

## Anisotropy of infrared-upconversion luminescence generation in porous silicon

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It is demonstrated that the infrared-upconversion luminescence generation from porous silicon, which was considered as an enhanced third-order nonlinear optical effect in our recent work, is anisotropic as the polarization vector of normally incident fundamental light is rotated. A new method was used to determine the anisotropy parameter  $\sigma$  of the third-order nonlinear optical tensor  $X^{(3)}$ . Due to the sensitivity of  $\sigma$  to the crystal structure and microscopic electronic properties, the difference of  $\sigma$  between porous silicon and crystalline silicon, particularly of their phases, demonstrates that the nanometer structure of porous silicon induces a dramatic change of the electronic band structure, but the strong anisotropic crystal property remains.

Recently, efficient room-temperature visible light photoluminescence (PL) (Ref. 1) and also electroluminescence (EL) (Ref. 2) from highly porous silicon (PS) have been observed. Since then, many studies<sup>3-11</sup> of PS have been carried out from many different points of view, aimed at both the fundamental understanding of the mechanism of light emission and the possible applications of PS in future optoelectronic devices.

In our recent work,<sup>12</sup> efficient infrared-upconversion luminescence from PS was observed under the excitation of 1.06- $\mu\text{m}$  radiation. This phenomenon was explained as an enhancement of the third-order nonlinear optical susceptibility  $X^{(3)}$  due to the quantum confinement effect arising from the nanometer structure of PS. It was considered that the upconversion luminescence is converted from the strong third-harmonic generation (THG) of PS.

In past years,<sup>13-16</sup> THG has been used as a probe of the bulk symmetry of crystals, especially semiconductors and metals which possess cubic symmetry and centrosymmetry. In essence, this technique makes use of the fact that the linear optical susceptibility is isotropic in character, whereas the third-order nonlinear susceptibility, because of its high tensorial rank, is not. In addition, THG has a bulk electric dipole source which bars any large resonantly enhanced surface electric dipole effects, and tends to be the sole source. It is these characteristics which lead to the use of THG as an unambiguous probe of anisotropic bulk symmetry properties. In this work, the anisotropic infrared-upconversion luminescence of PS is measured and the comparison with the THG of a silicon single crystal (*c*-Si) is given. It is found that the upconversion luminescence efficiency of PS versus the crystal orientation shows the same symmetry as that of the THG efficiency of *c*-Si, but their phases are significantly different.

The samples used were *p*-type Si(100) wafers with a resistivity of 18  $\Omega\text{cm}$ . The procedure of the sample preparation has been described previously.<sup>12</sup> The thick-

ness of PS layer was about 5–10  $\mu\text{m}$ , as determined by the anodization time. Under UV-light illumination, the sample emitted a bright homogeneous orange light.

The experimental arrangement is shown in Fig. 1. A passively mode-locked Nd:YAG (yttrium aluminum garnet) laser was used to generate 50-ps pulses at a repetition rate of 10 Hz. By using colored-glass filters, only 1.06- $\mu\text{m}$  light can enter the blackbox. The incident light beam, which had a diameter of  $\sim 1$  mm with a single-pulse energy of  $\sim 20$   $\mu\text{J}$  was directed at normal incidence onto a PS sample through a linear polarizer and a 1/2-wave plate mounted on a rotation stage for polarization rotation. Under this level of energy, we did not observe any time-dependent signal decay, which showed that the PS sample was not damaged by the laser illumination. The signal emitted from the PS was collected by a relative aperture 1:1.5 lens after removing the fundamental light, and detected by the photomultiplier and then recorded by an *X*-*Y* recorder after being treated by a boxcar averager. It was found that THG from air and the optical components was not a problem in our case.

The infrared-upconversion spectrum of PS was measured by inserting a monochromator between the lens and the photomultiplier and removing the polarizer and the 1/2-wave plate. The result is shown in Fig. 2, where, in addition to the narrow THG peak at 355 nm, there exists a broader luminescence band centered at the visible region. For *c*-Si, the THG signal was observed with the absence of the broad luminescence band in the upconversion region. In our previous paper,<sup>12</sup> it was considered that the broad infrared-upconversion luminescence band is converted from the strong THG of PS, which is quite similar to the visible light-emitting process of PS excited by external UV light, and the strong THG was attributed to a double-resonance-enhanced third-order nonlinear optical process. With the PS sample fixed, the upconversion luminescence efficiency was measured as a function of the rotation angle  $\Theta$  of the 1/2-wave plate (and hence the

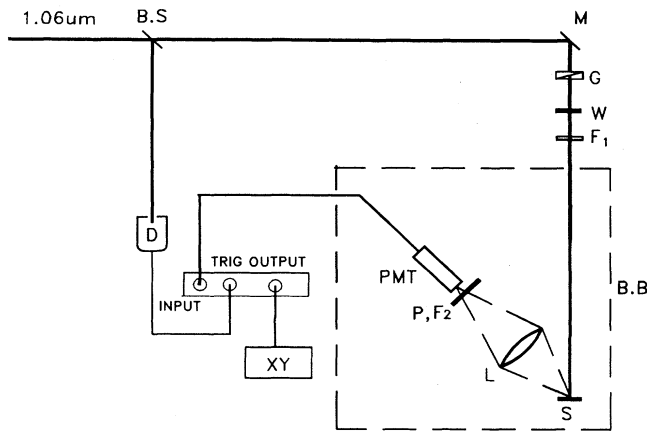


FIG. 1. A schematical illustration of the experimental setup. B.S.: beam splitter; M: reflection mirror; G: Glan prism; W: 1/2-wave plate; F1, F2: filters; S: porous Si sample; L: lens; P: polarizer; PMT: photomultiplier tube; D: photodetector; XY: x-y recorder; B.B: blackbox.

orientation of the incident electric field), as shown in Fig. 3. The THG efficiency versus the crystal orientation for linearly polarized light, which was incident upon a (100) *c*-Si surface, was also measured and is shown in Fig. 4. By comparing these two curves, it can be seen that the upconversion luminescence efficiency of PS shows the same fourfold symmetry and almost the same modulation depth as that of the THG efficiency of the *c*-Si. However, there is a phase difference of  $\pi$  between the two curves. These results demonstrate that PS has a strong crystalline anisotropic behavior and a different nonlinear optical response from that of *c*-Si. It is known<sup>14</sup> that, if silicon is changed from crystalline Si to noncrystalline Si, the only difference between curves of THG efficiency versus crystal orientation is the reduction of modulation depth rather than the change of phase. For amorphous Si (*a*-Si), the modulation depth of the THG efficiency versus the rotation angle is 0. Therefore, we consider that the third-harmonic photons are actually being generated mainly from the nanoscale crystalline structures, such as quantum rods or/and dots, in the PS layer, and thus its signal intensity possesses anisotropic characteristics as anti-

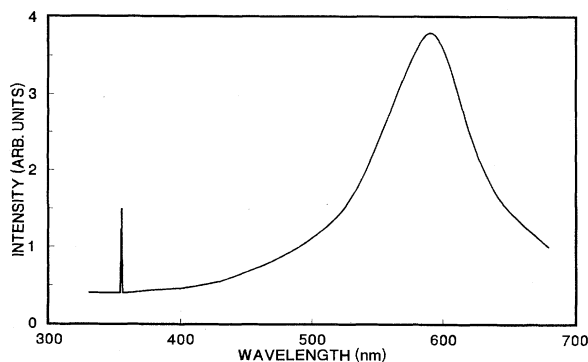


FIG. 2. The infrared-upconversion spectrum of porous Si excited by the 1.06- $\mu\text{m}$  radiation of a mode-locked YAG laser.

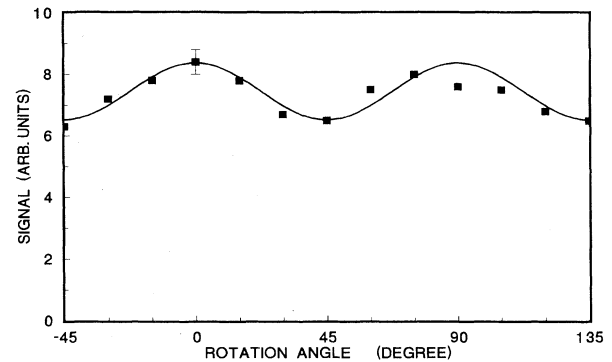


FIG. 3. Intensity of the infrared-upconversion luminescence signal of porous Si as a function of the angle between the fundamental electric-field vector and a crystal cubic axis. The solid line is the theoretical fitness to Eq. (5).

ipated. This radiation, with relatively high photon energy, is able to excite the visible luminescence of PS just as the external UV-light source does. The photoluminescence mechanism of PS may be related to different factors such as quantum confinement in Si nanostructures, surface states, and some possible Si-related luminescent species or compounds on PS internal surfaces, but the THG signal could only be generated mainly from crystalline nanostructures in PS. We believe this is a reasonable explanation for the anisotropy of infrared-upconversion luminescence generation observed in our experiments. Another possibility, that the THG occurs in the Si substrate, seems unlikely since the THG from *c*-Si is relatively too weak to excite the observable infrared-upconversion signal.<sup>12</sup> In addition, this possibility could not account for the phase difference between the two curves in Figs. 3 and 4.

To characterize the anisotropy of nonlinear optical susceptibility tensor, Moss and co-workers<sup>17,18</sup> introduced a complex anisotropy parameter  $\sigma$ , which is defined as

$$\sigma = 3X_{1122}^{(3)} / X_{1111}^{(3)} - 1, \quad (1)$$

where  $X_{1122}^{(3)}$  and  $X_{1111}^{(3)}$  are the two independent nonvanishing elements of the nonlinear optical susceptibility ten-

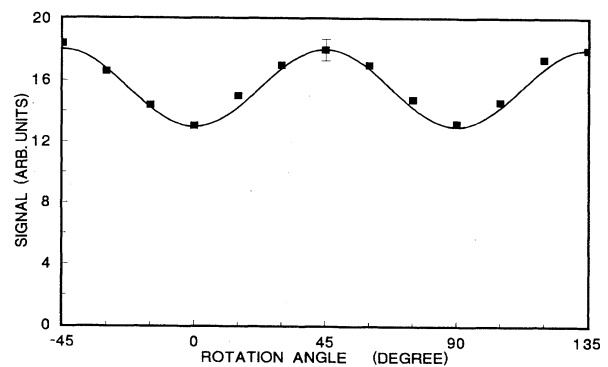


FIG. 4. Intensity of the THG signal of *c*-Si as a function of the angle between the fundamental field vector and a crystal cubic axis. The solid line is the theoretical fitness to Eq. (5).

sor  $X^{(3)}$ , and  $\sigma$  is proved to be more sensitive to the microscopic electronic properties of the solid than the absolute magnitude of  $X^{(3)}$ . Thus the THG can be used to probe not only the symmetry of the potential in which the electrons move but also the details of that movement itself. The quantitative analysis of the above experimental results can be done by determining the complex parameter  $\sigma$ . However, it was claimed in previous work<sup>13,14,18</sup> that  $\sigma$  cannot be determined solely from Fig. 3.<sup>13</sup> Burns and Bloembergen<sup>13</sup> and Moss, Van Driel, and Sipe<sup>18</sup> solved the problem by using a circularly polarized light. In the following, we present another method which can determine  $\sigma$  more accurately by simply using only linear polarized light.

In centrosymmetric crystals such as silicon with  $m3m$  symmetry, the lowest-order nonlinear optical effects are those associated with an induced polarization which is third order in the electric strength.<sup>19</sup> The  $i$ th Cartesian component of the induced polarization may be given phenomenologically as

$$P_i^{\text{NL}}(3w) = BE_i(\mathbf{E} \cdot \mathbf{E}) + (A - B)E_iE_jE_j, \quad (2)$$

where  $A = X_{1111}^{(3)}$ ,  $B = 3X_{1122}^{(3)}$ . For a linearly polarized beam at normal incidence on a (100) crystal face, the reflection third-harmonic field in air is given by<sup>10</sup>

$$\begin{aligned} \mathbf{E}(3w) = & -\frac{\pi}{(N+1)(N+n)} \left[ \frac{2}{n+1} \right]^3 E^3(w) \\ & \times \{ [(3A+B) + (A-B)\cos(4\Theta)] \hat{\mathbf{e}}_1 \\ & + (A-B)\sin(4\Theta) \hat{\mathbf{e}}_2 \}, \end{aligned} \quad (3)$$

where the unit vectors  $\hat{\mathbf{e}}_1$  and  $\hat{\mathbf{e}}_2$  lie in the plane of the surface and are parallel and perpendicular to the polarization direction of incident light beam, and  $\Theta$  is the angle between the incident  $\mathbf{E}$  field and the  $x$  axis of crystal.  $N = \sqrt{\epsilon(3w)}$  and  $n = \sqrt{\epsilon(w)}$ , where  $\epsilon(w)$  is the linear complex dielectric constant of the medium. If we express  $A$  and  $B$  into complex, that is

$$B/A = \alpha e^{i\phi} = \sigma + 1, \quad (4)$$

then, according to Eq. (3), we have

$$I \sim [5 + \alpha^2 + 2\alpha \cos(\phi)] + [3 - 2\alpha \cos(\phi) - \alpha^2] \cos(4\Theta), \quad (5)$$

and

$$\frac{I_{\max}}{I_{\min}} = \frac{4}{1 + \alpha^2 + 2\alpha \cos(\phi)}. \quad (6)$$

According to Eq. (3), if another polarizer, which is along  $\hat{\mathbf{e}}_2$ , is put in front of the photomultiplier tube (PMT), we obtain theoretically

$$I_{e2} \sim [1 - 2\alpha \cos(\phi) + \alpha^2] \sin^2(4\Theta). \quad (7)$$

In our case, we chose  $\Theta = 22.5^\circ$ , and from Eqs. (5) and (7), we have,

$$\frac{I(\Theta = 22.5^\circ)}{I_{e2}(\Theta = 22.5^\circ)} = \frac{5 + \alpha^2 + 2\alpha \cos(\phi)}{1 - 2\alpha \cos(\phi) + \alpha^2} = R. \quad (8)$$

The measured value of  $R$  for our PS sample is 4.2, and  $I_{\max}/I_{\min}$  in Fig. 3 is 1.3. From Eqs. (6) and (8), it is very easy to determine  $\alpha$  and  $\phi$  and thus  $\sigma$  of PS in a rather accurate way. As a result, we have

$$\alpha = 1.19 \pm 0.1, \quad \phi = 73^\circ \pm 3^\circ,$$

and  $\sigma = 1.31e^{i120^\circ}$ . For  $c$ -Si, the corresponding results are

$$\alpha = 1.24 \pm 0.1, \quad \phi = 18^\circ \pm 2^\circ,$$

and  $\sigma = 0.46e^{i69^\circ}$ , which coincide well with the results of Refs. 14 and 15, and thus verify the validity of our simple but more accurate method.

The difference of  $\sigma$  between PS and  $c$ -Si, in particular of their phase, indicates that the microscopic electronic property of PS is greatly different from  $c$ -Si; however, the crystalline anisotropy remains. In contrast to those of  $c$ -Si, the large magnitude and phase of  $\sigma$  of PS also support<sup>18</sup> the microscopic mechanism of infrared-upconversion luminescence generation proposed by our previous paper,<sup>12</sup> i.e., there exist some resonant excitation processes.

In conclusion, the anisotropy of the infrared-upconversion luminescence generation in PS has been studied. Detailed quantitative analysis shows that PS has a strong crystalline anisotropy, and that the microscopic electronic property of PS is greatly different from that of  $c$ -Si due to the nanometer structure.

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<sup>1</sup>L. T. Canham, Appl. Phys. Lett. **57**, 1046 (1990).

<sup>2</sup>N. Koshida and H. Koyama, Appl. Phys. Lett. **60**, 347 (1992).

<sup>3</sup>V. Vezin, P. Goudeau, A. Naudon, A. Halimaoui, and G. Bamchil, Appl. Phys. Lett. **60**, 2625 (1992).

<sup>4</sup>A. Halimaoui, C. Oules, G. Bomchil, A. Bsiesy, F. Gaspard, R. Hermo, M. Ligeon, and F. Muller, Appl. Phys. Lett. **59**, 304 (1991).

<sup>5</sup>R. Tsu, H. Shen, and M. Dutta, Appl. Phys. Lett. **60**, 112 (1992).

<sup>6</sup>V. Lehmann and U. Gosele, Appl. Phys. Lett. **58**, 856 (1991).

<sup>7</sup>R. P. Vasques, R. W. Fathauer, T. George, and A. Ksendzov, Appl. Phys. Lett. **60**, 1004 (1992).

<sup>8</sup>C. Tsai, K.-H. Li, D. S. Kinosky, R. Z. Qian, T.-C. Hsu, J. T.

Irby, and S. K. Banerjee, Appl. Phys. Lett. **60**, 1700 (1992).

<sup>9</sup>M. S. Brandt, D. H. Fuchs, M. Stutzmann, J. Weber, and M. Cardona, Solid State Commun. **81**, 307 (1992).

<sup>10</sup>Z. Y. Xu, M. Gal, and M. Gross, Appl. Phys. Lett. **60**, 1375 (1992).

<sup>11</sup>T. Ito, T. Ohta, O. Arakaki, and A. Haraki, in MRS Symposia Proceedings No. 256, edited by S. S. Iyer, R. T. Collins, and L. T. Canham (Materials Research Society, Pittsburgh, 1992), p. 127.

<sup>12</sup>Jian Wang, Hong-bing Jiang, Wen-cheng Wang, Jia-biao Zheng, Fu-long Zhang, Ping-hai Hao, Xiao-yuan Hou, and Xun Wang, Phys. Rev. Lett. **69**, 3252 (1992).

<sup>13</sup>W. K. Burns and N. Bloembergen, Phys. Rev. B **4**, 3437

- (1971).
- <sup>14</sup>D. J. Moss, H. M. Van Driel, and J. E. Sipe, *Appl. Phys. Lett.* **48**, 1150 (1986).
- <sup>15</sup>C. C. Wang, J. Bomback, W. T. Donlon, C. R. Hou, and J. V. James, *Phys. Rev. Lett.* **57**, 1647 (1986).
- <sup>16</sup>J. E. Sipe, D. J. Moss, and H. M. Van Driel, *Phys. Rev. B* **35**, 1129 (1987).
- <sup>17</sup>D. J. Moss, E. Ghahramani, J. E. Sipe, and H. M. Van Driel, *Phys. Rev. B* **41**, 1542 (1990).
- <sup>18</sup>D. J. Moss, H. M. Van Driel, and J. E. Sipe, *Opt. Lett.* **14**, 57 (1989).
- <sup>19</sup>Y. R. Shen, *The Principles of Nonlinear Optics* (Wiley, New York, 1984).