Improved electrochemical etching of macroporous silicon - the rôle of surfactants

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Since the discovery of macroporous silicon in 1990 by Lehmann and Föll [1], macroporous silicon growth has been extensively studied in n-type and also more recently p-type silicon [2]. In both reactions silicon is converted to SF_6^{2-}-ions which have a good solubility in aqueous solutions. In addition, in both reactions, hydrogen is produced. If larger bubbles are formed, they significantly disturb the macroporous silicon growth. Therefore, typically tensides or ethanol is added to the electrolyte to reduce the surface tension allowing only very small bubble formation.

We have studied in detail the effect of different tensides on the macroporous silicon growth in n-type silicon with lithographically predefined etch pits. Whereas for pores with diameters larger than a few microns, the type of tenside (anionic, cationic or non-ionic) does not change significantly the growth of the macropores, we found extreme differences for interpore distances of 1,5µm having pore sizes of 900 nm (Fig. 1). The cationic surfactant leads to branching of the pores, whereas the non-ionic surfactant allows the formation of straight pores, but with some narrowing of the pore diameter with growth even after compensation for diffusion. Only anionic surfactants give straight pores with constant diameter. The infrared spectra of the photonic crystal properties of these structures, exhibiting rectangular shape reflectivities inside the photonic bandgap support the high quality of these structures (Fig.2).

By analysing the dark current at the anodic potential of the etch process, the influence of the surfactant can be revealed. Both, cationic and non-ionic exhibit high dark currents up to 25% of the etching current, depending on their concentration (Fig. 3). A concentration not less than 0.1mM is required for effectual tenside action. The increased dark current is responsible for the widening of the pores at the pore openings. In contrast, anionic surfactant show very low dark current, independent of the tenside concentration.

We analyze these results in terms of the surface potential Φ_0, which is increased in the case of anionic surfactants and reduced in the case of cationic surfactants compared to that of pure water. The different band bending at the HF/Si-interface leads to a different thermal injection-rate of electrons in the conduction band of silicon, and thus to different dark currents. Please note, that for p-type silicon the situation is vice versa. There an improved electrochemical etching can be obtained for cationic surfactants [3].

[1] V. Lehmann and H. Föll, J. Electrochem. Soc. **140** (1990) 653.
[2] R.B. Wehrspohn, J.-N. Chazalviel, and F. Ozanam, J. Electrochem. Soc. **145** (1998) 2958.
[3] K.J. Chao, S.C. Kao, C.M. Yang, M.S. Hseu, and T.G. Tsai, Electrochem. Solid-State Lett. **3** (2000) 489.

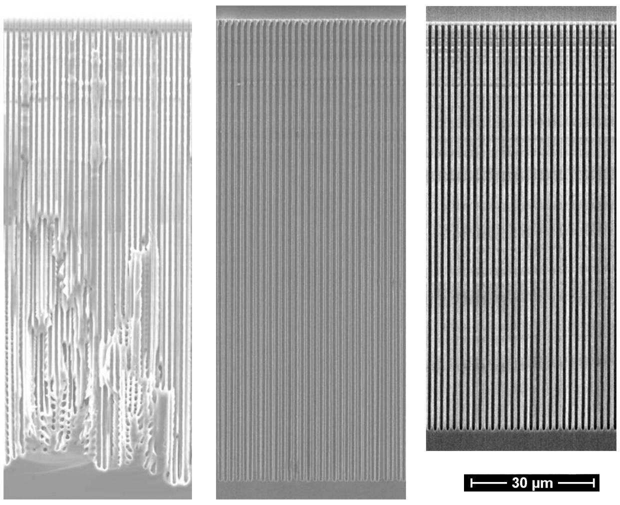

Figure 1: SEM images of air pores in silicon, etched with (a) cationic, (b) non-ionic, and (c) anionic surfactant added to the electrolyte (a=1.5µm, d=900nm).

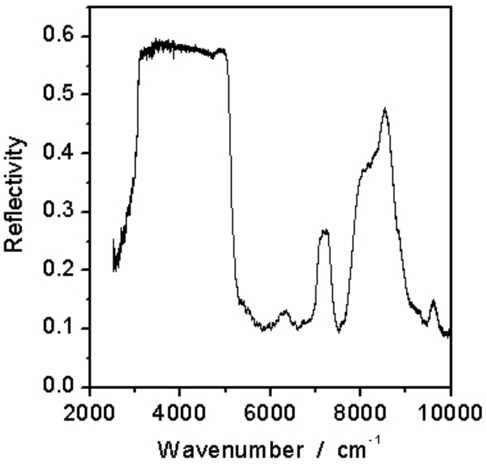

Figure 2: FTIR-spectrum for straight pores with interpore distance of 700nm, and diameter of 500nm.

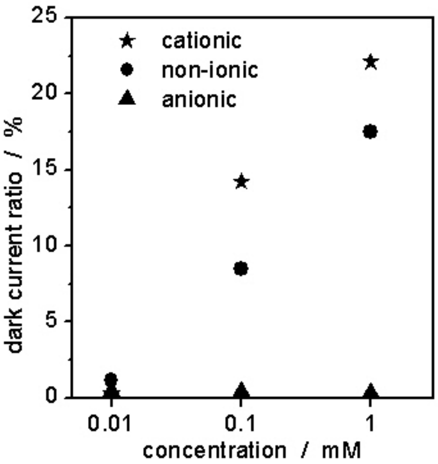

Figure 3: Dark current relative to the etching current as a function of the tenside concentration.