Mechanism and control of formation of porous silicon on \( p \)-type Si

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Abstract. A simple extension of Beale's and Lehmann's models for the formation of porous silicon layer on \( p \)-type silicon is proposed with a view to explain the experimental conditions necessary for obtaining either uniform vertical pores or non-uniform pore branching, as desired. A uniformity parameter is defined and correlated with the measured porosity. The dependence of the porosity and the uniformity factor with the various formation parameters of porous layer are studied experimentally and explained qualitatively.

Keywords. Porous silicon; \( p \)-type Si.

1. Introduction

The discovery of room-temperature photoluminescence (PL) of porous silicon has initiated an extensive research on both theoretical and experimental aspects especially because of its strong potential in its use in optoelectronic and photonic applications.

Porous silicon (PS) is formed by anodic etching of crystalline silicon in hydrofluoric acid. The specific structure of PS depends on various parameters like doping type and level of c-Si, HF concentration, formation current density, presence of illumination, surface morphology etc (Smith and Collins 1992). Depending upon the various parameters during formation, PS may be looked upon as either quantum wires or quantum sponges (Koshida et al 1992; Marusak et al 1993; Feng and Tsu 1994b; Jain et al 1994; Kocka et al 1996).

For optoelectronic applications, however, the near-vertical growth of pores and consequently that of the silicon pillars should be a pre-requisite to ensure reproducibility as well as isolation of the devices formed on a single wafer.

In this paper, we report a detailed study on \( p \)-type silicon to examine the growth of PS under various experimental conditions with a view to find out the favourable formation conditions for near-vertical growth of silicon pillars. The formation model proposed by Lehmann is extended in this paper introducing the concept of a uniformity parameter (Lehmann 1993).

2. Modelling of vertical PS growth

The basic prerequisites for electrochemical pore formation are passive state of pore walls and active state of pore tips (Feng and Tsu 1994a). Dissolution of silicon in HF occurs if holes are present in the surface. Thus, a surface depleted of holes is passivated. Hole depletion occurs if any hole reaching the solid-electrolyte interface is immediately consumed in the dissolution reaction. This is the case when the chemical reaction is not limited by the mass transfer in the electrolyte—a condition satisfied when the formation current density is below a critical current density value \( J < J_p, \).

However, when \( J > J_p, \) the reaction is limited by mass transfer of ions in the electrolyte. The dissolution of Si is controlled by the supply of reactants through the diffusion layer in the electrolyte, leading to a build up of surface charge in silicon due to accumulation of holes and resulting into electropolishing (Turner 1958).

In equilibrium macropore formation, a steady-state condition is assumed at the pore tips, i.e. the charge transfer due to holes exactly balances the availability of ions in the electrolyte (John and Singh 1995). In such a case, all holes will be consumed at the pore tips itself so that the pores grow vertically downwards with a constant cross-section. This is characterized by critical current density \( J_p, \).

Thus, if the localized current density, \( J_{tip} \) at any place is greater than \( J_p, \), then the steady-state condition for lateral electropolishing will be achieved when the cross-sectional area to \( J_{tip} \) increases to a value \( A_p, \) so that \( J_{tip} = J_p, \). This concept is realized at the initial stage of formation of the porous structure. The initiation of PS structure probably occurs at the locations of random inhomogeneities in the path of current flow through the interface (Beale et al 1985).

In regions of the inhomogeneities where the local current density is initially high so that \( J_{tip} > J_p, \), localized
lateral electropolishing should occur until \( J_{\text{tip}} \) becomes equal to \( J_{\text{ps}} \).

If the total number of inhomogeneities (nucleation centres) at the surface is \( N_{\text{ps}} \), then the current flow (\( J_{\text{ps}} \) per m\(^2\)) occurs through an effective area of \( N_{\text{ps}} A_{\text{ps}} \) so that

\[
(N_{\text{ps}} A_{\text{ps}}) J_{\text{ps}} = JA,
\]

(1)

\( A \) is the total cross-sectional area of the same and \( J \) the measured current density.

If the growth of pores were uniform, then the porous silicon thickness \( h_u \) would be given by

\[
(N_{\text{ps}} A_{\text{ps}}) h_u \rho = \frac{(JA)t}{ne} \times m_s,
\]

(2)

where \( n \) is the number of atoms required for dissolution of each silicon atom and \( \rho \) the Si density and \( n \), reported to be of the order of 2 (Beale et al 1985).

The porosity of vertically grown PS (no branching) will therefore be given by

\[
P_u = \frac{(N_{\text{ps}} A_{\text{ps}}) h_u \rho}{A h_u \rho} = \frac{N_{\text{ps}} A_{\text{ps}}}{A} = \frac{J}{J_{\text{ps}}}.
\]

(3)

It can be seen from (1)-(3) that

\[
h_u = \frac{(Jp_x)t m_s}{ne \rho},
\]

(4)

and

\[
P h_u = \frac{J t m_s}{ne \rho}.
\]

(5)

Thus, when PS growth is vertical, the porosity is a function of \( J \) and \( J_{\text{ps}} \) (in turn, dependent on HF concentration). However, the thickness of PS layer is independent of the current density and is only a function of \( J_{\text{ps}} \). This happens because of the fact that \( A_{\text{ps}} \) increases in proportion of \( J \) for a constant \( J_{\text{ps}} \).

If, however, the number of nucleation centres \( (N_{\text{ps}}) \) is very large, then the maximum limit to pore wall thickness is set by the pinch-off effect (Lehmann 1993) due to overlap of adjacent depletion layers so that the porous column dimension is twice the depletion width (\( \Delta W \)) (figure 1).

Under these circumstances, we have

\[
P_u = \left( \frac{d}{d + 2\Delta W} \right)^2 \frac{J}{J_{\text{ps}}},
\]

(6)

and

\[
N_{\text{ps}} = \frac{A}{(d + 2\Delta W)^2},
\]

since the number of pores per unit area is \( 1/(d + 2\Delta W)^2 \).

Thus, in this case, the porosity becomes a function of the pore diameter and the sample resistivity in the form given by

\[
d = \frac{2\Delta W}{\left( \frac{1}{\sqrt{P_u}} - 1 \right)},
\]

(7)

and the formation of pores will be possible only if

\[
N_{\text{ps}} \leq \frac{A}{4\Delta W^2} \text{ i.e. } n_{\text{ps}} \leq \frac{1}{4\Delta W^2}.
\]

(8)

It is quite obvious that heavily doped p-type silicon will give rise to a large number of nucleation centres in the vicinity of doping impurities (Beale et al 1985), since current flow can occur in such samples by tunneling and a larger fraction of area is then always amenable to offer the path of current flow. Due to the depletion layer width overlap and pinch-off effect, the columnar growth of the pores is highly likely in the case (Beale et al 1985; Lehmann 1993).

Equation (7) is indeed obeyed in the case of heavily doped layers as can be seen by inserting the results of Beale et al (1985) into (7). The number of nucleation centres necessary for vertical pores is given by

\[
N_{\text{ps}} \left[ \left( \frac{A}{N_{\text{ps}}} \right)^{1/2} - 2\Delta W \right]^2 = \left( \frac{J}{J_{\text{ps}}} \right) A.
\]

(9)

Thus, the number of nucleation centres per unit area \( (n_{\text{ps}}) \) for vertical PS growth (from (9) and (8)) is given by

\[
n_{\text{ps}} = \frac{N_{\text{ps}}}{A} = \left[ \frac{1 - (J/J_{\text{ps}})^{1/2}}{2\Delta W} \right]^2,
\]

(10)