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Thermally Annealed Sub-Monolayers of AlF_3 on Cu(100): An STM and XPS Study

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A steady and durable transition from rough and randomly oriented 2D aluminum fluoride clusters to ultra-thin films with defined arrangement is here reported. Scanning tunneling microscopy images show that the material deposited on top of Cu(100) reveals a smooth surface with a preferential arrangement and a transition in the morphology of the islands after performing a post-deposition annealing treatment at 575 K. X-ray photoelectron spectroscopy shows that the chemical environment of fluoride atoms remains unaltered after performing annealing treatments at this temperature. However, the tunneling voltage used to acquire STM images of the films changes from typical insulator values to metallic-like ones after annealing. These results suggest an important change in the local density of states of the aluminum fluoride islands after the post-deposition annealing treatment.

1. Introduction

As the ongoing miniaturization in nanotechnology reaches the sub-nanometre regime, the morphology and electronic structure of ultra-thin films have attracted widespread interest in the last years. In particular, aluminum fluoride (AlF_3) thin-films have been both of fundamental and technological importance for more than three decades.[1–14] The interest on this material has been boosted by its potential applications in nanometer-scale patterning due to the radiolysis observed under electron irradiation, that is the desorption of fluoride with the consequent formation of an aluminum metallic layer.[3,9–14] This approach has shown its potentiality to build aluminum nanowires on bulk AlF_3 substrates, which might be used as nano-interconnectors of electronic devices.[14]

The early growth stages of AlF_3 on Cu (100) have been studied by a combination of surface science techniques, including: thermal energy atom scattering (TEAS),[1] scanning tunneling microscopy (STM),[1–3] scanning tunneling spectroscopy (STS),[4] low-energy electron diffraction (LEED),[1] Auger electron spectroscopy (AES),[1,9] electron energy loss spectroscopy (EELS),[1] secondary electron emission (SEE),[1] and direct recoiling spectroscopy with time of flight analysis (TOF-DRS).[9] It has also been studied by DFT calculations,[4] as well as predicted by means of kinetic Monte Carlo (KMC) simulations.[2] In those studies the growth of AlF_3 at room temperature as a function of the surface coverage[2] and the thermal stability of the films[1,9] have been reported.

In the present work, we have carried out a detailed study of AlF_3 islands deposited onto Cu(100) surfaces in the sub-monolayer regime after they have been exposed to post-deposition annealing treatments. In order to get a better understanding of the effects of these treatments over the deposited AlF_3 islands, we have studied the annealing process by means of STM and X-ray photoelectron spectroscopy (XPS). We have observed that within a narrow temperatures window at around 575 K, the AlF_3 islands experiment an irreversible transition from the known dendritic shape without any preferential orientation respect to the substrate[2] to a rectangular shape preferentially aligned along the [110] Cu main directions.

2. Results and Discussion

After AlF_3 deposition was accomplished, the first step was focused on a morphological surface study. **Figure 1** shows a typical STM image of AlF_3 deposited on Cu(100) at room temperature. As it can be observed from the early stages of growth, the AlF_3 islands are imaged as bright protrusions developing dendritic shapes and being randomly distributed along the Cu(100) surface without showing any preferential orientation over it. As reported in the literature for films alike,[2,3]

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it is observed from the line profile acquired along the STM image that the apparent height of the islands are between 0.25–0.35 nm, that is one monolayer high, unveiling a rather rough top-most surface of the islands (see inset of Figure 1). At this point, it is worth recalling to be mentioned that a-AlF_3 lattice parameters are $a = 0.5$ nm and $c = 1.2$ nm.[15,16] However, as the STM images are a convolution of geometric and electronic contributions, the apparent height of the islands should not be directly interpreted as their geometric height. Hereon, we define one monolayer as the reported apparent height of AlF_3 islands during the growth of 2D films (0.25–0.35 nm).[1–3]

As we recently reported,[2] both sides of the substrate step-edges are completely decorated by islands, and narrow terraces (not wider than 17 nm) do not show any nucleation under the deposition conditions we used (see the experimental section), pointing towards a large diffusion coefficient of AlF_3 molecules. At this stage, stable STM images of AlF_3 islands can only be obtained by using relatively high positive sample bias voltages (V>+2.50 V). For bias voltages lower than + 2.50 V the islands are frequently swept away by the tip, as it is expected due to the insulating character of bulk AlF_3. After post-deposition annealing treatments were done, important changes were observed in the islands morphology. **Figure 2** shows a typical STM image of AlF_3 on Cu(100) after a post-deposition annealing treatment at 575 K has been performed. At this stage, the islands are no longer dendritic, and start showing a clearly rectangular shape. A statistical analysis of the islands orientation unveils a preferential alignment of them along the [110] *Cu* main directions. Remarkably, the islands do not decorate the step-edges anymore and their borders are imaged with brighter STM contrast. STM images of the rectangular islands can be acquired at relatively low voltages, that is +0.05 V, while before the annealing process it was not possible to acquire stable images at voltages below +2.50 V. This result suggests a modification in the electronic structure of the AlF_3 islands after performing the annealing treatment. Finally, some changes are also evident in the morphology of the Cu(100) substrate. In particular, Cu(100) step-edges look irregular as compared to the surface before the annealing process, showing a saw-tooth like shape, which implies a massive movement of *Cu* ad-atoms, as it can be clearly observed in Figure 2 (see the white line).

To complement these observations we studied the topography of the rectangular islands by performing an STM height profile analysis. **Figure 3**b shows the STM height profile acquired along the line depicted in Figure 3a. The analysis of several of these profiles revealed that the islands apparent height (0.10–0.12 nm) was 50% lower than previous to the annealing treatment. These results suggested that an important change had to be present in the islands, in their morphology and/or in their local density of States (LDOS). A careful observation of the islands borders unveiled relevant STM height differences between the borders that were in contact with the substrate step-edges and those that were not. While the islands borders pointing to the Cu(100) terraces showed an apparent height of ≈0.17 nm, the ones in touch with the step-edge of the substrate showed an apparent height of ≈0.35 nm. This result resembles the case of other insulator islands decorated by metallic atoms. In particular, similar rectangular islands with bright borders have been reported by Finetti et al.[17] who suggested that the bright borders observed in titanium oxide islands are originated by copper atoms expelled from the Cu(100) surface, which migrate to the

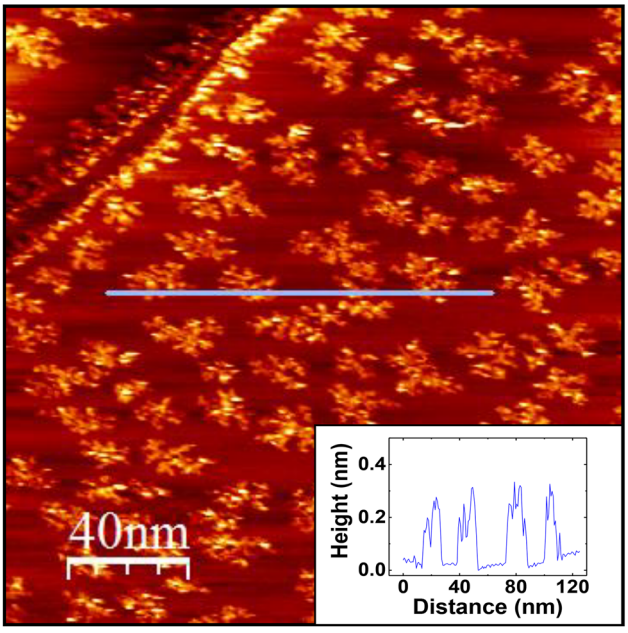

Figure 1. STM image (200 × 200 nm) of 0.35 ML of AlF_3 deposited on Cu (100), acquired at room temperature: The inset shows the STM apparent height profile acquired along the line depicted in the image. The STM image was acquired at a sample bias voltage of $V_S = +2.5$ V and a tunnel current of $I_T = 0.60$ nA.

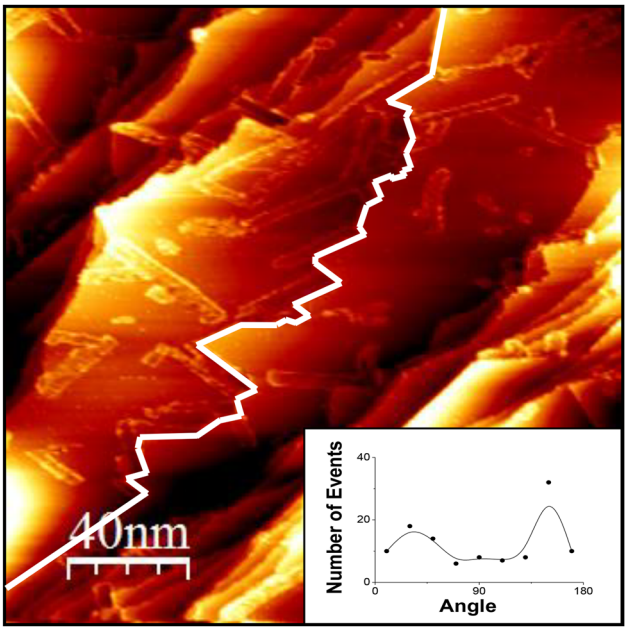

Figure 2. STM image (200 × 200 nm) of 0.35 ML of AlF_3 deposited on Cu (100), acquired after a post-deposition annealing process at 575 K was done. The inset shows the orientation distribution of the islands on the surface. The image was acquired at $V_S = +0.5$ V and $I_T = 0.60$ nA.

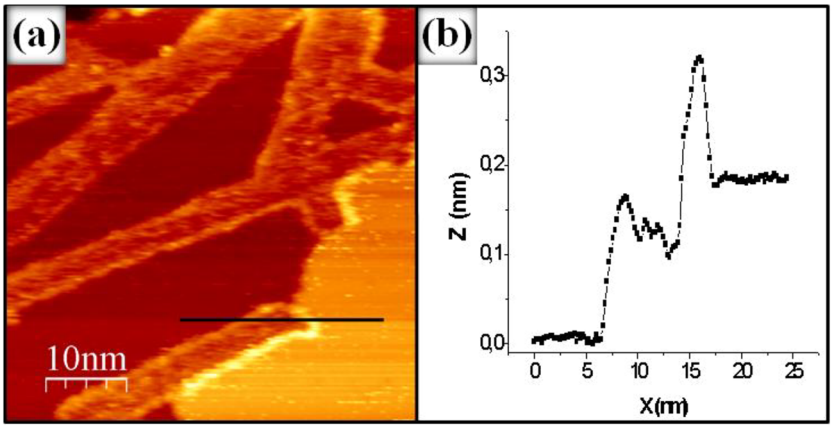

Figure 3. a) STM image (50×50 nm) of 0.35 ML AlF_3 deposited on Cu(100) after the post-deposition annealing treatment at 575 K was done. b) Typical STM apparent height profile acquired along the line depicted in the image. The image was acquired at $V_S = +0.6$ V and $I_T = 0.5$ nA.

edges of the islands. Taking into account that the copper steps are ≈0.18 nm height, we suggest that the borders of the rectangular AlF_3 islands might be fully surrounded by metallic atoms, for example *Cu* and/or *Al* atoms. In particular, for those borders in touch with the substrate step-edge the metallic atoms might be placed at the upper side terrace of the step-edge, explaining the observed STM height of ≈0.35 nm for these borders.

Finally, a further annealing treatment at 700 K results in the total desorption of all the islands from the surface (not shown here). After annealing at 700 K, no islands are visible, neither over terraces nor at the step-edges, which recover their typical smooth shape as in Figure 1. These results suggest that after annealing at 700 K aluminum fluoride desorbs from the Cu(100) surface, as it was already reported by AES measurements.[1]

In order to gain additional insight into the chemical environment of the fluoride atoms we performed XPS measurements. In **Figure 4**, the XPS spectrum in the region of the F1*s* signal for a sample with 0.35 ML of AlF_3 on Cu(100) is depicted. Figures 4a,b show the XPS spectra before and after the annealing process at 575 K was done. The *F1s* core level spectrum shows a main peak at 687.4 eV (FWHM = 2.34 eV) and a secondary peak at 685.1 eV (FWHM = 1.51 eV) before annealing (see Figure 4a). The presence of the secondary peak at lower binding energy is associated to the coexistence of minor species,[18,19] for example dangling bond of *F* ions in the boundary of the islands.[20] Thus, while the inland fluorine atoms will feel the full interaction with surrounding Al^+ cations, the *F1s* photoelectrons coming from those located at the islands edges may appear at lower binding energies, since they simply have less electropositive neighbors. Therefore, the intensity of the secondary peak would be proportional to the perimeter/area ratio of the islands. After the annealing treatment, Figure 4b shows that while the main peak remains at 687.4 eV (FWHM = 2.27 eV), the small secondary peak shows a clear decrease of 33% in intensity (see Figure S1, Supporting Information) and it is slightly shifted toward lower binding energy, 684.8 eV (FWHM = 1.35 eV). On the one hand, the first consequence of the annealing observed by STM is the smoothening of the islands, going from dendritic to compact shapes with a decrease of 31% in the perimeter/area ratio of the islands, which is in excellent agreement with the decrease in intensity observed by XPS (see Figure S1 and S2, Supporting Information). On the other hand, if this minor peak is ascribed to CuF_2, which has been previously reported in a broad range of energies between 664.3 and 685.9 eV,[21–24] it would only represent 4.7% of the total area of the *F*1s peak. Therefore, our XPS study rules out the formation of massive CuF_2, as the reason behind the observed changes. At this point, it is worth to be mentioned that in our sub-monolayer study of AlF_3 on Cu(100) the $Cu2P_{3/2}$ XPS spectrum shows mainly irrelevant information about the Cu(100) substrate and the Al2p peak is hindered by the $Cu3p_{3/2}$ peak (see Figure S3, Supporting Information).

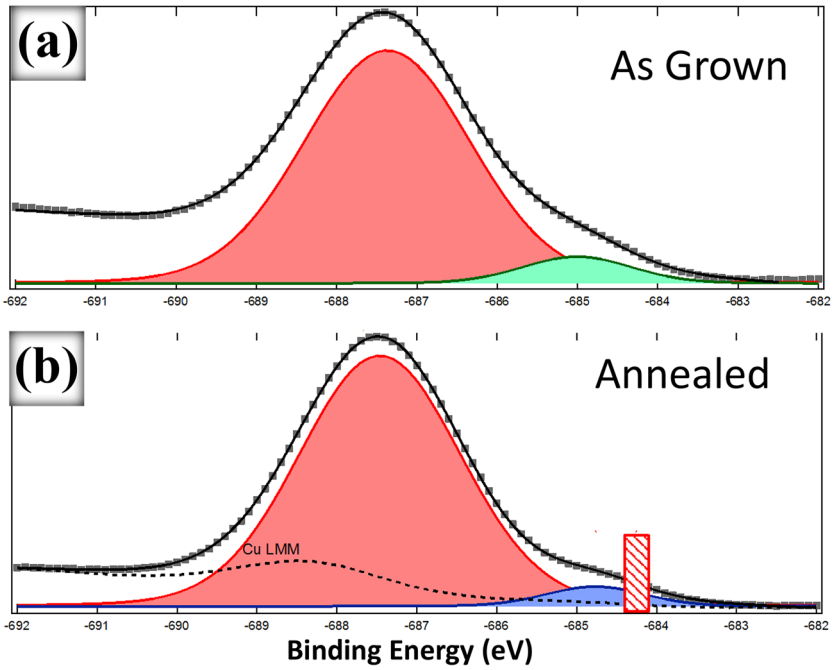

Figure 4. *F*1s XPS spectrum acquired "in-situ", for a sample with 0.35 ML of AlF_3 deposited on Cu (100). a) as grown, and (b) after a post-deposition annealing treatment at 575 K was done. The position corresponding to *F* in CuF_2 is pointed out in (b) with a red rectangle.[21]

Our combined XPS and STM results, confirm that the AlF_3 islands have

undergone a transition without any considerably change in the chemical environment of fluorine atoms. However, we cannot rule out a slight doping of the islands by metallic atoms, for example Cu and/or Al atoms in a concentration minor than 5%, which is beyond the resolution of our experimental setup. Nevertheless, we cannot discard that a transition towards a less insulating arrangement could occur. In this regard, this new arrangement may be intrinsically more conductive, or on the other hand may allow a denser packaging thus leading to thinner islands. Both situations might contribute to an increase in the tunneling current for a wider range of bias voltages in STM.

3. Conclusion

We have shown a transition of AlF_3 films (islands) over Cu(100) under post-deposition annealing processes at 575 K. We found that the islands shape changes from dendritic to rectangular with a preferential alignment along the [110] *Cu* main directions. At the same time, a strong change in the bias voltage is needed to acquire stables STM images. While, before the annealing at 575 K the bias voltage used was in agreement with typical values for insulator thin films, after this treatment the bias voltage values became more similar to those used to image metallic conductive surfaces. From XPS measurements, we rule out the formation of massive CuF_2 as the reason behind the changes in the islands but a transition per se or a doping of thinner islands may be responsible for the observed morphological and electrical features.

4. Experimental Section

The experiments were performed at room temperature using an ultra-high vacuum (UHV) system with a base pressure maintained in the low 10^{-10} mbar range. The Cu(100) substrate was cleaned in a secondary UHV reaction and preparation chamber by cycles of Ar^+ ion bombardment followed by annealing at 900 K. The temperature was measured by means of a chromel-alumel thermocouple in contact with the backside of the sample holder. Aluminum fluoride films were deposited *in situ* onto Cu (100) samples at room temperature (300 K) using a Knudsen cell charged with anhydrous AlF_3 (CERAC INC., Milwaukee, Wisconsin, USA, 99.5%) and heated at 820 K. The cell was carefully degassed and shuttered to avoid sample contamination. Vacuum conditions in the secondary chamber were in the low 10^{-9} mbar range throughout the evaporations. The typical deposition time for sub-monolayer depositions was between 1 and 2 min. STM images of the clean Cu(100) substrate and AlF_3/Cu(100) samples showed no evidence of contamination even after maintaining them during several hours in the secondary chamber. The samples were introduced into the UHV main chamber immediately after the preparation. The deposition rate of AlF_3 was 1.7×10^{-3} ML s^{-1}. The calibration procedure and analyses of the coverage were determined from a direct analysis of the STM images.

Post-deposition annealing treatment was carried out by radiation of a filament placed in the backside of the sample holder, so as to avoid electron bombardment to prevent radiolysis.[9] During the annealing treatments the samples were kept at the reported temperature during 15 min. Electrochemical etched tungsten tips were used for all STM experiments reported in this work. Image processing was performed using the WS × M free software.[25] Additional XPS measurements were carried out in-situ at a base pressure in the low 10^{-10} mbar range. Measurements were performed at room temperature and at a normal emission angle. The calibration of the XPS analyzer was based on the position of the $Cu2p_{3/2}$ peak. The spot size of the X-ray beam was around 4 mm^2. A monochromatic *Al* K_α X-ray-source was used (1486.5 eV).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Conflict of Interest

The authors declare no conflict of interest.

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Keywords

aluminum fluoride, thin-films growth, scanning tunneling microscopy, X-ray photoelectron spectroscopy

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