

Investigation of Mesoporous Structures for Thermoelectric Applications

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Abstract — Mesoporous silicon is an attractive material for thermoelectric application. For pore wall thicknesses around <100nm, phonons can not penetrate the porous layer while electrons still can, due to there smaller mean free path length. The resulting good electrical and bad thermal conductivity is a premise for efficient thermoelectric devices. This paper presents results regarding homogeneity, high porosity, and optimal pore wall thicknesses for porous silicon based thermoelectric devices.

Index Terms — electrochemical etching, mesoporous silicon, thermoelectric

I. INTRODUCTION

Porous silicon (PSi) has found various applications, e.g. in photonic devices [1], sensor systems [2] or drug-delivery devices [3]. In this paper electrochemically etched porous Si layers suitable for thermoelectric devices are discussed. Thermoelectric devices need a high electrical conductivity and low thermal conductivity. While in most materials electrical and thermal conductivity are coupled by the Wiedemann-Franz law, in porous material the big difference in mean free path lengths between electrons ($\approx 110\text{nm}$) and phonons ($\approx 300\text{nm}$) [4] allows for a decoupling of both conductivities.

In contrast to bulk silicon mesoporous silicon is well known to show a very low thermal conductivity as soon as the distance between pores becomes smaller than the mean free path length of the phonons, while the electrical conductivity stays high. Several papers describe efforts to enlarge the figure of merit ZT for thermoelectric application by optimizing porous materials [5 - 7]. This paper focuses on producing porous Si layers [8, 9] with pore walls sizes in the range of 20 - 100 nm.

II. EXPERIMENTAL DATA

Low doped silicon allows for larger mobilities of the electrons, which would be beneficial for the thermoelectric effect. Thus various electrolytes and etching conditions had been tested on low-doped material without getting reasonable porous layers. Thus in this paper we will only focus on mesopores etched on (100)-oriented highly doped n-type Si with resistivity of $(0.02 - 0.05) \Omega\text{cm}$. Etching has been carried out in the electrochemical cell described in detail in [10] without illumination. As electrolyte of 48 wt. % HF dissolved in acetonitrile in a volume ratio of 1:2 has been used.

All experiments have been performed at a constant temperature of $T = 20^\circ\text{C}$.

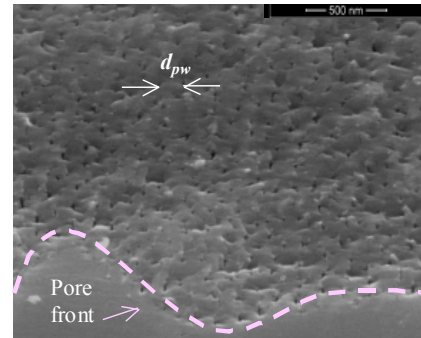


Fig. 1. SEM pictures of a cross section for pores. Electrochemically etched, 5 s, into n-type Si at 2 V for $(0.02 - 0.05) \Omega\text{cm}$ resistivity.

III. RESULTS UND DISCUSSION

Just by etching pore walls less than 100 nm the thermal conductivity is drastically reduced. In order to get a good electrical conductivity the pore walls should fulfill several properties:

- The porous layer should be uniform with a small spread of pore dimensions.
- The pore walls should be structurally as perfect as possible (not containing side pores, for example) to minimize scattering of carriers and thus the resistivity.

Since galvanostatically etched mesopores tend to show diameter oscillation (cf., e.g., [11, 12]) all mesoporous layers presented here have been etched under potentiostatic condition.

A typical result of mesopores with an average pore wall thickness of $d_{pw} \approx 100 \text{ nm}$ when etching 5 sec and 15 sec, i.e. just after finishing the pore nucleation, is shown respectively in Fig. 1 and Fig. 2a). The length of the pores is quite inhomogeneous, probably due to a small variation in the speed of pore nucleation at different position on the sample surface.

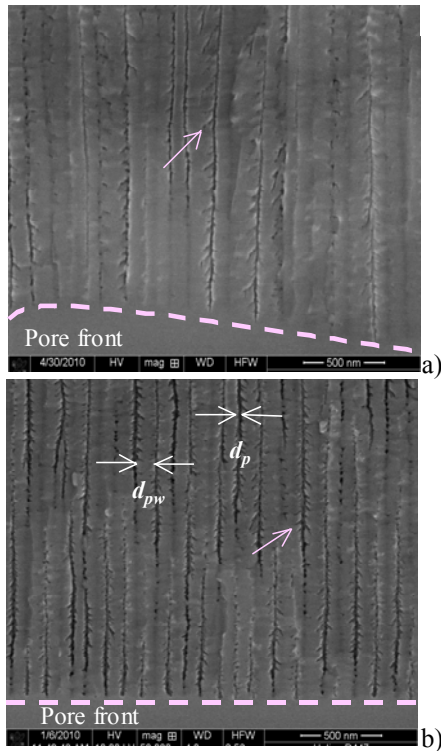


Fig. 2. SEM pictures of a cross section for pores in nucleation stage electrochemically etched a) 15 s, 2V; b) 30 min, 2V into n-type Si for (0.02 – 0.05) Ω -cm resistivity.

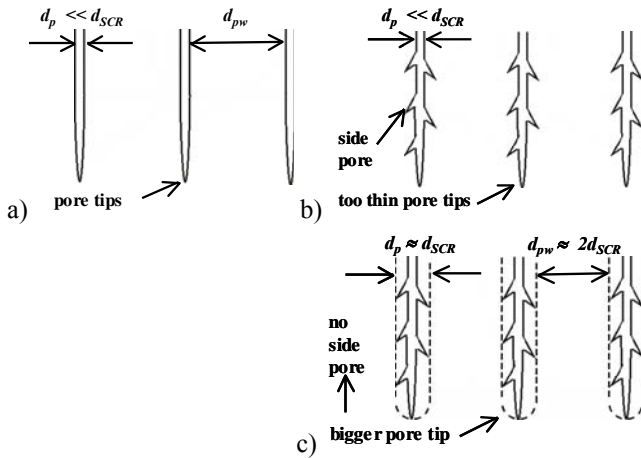


Fig. 3. Schematic illustrations for a model of the pore nucleation phase.

Etching for a longer time, e.g. for 30 min, the pore front becomes straight as shown in Fig. 2b). This is a general aspect of mesopore growth. Probably due to diffusion limitation increasing with pore length, the dissolution at the pore tips slows down, leading to a self-stabilizing adjustment of pore lengths. Since a straight pore front is essential for producing a thermoelectric device, the mesoporous layers have typically been etched to a length of 100 μ m, which is a thicker layer than necessary for the device. As visible in Fig. 2 for longer pores, the morphology changes from top to tip. Since a top layer can be polished off, the relevant pore morphologies are near the pore tips.

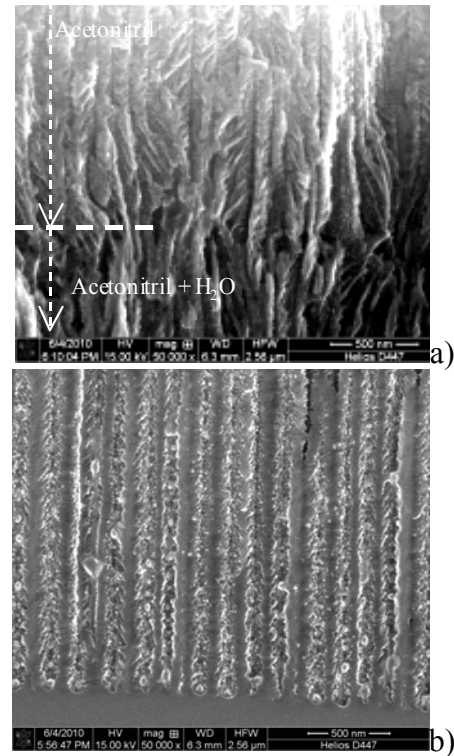


Fig. 4. SEM pictures of pores obtained with a “differential” electrolyte. Start with acetonitril containing 48 wt.% HF in a ratio of (2:1), growth with addition of water; a) overview (top region); b) pore tips.

The main problem when increasing the etch time is the formation of side pores. These side pores do not form instantly near the pore tips but their density and length increases with etching time; e.g. at the beginning of all experiments the pores have no side pores near the top, but after further etching many side pores are found near the top. This feature does not become perfectly clear from Fig. 2a) and Fig. 2b) but at least the trend becomes visible.

The nucleation phase has a substantial influence on the pore morphology. In the nucleation phase the pores are very thin and have a rather homogeneous pore density (Fig. 1). The pore wall thickness d_{pw} is around 100 μ m, which corresponds to $2d_{SCR}$ for the used resistivity, (d_{SCR} – thickness of the space charge region). As visible in Fig. 1 and Fig. 2, the pore diameter d_p is much smaller than the pore wall thickness d_{pw} . This geometry is illustrated in Fig. 3a). It is well known that optimal pore growth needs $d_p \approx d_{pw} \approx 2d_{SCR}$ (e.g. see [8]). For $d_p \ll 2d_{SCR}$ the electrical field around the pore tips will be drastically increased. Since the side pores have roughly the same diameter as the main pores, the strong increase of the electrical field around any small “bump” in a pore wall may trigger the formation of side pores, leading to pore morphologies as schematically shown in Fig. 3b), which correspond to the SEM images in Fig. 2b). So, to avoid side pore formation, a larger pore diameter could be helpful, as illustrated in Fig. 3c).

As e.g. discussed in [8] diameters of mesopores etched with aqueous electrolytes are larger in comparison to pores etched with organic electrolytes. Therefore H_2O was added to the electrolyte in a ratio acetonitril : H_2O : HF = 2 : 1 : 1.

Indeed, larger pore diameters d_p are found but the distance between the pores d_{pw} was larger as well, leading to the same morphologies as shown schematically in Fig. 3, just on a larger scale. Consequently side pores still occur.

Fig. 4 shows the resulting pores when starting the etching with pure organic electrolyte and adding water after roughly 5 seconds. As expected, a significant increase in pore diameter was found as shown in Fig. 4a). Subsequently a number of pores died out, leading finally to a pore morphology as shown in Fig. 4b) where again the pore walls are quite rough.

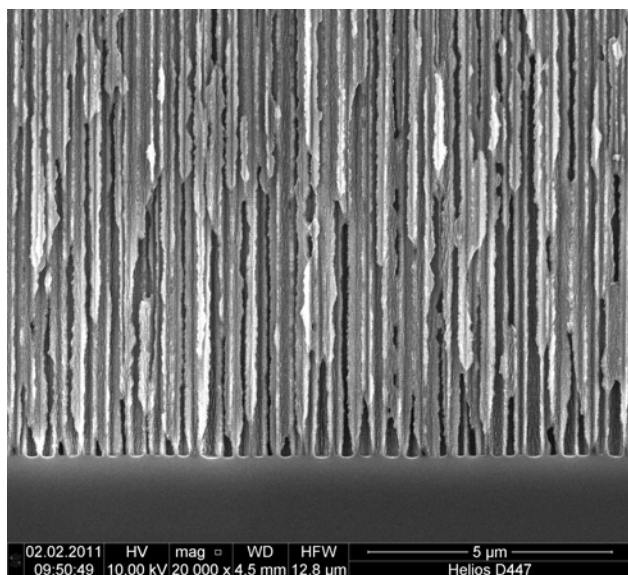


Fig. 5. SEM pictures of a cross section of pores etched with electrolytes acetonitril:HF in ratio (4:1) under galvanostatic condition for constant applied etching current 50mA for 30 min.

The water-free (as far as possible) electrolytes are the best ones. While many other electrolytes have been tried too, further improvements are still possible. Lowering the temperature a few degrees or increasing the viscosity of the electrolyte has been shown to improve pore morphologies in other cases, for example [13, 14] and need yet to be tried. Fig. 5 shows the best pore structures produced so far. The high growth rates of 3.3 $\mu\text{m}/\text{min}$ for 100 μm could be obtained. While not all goals are achieved yet, these pores already show promising results.

IV. CONCLUSION

The experimental results obtained permit to claim that silicon with low resistivity is an attractive material for thermoelectric application. The “water-free” electrolytes are the best ones for mesopore structure formation. Much work remains to be done and further optimization of the etching process is necessary.

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