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Organic and aqueous electrolytes used for etching macro- and mesoporous silicon

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The aim of this work is to explain the influence of the solvent molecules on silicon dissolution using several hydrofluoric acid containing "organic" electrolytes. The investigations focus on the morphology of the mesopores and macropores and the electrochemical valence of the overall reaction. Some basic properties of the electrolyte (polarity, tendency to form silicon oxide, and the H donor properties) were found to dominate the macropore formation in p-type silicon. For macropore formation the correct balance between the two main dissolution paths (direct silicon dissolution and dissolution via an anodic oxide) is very important. For mesopores in highly doped p- and n-type silicon the direct dissolution is dominant. The consequences of mixing organic and aqueous solutions are discussed.

1 Introduction In 1990 Lehmann and Föll [1] discovered that regular arrays of perfectly straight macropores (structure sizes according to the IUPAC norm: macropores >50 nm) with extremely large aspect ratios ("good" macropores) can be obtained in the n-Si/HF system in an aqueous electrolyte using back side illumination. The first paper dealing with organic solvent/hydrofluoric acid containing electrolytes for macropore formation was published 1994 by Propst and Kohl [2]. The authors studied the dissolution of silicon in the absence of water in hydrofluoric Acetonitrile [2] and obtained for the first time (rather poor) macropores in p-type silicon. In the following years, many papers dealing with macropores in p-type silicon and their possible formation mechanisms were published [see, e.g., 3–6] and various organic electrolytes have been used [see, e.g., 3–6]. While organic solvents essentially suppress the electrochemical oxidation of Si in comparison to an aqueous electrolyte, it has been shown that organic solvents can act as a mild oxidizing reactant for silicon, too. Song and Sailor, e.g., studied the oxidation of silicon in DMSO with infrared spectroscopy [11]. A number of quite different models has been published to explain the formation of macropores in p-type Si. Models referring to e.g. pore wall passivation [3], diffusion limited random walk [7], or surface instabilities give general scales for the pore morphology under certain conditions [8–10].

The detailed chemical reactions for the silicon dissolution are still under discussion [12]. Different dissolution mechanisms have been suggested for the interaction of the hydrogen passivated silicon surfaces and the aqueous or organic fluoride containing solutions. Several experiments indicate that the silicon surfaces are H-terminated after the etching and it is generally accepted that etching proceeds through sequential reactions of Si–H groups with F^- and H^+ to form Si–X. Subsequent steps involve chemical reactions of the Si–Si backbones with H_2O or HF [12]. The electrochemical reaction is always triggered by at least one hole in the semiconductor [13].

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In the present paper we studied the influence of different organic electrolytes on the electrochemical reactions and the morphologies of macroporous silicon.

2 Experiments Various p-type silicon specimens (0.1 Ω cm, 1 Ω cm, and 6 Ω cm, {100} oriented; 10 Ω cm and 20 Ω cm, {111} oriented; CZ-grown, polished, from MEMC) were used. The specimens were subjected to anodic etching under the following conditions: Galvanostatic current densities between 2–4 mA/cm^2 (applied from a KEITHLY 238 high current source), stabilized electrolyte temperature (20 °C), and no illumination of the sample.

Different organic electrolytes were used which have already been tested as suitable organic solvents for p-type macropore formation [2, 3, 5, 6]: acetonitrile (MeCN), dimethylformamide (DMF), dimethylsulfoxide (DMSO), tetrahydrofluran (THF), N-propanol, dioxane, and ethylacetate (ETA). All electrolytes were prepared from a 48% HF solution. Therefore always a small amount of water (~4 wt%) is present even in the organic solutions. The electrolyte was pumped through the cell and its temperature was kept constant at 20 °C by running it through a heat exchanger controlled by a PC. A Pt reference electrode was used in all cases to ensure reproducible results and quantitative control of the junction potential. Nitrogen gas has been bubbled through the electrolyte.

The pore morphologies were investigated by scanning electron microscopy (SEM) using a Philips XL30 microscope. The cleavage plane is always {110}.

3 Experimental results The formation of an anodic oxide with organic electrolytes that did not contain HF has been studied with galvanostatic experiments (0.1 mA cm^{-2}, p-Si, 4 Ω cm). The bubbling of nitrogen into the electrolyte was absolutely necessary for reproducible results. The resulting voltage curves are shown in Fig. 1 and Fig. 2. Figure 2 shows just the first few minutes which are obscured in Fig. 1 and starts all curves at nominal zero.

In order to study the influence of the organic solvent, macropores on (0.7–1.1 Ω cm) p-type Si (galvanostatic, 4 mA cm^{-2}, 120 min, 4 wt% HF) have been etched with MeCN, ETA, N-propanol, dioxan, HMPA, DMSO, DMF, and DMA as an organic solvent. In order to quantify the tendency to form macropores, the pore depth obtained after the 120 min. etching time as measured with the SEM was taken. If only a rough or wavy surface is formed, the roughness was interpreted as a macropore depth, too (see inset in Fig. 3). Figure 3 displays the average pore depth for the different electrolytes. A rough surface is formed in hydrofluoric MeCN, THF, N-propanol, dioxane, and ETA – followed by "proper" but still rather poor pores obtained with DMF and DMSO at 3 µm and 4 µm pore depth, respectively. The deepest pores (~5 µm) were obtained in hydrofluoric DMA. In the case of MeCN and ETA a mesoporous layer is formed. The general morphology was studied with transmission electron microscopy [14].

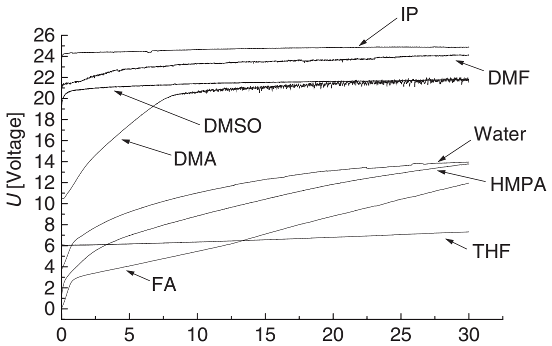

Fig. 1 Time development of the voltage for anodic oxide formation under galvanostatic conditions (0.1 m A cm^{-2}, p-Si, 4 Ω cm) in various organic solvents.

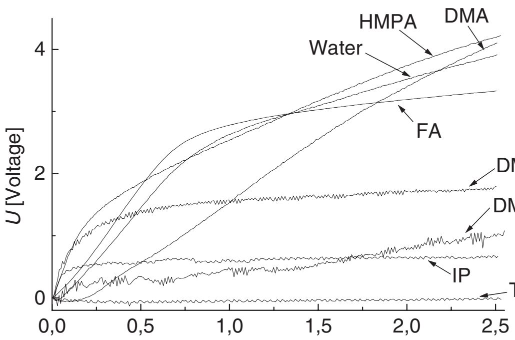

Fig. 2 Voltage vs. time curves for the first few minutes and normalized to zero Volts.

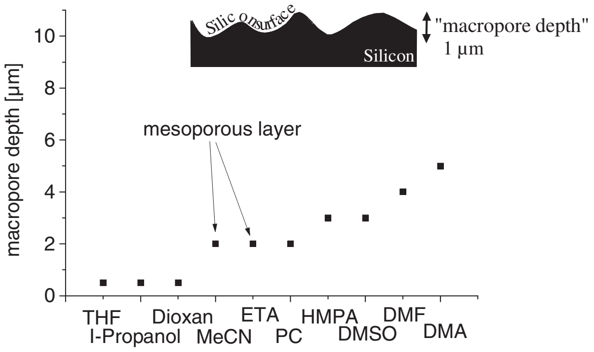

Fig. 3 Macropore depth as a function of the electrolytes used.

4 Discussion The voltage vs. time curves in Figs. 1 and 2 are induced by the electrolyte specific peculiarities for the formation of an anodic oxide layer. With increasing oxide layer thickness, the voltage has to be increased to allow for constant current flow. The slope of the voltage vs. time curves in the linear portion of the curves thus contains information on the speed of the oxide growth and the quality of the oxide layer formed with respect to its ability to impede current flow. The slopes of the $V(t)$ curves thus obtained are shown in Fig. 4. Formamide and water are obviously forming good oxide layers quite fast. In comparison to these solvents, DMF and DMA are mildly oxidizing reactants.

Since no HF was added to the electrolyte, no chemical oxide dissolution is possible. So after some time current flow will only be possible by providing current paths, i.e. cracks or pores through the oxide layer [15]. Each newly formed crack will produce a voltage peak for a short time. The roughness or noise level of the voltage curves thus reflect the roughness or homogeneity of non-linear events allowing current and thus voltage fluctuations thick oxide layers in the different electrolytes. Noisy curves indicate few and violent processes, while smooth hint at, e.g. many small pores forming and disappearing continuously. According to this interpretation, DMA and DMF are forming low quality oxides – these oxides then should be easy to dissolve in hydrofluoric acid containing electrolytes.

Before discussing the results in more detail we will add two properties of the tested electrolytes, extracted from the literature: the polarity of the electrolyte (Fig. 5) and the ability of the organic solvents to act as H donor (Fig. 6) (data for Figs. 5 and 6 taken from [16]). The organic solvents are ordered in both figures according to their ability to form macropores, described by the depth of the etched macropores after a fixed time as shown in Fig. 3. It becomes clear that in order to obtain “good” macropores, the electrolyte should have the following three properties:

- Medium oxidation of silicon as expressed in the slope of the $U(t)$ curve
- Good H donor capacity
- Large polarity.

Most of the papers dealing with macropores in n-type silicon agree with the opinion that two basic dissolution reactions take place at the tip of a pore in silicon: The first reaction path is the direct silicon dissolution and the second path is the silicon dissolution via an anodic oxide. So the necessity for the

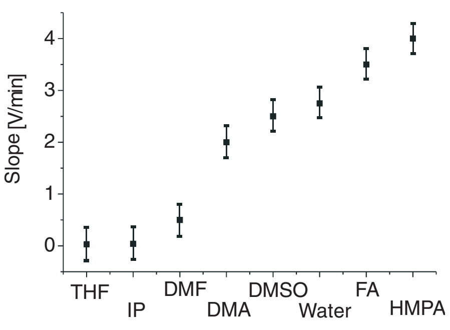

Fig. 4 Slope of the $U(t)$ curves from Fig. 2 for the various electrolytes investigated.

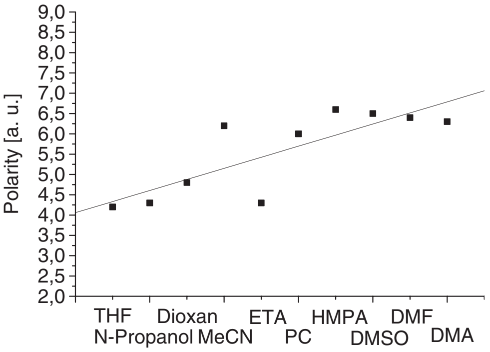

Fig. 5 Polarity of the organic solvents used for macropore formation vs. the tendency to form macropores.

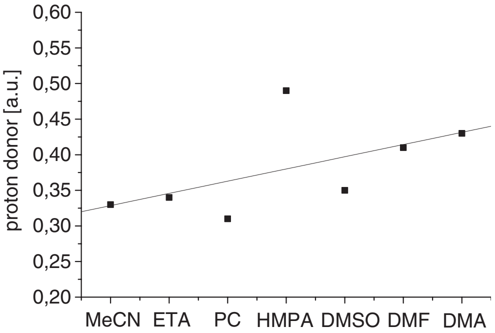

Fig. 6 Proton donor properties of the organic solvent molecules vs. the tendency to form macropores.

third property is quite obvious; silicon oxide can only be dissolved by HF, and if the electrolyte is not highly polar it can not easily dissolve HF to make it chemically available at the silicon electrolyte interface.

The meaning of the other two electrolyte properties are not so easy to understand. We will discuss them within the framework of the current burst model [17] which can easily adopt the experimental findings. Essential are the following properties of the direct dissolution process and the dissolution process via an anodic oxide:

– The H-termination of the silicon surface acts as the main passivation mechanism of the pore walls [16]. The decisive parameter for pore formation is the velocity of the H-passivation on different crystallographically oriented surfaces as a function of the composition of the electrolyte (and temperature). The selectivity between the passivated pore walls and the non passivated pore tips is the basic mechanism for pore formation. The better the wall passivation the higher is the dissolution rate at the pore tip. Consequently the direct dissolution is the main reason why pores are formed since it allows for an effective passivation of the silicon surface.

– If oxide is formed, no {*hkl*} dependent H-passivation of surfaces is possible. This leads to smooth silicon surfaces, if oxide formation and dissolution is the dominant chemical process (e.g. at high anodic potentials), and electropolishing of the silicon surface occurs [17].

According to the above list, an absolute necessity for (meso- or macro-) pore formation in silicon is the availability of H, and thus the H donor ability of the solvent is crucial. A clear trend is visible in Fig. 6: the better the H donor property, the better is the macropore formation. A more systematic study concerned with the effect of adding H donating molecules to MeCN and supporting this view is presented in [5].

If macropores are finally formed, will now depend on the balance between direct dissolution and oxide formation and dissolution. If the tendency to form stable oxide is too strong, e.g. for formamide which shows the highest value for the $V(t)$ slope in Fig. 3, no macropores can form because electropolishing (or, interestingly, micropore formation) occurs. If, in contrast, the tendency to form a stable oxide is too weak, e.g. for MeCN and ETA (which are not displayed in Fig. 4 because they do not form an oxide layer at all), only mesopores can be formed without a suitable oxide formation, thus there is no ability of an electropolishing reaction to smooth pore walls which is needed for macropore formation.

Some organic electrolytes (e.g. DMSO) act as mildly oxidizing reactants for silicon already chemically [11]. DMA, DMF, and DMSO occur in Fig. 4 as medium oxidizing solvents and, according to Fig. 3, allow for the best macropore growth. According to Fig. 4 pure aqueous HF electrolytes will form an oxide layer which is too stable to allow for good macropore growth on p-type silicon. Macropores will only be found if the oxidation process is weakened by limiting the hole supply – either by using n-type Si or very small potentials (and then current densities). With organic electrolytes, the donation of oxygen is more difficult in comparion to water which explains the reduced tendency to form stable oxide.

For n-type silicon and back side illumination, the balance between direct dissolution and dissolution via an oxide layer can be optimized for water, too; it corresponds to a current density at the pore tip that equals j_{ps} [1]. Using organic electrolytes and back side illumination, however, the pores tend to become extremely small [18] and the walls are rough, since now the oxide formation in comparison to water is too weak.

5 Conclusion This work was to study the influence of the organic solvent molecules on the macropore formation in p-type silicon. It was found that essentially the polarity, the (quantifiable) tendency to oxidize Si, and the H donor properties are the major parameters governing pore formation. The proportion of direct silicon dissolution and dissolution via an anodic oxide encoded in these properties is the major factor responsible for the various pore morphologies and electrochemical reactions. This proportion is also a function of the hole supply; taken all factors together, pore formation in Si can be understood from general principles for all electrolytes used so far.

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