

# Anisotropic photoluminescence from porous silicon layers made under polarized illumination: Origin of contradictory experimental observations

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A detailed study has been performed on the anisotropic photoluminescence of porous silicon (PSi) layers formed by the electrochemical anodization under polarized illumination. Emphasis is placed on the different effects of the photoelectrochemical dissolution process and the electroless photochemical counterpart on the direction of the anisotropy. Our experimental results indicate that the two dissolution mechanisms induce photoluminescence anisotropy in totally different directions: in photoelectrochemically etched PSi samples, a maximal degree of polarization is observed only when the polarization ( $E_{\text{exc}}$ ) of the excitation light is *parallel* to the polarization ( $E_{\text{etch}}$ ) of the illumination light, while in photochemically etched samples it is observed when  $E_{\text{exc}}$  is *perpendicular* to  $E_{\text{etch}}$ . The former and latter results are explained, respectively, by the thinning and disintegration of the Si nanostructures oriented parallel to  $E_{\text{etch}}$  during the etching treatments. © 2003 American Institute of Physics. [DOI: 10.1063/1.1540746]

## I. INTRODUCTION

Over the last decade, nanocrystalline Si materials have attracted much attention for their efficient visible luminescence.<sup>1</sup> In particular, porous silicon (PSi) has an advantage for electrical excitation<sup>2,3</sup> because it has a network of interconnected Si nanocrystals. The mutually connected Si nanocrystals, or Si nanochains, are also responsible for some other unique optoelectronic properties of PSi, including the polarization memory effect<sup>4–11</sup> and a large birefringence.<sup>12,13</sup> The polarization memory effect is a phenomenon that excitation with linearly polarized light results in photoluminescence (PL) which is partially polarized in the same direction as the excitation light.<sup>14,15</sup> In the case of PSi, this is ascribed to the selective photoexcitation of randomly oriented Si nanochains.<sup>16</sup> A large birefringence is also observed in some PSi samples, and is attributed to Si nanochains organized in a specific direction. Optical devices based on this large birefringence have been demonstrated.<sup>17,18</sup>

These birefringent PSi layers exhibit anisotropic PL, that is, the PL intensity and/or its degree of linear polarization depends significantly on the polarization ( $E_{\text{exc}}$ ) of the excitation light.<sup>19</sup> Similar anisotropic PL has also been reported for PSi layers made by electrochemical etching under linearly polarized illumination.<sup>19–21</sup> This implies that anisotropic nanostructures can be formed photoelectrochemically, based on the absorption anisotropy in linear Si nanochains. We should note, however, that there is a large discrepancy in reported experimental results on the direction of this anisotropy. Polisski *et al.*<sup>19,20</sup> observed a maximal degree of linear polarization when  $E_{\text{exc}}$  was *perpendicular* to the polarization ( $E_{\text{etch}}$ ) of the etching illumination. On the contrary, in our previous experiment<sup>21</sup> based on *n*-type samples, a maximal degree of linear polarization was only observed when  $E_{\text{exc}}$

was *parallel* to  $E_{\text{etch}}$ . We suggested that a large difference in the intensity of illumination might have resulted in this discrepancy, probably through the predominance of photochemical and photoelectrochemical etching reactions in the former and latter experiments, respectively. The detailed effects of these reactions, however, were left unresolved.

In this study, we have investigated in more detail the effect of polarized illumination on the luminescence anisotropy of PSi samples. We used *p*-type wafers and illuminated them either during or after the formation of PSi layers. This made it possible to separate the effect of the electroless photochemical dissolution process that might be competing with the photoelectrochemical counterpart during the light-assisted anodization.

## II. EXPERIMENT

Single-crystal Si wafers of *p*-type (100) 0.01–0.02  $\Omega$  cm were etched either electrochemically or photoelectrochemically by anodization in a solution of 55% HF:C<sub>2</sub>H<sub>5</sub>OH = 1:3. The anodization current density and time were 20 mA/cm<sup>2</sup> and 30 min, respectively. The electrochemically etched samples were then subjected to polarized photochemical etching in the same solution under open-circuit conditions. In both photoelectrochemical and photochemical treatments, we used a 150-W halogen lamp equipped with a fiber-bundle light guide and a collimating lens. To obtain linear polarization, a film polarizer was placed between the light source and the sample. Also, a long-wavelength pass filter with a cutoff wavelength of 660 nm was used. This ensured uniform illumination over sufficient PSi thickness, because the penetration depth for the filtered light ( $\lambda > 660$  nm) was significantly larger than that for the PL excitation light ( $\lambda = 488$  nm).<sup>1</sup> Another reason for using the filter was that we had found that the filtered illumination remarkably enhanced the PL efficiency of PSi layers.<sup>22</sup> The PSi samples thus pre-

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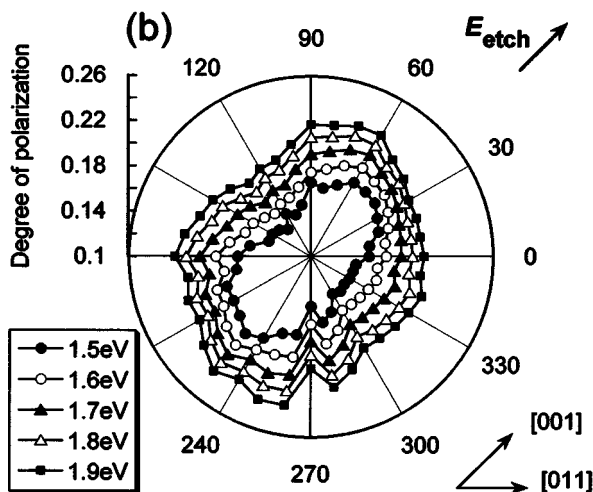
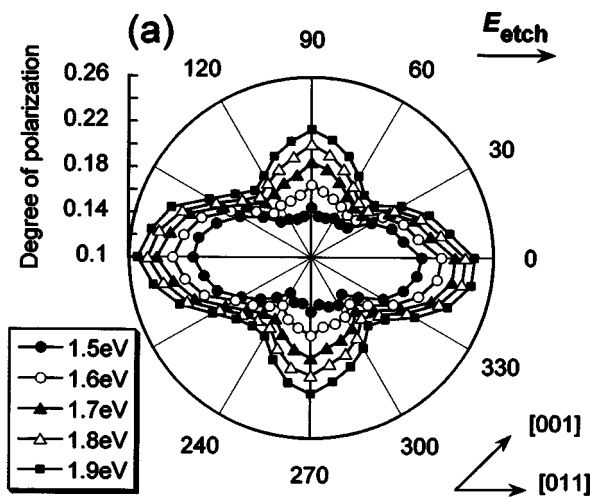


FIG. 1. Anisotropic responses of the PL from PSi samples made by photoelectrochemical anodization under polarized illumination. The degree of linear polarization is plotted as a function of the angle between the polarization ( $E_{\text{exc}}$ ) of the excitation light and the [011] axis of the Si substrate. The polarization ( $E_{\text{etch}}$ ) of the etching light is parallel to the [011] axis in (a) and [001] axis in (b).

pared were actually unstable under laser irradiation<sup>23</sup> and could not be employed in the measurement of PL anisotropy. Therefore, all the PSi samples were slightly oxidized electrochemically<sup>24</sup> in aqueous 0.1-M  $\text{H}_2\text{SO}_4$  at 2.3  $\text{mA}/\text{cm}^2$  for 19 min immediately after the photoelectrochemical anodization or photochemical etching.

The anisotropy in PL was evaluated by measuring the degree of linear polarization  $P = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp})$  for various polarization directions of the excitation light.<sup>21</sup> Here,  $I_{\parallel}$  and  $I_{\perp}$  are the intensities of the PL components polarized parallel and perpendicular to  $E_{\text{exc}}$ , respectively. The excitation light source was a 488-nm  $\text{Ar}^+$  laser.

### III. RESULTS

#### A. PSi samples illuminated during anodization

Figure 1 shows the measured polarization anisotropy of the PL from photoelectrochemically etched PSi samples. In

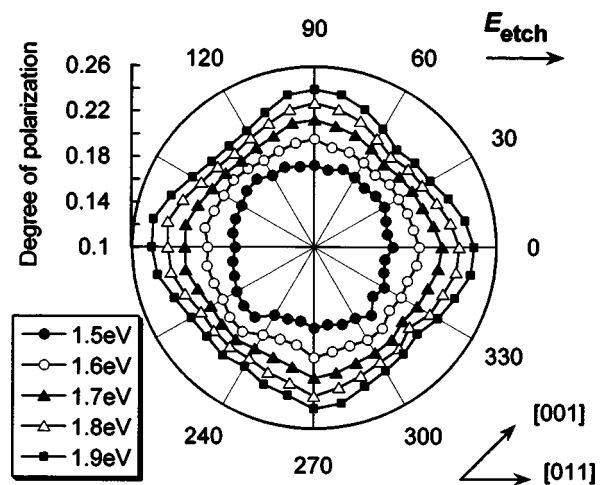


FIG. 2. Anisotropic response of the PL from a PSi sample made by anodization in the dark and subjected to electroless photochemical etching for 30 min with polarized light.

the figure, we show the degree of polarization as a function of the angle between  $E_{\text{exc}}$  and the [011] axis of the Si substrate for several emission energies. The sample of Fig. 1(a) was anodized under the condition of  $E_{\text{etch}} \parallel [011]$ , whereas the sample of Fig. 1(b) was prepared for  $E_{\text{etch}} \parallel [001]$ . In both cases, a maximal degree of linear polarization is observed when  $E_{\text{exc}}$  is parallel to  $E_{\text{etch}}$ . This behavior is basically the same as that of  $n$ -type samples reported before,<sup>21</sup> although these  $p$ -type samples show smaller dispersion of anisotropy. The small maxima appearing at the  $\langle 110 \rangle$  directions at high emission energies are characteristic of oxidized PSi samples,<sup>25</sup> and should be attributed to the electrochemical oxidation in  $\text{H}_2\text{SO}_4$  solution.

#### B. PSi samples illuminated after anodization

The corresponding results for the photochemically etched PSi sample are shown in Fig. 2. The photochemical etching time of this sample is 30 min, which is the same as the photoelectrochemical anodization time of the samples of Fig. 1. It seems that the polarized photochemical etching after anodization produces no preference of linear polarization for  $E_{\text{exc}} \parallel E_{\text{etch}}$ , although it does enhance the PL intensity to the level close to that of the photoelectrochemically etched samples, as shown in Fig. 3.

The photochemical etching, however, induces significant anisotropy in the other direction when the etching time is fairly long. Figure 4 shows the results of a PSi sample photochemically etched for 90 min. A maximal degree of linear polarization is observed when  $E_{\text{exc}}$  is perpendicular to  $E_{\text{etch}}$ . This trend is similar to those reported by Polisski *et al.*<sup>19,20</sup>

The prolonged photochemical etching with polarized light also gives rise to some other important changes in the PL properties of PSi samples. These are summarized in Fig. 5, where we show the PL intensity, the average degree of linear polarization, and the emission anisotropy as a function of photochemical etching time. Under the conditions employed here, the anisotropy begins to appear at an etching time between 60 and 75 min. Beyond this time, the PL intensity drastically increases, and the average degree of polar-

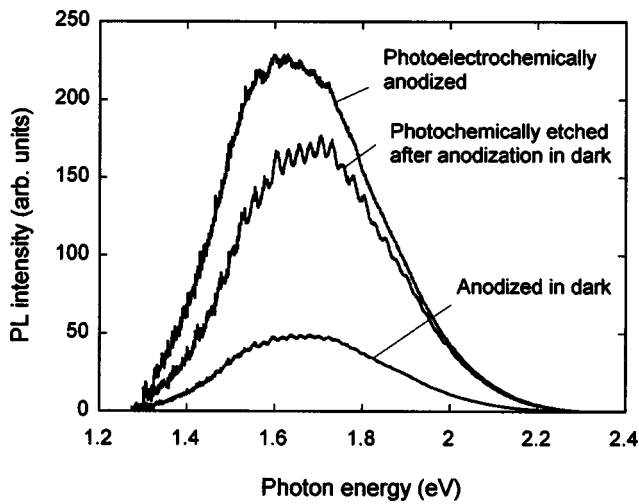


FIG. 3. PL spectra of the PSi samples of Fig. 1(a) (photoelectrochemically anodized) and Fig. 2 (photochemically etched). Also shown is the PL spectrum of a PSi sample prepared by anodization in the dark and subjected to no photochemical treatments.

ization decreases. In addition, it is also observed that the glossy surface of the samples changes into rough and matte, suggesting that microscopic mechanical damage is taking place in the PSi layers.

IV. DISCUSSION

It is clearly demonstrated in Figs. 1 and 2 that the electroless photochemical etching treatment employed here has a significantly weak effect compared to that of photoelectrochemical etching. This is because the primary photocurrent density ( $\approx 1.3 \text{ mA/cm}^2$ ) is much smaller than the anodization current density ( $20 \text{ mA/cm}^2$ ) as noted in a previous report.<sup>21</sup> The anisotropic PL shown in Fig. 1 can then be attributed to photoelectrochemically thinned Si nanochains oriented parallel to  $E_{\text{etch}}$ , as schematically shown in Fig. 6(a). These chains are preferentially thinned because of their higher pho-

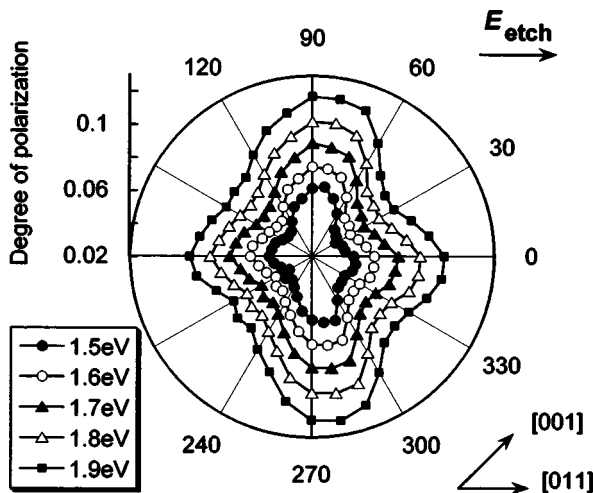


FIG. 4. PL anisotropy of a PSi sample subjected to polarized photochemical etching for 90 min after anodization in the dark.

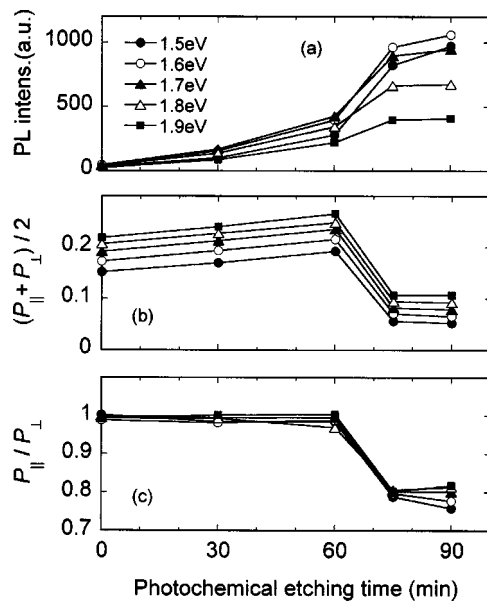


FIG. 5. PL intensity (a), the average degree of polarization (b), and the anisotropy of PL (c) as a function of the period of polarized photochemical etching.  $P_{\parallel}$  and  $P_{\perp}$  denote the degrees of polarization when the polarization ( $E_{\text{exc}}$ ) of the excitation light is parallel and perpendicular to the polarization ( $E_{\text{etch}}$ ) of the etching light, respectively.

toconductivities under polarized illumination. According to the quantum confinement model, these thinner structures should have higher emission efficiencies than the less etched ones, that is, those oriented perpendicular to  $E_{\text{etch}}$ . This results in a larger degree of polarization for  $E_{\text{exc}} \parallel E_{\text{etch}}$  and smaller one for  $E_{\text{exc}} \perp E_{\text{etch}}$ , which is consistent with the experimental results shown in Fig. 1.

It is important to note that the photoelectrochemical dissolution reactions at these Si nanochains become significantly suppressed as the thinning proceeds, owing to an increase in their resistivity. Therefore, the photoelectrochemical reactions only form narrow Si “nanowires” in the direction parallel to  $E_{\text{etch}}$ . In contrast, it is very plausible that the electroless photochemical etching reactions

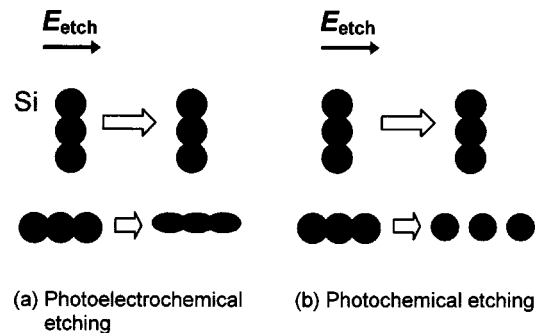


FIG. 6. Possible model for the observation of different optical anisotropies in PSi samples. The polarized illumination for etching preferentially works on those Si nanochains oriented parallel to its polarization ( $E_{\text{etch}}$ ). As a result, the Si nanochains become thinner in photoelectrochemically etched samples (a), while many of them tend to disintegrate in photochemically etched samples (b).

break many of the Si nanochains oriented parallel to  $E_{\text{etch}}$ , leaving number of Si “nanodots” (of course these are not true “dots” and should be connected somehow, most probably in the direction normal to the sample surface) as shown in Fig. 6(b). These Si “nanodots” are highly luminescent due to their lower dimensions, and their PL is basically unpolarized. PSi samples with these structures will show higher PL efficiencies and lower average degrees of polarization, and these properties are actually observed in our photochemically etched PSi samples (Fig. 5). The small anisotropy in the direction perpendicular to  $E_{\text{etch}}$  (Fig. 4) can be explained by the contribution of those Si nanochains oriented perpendicular to  $E_{\text{etch}}$  that have survived the photochemical process. Breaking the network of Si nanocrystals, in addition, makes the surface of PSi samples rough, which is also consistent with the experimental observation.

## V. CONCLUSION

This study has resolved the contradictory experimental results regarding the direction of PL anisotropy in PSi samples anodized under polarized illumination. The important point is that the anodization under illumination involves two mutually competing processes: the photoelectrochemical dissolution and the electroless photochemical dissolution. Our experimental results based on *p*-type wafers have shown that the former and the latter processes result in such different anisotropic responses that a maximal degree of polarization is observed for  $E_{\text{exc}} \parallel E_{\text{etch}}$  and  $E_{\text{exc}} \perp E_{\text{etch}}$ , respectively. Since our light intensity is relatively weak, the photoelectrochemical process is thought to have overcome the photochemical counterpart in our previous experiment.<sup>21</sup> In contrast, many Si nanochains in the samples of Polisski *et al.*<sup>19,20</sup> are likely to have suffered from photochemical dissolution reactions significantly, because their illumination intensity is very high (2–500 mW/cm<sup>2</sup>). The different optical responses can be attributed to the different effects of these dissolution processes on the Si nanochains oriented parallel to  $E_{\text{etch}}$ : the photoelectrochemical process only makes them thinner preserving the connections between Si nanocrystals, while the photochemical process can break the connections and produce many low-dimensional structures.

## ACKNOWLEDGMENTS

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