Nascent and Metastable Phases in Nanostructure Evolution on Silicon

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Advanced miniaturization in feature size of silicon nanostructures by photoelectrochemical conditioning allows preparation of hitherto unequalled small dimensions. Possible applications include photonic bandgap materials where the photonic energy gap is shifted towards the visible spectral range and new light coupling devices in photodiodes and photovoltaic solar cells. The fabrication of ordered pore arrays, for instance, necessitates the investigation of the parameter dependency of self organized structurization.

In dilute, slightly acidic fluoride containing solutions, potential controlled experiments enable us to follow the very early nanopit formation at specific sites of H-terminated Si (111) towards a transitory metastable phase where mesa-type features, between 80 nm and about 200 nm in size, are formed. The surface nanotopography is analyzed using contact mode atomic force microscopy (CM AFM) and Fig. 1 shows a typical example of such a feature. Interestingly, it is found that the sidewalls of the mounds show angles with respect to each other which are partly unexpected for a (111) surface with C_{3v} symmetry. Even right angles are observed in AFM experiments as shown in Fig. 1. These phenomena

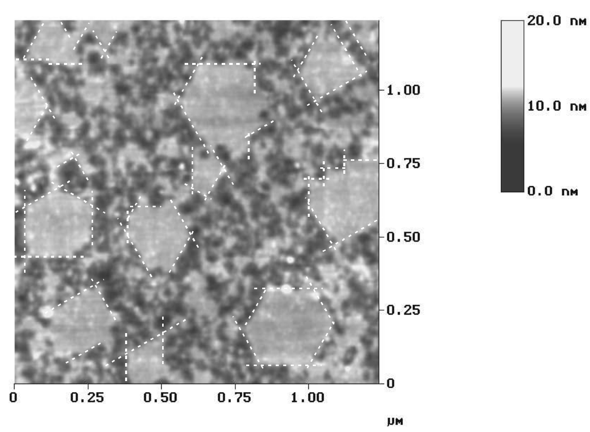

Fig. 1. AFM micrograph of FZ n-Si (111) obtained after anodisation under illumination in 0.2 M NH_4F, pH 4 by scanning from open circuit potential (ocp) to + 0.3 V positive of ocp; charge passed 3.9 mC/cm^2.

can be explained by considering the imaging process of CM AFM and the crystallographic orientation of crystal facets adjacent to the (111) main plane. It turns out that the shapes of the mounds can be constructed using the low index {110}, {113} and {111} faces. Although the latter two crystal faces are inclined towards the main (111) face, their rather little height of some nanometers constitutes that the inclination of these planes can not be resolved due to the considerably larger radius of the imaging tip. It is well known that the contributing crystal faces have all been successfully H-terminated in a (1x1) manner [1-3]. Since (1x1) H-terminated Si is also known to exhibit exceptional stability, we explain the observed metastability by the stability of the sidewalls and of the (111) top surface of the mounds. Nevertheless, the weakened bonding of atoms at edges between planes finally results in further dissolution which is also observed in the AFM images.

The data show the influence of rather minute changes in concentration of NH_4F and pH on the topography: with increasing concentration and decreasing pH, the photocurrent and hence the divalent dissolution rate increases, allowing us to monitor the transition from very small corrugation via mesa formation to a stage where the decomposition of these mesas sets in. The dissolution charges vary from about one bilayer (BL) to 22 BL where pores of 16 nm depth and about 100 nm width are formed and mesas still persist.

In subsequent work we intend to prepare nanopores and – mounds by scanning probe microscopy induced seed formation.

References:

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