Nano-photonic crystal formation on highly-doped n-type silicon*

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(Received 4 October 2014)

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We present a novel electrochemical technique for the fabrication of nano-photonic crystal structures. Based on a specially designed electrolyte, porous silicon (PSi) layers with different porosities are possible to be produced on highly-doped n-type silicon substrate by varying the applied current density which determines the size and the morphology of pores. By applying an alternative current density modulation during anodization, porous silicon photonic crystals are obtained using HF-containing electrolyte without oxidizing components. The current burst model (CBM) is employed to interpret the mechanism of the formation of the macropore porous silicon.

Document code: A **Article ID:** 1673-1905(2015)01-0010-3

DOI 10.1007/s11801-015-4181-4

Porous silicon (PSi) photonic crystal has become a very interesting material owing to its potential application in many fields, such as sensors, solar cell and photoluminescence (PL)[1-5]. The main advantages are easy preparation, low cost and tuning characteristics of refractive index[5,6]. The most common preparation method of PSi is electrochemical etching. But this technique often needs illumination, and it is difficult to prepare multilayer PSi on n-type silicon. Lenshin et al[6] obtained the multilayer PSi by electrochemical etching on an n-type single-crystal silicon wafer with a highly doped p-type layer epitaxially deposited on the surface. Other researchers[7] made good effort to obtain multilayer PSi on n-type single-crystal silicon wafer by adding strong oxidants, such as CrO_3 and $KMnO_4$. But the oxidants may introduce metal impurity in PSi layer. So H_2O_2 may be an ideal substitute, because it will not introduce impurity. Ge et al[8] found that if a high hydrofluoric acid (HF) concentration and a high current density can be applied simultaneously, it is possible to produce nice nano-sized macropores via HF/H_2O_2 electrolyte on highly-doped n-type silicon without illumination, and they also think that the concentration of H_2O_2 has little effect on the formation of macropores. In most previous reports, the preparation of PSi by electrochemical etching method must use illumination or oxidant.

In this paper, we demonstrate that it is possible to produce distributed Bragg reflector (DBR) without illumination on highly-doped n-type silicon. Field emission scanning electron microscopy (FESEM) images show that the porous materials with macropores have nice surface morphology, and they are smooth on layer interface. Pore size is about 50–80 nm. The experimental result and the theoretical analysis show that this method is good for the fabrication of multilayer PSi. Moreover, the interpretation of macropore PSi formation mechanism is also discussed.

PSi samples were prepared on highly-doped n-type (100) silicon wafers with resistivity from 0.01 Ω/cm to 0.02 Ω/cm, which were electrochemically etched in double etch tank. The electrolyte was a mixture of aqueous HF with weight ratio of 48% and ethanol with volume ratio of 99.7% in a variety of concentrations, where the concentration is expressed in volume ratio unless otherwise stated. Galvanostatic conditions of 50–100 mA/cm^2 from a Labview system based current source with a tolerance down to 0.01 mA were applied. For the fabrication of DBR, we first prepared single layer PSi, and two current densities of 50 mA/cm^2 and 100 mA/cm^2 were applied during the etching process, respectively. Then, alternative current densities of 50 mA/cm^2 for 3 s and 100 mA/cm^2 for 2 s were applied for fabrication of DBR. After etching, the samples were rinsed with pure ethanol and dried in vacuum drying oven. The morphological analysis of the prepared films was undertaken by using FESEM (SUPRA 55VP) operated at 20 kV.

In order to get PSi photonic crystal, we investigate the pore morphologies and the etching speeds with different current densities of 50 mA/cm^2 and 100 mA/cm^2. All samples were anodized using the same electrolyte with volume ratio of HF to ethanol of 1:3 and the duration of 10 min. Fig.1 shows the cross section and top-view FE-

* This work has been supported by the National Natural Science Foundation of China (No.61265009), the Excellent Youth Foundation of Shihezi University (No.2012ZRKXYQ-YD20), and the Doctoral Research Foundation of Shihezi University (No.RCZX201327).

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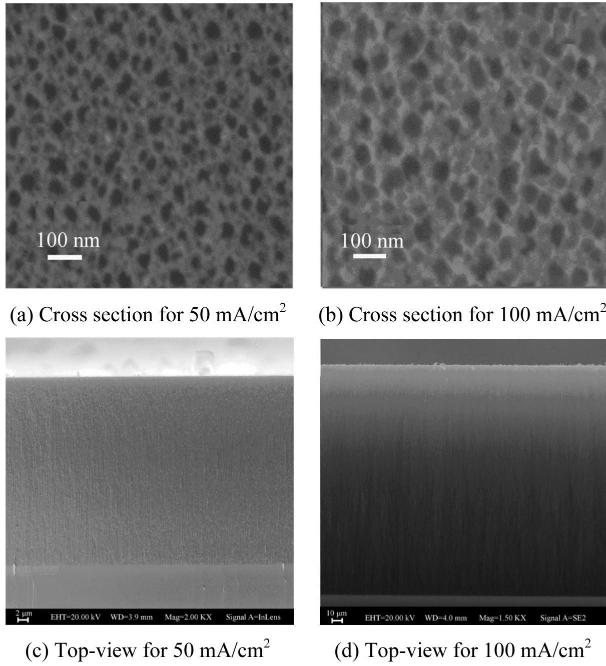
SEM images of PSi formed at 50 mA/cm^2 and 100 mA/cm^2. As shown in Fig.1(a) and (c), in the PSi formed at 50 mA/cm^2, heavily branched mesopores are created with depth of 28 μm, and we can calculate that the etching speed is 46.7 nm/s and the pore size is about 50 nm. As shown in Fig.1(b) and (d), when the etching current density is increased to 100 mA/cm^2, the pores become straighter, and the pore size is increased to about 70 nm. The etching speed also reaches 76.7 nm/s. The etching speed is increased with the increase of current density, but the growth is not linear. The similar results can be seen in previous work[8].



(a) Cross section for 50 mA/cm^2 (b) Cross section for 100 mA/cm^2

(c) Top-view for 50 mA/cm^2 (d) Top-view for 100 mA/cm^2

Fig.1 Cross section and top-view FESEM images of PSi formed by different current densities

According to the definition of PSi porosity, the porosity p can be expressed as

$$p = \frac{m_1 - m_2}{m_1 - m_3}, \tag{1}$$

where m_1 is the weight of silicon before anodization, m_2 is the weight of silicon after anodization, and m_3 is the weight of silicon after removing PSi. Thus, we can get that the porosities of samples formed at 50 mA/cm^2 and 100 mA/cm^2 are 80% and 65%, respectively.

According to Bruggeman effective medium model, the effective refractive index of PSi layer can be shown as[9]

$$(1-p)\frac{n_{\mathrm{Si}}^2 - n_{\mathrm{e}}^2}{n_{\mathrm{Si}}^2 + 2n_{\mathrm{e}}^2} + p\frac{n_{\mathrm{air}}^2 - n_{\mathrm{e}}^2}{n_{\mathrm{air}}^2 + 2n_{\mathrm{e}}^2} = 0, \tag{2}$$

where p is the porosity of the PSi layer, n_{Si} is the refractive index of the PSi layer, and n_{air} is the refractive index of air. Because the refractive index of air can be thought as 1, Eq.(2) can be expressed in another form as

$$n_{\mathrm{e}} = \sqrt{n_{\mathrm{Si}}^2(1-p) + p}\ . \tag{3}$$

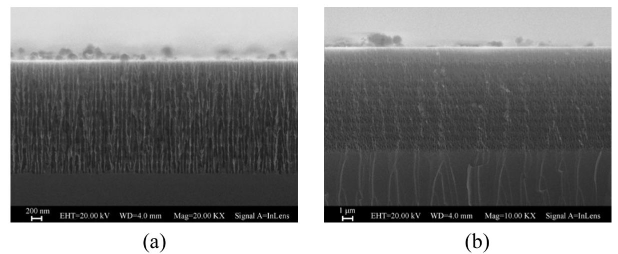
Thus, we can get that the effective refractive indices of the PSi layers with high and low porosities are 1.7 and 2.1, respectively.

As mentioned above, the pore size and morphology are intimately related to the applied current density and HF concentration. Thus, PSi layers with different refractive indices can be obtained by varying the current density. The simulation of the DBR reflectivity is performed using a transfer matrix method, which includes the effect of oxidation on the reflective index[10]. The photonic band gap can be expressed as

$$\lambda_{\max} = \frac{2}{m}(n_{\mathrm{h}}L_{\mathrm{h}} + n_{\mathrm{l}}L_{\mathrm{l}}), \tag{4}$$

where m is the spectral order, L is the thickness of the PSi layer, n is the average refractive index of the layer, and the subscripts of h and l indicate high porosity and low porosity, respectively.

Fig.2 shows FESEM images of two DBRs obtained by applying alternative current densities during the etching process. The anodizing solution is composed of HF and ethanol with volume ratio of 1:3. Fig.2(a) shows the sample which is formed by anodization at 100 mA/cm^2 for 1 s followed by an anodization at 50 mA/cm^2 for 1.5 s. Fig.2(b) shows another sample which is formed by anodization at 100 mA/cm^2 for 2 s followed by an anodization at 50 mA/cm^2 for 3 s. From the FESEM images, we can get that the DBR depths are 4.3 μm and 2.2 μm, respectively. Considering the error of measurement, we may conclude that the etching speed does not change when the etching time becomes longer.



(a) (b)

Fig.2 Cross section SEM images of PSi reflector formed by alternative current densities of (a) 100 mA/cm^2 for 1 s followed by 50 mA/cm^2 for 1.5 s and (b) 100 mA/cm^2 for 2 s followed by 50 mA/cm^2 for 3 s

Fig.3 shows the simulated and experimental results of reflectance spectra. From Fig.3, we can get that when the etching time doubles from 1 s and 1.5 s to 2 s and 3 s, the middle wavelength of the band gap also doubles. It shows that the etching time can not affect the effective optical thickness (EOT) of PSi layers. That is to say, when the etching time doubles, the EOT also doubles. And when the current density is changed, the band gap can be tuned in other areas.

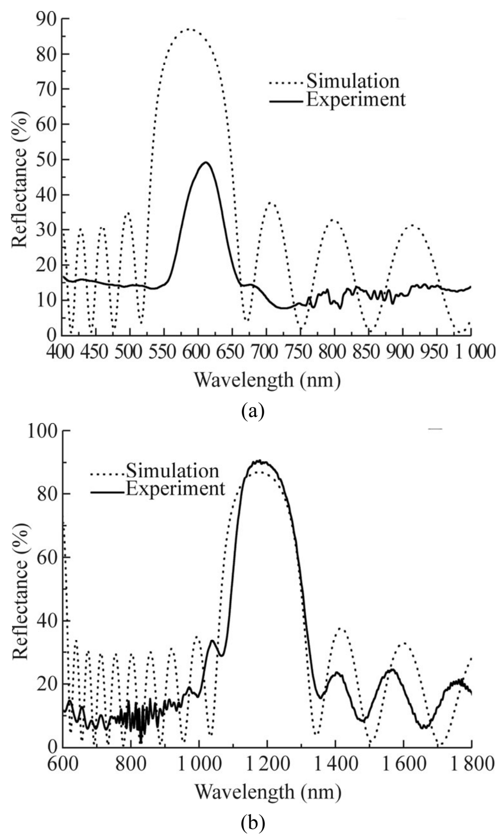


Fig.3 Experimental and simulated spectra of DBRs formed by alternative current densities of (a) 100 mA/cm^2 for 1 s followed by 50 mA/cm^2 for 1.5 s and (b) 100 mA/cm^2 for 2 s followed by 50 mA/cm^2 for 3 s

According to the space charge region (SCR) model, for highly doped n-type Psi, the pore wall thickness should be more than 100 nm, as discussed by Ge et al[8]. But from Figs.1 and 2, the pore wall is far less than 100 nm. It indicates that the macropore formation in our experiments is not primarily caused by SCR effects. In our cases, the low concentration (<25%) and large current density (>50 mA/cm^2) are the prime factors. Current burst model (CBM) is often thought to be able to interpret all silicon electrochemistry phenomena. This model has three characteristics of fast direct silicon dissolution, fast silicon oxide generation and extremely slow dissolution of the generated oxide[11]. For HF, the lower concentration leads to the higher fluorine ion concentration. Fluorine as one of the very lively non-metals has strong ability of oxidation. The higher current density means that the more available electronic holes can participate in chemical reactions. Thus, the macropore PSi formation can be well interpreted by CBM.

In conclusion, PSi photonic crystals with the pore size of about 80 nm were prepared by electrochemical etching method on highly-doped n-type silicon. It is found that the well dispersed macropores can be successfully fabricated by specially designed etching solution without illumination or oxidant. Theoretical calculation and experimental results of the PSi photonic crystals are consistent. Furthermore, we demonstrate the feasibility of the band gap selection by controlling the etching time, which suggests an interesting possibility for the application of PSi devices.

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