Making and Using Macroporous p-Type Silicon with Modulated Pore Diameters

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Abstract — **Macropores in Si have many potential uses. For some applications macropores in p-type Si with a defined diameter profile are needed. Producing these pores is more difficult than in n-type Si, where the backside illumination necessary for pore formation offers an additional degree of freedom for controlling pore properties. The paper elucidates the mechanism of pore diameter modulations in p-type Si and discusses two applications. First, the making of superior anodes for Li ion batteries; second, the production of uniform Si nanoparticles.**

Index Terms — **Macropores, pore modulation, porous Si, Si particles, Si anode.**

I. INTRODUCTION

Macroporous Si has been prepared in different ways and forms in the past, but the modulation of the pore diameter has been restricted to n-type Si, where various models for the pore growth are known [1 - 7]. Macropores provide for an impressive number of possible applications; the reviews [3, 8 - 10] supply in-depth information about the making and the use of macropores. On the other hand, until recent reports of applications using p-type Si [11, 12], it was believed that the modulation of pores in p-type Si was nearly impossible.

p-type porous Si is of importance for applications where an excess of holes is necessary, e.g. for metal deposition, but also for other reasons. Macropores in p-Si discussed in this paper are typically around 1 μm in diameter and 5 - 150 μm deep. Their growth is initiated by providing nucleation at lithographically defined positions, resulting in ordered pore arrays. In what follows only macropores with modulated diameters in p-type Si will be considered because they are instrumental e.g. for:
1. Making superior anodes for Li ion batteries.
2. Making Si nano needles with defined geometries.

Producing defined pore diameter modulations in p-type Si is, however, not an easy task. The first part of the paper therefore will introduce into this topic.

During steady-state growth of macropores the pore diameter d_P and the distance d_W between pores is constant. The volume V of Si dissolved per time increment Δt is constant and given by $V \propto n \cdot Q$; with n = valence of the dissolution process (= number of electrons needed to flow through the external circuit in order to "dissolve" one Si atom), $Q = I \cdot \Delta t$ = total charge transferred during Δt.

Changing the external current I by some dI changes the dissolved volume by an amount $dV \propto dI \cdot n \cdot \Delta t$ as long as the valence n is constant. That is not necessarily the case. The system can and often will react by changing the dissolution valence n but that is not important for what follows and will be neglected.
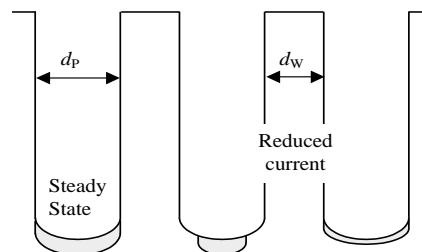

Fig. 1. Incremental pore growth at steady state (left) and the two extremes for a decrease in current.

Introducing the nominal current density j (= current/pore area), the change in dissolved volume thus is $dV \propto dj$. The concomitant change in the pore diameter, however, is still undetermined as schematically shown in Fig. 1 since the pore could keep the old diameter by growing slower or faster, or keep the old growth rate and thus the current density by changing the diameters accordingly, to name the extremes. It also could implement a mixture of the two extremes. In order to understand and thus to control what will happen upon a change of the current, more information about pore growth is needed. In particular, one needs to consider what kind of factors influence or determine the internal length scales of the system. A list of major input parameters includes:

Doping type and level: Doping determines the width of the space charge region d_{SCR}, which in turn determines (always up to a point) the minimal width of the pore wall thickness $d_{Wall}(min) \approx 2d_{SCR}$. Macropore growth is only possible if electrical breakdown and tunneling through the SCR does not happen and thus restricted to lightly doped Si.

Applied potential U: Since the width of the SCR also depends on the potential, n-type and p-type silicon must be considered separately. For p-type Si, pore growth proceeds in the forward part of the IU characteristics. The SCR width is thus on the small side and changes if the current requires changes in the potential.

For n-type Si pore-etching proceeds in the reverse part of the characteristics and current flow must be enabled by illumination (typically of the sample backside). Larger

d_{SCR} can be realized in this way and changes in current are possible for constant U by adjusting the illumination intensity.

Self-organization features. It is known that macropores in n-type Si tend to maintain a constant nominal current density while macropores in p-type Si do not. n-macropores thus can and will always reduce their diameters if the current is decreased, and increase their diameter for increasing current as long as the minimal pore wall width d_{Wall} has not yet been reached. Macropores in p-type Si have no preference for specific current density as long as it is not above a critical value and thus tend to always grow to a maximum diameter given by the nucleation geometry and the condition $d_W \approx 2d_{SCR}$.

These points alone would allow "easy" modulation of n-macropore diameters and no modulations of p-macropore diameters. There are indeed many investigations concerning "modulated" macropores in n-Si [1 - 7] and hardly any for p-Si. Experimentally it is observed that modulating the diameter of macropores in n-Si, while easy in principle, is not easy in practice but still much easier than in p-type Si. Since modulated pore diameters are mandatory for key applications [11, 12] they have been investigated in some detail in the group of the authors. The key topic for success is one more parameter that influences the dissolution process during pore formation: diffusion-controlled passivation kinetics.

II. PASSIVATION KINETICS AND DIFFUSION LIMITATION

Pore growth results if current flow is restricted to the pore tip, which in turn demands that the sidewalls are "passivated" against current flow at all times. The term "passivation" is used broadly and includes all effects that prevent current flow. This includes always the saturation of the Si surface bonds by some species (typically hydrogen) that passivate electronic states in the interface to the electrolyte in such a way that no appreciable interface charge densities are found. Only in this case will the junctions behave like textbook junctions that have their parameters determined by external parameters. Pore etching in this model relies on etching being faster than passivation at the pore tip areas and far slower or zero at the wall areas.

A growing pore continuously generates fresh and thus not yet passivated surfaces. The passivation of these fresh surfaces takes some time. Passivation must neither be too fast, preventing continues etching of the pore bottom, nor too slow, making pore walls susceptible to attack. These mechanisms show up most clearly when using high concentration of acidic acid in an aqueous electrolyte for etching macropores in n-Si using backside illumination. An optimum acidic acid concentration is found, above which the dissolution at the pore tips drastically decreases, while the stability of the pore walls and the sample surface continuously improves with increasing acidic acid concentration [13, 14]. Two more features well known for pore etching are tightly related to the surface passivation: dependence of the dissolution on the crystal orientation and changes of pore morphologies as a function of pore length, i.e. on concentration changes of products and educts induced by diffusion through the length of the pores. The most prominent examples are the current line oriented pores in InP and other semiconductors. These pores can only grow under a layer of crystallographically oriented pores, which provide the necessary diffusion limitation for the species relevant for the crystallographically dependent passivation of pore walls [15].

In this paper a further example for the importance of diffusion limitation for macropore etching will be discussed, i.e. adding approx. 0.01 M of polyethylene glycol (PEG) to the "standard" electrolyte: 5 wt.% of hydrofluoric acid (HF) dissolved in Dimethylformamide (DMF). PEG increases drastically the viscosity of the electrolyte; it hardly interferes with the etching properties of an electrolyte for not-so-deep and un-modulated pores. However, it enables deep pores and easy pore diameter changes in p-type Si, even for shallow pores (e.g. for 10 μm pore length), which is nearly impossible without addition of PEG. The effect of PEG to allow for diameter modulation has been studied in two experiments by FFT impedance spectroscopy (IS) when applying sudden changes in the current density. The impedance measurements have been performed every 2 seconds by applying 30 frequencies between 10 Hz and 20 kHz simultaneously to the current and analyzing the linear voltage response. The current density profile is shown in Fig. 2; it starts with 19 mA/cm^2 for 5 min., then 3 mA/cm^2 for 10 min., and finally 19 mA/cm^2 for 2 min. Fig. 2 shows the results of the impedance analysis for experiments without (Fig. 2a) and with addition of PEG (Fig. 2b). With PEG a significant diameter modulation was found, no significant modulation was visible in SEM images without PEG. Correspondingly strong differences are found for the impedance results. Especially the time constants τ_1 and τ_2 show a significant difference. Without PEG the time constants τ_1 and τ_2 are much larger and the step like change in current density is nearly invisible in the curves. With PEG the step like change in current density is clearly visible in the curves for τ_1 and τ_2; in addition in the curve for τ_3 clearly a relaxation with a time constant in the order of one minute is visible. This time corresponds well to the length of the shoulder in the pore for the transition from large to small pore diameter.

The experiments with PEG show larger absolute values for all resistances in Fig. 2 which just reflects the overall smaller dissolution rate in this highly viscous electrolyte. It is no contradiction to find better pore growth for larger transfer resistances because good pore etching is not just dissolution of silicon but dissolution of silicon with a high selectivity between dissolution of pore walls and pore tips. Obviously the time constants are more sensitive to this selectivity between pore walls and pore tips than the transfer resistances, i.e. the decisive category for understanding surface passivation is most probably speed and not strength. In case of optimal pore formation, i.e. when adding PEG, a reduced current density leads to a drastic increase of the impedance time constants in Fig. 2b); such difference in local current density exists in each pore between pore walls and pore tips and thus leads to a self amplification of the selectivity for the passivation

(and thus dissolution) of pore tips and pore walls. This self stabilizing effect is missing in the experiment without PEG.
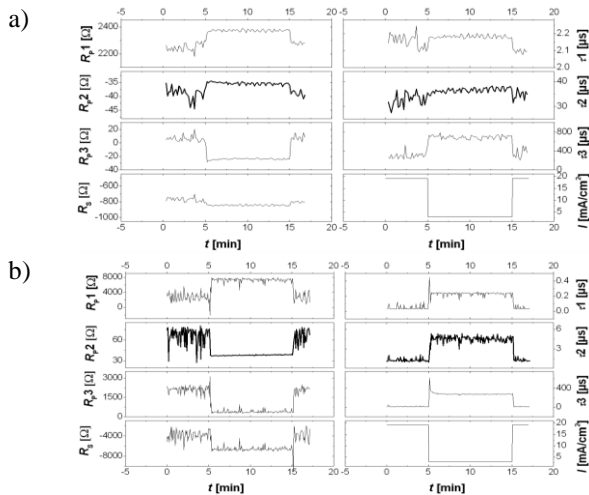
a)

b)

Fig. 2. Comparison of the relevant IS parameters of pore diameter modulations a) without and b) with PEG addition to the electrolyte [16].

The high viscosity of the PEG containing electrolyte does not only enforce a strong difference in the concentration at pore top and pore tip (which in principle is a drawback for fast pore formation) but may allow for concentration gradients between pore tip and nearby pore walls, necessary to allow for the selectivity in local silicon dissolution rates, i.e. good pore formation.

In what follows only optimized electrolytes with PEG additions are being used. This allows a defined diameter change of growing pores at a pre-determined depth. Further diameter changes at larger depth must take into account that the first diameter variation changed the system (it provides for some geometric diffusion limitation, for example, if the diameter was decreased). In the end, a complex $j(t)$ profile is implemented and controlled via in-situ FFT IS.

The possibility of implementing controlled pore diameter variations will now be applied to the production of superior Si microwire anodes for Li ion batteries and the formation of uniform size-controlled Si nano needles.

III. MAKING SUPERIOR SI MICROWIRE ANODES FOR LI ION BATTERIES BY MODULATING PORE DIAMETERS IN P-TYPE SI

Pore modulation in p-type Si allows for the fabrication of Si microwire array anodes for Li ion batteries. Fig. 3. shows a SEM micrograph of an anode with the highest capacity theoretically possible (4200 mAh/g) that is stable for at least 80 charge/discharge cycles [17].

The optimized Si microwire anode necessitates

- that the free space between the wires is as small as possible, just what is needed to accommodate the volume change of the Si during lithiation and allowing contact to the electrolyte (via formation of a so-called solid electrolyte interface or SEI,
- that the wires are as long as possible, and
- that the surface of the wires is preserved to allow the deposition of (minimum amounts) of Cu as efficient current collector.

In this context it is necessary to point out that in a real battery system the capacity of the anode must always be considered with respect to the combined weight of i) Si, ii) the weight of electrolyte the Si must be immersed in, and iii) the weight of the current collector. The weight of the items ii) and iii) determines the total weight; keeping it to a minimum necessitates the optimized Si microwire geometry outlined above and illustrated in Fig. 3. This structure can be only accomplished through pore diameter modulation. Fig. 4 shows a micrograph of a macroporous Si sample with modulated pore diameters to prepare Si microwires akin to the ones in Fig. 3.

Diameter modulations are necessary to:

- Produce the stabilizing planes that avoid "collapse by stiction". The thicker parts of the wires, preventing stiction, are produced by reducing the diameters of the original pores (see encircled sections of the pores of Fig. 4). After chemical over etching, the original pore walls collapse to form the microwires; additionally there is still some material left between the wires at the positions of the diameter reductions, very efficiently preventing collapse by stiction, as shown in Fig. 3.
- Pore diameters are increased close to the pore bottom. The microwires are then very thin at the interface to the Si substrate and can be easily detached by "pulling".
- The pore diameter is slowly increased as a function of depth so that less material needs to be removed in the depth of a pore during over-etching. This counterbalances the effect of reduced etching rates in depth.
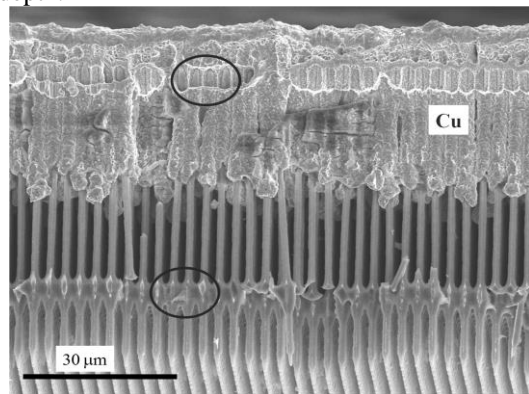

Fig. 3. Optimized Si microwire anode. In the upper section the wires are embedded in Cu, assuring a good mechanical and electrical contact. The encircled sections point to supporting layers that avoid stiction and allow easy processing.
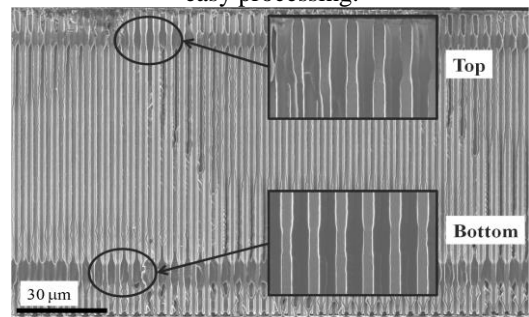

Fig. 4. Macroporous Si for the preparation of microwires (see Fig. 3). The encircled pore diameter reductions are necessary for the formation of support layers.

IV. MAKING Si NANO RODS WITH DEFINED GEOMETRIES AND HIGH YIELDS

Through pore modulation in Si one may prepare also micro/nano Si particles with defined sizes and shapes, single crystalline. An example of the particles enabled with pore modulation is shown in Fig. 5.

The fabrication process could be divided in the following two main steps. Exact details of the fabrication process will be published elsewhere.

- Electrochemical etching of macropores with periodic diameter increases ("bulges") are produced. The length between two bulges corresponds to the length of the final particles. The diameter can change abruptly or slowly between two values, according to the desired shape of the particles. The number of bulges translates into the number of particles that can be produced per microwire, obtained as before by overetching. An example of pores is shown in Fig. 6.

- The second step, as for the preparation of microwires, is chemical etching of the pore walls producing particles. The minimum etching time is determined by the time needed to etch away the distance between the bulges, liberating the nano rods. The etching time can be extended if the desired diameter of the nano rods needs to be smaller.
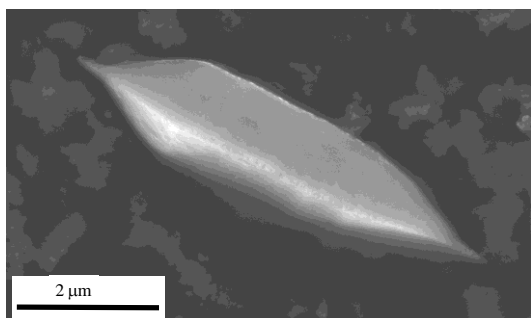

Fig. 5. Example of Si particle produced from macroporous Si with modulated pore diameter.
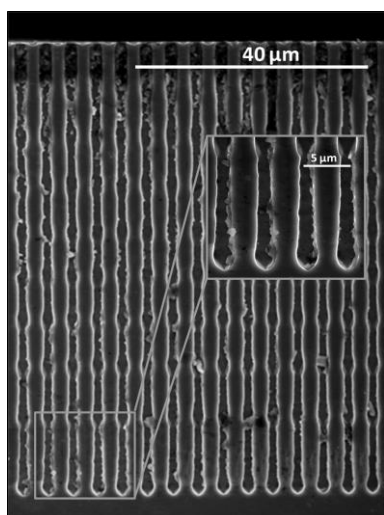

Fig. 6. Macroporous Si with modulated pore diameters, for the preparation of Si nano rods. The close-up section depicts the last modulations.

CONCLUSION

Pore modulation in p-type Si can be accomplished through current modulation in time, and the selection of adequate additives like polyethyleneglycol, which help for the passivation of pore walls.

Macroporous p-type Si with modulated pores is of great interest for different applications, like the preparation of high capacity Si wire anodes for Li-ion batteries, and Si nano rods for biological purposes.

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