at room temperature: (a) growth of 2 ML(001) and 3 ML(001) KCl islands with polygonal shape; (b) and (c) completion of the first and second layers, resulting in a 3 ML(001) (b) and 5 ML(001) ultra-thin KCl film (c), respectively. (d) ball model of the first and second KCl(001) layers.

A subsequent increase of the deposited KCl amount led to a development of the existing 2 ML(001) and 3 ML(001) islands, which exhibit more and more a polygonal shape (see Fig. 2(a)). The edges of the polygonal shaped islands exhibit in most cases angles of 90°, which can deviate due to a coalescence of islands or due to edges that have a high kink density leading to edge orientations other than <001>.

Interestingly, we observed that in many cases the tunneling current from KCl islands was modulated by the 7 × 7 structure lying underneath, i.e. we could still observe the 3-fold symmetry structure originating from the Si(111) 7 × 7 reconstructed surface through the KCl islands (see Supplementary Fig. S2(a) online). This strongly indicates that the 7 × 7 reconstruction of the underlying Si(111) surface is unaltered and still intact, similar to the herringbone geometry of the Au(111) surface covered with NaCl islands.11,12

An atomically resolved STM image of a polygonal 2 ML(001) KCl island is shown in Fig. 3(a). The lattice parameter determined from the 2D FFT of this image (see Fig. 3(b)) equals (4.6 ± 0.3) Å in good agreement with the sub-cell dimension of either the anions or cations (aKCl/√2 = 4.45 Å). The angle between the surface vectors was determined to be 90° ± 11°, with the error resulting mainly from the drift of the STM imaging.

Up to the saturation of the Si(111) 7 × 7 surface, the growth of the first layer proceeds in a 2 ML(001)/3 ML(001) growth mode as already reported for the initial growth of NaCl(001) overlayers on Ge(001).5 Prior to the growth of the second layer, an almost complete 3 ML(001) flat layer can be obtained as shown in Fig. 2(b), with an apparent height of ~6 Å (see also Fig. 2(d)). A simple analysis of the high-resolution STM images (as shown in Fig. 4(a)) and the corresponding Fourier transform (see Fig. 4(b)) recorded on the first complete layer confirms that the layer is still in its (001) epitaxy. However, a perfect (001) lattice can only be found in small regions whereas the lattices of the regions differ in their lateral orientations - in other words the film is polycrystalline. A rather high density of defects can be observed,
which is a signature that the small initial KCl islands (Fig. 2(a) and (b)) do not all have the same orientation on the Si(111) surface before the films gets closed - when the film closes dislocations and grain boundaries are formed similar to the case of NaCl on Ag(001).

During the growth of the first and second layers, we found occasionally some small areas corresponding to disruptions of these layers, where triangular shaped islands can be observed. One of such islands and the corresponding 2D FFT are presented in Fig. 3(c) and 3(d). The structure possesses a six-fold symmetry with a lattice constant of (4.6 ± 0.3) Å which agrees well with the lattice parameter of the KCl(111) plane (a_{KCl} / \sqrt{2} = 4.45 Å). The triangular islands can thus unambiguously be assigned to KCl(111) islands.

To investigate the growth of the KCl thin films at high temperature and to promote the formation of large areas of KCl(111) layers, we performed depositions of KCl at 400 K and 430 K on clean Si(111) surfaces. The amorphous layer described at RT was not observed at elevated growth temperature. Fig. 5(a) presents islands grown at 400 K with clearly two different structures (see areas A and B in Fig. 5(a)). Both structures have the same apparent height of (4.0 ± 0.5) Å within the error bars. The first structure A can clearly be associated with that of small square shaped islands and thus assigned to 2 ML(001) KCl islands. We also observe the presence of small square shaped islands with an apparent height of (6.0 ± 0.5) Å assigned to 3 ML(001) islands and 3 ML(001) patches at the edges of islands (see Fig. 5(a) and (b)). The analysis of the atomically resolved STM images and the corresponding 2D FFT (see Fig. 5(b) to (d)) unambiguously reveal that the second structure B possesses a six-fold symmetry, yielding 60° and 120° islands corners and a lattice constant close to 4.5 Å, which corresponds to the lattice of either the Cl or Na ions in the (111) plane. Thus, we assign the second structure B to KCl(111). Note that we define a monolayer (1 ML(111)) as an atomic layer that contains either only potassium or chlorine atoms (Fig. 5(f)). The height of the ML(111) is then the distance between two atomic layers (a_{KCl} / 2\sqrt{3} = 1.82 Å), and multiple layers will be an integer multiple of the latter height. The apparent height of the B islands is well above the physical thickness of 2 ML(111) KCl layers (3.64 Å) and lower than the geometrical 3 ML(111) height of 5.46 Å, suggesting that the KCl(111) areas consist of 3 ML(111). We note that formation of similar alkali halide structures have been observed before, consisting of 3 ML NaCl(111) islands grown on Al(111) and Al(001). Interestingly, the 7 × 7 structure can be distinguished in STM images underneath the KCl(111) islands, which strongly indicates that the growth of the (111) KCl structure does not alter the 7 × 7 reconstruction (see Supplementary Fig. S2(b) online). For all KCl(111) islands, the surface directions of the islands are the same as for the Si(111) surface, e.g. [110]_{KCl(111)} and [110]_{Si(111)} are parallel.

A higher deposition temperature (430 K) favors the growth of very large KCl(111) areas on the Si(111) surface as shown by high resolution STM images (see Fig. 5(e) and Supplementary Fig. S3 and S4 online) and supported by 2D FFT of such areas. In agreement with the above discussion, we assign these KCl(111) areas to 3 ML(111) (see Fig. 5(f)). Apart from the very large (111) areas we observe, however, also small areas where the film has a higher thickness, with an apparent height difference of ~2 Å above the (111) layer (see Supplementary Fig. S3 and S4).
in the case of a Knudsen cell, $K_2Cl$ the evaporated species drastically depends on the evaporation source.

**Discussion**

We will focus in the following on the mechanisms which could explain the growth of (111) areas at high temperature. It has been reported that the formation of NaCl(111) islands is possible on Al(111) and Al(001) by conversion of NaCl(001) to NaCl(111) upon Na post-deposition onto a stoichiometric NaCl(001) film with the sample kept at RT. The obtained islands possess Na-Cl-Na triple layer structure. In our experiments, the apparent height of the (111) layers is consistent with the thickness of a 3 ML(111) layer. We thus assume that such layers have a K-Cl-K structure, in analogy with the model reported by Hebenstreit et al. The formation of KCl(111) areas in our experiments would thus result from an excess of potassium on our surfaces.

Fig. 5(e) and Supplementary Fig. S3 and S4 online). Such regions are either square shaped or have a polygonal shape. Even though the atomic structure of these islands appears less organized than in the RT case, 2D FFT confirms that these higher islands correspond to KCl(001). In agreement with our observations at RT and 400 K, we assigned these higher islands to 3 ML(001) islands. It can be further noted that small atomically poorly organized areas have been also formed (denoted mixed area in Fig. 5(e)), which could correspond to mixed (111) and (001) zones.

**Conclusions**

In conclusion, we have conducted an in-situ characterization of the atomic structure and morphology of KCl films grown on Si(111)$^7 \times 7$ by means of STM. Our work shows that the stacking, termination and consequently the polarity of such films can be tuned by adjusting the growth temperature - an approach that can most likely be extrapolated also to other alkali halide thin films on Si(111)$^7 \times 7$. Such KCl films with controllable polarity are suitable for the growth of organic molecules which are electronically decoupled from the conductive Si(111) substrate. Furthermore, these ultra-thin layers can be successfully employed for the growth and the subsequent removal of metal nanoparticles from the Si substrate by dissolution of the KCl layer in liquid as it will be shown in a forthcoming paper.

**Methods**

Ultra-thin KCl films have been grown under UHV (base pressure $3 \times 10^{-10}$ mbar) on n-doped Si(111) substrates misoriented by $1^\circ$ towards the [112] direction. The $7 \times 7$ reconstructed (111) surface was obtained using a standard heating procedure.
described elsewhere. KCl powder was evaporated from a Knudsen cell with a molybdenum crucible using a commercial electron beam Omicron EFM 37 evaporator. KCl depositions were performed with the sample kept at room (RT) and high temperatures (400 K–430 K) with a constant deposition rate of ~2 ML/min.

In the case of KCl(001), one monolayer of KCl(001) (ML(111)) is defined to be one atomic layer that contains potassium and chlorine atoms. In this case the monolayer is stoichiometric, and the height of the ML(111) is the distance between two atomic layers \(a_{\text{KCl}} / \sqrt{2} \times a_{\text{KCl}} \approx 6.29 \text{ Å} \) with multiple layers being an integer multiple of the latter height. In the case of KCl(111), we define for simplicity reasons a monolayer as an atomic layer that contains either only potassium or chlorine atoms. Note that in this case, a monolayer is certainly not stoichiometric. The height of the ML(111) is then the distance between two atomic layers \(a_{\text{KCl}} / 2 \sqrt{3} \) and multiple layers will be an integer multiple of the latter height.

For the depositions at high temperatures, resistive DC heating was applied to the sample. The temperature readings were calibrated using an IR pyrometer for the spot where the STM measurements were performed. The accuracy of the temperature measurement is ±20 K. The samples were examined in-situ by an OmicronTM STM operating in the constant current mode using chemically etched tungsten tips. The optimal sample bias was in the range of −1.7 V to −2.1 V, whereas the setpoint was below −300 mV. We would like to mention that the imaging was only possible with negative sample bias voltages. Atomically resolved STM images were analyzed in terms of two-dimensional (2D) fast Fourier transforms (FFT) using the plane-fitted STM data processed in Gwyddion.

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