Porous Si Formation on Highly Doped n-type Samples:
Novel Considerations on the Origin of the Current-Voltage Characteristics

H. Jungblut* and H .J. Lewerenz
Hahn-Meitner-Institut Berlin GmbH,
Bereich Solarenergieforschung, Glienicker Str. 100,
14109 Berlin, Germany

For the divalent dissolution of Si in fluoride containing solutions leading to porous silicon formation, present models need valence band holes to initiate the process [1]. In n-Si, the excess holes are provided by illumination. On higher n-doped Si ($N_D > 10^{17}$ cm^{-3}), initial stages of porous Si formation are found also in the dark although the hole concentration is neglegibly small. A convincing explanation for this finding is still lacking.

We study the process in more detail by systematical investigation of dark current-voltage characteristics of n-Si(111) with different dopant densities ($N_D = 2x10^{19}$ cm^{-3} ... $2x10^{17}$ cm^{-3}) in dilute NH_4F (Fig. 1). The extrapolated onset of the anodic current reflecting divalent dissolution (e.g. arrow in Fig. 1) is shifted from –0.34 to +4.4 V/SCE for decreasing N_D. The calculated potential drops in the semiconductor ΔU_{sc} increase from 0.05 to 4.6 V while the potential drop in the Helmholtz layer ΔU_{HH} remains nearly constant (0.52 ± 0.05 V) in all cases [2].

For an explanation, we can exclude Fowler-Nordheim-type electron tunneling from the valence band to the conduction band resulting in a hole at the Si/electrolyte interface because a band bending of at least 1.1 eV (band gap) would be necessary. This is in contrast to our findings, particularly for the highly doped n^+ samples. For the interpretation of our results, we refer to the observation of an energetic shift of surface states proportional to the potential drop in the Helmholtz layer which was reported earlier for Ag(100) [3]. The constant ΔU_{HH} found in our experiments for current onset conditions suggests the existence of an electron-injecting state 0.3 – 0.5 eV below the conduction band edge extending into the Helmholtz layer. This state is shifted proportional to ΔU_{HH} and for sufficiently large ΔU_{HH} electron injection is facilitated (Fig. 2).

In Fig. 1, an increasing broadening of the current onset with decreasing N_D is observed. Because larger potentials must be applied to get comparable ΔU_{HH}, also an increasing potential difference must be applied to shift the state beyond the conduction band edge. From this, the width of the energy distribution being assumed as Gauss shaped can be estimated to be ≤ 50 meV. Thus electron injection due to outer or inner sphere charge transfer in the conventional sense can be excluded (reorganisation energy ≈ 1 eV).

We suggest that the electron injecting step replaces the first step in the dissolution model proposed by Allongue et al. [1] consisting of the capture of a (light induced) hole at only twofold coordinated kink site atoms. Electron injection on highly n-doped samples in the dark as well as hole capture on moderately n-doped illuminated samples leads to a surface radical initiating the subsequent dissolution reaction. Respective corrosion reactions leading to initial por-Si formation are also observed by AFM on highly n-doped Si in the dark (Fig. 3).

References:

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* Corresponding author. Fax: ++49 30 8062 2434
E-mail: jungblut@hmi.de

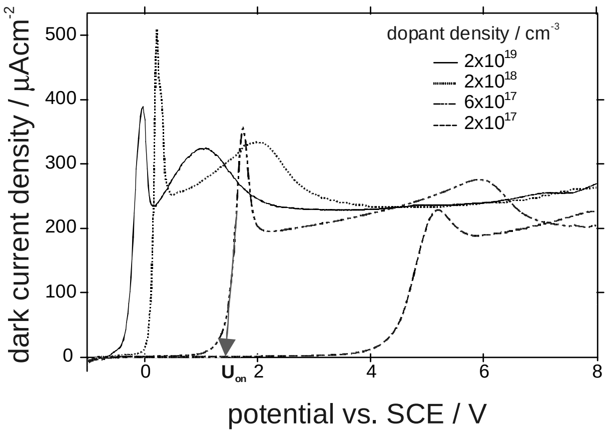

Fig. 1. Dark current-potential characteristics of differently doped n-Si(111) in 0.1 M NH_4F.

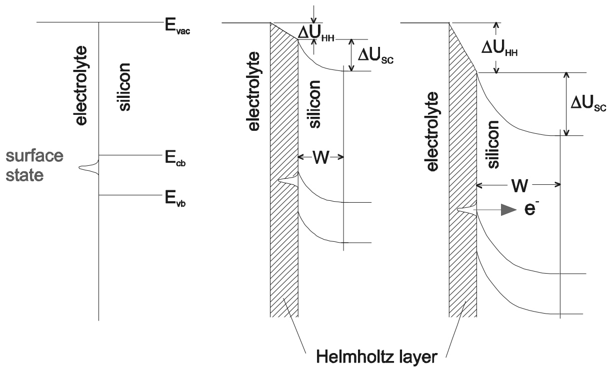

Fig. 2. Schematic illustration of the energetic shift of an electron injecting interface state with increasing ΔU_{HH}.

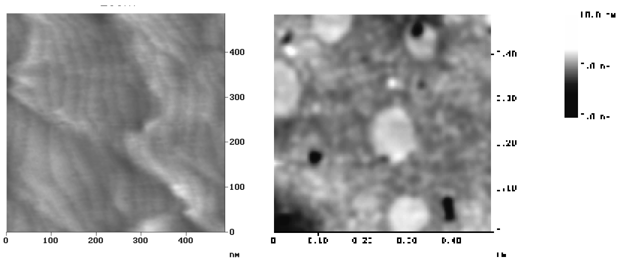

Fig. 3. Left: AFM image of H-terminated n-Si(111). Right: surface topography after sample emersion at the first dark current maximum. $N_D=2x10^{18}cm^{-3}$.