

Initial stages of the growth of CaF₂ on Cu(111) visualized by STM

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The epitaxial growth of insulators on semiconductor surfaces is a topic that has attracted widespread interest in recent years. In particular, a strong effort has been devoted to study the growth of CaF₂ on Si(111) and (100) surfaces [1] because of the potential interest for novel Si-based quantum effect devices, such as Resonant Tunnelling Diodes operating at 300 K [2]. Much less is known concerning the epitaxial growth of insulators on metal surfaces. We briefly report here on the early stages of the growth of CaF₂ on Cu(111), a highly mismatched system (the lattice parameters are 0.543 nm versus 0.361 nm) as visualized by STM.

Deposition of 0.4 TL at 300 K produces initially the decoration of the steps of the substrate from the lower side. Once that the steps are saturated, islands irregular in shape and 1.2-1.9 nm in height (4-6 TL) nucleate at the terraces as shown in Figure 1. The density of islands on the terraces is $3 \times 10^{10} \text{ cm}^{-2}$. The Cu(111) lattice can be atomically resolved in the patches of the surface between the islands, showing that, unlike Si(111) [1, 2], there is no CaF wetting layer with the Ca atoms bonded to Si, onto which the following molecules can grow epitaxially. Most of the CaF₂ molecules stay intact as they contact the Cu(111) surface and diffuse on it to nucleate and form the observed islands. There are, however, indications (not shown) of a very limited reaction between the Cu(111) substrate and the CaF₂ molecules in the form of some dark, triangular shaped defects of unknown nature, but not detected in the clean Cu(111) surface [3]. It is important to note that in order to decorate the steps of the Cu substrate, the diffusion length of CaF₂ molecules at 300 K has to be larger than the average distance between steps, i.e. 100 nm. Fig. 2 shows that increasing the amount of CaF₂ evaporated at 300 K to 1.7 TL simply increases the density of islands nucleated on the terraces to $1.2 \times 10^{11} \text{ cm}^{-2}$, but not their height, which is still 4-6 TL. The islands show ramified or dendritic shapes, indicating that the diffusion along the steps at 300 K is not fast enough to produce islands with compact shapes. After deposition at 550 K the steps are still decorated but the islands at the terraces have now a clearer triangular shape. Atomic resolution images between the islands show the, mostly undisturbed, lattice of Cu(111). The dark triangular defects associated to CaF₂ deposition are still clearly visible. The standing waves produced by quantum interference of the electrons of the surface state of Cu(111) scattered off defects and impurities, are detected even at 300 K. This indicates that these defects act as strong scattering centres for the 2D surface electron gas. Attempts to image the islands simultaneously with the substrate at reduced sample voltage of the order of 2 V fail and the islands are, in fact, swept away by the tip during scanning. The islands can only be imaged with tunnelling voltages of the order of +6 V, which indicates that the gap of insulating CaF₂ (12.1 eV in the bulk) must be almost completely developed in islands only 1.4-1.8 nm (4 to 6 TL) high. Fig. 3 shows that after deposition of 0.4 TL with the substrate at 750 K the islands do not decorate preferentially the steps anymore. In fact, they appear to nucleate randomly at the surface without special preference for the steps of the substrate. The island density is $5.4 \times 10^{10} \text{ cm}^{-2}$. The CaF₂ molecules can easily reach the steps, since they diffuse certainly a larger distance at 750 K than at 300 K, but, however, they are not trapped there. Thus, the energy of the CaF₂-Cu bond must be small enough, so that, even the enhanced atomic coordination at the steps is not able to provide a preferential nucleation site to trap them there. A weak CaF₂-Cu interaction is also suggested by the fact mentioned above that the islands can easily be removed from the surface by scanning with the STM tip at sample voltages of the order of 2 V. Figure 4 demonstrates that the shape of the islands changes strongly with increasing

temperature from dendritic (compare to Figure 2) to triangular with two orientations. The top surface of the islands is atomically flat. The LEED pattern observed shows a superposition of the diffraction spots reflecting the unit cells of $\text{CaF}_2(111)$ and $\text{Cu}(111)$. This indicates that the islands are (111) oriented and strain relaxed. This is also suggested by the fact that most of the observed island heights are integral multiples of the F-Ca-F trilayer height, i.e. 0.315 nm.

References:

- [1] L.J. Schowalter and R.W. Fathauer *Crit. Rev. Sol. State Mat. Sci.* 15, 367 (1989).
 [2] A.I. Yakimov *et al* , *Appl. Phys. Lett.* 81, 499 (2002).
 [3] F. Calleja *et al* , *Surface Sci.* submitted.

Figures:

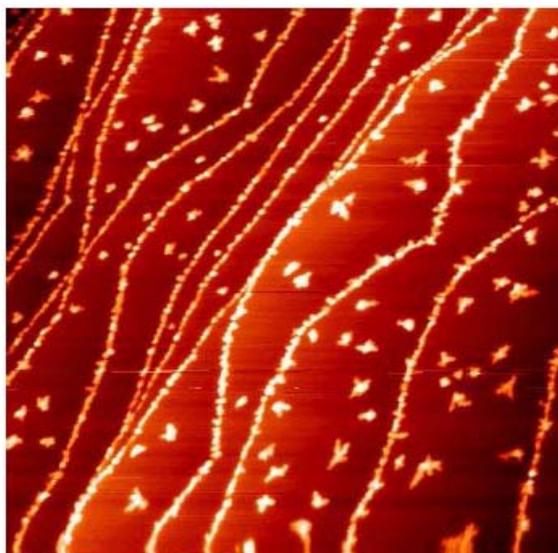


Fig. 1. 500 nm x 500 nm STM image recorded after 15 sec deposition of CaF_2 on $\text{Cu}(111)$ at 300 K. The sample voltage is +6V

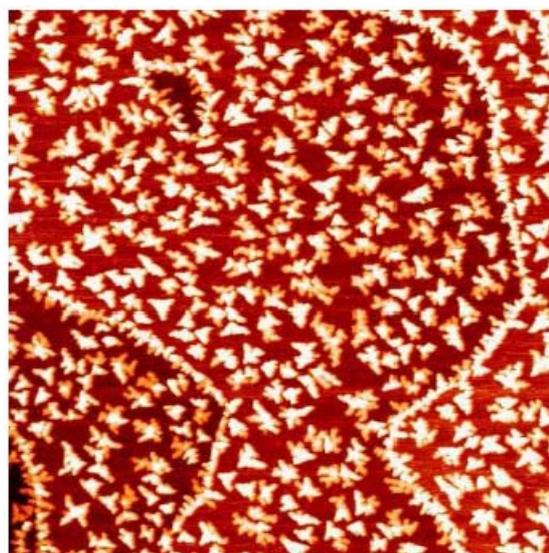


Fig. 2. 500 nm x 500 nm STM image after 70 s deposition of CaF_2 on $\text{Cu}(111)$ at 300 K.

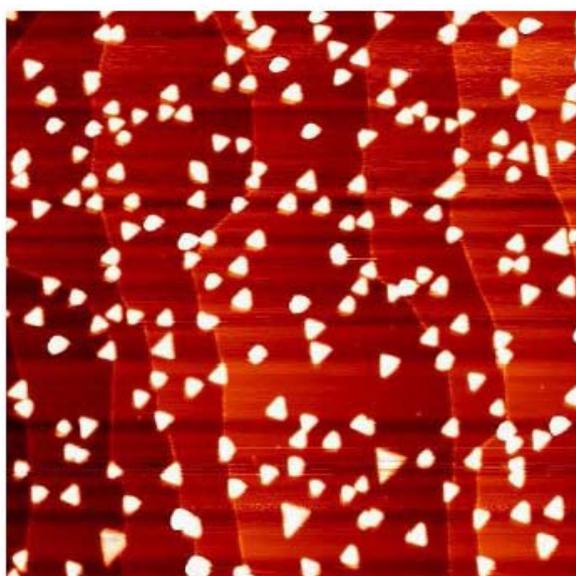


Fig. 3. 500 nm x 500 nm STM image after 15 sec deposition of CaF_2 on $\text{Cu}(111)$ at 750 K

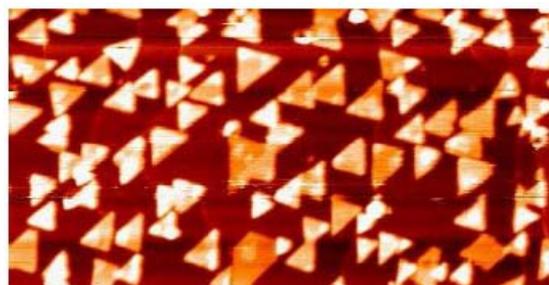


Fig.4. 500 nm x 500 nm STM image recorded after 70 sec deposition of CaF_2 on $\text{Cu}(111)$ at 750 K