

Site Specific Electrolyte Interaction at Terraced Si (111) Surfaces

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Luminescent porous silicon is a well known material for almost two decades. Despite its interesting features and many applications [1,2], almost nothing is known about the very early phases of its formation when the pore depth is too small to allow pore propagation based on quantum size effects [3]. Also, the origin of pore wall stabilization in the nascent phase of porosity evolution is hitherto unknown. We have therefore performed potentiostatic and chronoamperometric photoelectrochemical experiments in the alternative parameter space of dilute NH_4F solution at pH values between 4 and 4.5 using small overpotentials on float zone (FZ) Si because of its much lower defect density and oxygen content compared to Czochralski (CZ) Si allowing better assessment of the influence of the topography on the pitting process. As will be shown below, the surface nanotopography plays a decisive role in immobilization of counterions resulting in extremely localized current flow. In this respect, this finding has considerable relevance also for localized electrodeposition processes allowing feature sizes in the self organized mode of about 12-15 nm.

The photoelectrochemically conditioned surfaces are investigated using contact mode atomic force microscopy (CM AFM) after anodic polarization of 0.1 V from open circuit (ocp) and for anodization times at this potential between 15s and 60s resulting in dissolution charges between 0.53 mCcm^{-2} (pH 4.5) and 10 mCcm^{-2} (pH 4 and $0.2 \text{ M NH}_4\text{F}$). The earliest detectable corrosion is shown in Fig. 1. Besides the zig-zag arrangement of the atomic terraces, first nanometer sized pits at reentrant sites of the topographic structure are visible. They are one atomic bilayer deep (0.314 nm) and possess diameters of about 12-15 nm. In advanced stages of this divalent process, where only two charge carriers are needed for the extraction of one silicon atom, the structure changes towards parallel aligned step edges and pits mostly occur beneath these edges. Increased corrosion results in trench formation and the alignment of the trenches can be correlated to low index crystallographic orientations. As a result, atomically flat mounds whose sidewalls are made of low index (1x1) H-terminated faces are formed. The locality of these processes is described by modelling the electrostatic potential between the few F^- counterions needed for the charge balance and the surface nanotopographic features, for example, the corners of step edges. Considering attractive forces, the electrolyte Debye length and repulsive so-called non DLVO forces [4], anion immobilization near the corner of a step edge in the zig-zag structure is postulated as shown schematically in Fig. 2. The very local electrostatic field results in deflection of light generated excess minority carriers towards these sites which mostly diffuse to the localized spherical space charge region where they are deflected towards the surface oxidizing fully coordinated Si atoms with resulting solvolytic splitting of the backbonds.

We presently investigate whether the observed site specificity of the dissolution process also occurs in the self organized deposition of metal nanoclusters on these surfaces.

References

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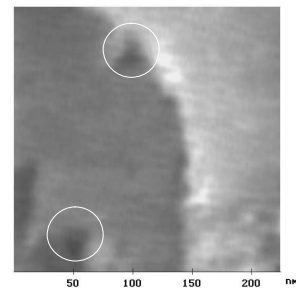


Fig. 1. AFM micrograph of FZ n-Si(111) after anodization from ocp to 0.1 V positive of ocp under illumination.

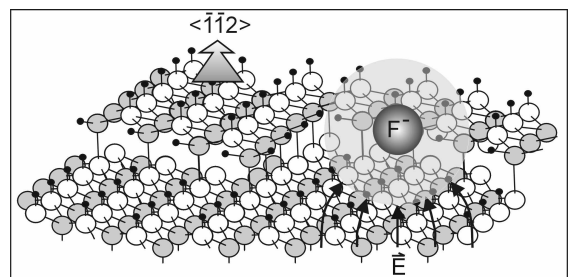


Fig. 2. Anion immobilization at a reentrant site; the solvation shell is indicated by the transparent sphere and the localized electrostatic field lines are shown as arrows; open spheres: topmost silicon atoms terminated by H-atoms (black spheres (see text)).