

## WATER/L-ALANINE INTERACTIONS: HYDROPHILICITY VS. HYDROPHOBICITY

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L-alanine is a non-essential chiral amino acid with a non-reactive hydrophobic methyl group as a side chain. However, it exhibits a relatively high solubility in water which is due to its zwitterionic form. Cleaved (011) and (120) surfaces of single crystals of L-alanine grown from aqueous solutions have been characterized by atomic force microscopy (AFM) at room temperature as a function of the relative humidity (RH). Their behaviour is radically different: while (011) surfaces are highly hydrophilic, (120) surfaces are highly hydrophobic.

The AFM experiments have been performed in a glove box with a 5500 Agilent Technologies AFM (Agilent Technologies, USA) under controlled humidity using microfabricated silicon cantilevers with force constants  $k_c \sim 40$  N/m and ultrasharp silicon tips (tip radius  $R < 10$  nm) (NanoAndMore GmbH, Germany). RH inside the box was decreased or increased by flowing dry nitrogen or by bubbling nitrogen through MilliQ water, respectively. The single crystals were cleaved inside the glove box at the lowest achieved RH ( $< 5\%$ ).

Figure 1(a) shows an AFM image in acoustic mode (amplitude) taken immediately after cleavage at low humidity (RH  $\sim 5\%$ ) of a (011) surface. The surface exhibits a combination of well-defined long and shorter straight steps. The measured step height is  $\approx 0.5$  nm, in agreement with the distance between two adjacent (011) planes (0.52353 nm). The effect of humidity is quite drastic on the (011) surfaces. Already at 20% RH [Fig. 1(b)] important morphological changes can be observed at the surface. Islands with heights of  $\approx 0.3$  nm are formed on the terraces. As humidity increases the islands grow two-dimensionally and at RH  $\sim 50\%$  [Fig. 1(c)] the original steps are hardly identified. At this humidity the islands have merged forming terraces with irregular edges covering the entire surface [Fig. 1(d)]. At high humidity (RH  $> 70\%$ ) holes appear at the surface indicating large dissolution of the crystal. For higher humidity, tip perturbation of the surface can be observed as a strong dissolution process at the areas where the tip has been scanning.

Freshly cleaved (120) surfaces show well-defined steps along the crystallographic  $c$ -axis, as shown in Fig. 2(a). The measured step height was found to be  $\approx 0.5$  nm, again in agreement with the distance between two (120) adjacent planes. Surfaces showing mostly steps in the [001] direction remained unaffected upon exposure to water vapour up to high humidity (RH  $\sim 75\%$ ). At high humidity conditions the scanned regions become perturbed due to the tip but when the surroundings of the observed area are imaged, it is found that they remain essentially unaffected [Figure 2(b)]. The stability of the morphology of the surface is a proof of the hydrophobic nature of the (120) face. A closer look to what happens on the steps growing perpendicularly to the [001] direction reveals some anisotropic degree of hydrophilicity. This is shown in Fig. 2 (c), where we observe that the long step edges remain unperturbed while nanoneedles aligned along

the [001] direction are formed. A further proof that water preferentially interacts in such regions is given by the phase image shown in Fig. 2(d) where a high phase contrast is observed due to water absorption. We also observe the formation of needles on the terraces. Starting from small crystals that deposits on the surface the needles grow in the [001] direction.

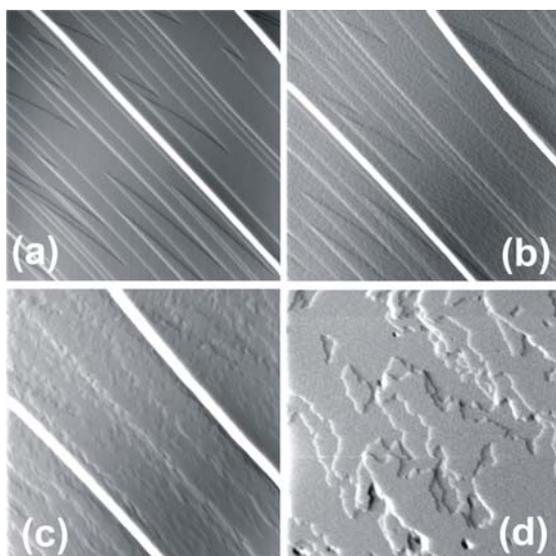


Figure 1: Evolution of amplitude AFM images of a L-Alanine (011) surface as a function of RH: (a) ~ 5%, (b) ~ 20% and (c) ~ 50%. Figure (d) shows a zoom of a surface region taken at RH ~ 50%.

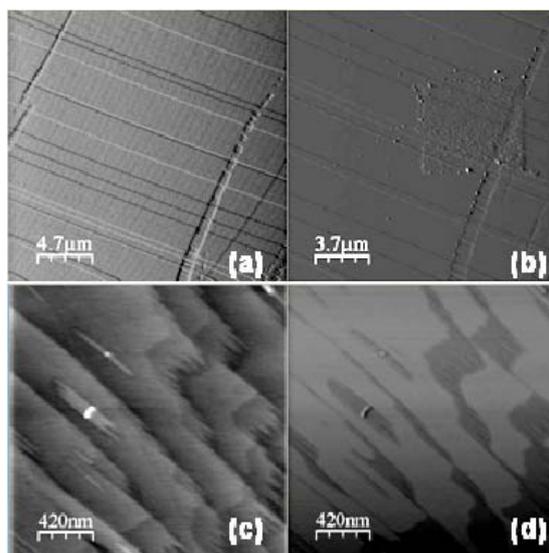


Figure 2: Evolution of AFM images of a L-Alanine (120) surface as a function of RH; (a) ~ 5%, (b) ~ 10% [after exposure at ~75%] and (c) ~ 45%. (d) phase image of (c)