FORMATION OF MESOPORES WITH LARGER DIAMETERS

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During the electrochemical etching of silicon in HF containing electrolytes, different types of pores can be formed. Micropores (pore diameter smaller than 5 nm) have received most attention after Canham [1] and Lehmann [2] discovered the luminescence of microporous silicon. In the last years, mesoporous silicon (diameters 5-50 nm) is more and more used for fabrication techniques, especially for producing silicon-on-insulator (SOI) wafers. Currently, a third type of pores, the macropores (with diameter larger than 50 nm up to several microns) allow for the best controlled growth conditions and an extremely large variety of different structures. In this work we deal with an intermediate kind of pores which grow (like mesopores) by electrical breakdown of the silicon electrolyte interface but which show diameters larger than 50 nm. We will still call them mesopores, dissenting from the IUPAC scheme.

The parameter dependence of these mesopores has only been scarcely investigated (Theunissen [3] in the seventies and recently Lehmann et. al. [4]). The goal of our work is to drastically enhance the growth speed of pores with macropore dimensions while at the same time to push further down the size limit for the macroporous regime of well defined pores.

We used standard n-type (100)- and (111)-wafers with 0.7 and 0.014 Ωcm and anodized them in the dark in a custom-build etching set up with a high precision potentiostat / galvanostat. HF concentrations were 5 resp. 15% wt. (aqueous) with current densities of 10 and 80 mAcm^{-2}. The samples were then analyzed in plain view and cross section using electron and optical microscopy.

We will illustrate the different morphologies for the noted conditions: As can be seen exemplary in **Fig. 1** and **2** at 5 % wt. HF two layers with different morphology form while at 15%wt HF only one type of pore is growing (cf. **Fig. 3**) and that at quite high speed (160 µm/h) compared to "normal" macropore growth (approx. 60 µm/h). The pores seem to reshape current flow while still growing along crystallographic directions which is visible at higher magnifications. We will show examples of pores etched in organic electrolytes with and without the addition of conducting salts. The behavior for different substrate orientations will be compared. Possible interpretation of the formation mechanisms will be given in the framework of the so called current burst model including a comparison to III/V semiconductor pores where the goal mentioned above is easy to achieve.

References:

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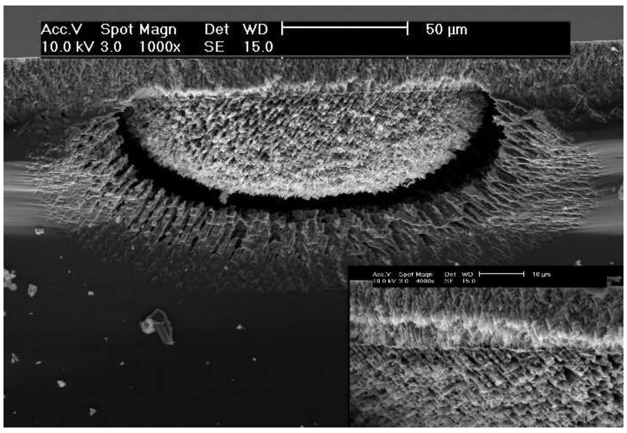

Fig. 1: SEM cross section of the mesoporous structure (n-Si 0.7 Ωcm, 10mA, 5 %wt HF, 60min). A uniform layer of approx. 20 µm covers the etched surface. At several points a secondary pore structure formed below with a different morphology. **Inset:** Magnification of the interface between both porous layers.

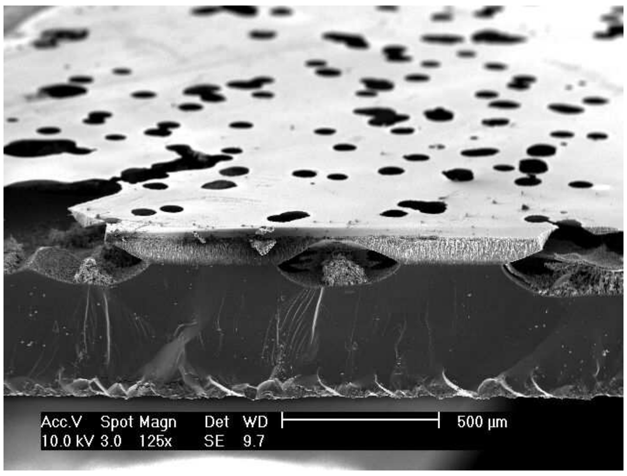

Fig. 2: Surface and cross section of a typical porous layer (n-Si 0.7 Ωcm, 80mA, 5 %wt HF, 60min): The remainings of "hedgehog" - like structures (cf. **Fig. 1**) which appear below large openings at the surface.

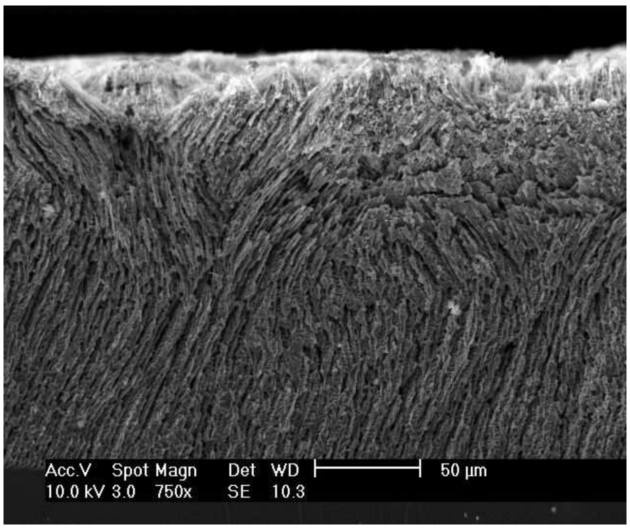

Fig. 3: Sample which has been anodized under high current densities (80 mA/cm^2) in 15 %wt aq. HF. Pores show an interesting behavior as they are still obeying crystallographic directions but assemble in a manner which seems to shape current paths.

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