# IMPEDANCE SPECTROSCOPY AS A POWERFUL TOOL FOR BETTER UNDERSTANDING AND CONTROLLING THE PORE GROWTH MECHANISM IN SEMICONDUCTORS

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Abstract: This work shows new results towards a better understanding of macropore growth in semiconductorphenomenology by using *in-situ* FFT impedance spectroscopy. A new interpretation of the voltage impedance is proposed. In particular, the pore quality could be quantified for the first time *in-situ*, especially by extracting the valence of the electrochemical process. The study paves the way towards an automatized etching system where the pore etching parameters are adjusted *in-situ* during the pore etching process.

Key words: FFT impedance spectroscopy, macropore, electrochemical etching

### **1. INTRODUCTION**

The electrochemical pore formation in Si is a topic [1] with many potential applications and much progress was made towards the development of production technologies [2] and many product prototypes were advanced (see [3] and references therein). Nevertheless, despite all of this work, no product based on porous Si can be found on the market at present. Among the main reasons for this is the still not fully understood mechanism of pore formation, or more generally, the many open questions in the field of electrochemistry of semiconductors. As an example, many envisioned applications demand precise control of the pore quality (e.g. diameter variations, pore wall roughness) and the present understanding of pore formation mechanisms, although rather advanced in some respects, does not ensure the full control of the etching process as it would be needed.

In this work, we show how impedance spectroscopy can be used for the purpose of controlling the macropore growth in n-Si. In particular, it is shown how one can extract the dissolution valence at the pore tips from the measured impedance. This number is used as a quantification of the pore quality. Determining this number *in-situ* can pave the way toward the implementation of an automatized etching system.

### 2. EXPERIMENTAL

n-Si wafer with low doping levels corresponding to a resistivity of 5  $\Omega$ cm are used for etching macropores. The substrate orientation is (100) with an n<sup>+</sup> layer on the backside of the wafer for good ohmic contact to the sample. The etching is done using backside illumination (BSI) [4]. The samples were pre-structured by standard photolithography before etching; the nucleation pattern was a hexagonal lattice with a lattice constant of  $a = 4.2 \,\mu\text{m}$ . The electrolyte consisted of 5 *wt.*% HF in an aqueous electrolyte. The temperature of electrolyte was fixed at 20°C. The FFT impedance spectrometer embedded with the etching system provided by the ET&TE GmbH, Germany was used to extract information concerning pore growth during the etching process.

### 3. **RESULTS AND DISCUSSION**

For voltage impedance a small perturbation signal is applied to the anodization voltage and the response in the etching current is measured. Fig. 1a shows the I-V curve of n-Si in contact with HF under BSI. One can easily see that a change in the voltage causes a variation in the current. Since during the macropore etching the etching voltage must be in the saturation regime of the IV curve [2], the linearity condition is fully fulfilled. However, another problem can be seen, i.e. being in the saturation regime, any perturbation in the voltage generates a minute variation of the current. In order to separate the measured signal from noise, strong requirements are imposed to the measuring hardware as well as data processing software.

#### Impedance Spectroscopy

Fig. 1b shows a tipical Nyquest plot of the measured impedance. The squares indicates the measured data. The data is fitted using the following model:

$$Z(\omega) = R_s + \frac{1}{\left(\frac{i\omega\tau}{\left(R_p + \Delta R_p\right)\left(1 + i\omega\tau\right)} + \frac{1}{R_p\left(1 + i\omega\tau\right)}\right) + i\omega C_p}$$
(1)

where  $R_s$  is the serial resistance accounting for the voltage losses at the contacts and electrolyte,  $R_p$  and  $\Delta R_p$  are the chemical transfer resistances which in our model are frequency dependent,  $\tau$  is a time constant and  $C_p$  is the parallel capacitance describing the capacitive nature of the reaction interface. A full derivation of the above model can be found elsewhere [5]. The solid fitting curve in Fig. 1b shows a very good match between the fit model and the measured impedance.



Fig. 1. The IV curve of the n-Si/HF interface with BSI illumination (a). The Nyquist plot of the measured voltage impedance together with the fitting curve (b).

Generally, interpreting the impedance data for macropore formation under back side illumination (BSI) for all kinds of etching conditions is nearly impossible since a lot of electrochemical dissolution processes can occur in parallel, e.g. the (desired) photoinduced dissolution of Si at the pore tips, the (undesired) dissolution of Si at the pore walls by electrical breakthrough current, or the formation of side pores. Therefore the voltage impedance can look much more complicated than for the formation of "nice" macropores as described in this paper.

While the capacitive behavior of the measured impedance during macropore formation could be well described by other authors [6], most challenging is the measured "inductive" loop. As it was mentioned above,  $R_p$  and  $\Delta R_p$ , which represent the intersection points of the inductive loop with

the abscissa axis, are related to the chemical processes that take place at the reaction interface. Under the optimal pore growth conditions this is solely represented by the pore tip. The main reactions at the pore tip, involving charge transfer, represent the Si dissolution. We claim that the  $R_p$  and  $\Delta R_p$  represent the dissolution reactions which are slow, i.e.  $R_p$  for  $\omega \rightarrow 0$ , and fast, i.e.  $R_p + \Delta R_p$  for  $\omega > 0$  correspondingly. Hence the parallel resistance is determined by two processes with different reaction rates: fast and slow. We assign this to the two well known and accepted main reactions for dissolution) and tetravalent (slow, purely chemical dissolution of the oxide in order to dissolve Si).

Without going into too many details here (more can be found in Ref. [5]) the measured  $R_p$  and  $\Delta R_p$  can be used to calculate a quantity *n* which describes very well the quality of the obtained macropores. It is defined as:

$$n = \frac{4}{2 - \frac{\Delta R_p}{R_p + \Delta R_p}} \tag{2}$$

Analysing the time behaviour of n we concluded that it represents the dissolution valence at the pore tip. That is, by using the voltage impedance this magnitude can be *in-situ* measured. It is important to mention that the dissolution valence was earlier measured via gravimetry and a value of 2.7 was found [7]. As it will be further shown, the measured values in this work fit very well with the advanced numbers.

Fig. 2a and 2b show two type of pores etched under nonoptimized conditions: in (a) macropores are etched with a small diameter such that the pore walls are fully conductive, i.e. the photogenerated holes can penetrate the pore interspacing and be consumed in electrochemical reactions at the pore walls; in (b) are shown pores etched with a very large diameter such that the pores walls are insulating; later, however, the anodization voltage is increased such that the pores become star or petal-shaped with features which due to their sharp geometries advantage the current flow.



Figure 2. SEM cross section of macropore etched under unoptimized conditions leading to too

larger interspacing between the pores (a) or an extremely large diameter and star- or petal-like shape of the macopores (b). The measured dissolution valence for both cases (c).

Fig. 2c shows the calculated dissolution valence from the measured impedance data. Striking is the value of 3 which for the case of small diameter pores is hardly reached while the large diameter pores reach this value relatively fast, however after almost 200 min decreasing.

The maximum value of the valence can be 3 if the electrochemical reactions would take place exclusively at the pore tip, or it reduces to 2 if etching n-Si in the dark [2]. Since the measured valence is an average describing the dissolution at the pore tip as well as the (unwanted, but unavoidable) dissolution at the pore walls it becomes obvious why the values in Fig. 2c are situated between 2 and 3. Obviously, the small diameter pores, where the holes penetrate easily between the pores and thus increase the leakage current, exhibit an average valence well below 3, i.e. due to a strong component of the divalent dissolution. In contrast, when etch large diameter pores, due to completely insulating pore walls, the measured valence reached very fast 3, however decreasing toward 2 once the voltage is too high and the macropores become the star or petal-shape hence increasing the leakage current via the pore walls, i.e. the divalent dissolution.



Fig. 3. The SEM image in cross section which shows good and bad macropores on the same sample (a). The extracted dissolution valence (b) for the structure in (a). A SEM picture of the sample in cross section where the pore growth did function well (c) and the extracted dissolution valence from the impedance data (d).

For etching homogeneous macropores the leakage current, i.e. the divalent dissolution of the pore walls might be very small. Measuring *in-situ* 

the dissolution valence might help to assess the moment when leakage current gets to large and eventually try to avoid it by readjusting the etching parameters. Fig. 3 shows such an example. The SEM picture in Fig. 3a shows the cross section through a porous structure which at the first glance seems to be etched perfectly. However, a closer inspection reveals that there are regions on the sample of bad grown macropores, in particular where the diameter is not constant and also the lattice is destroyed. The measured valence, according to Fig. 3b, shows a fast increase to 3 indicating a good start of the etching. After 300 min the dissolution valence starts to decrease toward 2 indicator that the leakage current through the walls becomes dominant and the porous structure is compromised. Fig. 3c illustrates a SEM picture in cross-section through a sample that was etched perfectly. The very homogenous macropores and good pore quality can easily be observed. The valence reaches very fast a value of 3 where it remains for longer time.

Without impedance analyses during the pore etching the only way to check if the pores grow perfectly is the analysis at the illumination intensity as a function of time. For the sample shown in Fig. 3a the illumination intensity gave signs for a problems in the macropores etching only after 400 min. By means of the impedance, however, already at the 250 min it could be observed that the etching process is not under optimized condition. Having the valence as a quality monitor tool allows at an early stage the readjustment of the etching parameters which could easily save the etched structure. After 400 min no parameter adapting allows to re-establish the normal etching process and the porous structure is considerably destroyed. Hence the voltage impedance becomes a very powerful tool that can be effectively used in order to *in-situ* control the etching process.

### 4. CONCLUSIONS

The data extracted from the voltage impedance allows one to estimate the dissolution valence at the pore tip at any instance in time. This is for the first time that such precise information about the development of the pore tip state could be obtained. By comparing the valence with the quality of the pores, it could be concluded that the optimum pore growth takes place at a valence of  $n \sim 3$ . This justifies the assumption that the pores advance while producing, and ulterior dissolving, oxide at the pore tips. As a next step a special model is to be developed for the purpose of explaining the growth mechanism of the macropores under optimized conditions.

# ACKNOWLEDGEMENTS

Parts of this work have been supported by the Alexander von Humboldt Foundation.

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