

Porous Formation Regime Transition in Anodising p-type Silicon: The Origin of Macropores

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INTRODUCTION

Anodising silicon in HF solution permits to obtain porous silicon (PS) with pore size in the nm range [1]. Below a certain current density the growth of PS is not stationary but it shows a transition from homogeneous nanopores to macropores filled by a nanoporous body (Fig. 1). Surprisingly, this transition occurs in spite of constant anodising conditions [2]. The transition is the origin of the macroporous structure [3] (μm range) since the dissolution of the nanoporous body in the course of anodisation or after a subsequent immersion in an etchant reveals the silicon skeleton [4].

RESULTS

With the (100) p-type $10\text{-}15\ \Omega\cdot\text{cm}$ and the 35 wt% HF ethanoic solution used in this work, the behaviour change occurs between 2.2 and 20 mA/cm^2 . The transition has a minute influence on the formation rate of the layer, which is nearly constant with time but decreases with the current density increase.

The valence values permit to determine the ratio of electrochemical to purely chemical dissolutions. This ratio is about 9 for 2.2 mA/cm^2 and 8 C/cm^2 . It expands by a factor 10 when increasing the current density from 2.2 up to 20 mA/cm^2 . The ratio reduces by a factor 2.5 when tripling the charge (at 2.2 and 20 mA/cm^2).

Taking the benefit of the skeleton formation various patterned surfaces were fabricated (Fig. 2) by chemical etching of the PS layer in 1 M NaOH [4]. The motif size has a narrow distribution that is independent of the crystalline orientation. The anodisation/etching patterning method can be an easy-to-handle alternative to more sophisticated one that use photolithography for producing faceted surface.

DISCUSSION

A valence above 2 can be interpreted as a regime that tends to electropolishing. A value below 2 signifies that chemical dissolution occurs during anodisation. The valence informs if the emptiness of a macroporous structure is due to electropolishing at the bottom of the pore or chemical dissolution.

The top view pictures allow determining the size of the motif i.e. the diameter of the columnar grains (Fig. 3). The depth and size dependence of the PS layer suggests that the nanoporous columnar grains grow in diameter while penetrating the bulk silicon until the diameter reaches its maximum size. This size is the same for 2.2 and 20 mA/cm^2 (Fig. 3). The only difference is that at 2.2 mA/cm^2 silicon walls separate the columnar grains.

The factor that controls the skeleton appearance has not been understood yet. However a carrier transportation dependence is most likely. Indeed, using various resistivities (4 up to 20 $\Omega\cdot\text{cm}$) demonstrates that a high resistivity and low current density favour the transition.

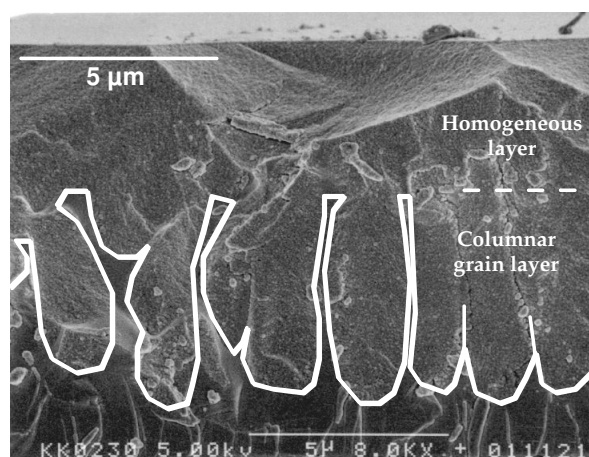


Fig. 1. Side view of a (100) sample anodised for 60 min at 2.2 mA/cm^2 .

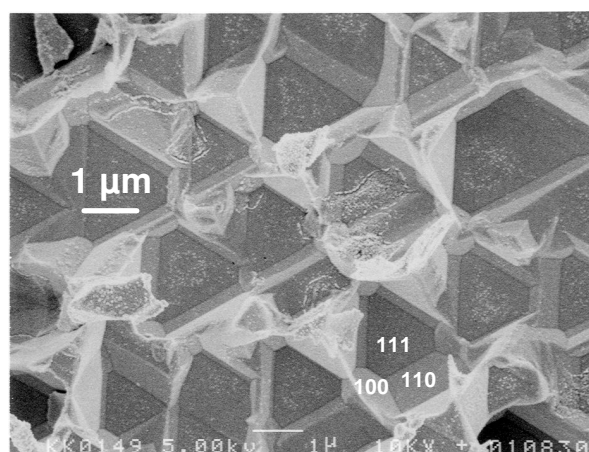


Fig. 2. Top view of a (111) wafer anodised for 60 min at 2.2 mA/cm^2 and subsequently immersed in 1 M NaOH.

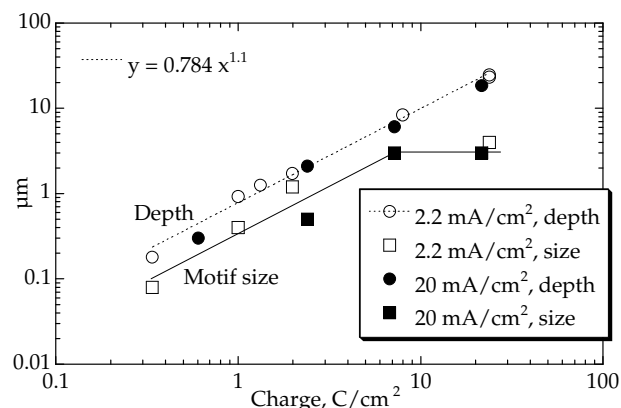


Fig. 3. Maximum size of the motif (square) together with the depth (circle) of the PS layer as a function of the charge. The solid line is a guide to the eye for the trend of the motif size series, its non-horizontal segment is parallel to the fit of the 2.2 mA/cm^2 depth series.

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