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 ($J < J_{ps}$).

However, when $J > J_{ps}$, 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_{ps} .

Thus, if the localized current density, J_{tip} at any place is greater than J_{ps} , then the steady-state condition for lateral electropolishing will be achieved when the cross-sectional area to J_{tip} increases to a value A_{ps} so that $J_{tip} = J_{ps}$. 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 $J_{tip} > J_{ps}$, localized

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lateral electropolishing should occur until J_{tip} becomes equal to J_{ps} .

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

$$(N_{ps}A_{ps})J_{ps} = JA, \quad (1)$$

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

$$(N_{ps}A_{ps})h_u\rho = \frac{(JA)t}{ne} \times m_s, \quad (2)$$

where n is the number of atoms required for dissolution of each silicon atom and ρ 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

$$P_u = \frac{(N_{ps}A_{ps})h_u\rho}{Ah_u\rho} = \frac{N_{ps}A_{ps}}{A} = \frac{J}{J_{ps}}. \quad (3)$$

It can be seen from (1)–(3) that

$$h_u = \frac{(J_{ps})tm_s}{ne\rho}, \quad (4)$$

and

$$P_u h_u = \frac{Jtm_s}{ne\rho}. \quad (5)$$

Thus, when PS growth is vertical, the porosity is a function of J and J_{ps} (in turn, dependent on HF concentration). However, the thickness of PS layer is independent of the current density and is only a function

Figure 1. Schematic diagram of uniform pores where d is pore diameter and $2\Delta W$ is the separation between two consecutive pores.

of J_{ps} . This happens because of the fact that A_{ps} increases in proportion of J for a constant J_{ps} .

If, however, the number of nucleation centres (N_{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 (ΔW) (figure 1).

Under these circumstances, we have

$$P_u = \left(\frac{d}{d + 2\Delta W} \right)^2 = \frac{J}{J_{ps}}, \quad (6)$$

and

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

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

$$d = \frac{2\Delta W}{\left(\frac{1}{\sqrt{P_u}} - 1 \right)}, \quad (7)$$

and the formation of pores will be possible only if

$$N_{ps} \leq \frac{A}{4\Delta W^2} \text{ i.e. } n_{ps} \leq \frac{1}{4\Delta W^2}. \quad (8)$$

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

$$N_{ps} \left[\left(\frac{A}{N_{ps}} \right)^{1/2} - 2\Delta W \right]^2 = \left(\frac{J}{J_{ps}} \right) A. \quad (9)$$

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

$$n_{psc} = \frac{N_{ps}}{A} = \left[\frac{1 - (J/J_{ps})^{1/2}}{2\Delta W} \right]^2, \quad (10)$$

and the pore dimension d is given by

$$d = \frac{2(\Delta W)}{[(J_{ps}/J)^{1/2} - 1]}.$$

Thus the pore dimension is found to be strongly dependent on the doping concentration.

It is obvious that if n_{ps} is less than n_{psc} , then the pore walls will not be passivated by the pinch-off effect and the branching of the pores will be a possible phenomenon.

The critical nucleation centre density (n_{psc}) decreases and thus approaches towards the actual centre density (n_{ps}) as J approaches J_{ps} and ' ΔW ' decreases (i.e. for lower resistivity) as long as the actual n_{ps} is not dependent on either J or ΔW .

3. Pore branching and uniformity

The morphology of pores formed depends on a number of parameters such as the surface roughness, doping type and density, anodizing current and voltage, pH and concentration of HF solution etc (Feng and Tsu 1994c). Depending upon these parameters, the pores may have fir-tree-shaped structures with interconnected branches underneath or well-defined unbranched vertical wells. In general, unless the surface is very polished and intentionally patterned, doping density is high and the anodization potential, HF concentration are of right magnitude, the pores exhibit branching and non-uniformity (Lehmann 1993).

The measured porosity (P_m) of PS will be different from that for uniform growth due to pore branching and can be expressed as

$$P_m = \frac{\text{mass of silicon dissolved}}{\text{mass of the porous layer}}$$

$$= \frac{\left(\frac{JA t}{ne}\right) \times m_s}{A h_m \rho} = \left(\frac{J t m_s}{n e \rho}\right) \times \frac{1}{h_m}, \quad (11)$$

where h_m is the thickness of the porous layer in the direction of external current density. Combining (5) and (11), we have

$$\frac{h_m}{h_u} = \frac{P_u}{P_m} = u,$$

where u is defined to be a measure of uniformity of the formed porous layer. In the case of a vertical pore growth, we have $h_m = h_u$ and $u = 1$. The uniformity factor (u) can be estimated from the relation

$$u = \frac{P_u}{P_m} = \frac{J/J_{ps}}{P_m}. \quad (12)$$

The measured porosity (P_m) for a given J will be higher

due to pore branching than that for a uniform PS growth. At lower current density ($J < J_{ps}$), holes are depleted from the silicon surface resulting into a preferential transport of holes from the bulk to the surface irregularities. This implies that higher current density will lead to lower non-uniformity (John and Singh 1995).

4. Experimental

Silicon wafers of p -type and (100) orientation and 7 cm^2 area, having resistivity of $1\text{--}2 \Omega\text{-cm}$ were anodized in a cell specially developed for the purpose. The wafers were texturized by standard anisotropic etching process that leads to the formation of pyramidal structures with exposed (111) planes.

The wafer actually acts as a seal between the front and rear regions. The front region of the cell was filled with $\text{HF}:\text{CH}_3\text{OH}$, while the rear portion was immersed in KCl solution. The back contact metallization was done by screen printing of silver aluminium paste and its subsequent firing. The textured samples were anodized by a constant current supply (Bandopadhyay *et al* 1996).

The gravimetric method was employed to determine the porosity of the samples (Amato 1995). Samples, before and after anodization, were weighed by the micro balance model No ADN200W. Then, the porous layers were removed by dipping the samples in NaOH solution and the wafers were again weighed.

The porosity was then determined by using the relation

$$P_m = \frac{m_1 - m_2}{m_1 - m_3},$$

where m_1 is the mass of the sample before anodization, m_2 the mass of the sample after anodization and m_3 the mass of the sample after complete dissolution of the porous layer.

SEM techniques have been used to provide some of the detailed direct information about the thickness of the porous layers and the branching of pores in these layers.

5. Results and discussion

5.1 Role of formation current density

Figure 2 shows the variation of measured porosity (P_m) as a function of current density (J) for a fixed HF concentration (mixed in 1:1 proportion with CH_3OH) and fixed time of anodization. The porosity (P_m) increases with increasing J .

The thickness (h_m) of the porous layer has been estimated from the mass of the porous layer and is given by

$$h_m = \frac{m_1 - m_3}{A \rho}.$$

Figure 3 and table 1 show the variation of estimated h_m with the current density (J). It is observed that h_m increases with increase in J . Figures 4 and 5 show two typical scanning electron micrographs of porous silicon layers at 45° tilt angle. It is seen from these figures and table 1 that the thickness of porous layers as measured by SEM technique agree fairly well with those measured by gravimetric methods.

It has been seen from the simple model presented

Figure 2. Variation of measured porosity (P_m %) with etching current density (J) when other etching parameters are constant.

Figure 3. Variation of porous layer thickness (h_m) with etching current density.

here that for a given passed charge (JAt) more branching will lead to a lower PS layer thickness and consequently higher porosity than that would be observed for uniform vertical pore growth. Thus, it appears from this study that as the fractional increase of P_m ($\Delta P_m/P_m$) is much less than the fractional increase of J ($\Delta J/J$) and since h_m increases with increasing J , the average thickness (h_m) approaches towards the uniform growth thickness (h_u) with increasing J .

The degree of uniformity is examined by investigating the variation of the uniformity (u) with the formation current density (J). Figure 6 shows that with increasing J , u is found to increase almost linearly with J . Table 1 shows the different values of P_m , h_m , u and h_u as functions of current density. It is seen from table 1 that u lies in the range 0.04–0.17 for the current densities in the range of 10–70 mA/cm². This can be explained from the consideration that as the critical density of

Figure 4. SEM of porous silicon formed under anodic etching by $J = 10$ mA/cm² in 48% HF for 5 min, estimated $h_m = 4.25$ µm.

Figure 5. SEM of porous silicon formed under anodic etching by $J = 50$ mA/cm² in 48% HF for 5 min, estimated $h_m = 9.6$ µm.

Table 1. Values of measured porosity, PS layer thickness for non uniform (h_m) and 100% uniform (h_u) and uniformity (u) for different etching current densities.

J (mA/cm ²)	P_m (%)	h_m (μ m) (from gravimetric method)	h_m (μ m) (by SEM tech.)	u (%)	h_u (μ m)
10	48.7	4.7	4.25	3.64	129
30	78.2	7.6	7.8	6.8	112
40	83.1	8.3	8.6	8.5	98
50	83.3	9.9	9.6	10.6	93
60	86.8	14.0	—	12.3	114
70	89.4	15.1	—	13.9	108

Figure 6. Variation of uniformity ($u\%$) with etching current density.

nucleation centres (n_{psc}) decreases with J almost linearly according to (10), an increase in J will favour the vertical pore growth since the actual density of nucleation centres (n_{ps}) approaches n_{psc} with increasing current density.

It is apparent from the present study that in the range of current densities considered here (10–70 mA/cm²), the uniformity factor is not very high (≤ 0.17). The uniformity factor is increased by increasing J , but it is likely that at high current density the pore tips lead to increased oxide formation (Feng and Tsu 1994c). Thus, it seems that it is preferable to either increase n_{ps} by pattern formation on the surface and creating the required value of $n_{ps} \approx n_{psc}$ and/or lowering the value of n_{psc} by increasing ΔW or in other words, decreasing the doping concentration of the sample.

The fact that the anodizing current mainly flows through the pores and not through the whole area (A) of the sample was examined by calculating the number of electrons required for the removal of every silicon atom estimated from the weight change of the wafer during anodization as follows:

Table 2. Number of electrons (n) required for dissolution of one silicon atom during electrochemical etching of p-type Si for different values of etching current density (J).

J (mA/cm ²)	m_1 (g)	m_2 (g)	m_s (g)	n
10	1.0251	1.0214	4.656×10^{-23}	1.7
30	0.9987	0.989		1.9
40	1.1263	1.115		2.2
50	1.0431	1.0296		2.3
60	0.9769	0.9571		1.9
70	1.081	1.059		1.9

$$(m_1 - m_2) = \frac{JA t}{ne} m_s, \quad (13)$$

where m_s = mass of each Si atom.

It is found that n is of the order of 2 indicating that the flow is essentially through the pores and on an average, two electrons are required for each silicon atom removal. It was, however, observed (table 2) that n increases in general with increasing J and values of n were found to lie in the range 1.7–2.3.

5.2 Role of methanol content in HF electrolyte

The role of methanol in the formation of PS layer has been examined by anodization of silicon in the same HF concentration with different proportions of methanol.

It is seen from table 3 and figures 7 and 8 that with increasing methanol proportions in HF, the average PS layer thickness and the uniformity factor (u) decreases for a given current density. This is possibly because of the fact that methanol acting as a wetting agent removes the hydrogen bubbles from the pore walls leading to the branching of pores.

The pore formation rate (average thickness per unit time) is found to follow the relation

$$r = 10^{[0.89 \times \log_{10} J - 1.2]}, \quad (14)$$

as suggested by Lehmann *et al* (Feng and Tsu 1994a) for 1:1 HF (48%)–methanol electrolyte.

5.3 Role of HF concentration

Figures 9 and 10 show the dependence of porosity and

uniformity factor with increasing HF concentration. It is found that porosity increases linearly with HF concentration, whereas the uniformity factor decreases.

This can be explained with reference to the change in n_{psc} . As HF concentration increases, the value of J_{ps} also increases leading to the increase of the critical nucleation centre density needed for near vertical growth. This leads to lower values of n_{ps}/n_{psc} with increasing

HF concentration and thus more pore branching. This observation is further corroborated by reflectance studies of PS (to be communicated separately).

The fact that increase of HF concentration leads to less uniformity and consequently more pore branching can be observed directly by examining the SEM micrographs taken from a direction perpendicular to the thickness of porous layer (figures 11 and 12). The black

Table 3. Values of measured porosity (P_m), PS layer thickness (h_m) and uniformity (u) for different methanol proportions in the electrolyte.

CH ₃ OH : HF	P_m (%)	h_m (μ m)	u (%)
1 : 1	78.0	6.3	6.8
1 : 2	75.0	7.4	7.1
1 : 3	74.4	8.2	7.2
1 : 5	72.4	8.9	7.3
0 : 1	51.5	9.9	10.3

Table 4. Values of measured porosity (P_m), PS layer thickness (h_m) and uniformity (u) for different HF concentrations.

C (wt%)	P_m (%)	h_m (μ m)	u (%)
48	83	2.5	2.1
36	74	2.1	3.2
30	77	1.3	3.7
24	63	2.3	5.6
18	61	2.0	7.6

Figure 8. Variation of uniformity (u %) with HF, methanol ratio in the electrolyte.

Figure 7. Variation of PS layer thickness (h_m) with HF, methanol ratio in the electrolyte.

Figure 9. Variation of measured porosity (P_m %) with HF concentration (wt%).

Figure 10. Variation of uniformity ($u\%$) with HF concentration (wt%).

Figure 11. SEM micrograph of porous silicon (HF=24%, $J=10 \text{ mA/cm}^2$) showing branching of pores.

holes in these micrographs show pores formed in the direction perpendicular to the thickness of porous layers and thus these indicate the branching of pores. Figures 11 and 12 clearly show that more branching occurs at higher HF concentration.

6. Conclusions

A simple model based on Beale's and Lehmann's ideas, for uniform porous layer formation on p-Si has been developed correlating the various growth parameters of vertical and uniform pores with the pore formation parameters. A concept of non-uniformity has been

Figure 12. SEM micrograph of porous silicon (HF=48%, $J=10 \text{ mA/cm}^2$) showing branching of pores.

introduced to characterize the quality of PS layer in respect of pore-branching and near-vertical growth of pores. A factor called 'uniformity factor' has been defined and its dependence on experimental and physical parameters of porous layer studied. The simple model developed here has been utilized to explain the different experimental observations.

With increase in J and/or decrease in HF concentration, the uniformity factor increases leading to better vertical growth. With more methanol proportion in HF electrolyte, the uniformity factor decreases giving more branching. The results can be explained with reference to the critical density of nucleation centres on the silicon surface.

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References

- Amato G 1995 *Jpn. J. Appl. Phys.* **34** 1716
- Bandopadhyay S *et al* 1996 *Bull. Mater. Sci.* **15** 725
- Beale M I *et al* 1985 *J. Cryst. Growth* **73** 622
- Feng Z C and Tsu R 1994a *Porous Silicon (WS)* 17
- Feng Z C and Tsu R 1994b *Porous Silicon (WS)* 99
- Feng Z C and Tsu R 1994c *Porous Silicon (WS)* 301
- Jain V K *et al* 1994 *Bull. Mater. Sci.* **17** 551
- John G C and Singh V A 1995 *Phys. Rep.* 263
- Kocka J *et al* 1996 *Thin Solid Films* **276** 187
- Koshida N *et al* 1992 *Appl. Phys. Lett.* **60** 20
- Lehmann V 1993 *J. Elec. Soc.* **140** 2836
- Marusak H P *et al* 1993 *Appl. Phys. Lett.* **63** 5
- Smith R L and Collins S D 1992 *J. Appl. Phys.* **71** 1
- Turner D R 1958 *J. Elec. Chem. Soc.* 402