Crystal orientation dependence of macropore formation in n-Si with backside-illumination in HF-electrolyte

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Abstract

The formation of macropores on anodically biased n-type silicon with backside-illumination was investigated as a function of crystal orientation and bias voltage. Specimens were cut from bulk crystals with various orientations from {100} to {111}, polished and subjected to anodic etching in HF. The resulting pores were investigated on cleaved samples by SEM. All pores were found to grow in either a $< 100 >$ direction or a $< 113 >$ direction, depending on the misorientation angle. This finding applies also to the branching of a single pore. The results can be understood if the valence for the dissolution reaction is approximately 2.6 in $< 100 >$ and approximately 4 in the $< 113 >$ direction, and if all other directions are not allowed for the growth of pores in Si.

keywords: macropore formation, crystal orientation dependence, $< 113 >$ orientation, anodic potential dependence

1 Introduction

Applying an anodic bias on a silicon HF contact allows to create pores which differ extremely in size, morphology and physical properties depending on the experimental setup [1, 2]. In this paper we discuss the formation of macropores in n-type silicon with backside illumination as shown in Fig. 1 [1, 2, 3, 4]. In contrast to the well-known porous silicon layer (PSL) with pores in the nm-region, macropores form only in n-type Si, their diameters are in the micrometer scale. Macropores are frequently lined with PSL, demonstrating that at least two independent pore formation mechanisms exist. Using a standard photolithography for generating etch pits as nucleation centers for pore growth, a very regular array of pores can be generated, which may serve as a starting point for a Si-microstructuring technique [5] or to create a "photonic crystal" [6]. (100)-oriented silicon shows a preferential growth in [100]

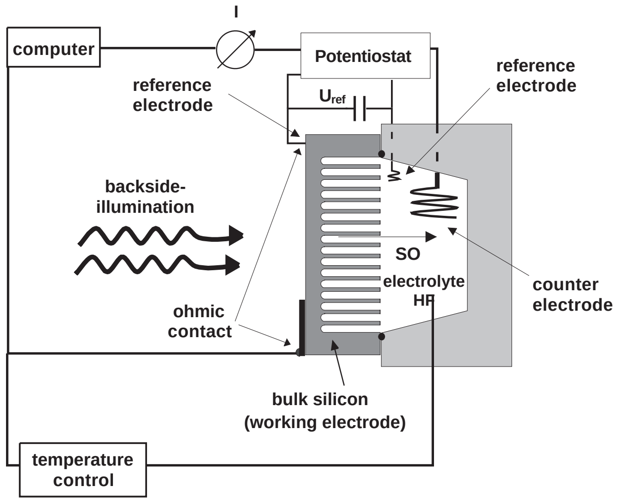

Figure 1: Schematic view of the macropore etching cell. For fixed values of anodic potential U and temperature of the electrolyte T the etching current I is computer controlled by regulating the backside illumination intensity on a wafer with surface orientation SO.

direction. One macropore experiment was done with {111} Si. The result was interpreted as a tree-like pore growth with pores in $< 100 >$ direction [7]. This paper systematically investigates the macropore formation for various orientations of the silicon surface between (100) and (111) orientation. The concept of "Random pores"was employed, i.e. no prestructured etch pits as nucleation centers for the pore growth were used.

2 Experimental set-up

Since no industrially produced Si is available with arbitrary orientation of the surface, silicon specimen (1 cm x 2 cm) were cut from the tail end of a n-Si crystal (4 Ω cm, (100)). Eight orientations from (100) (cutting angle α= 0) to (111) (α= 54.7) were prepared using a modified diamond ID saw. The saw damage was removed by lapping 80 μm and polishing the wafers with an acidic diamond suspension. The exact orientation of the surface was checked by a Laue transmission analysis getting an accuracy of 0.5. Taking a 4 w% HF-solution with a tenside for the reduction of the surface tension and a PC-controlled temperature of 20 C of the electrolyte, the pores are etched with a current density $j = 5.6$ mA/cm^2 for various anodic potentials between 1.5 V and 4 V. The pore growth is investigated by breaking the sample parallel to the $(01\bar{1})$ plane and SEM analysis of the cross section of the pore structure.

3 Results and discussion

Fig. 2 shows typical micrographs of pores in samples with a misorientation relative to [100] of 8 or 19.5 respectively. The main pores are easily identified, their growth direction is exactly [100]. A certain wavyness of the side wall of the pores on one side suggests the beginning of side pore formation, but no side pores of definite orientation are observed. However, care has to be taken in interpreting the SEM images, because side pores in directions not contained in the$(01\bar{1})$ cleavage plane would not be detected. The growth direction of the main pore remains exactly [100] up to misorientations of 43.3° (largest misorientation available). On $\{111\}$ oriented Si wafers, however (misorientation relative to $\{100\} = 54.7°$), the growth direction is [311]. The length of the pores - all conditions being equal - reduces from typically (50 - 55) μm in the [100] direction to about 35 μm in the [311] direction. The formation of side pores of definite orientation is observed for misorientations of the wafer surface ≥ 35.2 [(211)](Fig. 3 and Fig. 4). These side pores show a mirror symmetry to the cleavage plane, i.e. they are not contained in the cleavage plane. The growth direction of the side pores is $< 113 >$.

All experimental results can be explained quantitatively on the basis of two fundamental assumptions:

- Pores can only grow in $< 100 >$ and $< 113 >$ directions.
- For the growth velocities ν at equal current densities the following relation holds:

$$\nu_{100}/\nu_{113} \approx 4/2.6 \tag{1}$$

The ratio 4 / 2.6 was calculated from the length of the pores; it transforms into a condition for the valences n for the dissolution reaction: $n_{100}/n_{113} \approx 2.6/4$. The exact ratio might be somewhat bias dependent, but could be measured independently. A simple geometric calculation now defines the crystal direction for which pores are growing most quickly into the bulk, corresponding to the main pores, and the second fastest direction, corresponding to the side pores. With the given ratio of the growth velocities, a change-over from a $< 100 >$ growth direction to a $< 311 >$ growth direction would be expected for an angle α very close to 54.7. A particularly interesting feature for (111) orientation is found if the (111) plane is viewed at various depths below the original sample surface. In parts of the (111) sample an arrangement of the

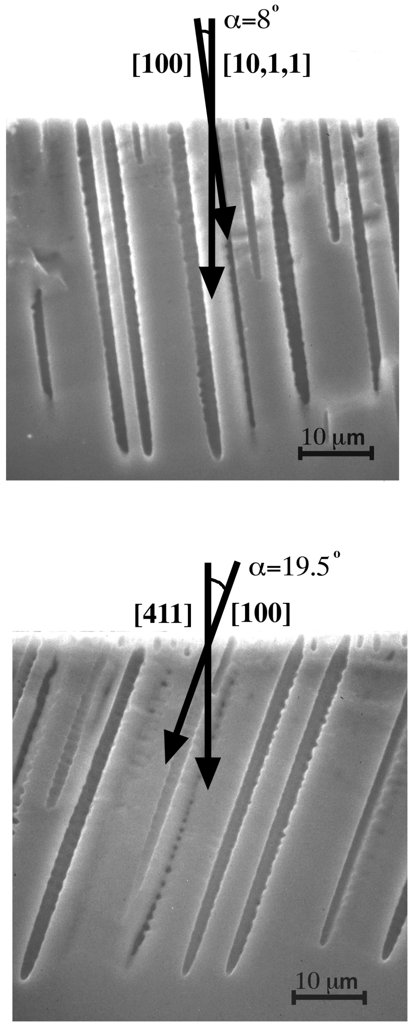

Figure 2: SEM-photograph of the pore cross section of a $(01\bar{1})$ plane for different orientations of the wafer surface. The main pores are growing in [100]-direction. a) Surface orientation (10,1,1). b) Surface orientation (411).

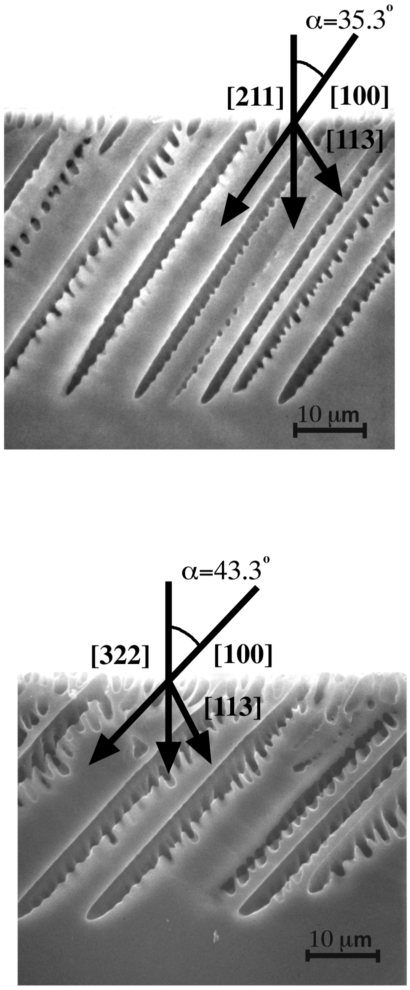

Figure 3: SEM photographs of the pore cross-sections of a $(01\bar{1})$ plane for different orientations of the wafer surface. The main pores are still growing in [100]- direction Side pores are growing in $< 113 >$ direction. a) Surface orientation (211). b) Surface orientation (322).

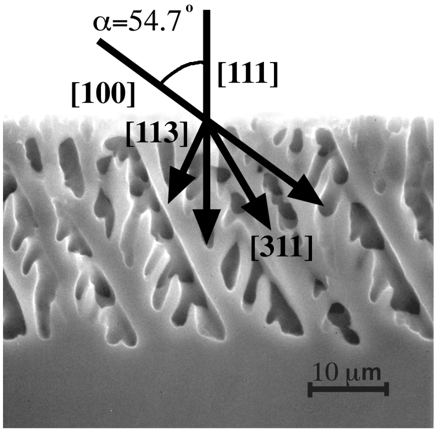

Figure 4: For (111) orientation of the surface the main and the side pores are growing in $< 113 >$ direction, resulting in a threefold symmetry of the pore-structure.

pore cross-sections on the edges of equilateral triangles is found in a depth of 15 μm to the wafer surface (Fig. 5). This may be explained by a model based on symmetrical restrictions which is shown schematically in Fig. 6. Because of the three-fold crystal symmetry in [111]-direction each pore nucleus (on a perfect wafer surface) generates three equivalent main pores. Since side pores grow in [113], [131] and [311]-direction and may converge creating a new nucleus for three new pores, this results in a tree-like morphology leading - in a depth T of the sample - to an arrangement of the pore cross-sections on the edges of equilateral triangles of which the corners belong to the main pores. The midperpendiculars of the triangles run parallel to the $\{01\bar{1}\}$-planes of the silicon structure. The cross-sections within the triangles may belong to side pores of higher order.

4 Conclusions

The results demonstrate that macropore formation is poorly understood. The anisotropy of the crystal structure is very important, a fact not contained in the existing models concerning macropore formation. A (not yet existing) theoretical model has to take into account not only the space charge region of the semiconductor and the diffusion of the minority carriers but also the anisotropy of the crystal structure. The surprising predominance of the $<$ $113 >$ direction is presently not understood. It is known that $< 113 >$

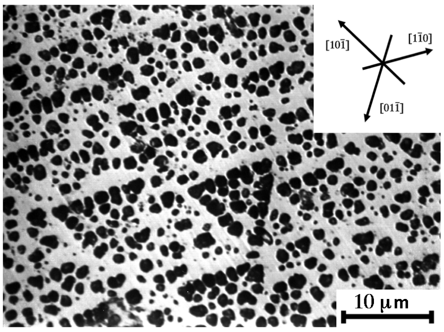

Figure 5: Pore cross-sections on (111) Si in a depth of 15 μm. In parts of the sample the cross-sections are arranged on the edges of equilateral triangles.

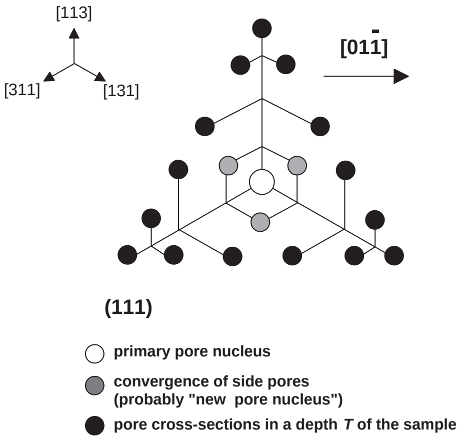

Figure 6: Three-fold pore structure on (111) Si projected onto the (111) plane.

directions or {113} planes have a certain bearing on defects in Si [8], but the particular significance of $< 113 >$ in the diamond structure is not yet clear.

References

[1] H. Föll, Appl. Phys. A, **53**, 8 (1991)

[2] R.L. Smith, and S.D. Collins, J. Appl. Phys., **71**, R1 (1992)

[3] V. Lehmann, J. Electrochem. Soc., **140**, 2836 (1993)

[4] V. Lehmann, Thin Solid Films, **225**, 1 (1995)

[5] S. Ottow, V. Lehmann, and H. Föll, J. Electrochem. Soc., **143**, 385 (1996)

[6] U. Grünning, V. Lehmann, S. Ottow, and K. Busch, Appl. Phys. Lett., **68**, 747 (1996)

[7] V. Lehmann, H. Föll, J. Electrochem. Soc. **137**, 653 (1990).

[8] S. Takeda, M. Kohyama in *Microscopy of semiconducting materials*, edited by A.G. Cullis, A.E. Staton-Bevan and J.L. Hutchinson (Royal Microscopical Society, Oxford, (1993), p.33