

## Porosity Determination Equation for Porous Silicon

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**Abstract:** Through the studying of the carriers moving of the porous and the definition of  $S_{\text{BET}}$ , the equation of the relationship among the porosity, the current density and the etching speed can be deduced. Here, it is shown that for porous silicon made from p-type silicon, there is a universal relationship, it is possible to determine the change in porosity with respect to etching under a set etching current density. This relationship is checked against experimental data from several reports on these etching parameters, and they confirm the validity.

**Key words:** porosity; porous silicon; luminescence intensity

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### 1 Introduction

The discovery of porous silicon (PS) visible luminescence by Canham<sup>[1]</sup> has generated considerable interest. The potential of using silicon-based optoelectronic devices seems to have increased with this discovery. Since then, the luminescence mechanism of the PS has been investigated by many workers<sup>[1-4]</sup>. However, there remains some drawbacks with respect to the optical characteristics of PS; the luminescence spectrum is too broad, and there exists the problem of stability and repeatability. However, recently Vincent<sup>[5]</sup> and others<sup>[2,3]</sup> showed that with multilayer PS, it is possible to compress the half width using distributed Bragg reflectors which also results in increase in luminescence intensity. This injects fresh impetus into the research on Si-based optoelectronic devices. In order to produce multilayer PS with different refractive indices, it is necessary to have an established

procedure that can provide a guide on the feasibility in porosity and thickness required. It is the aim of this report to demonstrate that it is possible to establish a universal relationship among porosity, etching current density and etching rate for PS fabricated from p-type silicon. With this relationship, it is hoped that the design of multilayer PS can be less of a trial and error and be more easily.

### 2 Theory

P-type silicon produced PS is chosen as the starting point because its etching current mechanism is simple; the etching depends on the exchange of holes and silicon trifluoride ions<sup>[6]</sup>, and since hole is the majority carrier in p-type silicon, therefore the etching current density depends on the majority carrier only. Whereas for n-type silicon, hole is the minority carrier and the etching depends strongly on external light source that generates extra electron hole pairs. This complicates the

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etching process, as the etching current density also becomes a function of the photo-generated hole density. We further assume that the etching velocity can be represented by a mean value. The assumption is that in order to have effective etching<sup>[7]</sup>, the etching rate should be low and does not vary significantly across the etching surface. Too high an etching rate would result in electro-polishing. And if the etching rate varies significantly across the etching surface, second order effect would appear which makes the final equation non-linear. For p-type silicon, anodisation is a function of the following parameters: the hydrofluoric acid (HF) concentration, the etching current density ( $J$ ), and the hole concentration ( $n_p$ ). Under any anodisation condition, the HF concentration is fixed, so the variables are  $J$  and  $n_p$ . And in p-type silicon, the hole carrier is a majority carrier whose concentration would not change during the etching period, therefore it can be considered as a constant. Then only one variable (the current density  $J$ ) is left. During etching, the sample has in effect two layers: the bulk and the porous silicon, therefore, we assume that it has two components, one derives from the silicon bulk at the base of the PS layer, i. e., bottom of the pores, and can be defined as follows,

$$J_b = \frac{n_p V e}{S t} \quad (1)$$

where  $e$  is the elementary charge,  $S$  is the area of the etched silicon,  $n_p$  is the hole density,  $V$  is the total volume of the pores, and  $t$  is the total time of etching.

If  $z$  is the etch thickness of the silicon separately, then the porosity is defined by  $P = \frac{V}{S z}$ .

Substituting  $P$  and  $v_e$  (the etching velocity) into equation (1), we have

$$J_b = n_p e P \frac{z}{t} = n_p e P v_e \quad (2)$$

Another current flows through the surface of silicon columns where the depletion region is formed<sup>[8]</sup>. This etching current component is de-

fined as

$$J_e = \frac{Q_e}{S t} \quad (3)$$

here,  $Q_e$  is the surface charge accumulates during etching and is defined as,

$$Q_e = Y S e n_p e \quad (4)$$

where  $Y$  is a function of HF concentration and is a constant in equation (4), and

$$S_e = S_{BET} V = S_{BET} P S z \quad (5)$$

and  $S_{BET}$  is the specific surface area derived from BET equation<sup>[9]</sup>.

Thus,

$$J_e = Y S_{BET} P v_e n_p e \quad (6)$$

Then the total current density  $J$ , when the current flows in the sample, is the sum of these two current components,

$$J = J_b + J_e = n_p e P v_e (1 + Y S_{BET}) \quad (7)$$

Rearranging equation (7),

$$\frac{P v_e}{J} = \frac{1}{n_p e (1 + Y S_{BET})} = \kappa \quad (8)$$

$J_b$  is derived from the silicon bulk at the base of the PS layer (i. e., bottom of the pores), whereas  $J_e$  flows through the surface of silicon columns where the depletion region is formed<sup>[8]</sup>. The total current flow,  $J$ , is the sum of  $J_b$  and  $J_e$ . Thus, for p-type silicon, the ratio of the product of porosity and mean etching velocity over the etching current density is a constant  $\kappa$ , which is inversely proportional to the carrier concentration  $n_p$ . Here  $Y$  is a function of HF concentration and  $S_{BET}$  is a constant too. In that case, the right hand side of equation (8) can be considered as constant.

### 3 Discussion

In order to verify the validity of equation (8), we used experimental results from four reports<sup>[3, 5, 10, 11]</sup> to derive  $\kappa$ . Table 1 shows the derivation of  $\kappa$  using the reported experimental data, and it shows that within the experimental errors, the  $\kappa$  values for each preparation condition agree well with one another.

Table 1 Comparison of Theoretic Values and Equation with Experimental Results

	Porosity	Etching Current Density	Etching Time	Etching Thickness	Mean Etching Rate	$pveJ^{-1}$
	$P/\%$	$J/(\text{mA} \cdot \text{cm}^{-2})$	$t/\text{s}$	$z/\text{nm}$	$ve/(\text{nm} \cdot \text{s}^{-1})$	$/ (10^{-4} \text{cm}^3 \cdot \text{A}^{-1} \cdot \text{s}^{-1})$
Sample 1	65	5	20	86	4.3	0.559
Ref. [1]	78	25	20	360	18	0.561
Sample 2	75	20	600	$3.9 \times 10^3$	6.5	0.2438
Ref. [8]	79	20	600	$3.7 \times 10^3$	6.17	0.2437
	65	20	600	$4.5 \times 10^3$	7.5	0.2438
Sample 3	53	25			2.1	0.0445
Ref. [4]	62	49.7			3.5	0.0436
	75	82.8			5.5	0.0436
Sample 4	41	10	1800	$3.3 \times 10^4$	18.33	0.752
Ref. [9]	50	20	1800	$5.4 \times 10^4$	30.00	0.750
	71	45	1800	$8.5 \times 10^4$	47.22	0.745

The table shows the derivation of  $\kappa$  using experimental data from four References. For each sample, the  $\kappa$  value is found to be a constant within experimental error. We can see that if we can measure the porosity, then the etching rate can be determined under various  $J$  values. Here, we have assumed that the HF concentration is fixed. Different HF concentrations would produce different  $\gamma$  values and therefore different  $J$  values. Nevertheless, it demonstrates that in producing a multi-layer PS, we can produce different porosities by controlling the etching rate for a pre-determined etching current density.

## 4 Conclusion

Thus, we have shown that for p-type silicon, the porosity, the etching velocity and the etching current density are related. This is verified from using experimental results from four reports and our results, and this relationship can be used to determine the porosity (or the etching rate) easily instead of measuring the porosity (or the etching rate) each time. By using the relationship estab-

lished, we then can select a set of etching conditions to produce a desired PS structure/layer thickness.

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## 光电材料多孔硅的多孔度理论计算方程

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**摘要:** 在制备多孔硅材料时, 多孔硅的多孔度和厚度与电解电流强度、电解时间以及氢氟酸的浓度有关. 如果氢氟酸的浓度保持不变, 通过改变电解时间和电解电流强度就可以得到所需多孔硅的多孔度及厚度. 但现在一般都通过测量设备来重复测量多孔硅的多孔度及厚度, 特别是多层多孔硅, 很难严格控制其厚度. 为此, 通过对多孔硅中载流子运动的研究, 结合 BET 方程中的  $S_{\text{BET}}$  定义, 推导出多孔硅的多孔度、电解速度和电解电流强度之间的关系表达式. 通过该理论公式, 就可以保证精确得到多孔硅的多孔度及厚度. 该理论公式得到了实验的验证.

**关键词:** 多孔度; 多孔硅; 发光强度

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