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ANISOTROPIC INFRARED-UP-CONVERSION LUMINESCENCE GENERATION IN POROUS SILICON*

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It is demonstrated in this paper that the infrared-up-conversion luminescence generation from porous silicon, considered as an enhanced third-order nonlinear optical effect by the recent work, is anisotropic as the polarization vector of normally incident fundamental light is rotated. A new method has been used to determine the anisotropy parameter σ of the third-order nonlinear optical tensor $\chi^{(3)}$. Due to the sensitivity of σ to the crystal structure and microscopic electronic properties, the difference in σ's between porous and crystalline silicon, particularly in their phases, demonstrates that the nanometer structure of porous silicon induces a dramatic change of the electronic band structure, but the strongly anisotropic crystal property remains unchanged.

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I. INTRODUCTION

Recently, efficient room-temperature visible light photoluminescence (PL)[1] and also electroluminescence (EL)[2] from highly porous silicon (PS) have been observed. Since then, a lot of studies[3-11] of PS have been carried out from different points of view, aiming 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[12], the efficient infrared-up-conversion luminescence from PS was observed under the excitation of a 1.06 μm radiation. This phenomenon was explained as an enhancement of the third-order nonlinear optical susceptibility $\chi^{(3)}$ due to the quantum confinement effect arising from the nanometer structure of PS. It was considered that the up-conversion luminescence is converted from the strong third-harmonic generation (THG) of PS.

For the past years[13-16], THG has been used as a probe for the bulk symmetry of crystals, especially semiconductors and metals which possess cubic-symmetry and centro-symmetry.

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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 that lead to the use of THG as an unambiguous probe of anisotropic bulk symmetry properties. In this work, the anisotropic infrared-up-conversion luminescence of PS is measured and the comparison with the THG of silicon single crystals (c-Si) is given. It is found that the up-conversion 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.

II. EXPERIMENTAL SETUP

The samples used were p-type Si(100) wafers with a resistivity of 18 Ω·cm. The procedure of sample preparation has been described previously[12]. The thickness of PS layer was about 5–10 μm as determined by the anodization time. Under UV-light illumination, the sample emitted a bright homogeneous orange-light.

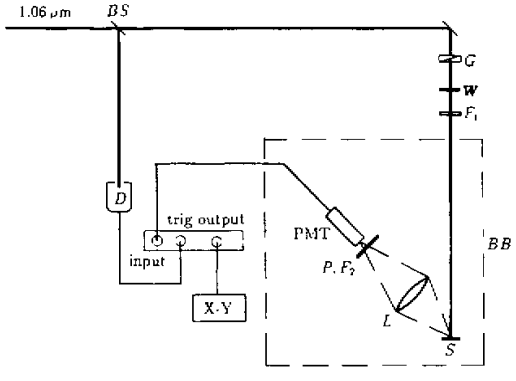

Fig. 1. Schematic diagram of the experimental setup. *BS*: beam splitter; *M*: reflection mirror; *G*: glan prism; *W*: 1/2 wave plate; F_1, F_2: filters; *S*: porous Si sample; *L*: lens; *P*: polarizer; PMT: photomultiplier tube; *D*: photodetector; X-Y: X-Y recorder; *BB*: blackbox.

The experimental arrangement is shown in Fig.1. A passively mode-locked Nd:YAG laser was used to generate 50 ps pulses at a repetition rate of 10 Hz. By using colored-glass filters, only 1.06 μm light can enter the blackbox. The incident light beam which had a diameter of 1 mm with single pulse energy 20 μJ was directed at normal incidence onto PS sample through a linear polarizer and a 1/2 wave plate mounted on a rotating stage for polarization rotation. Under this level of energy we did not observe any time-dependent signal decaying, 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 treated by a boxcar averager. It was found that THG from the air and the optical components caused no trouble in our case.

III. RESULTS AND DISCUSSIONS

The infrared-up-conversion 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 broad 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 up-conversion region. In our previous paper[12], it was considered that the broad infrared-up-conversion luminescence band was 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.

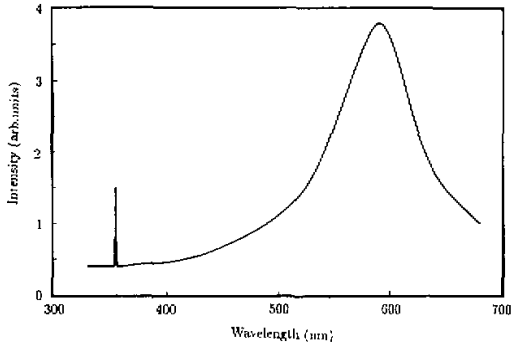

Fig. 2. Infrared-up-conversion spectrum of porous Si excited by the 1.06 μm radiation of a mode-locked YAG laser.

With the PS sample fixed, the up-conversion luminescence efficiency was measured as a function of the rotation angle Θ of the 1/2 wave plate (and hence the 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 up-conversion 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 π 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. As it is known[14], if silicon is changed from crystalline to non-crystalline, the only difference between the curves of the 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 zero. Therefore, our result gives an evidence that the a-Si phase is unlikely to be explained by the possible mechanism of visible light

emission from PS as suggested by Vasques *et al.*[7]

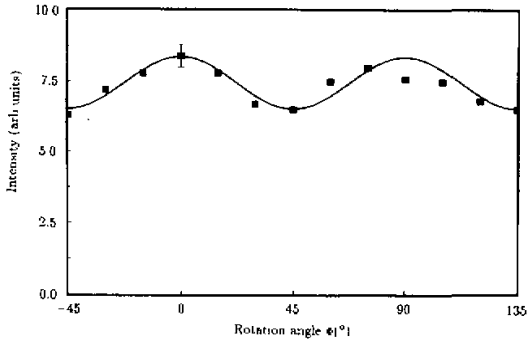

Fig. 3. Intensity of infrared-up-conversion luminescence signal of porous Si as a function of angle between the fundamental electric field vector and a crystal cubic axis. The solid line is a theoretical fitting to Eq.(5).

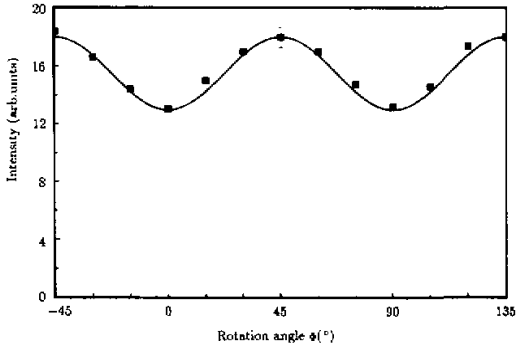

Fig. 4. Intensity of THG signal of c-Si as a function of angle between the fundamental field vector and a crystal cubic axis. The solid line is a theoretical fitting to Eq.(5).

To characterize the anisotropy of nonlinear optical susceptibility tensor, Sipe *et al.*[17,18] introduced a complex anisotropy parameter σ, which is defined as

$$\sigma = 3\chi^{(3)}_{1122}/\chi^{(3)}_{1111} - 1 \,, \tag{1}$$

where $\chi^{(3)}_{1122}$ and $\chi^{(3)}_{1111}$ are the two independent nonvanishing elements of the nonlinear optical susceptibility tensor $\chi^{(3)}$, and σ is proved to be more sensitive to the microscopic electronic properties of the solid than the absolute magnitude of $\chi^{(3)}$. 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 σ. However, it was claimed in previous work[13,14,18] that σ cannot be determined solely from Fig.3[13]. Bleombergen *et*

al.[15] and Sipe et al.[18] solved the problem by using a circularly polarized light. In the following we present another method which can determine σ more accurately by using only the 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 of the third order in the electric strength[19]. The ith Cartesian component of the induced polarization may be given phenomenologically as,

$$P_i^{\mathrm{NL}}(3\omega) = BE_i(\boldsymbol{E}\cdot\boldsymbol{E}) + (A-B)E_iE_iE_i\ , \tag{2}$$

where $A = \chi^{(3)}_{1111}$, $B = 3\cdot\chi^{(3)}_{1122}$. For a linearly polarized beam at normal incidence on a (100) crystal face, the reflection third harmonic field in air is given by[10]

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

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

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

then according to Eq.(3), we have

$$I \sim (5+\alpha^2+2\alpha\cos\phi) + (3-2\alpha\cos\phi-\alpha^2)\cos(4\Theta)\ , \tag{5}$$

and

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

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

$$I_{\hat{e}_2} \sim (1-2\alpha\cos\phi+\alpha^2)\sin^2(4\Theta)\ . \tag{7}$$

In our case, we choose $\Theta = 22.5°$, and from Eqs.(5) and (7), we have

$$\frac{I(\Theta=22.5°)}{I_{\hat{e}_2}(\Theta=22.5°)} = \frac{5+\alpha^2+2\alpha\cos\phi}{1-2\alpha\cos\phi+\alpha^2} = R\ . \tag{8}$$

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 α and ϕ and thus σ of PS quite accurately. As a result, we have $\alpha = 1.19\pm0.05$, $\phi = 73°\pm3°$, and $\sigma = 1.31\,e^{i120°}$.

For c-Si, the corresponding results are $\alpha = 1.24 \pm 0.05$, $\phi = 18° \pm 2°$, and σ=0.46e$^{i69°}$, which coincide well with the results in Refs.[14] and [15], and thus verify the validity of our simple but more accurate method.

The difference of σ's, in particular their phases, between PS and c-Si indicates that the microscopic electronic property of PS is quite different from c-Si; however, the crystalline anisotropy is retained. In contrast with those of c-Si the large magnitude and phase of σ of PS also support[18] the microscopic mechanism of infrared-up-conversion luminescence generation proposed in our previous paper[12], i.e., there exist some resonant excitation processes.

IV. CONCLUSION

The anisotropy of the infrared-up-conversion luminescence generation in PS has been studied. Detailed quantitative analysis shows that PS has a strong anisotropy in crystals, which is in contradiction with the hypothesis of a-Si phase mechanism for PS luminescence, and the microscopic electronic property of PS is considerably different from that of c-Si due to the nanometer structure.

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