Nonlinear phenomenon in nanocrystallites produced by laser-induced etching of silicon

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Abstract

Self-phase modulation of continuous wave argon-ion laser beam by a medium containing silicon nanocrystallites is reported here. Refractive index of nanocrystallites shows nonlinear behavior with the intensity of probing laser beam when size of nanocrystallites is decreased below 8 nm. A simple quantitative explanation for the observed optical fringes is given in terms of distribution of sizes of nanocrystallites and intensity of laser beam. Nonlinear optical response of silicon nanocrystallites is found to have a strong correlation with the size of nanocrystallites, which are determined by the Raman scattering and photoluminescence using two-dimensional quantum confinement effects of phonons and electrons, respectively.

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1. Introduction

The nonlinear optical properties of nanometer size semiconductors have been a topic of great interest in recent years [1-10]. Porous silicon (PS), in particular, has been reported [6-10] to possess optical nonlinear properties, which may make PS a promising material to be used in several nonlinear optical applications such as optical switching. Medium containing nanocrystallites of silicon (Si) acts as a dielectric-like medium whose dielectric properties can be exploited by the light to observe nonlinear optical response. Recently, laser-induced etching of Si wafer has been used as a technique for creation of nanocrystallites of Si of desired size with narrow size distribution [11,12]. The optical properties such as nonlinearity associated with changes in refractive index are significantly affected by the presence of nanocrystallites [8,10] and size distribution of nanocrystallites. This can lead to well-known phenomena of self-focusing and self-phase modulation [13]. For better understanding of the physics of the nanocrystallites and
their possible applications in practical devices, more investigations on the optical properties of the nanocrystallite ensemble are yet to be explored.

Cotter et al. [5] have reported the third-order optical nonlinearity of nanometer-size semiconductors caused by electronic quantum confinement. Many authors [6-8] have used Z-scan technique to measure the third-order nonlinear susceptibility of PS resulting from the quantum confinement of Si. Vijayalakshmi et al. [7] have found that there is a strong correlation of the optical properties with the sizes of Si nanoclusters. A negative refractive index is observed in free-standing PS layers due to dominant contribution of the optical Stark effect [8]. Maly et al. [9] have shown that the picosecond absorption nonlinearity in PS is due to recombination of carriers in localized surface states and the free carriers in the core of Si nanocrystallites. Significant photo-induced refractive index changes have been observed in PS Fabry-Perot resonators and are presumably caused by the charge carrier accumulation in nanocrystallites [10]. It is proposed that the ensemble of nanocrystallites acts as a dielectric-like medium where optical nonlinearity exists [6-10]. When an electromagnetic radiation with sufficiently high intensity interacts with the porous medium or the nanocrystallites, optical nonlinearity (i.e., nonlinear behavior of refractive index) is observed in it. Light-induced electric dipoles oscillating with the frequency of light are formed inside the nanocrystallites. Oscillator strength of these electric dipoles is expected to increase with the intensity of electric field associated with the incident photon as well as decrease in size of nanocrystallites.

Recently, Koker and Kolasinski [14] have reported the formation of optical patterns by a photochemically fabricated PS film. They have explained it by the optical interference and Fresnel diffraction of light from the bottom interface of the film. Similar diffraction fringes have been seen earlier in the liquid crystals due to self-focusing of laser beam [15-18]. We believe that the optical fringes from nanocrystallites of silicon can be explained by the self-phase modulation of laser beam [13]. In view of this, we have studied the formation of the optical fringe pattern with different laser etching times, which control the size of nanocrystallites in Si substrate. Nanometer size crystals (<10 nm), which are much smaller than the wavelength of laser beam, have strong dipole-induced interaction of nanocrystallites of Si with electric field of incident laser beam. The optical fringe pattern observed on the screen contains information about changes in refractive index and their correlation with nanocrystallites size distribution in PS. The formation of optical fringe pattern depends upon size of nanocrystallites in PS film.

In this paper, we report the optical fringe pattern of nanocrystallites during laser etching of Si. Influence of the size distribution of nanocrystallites is discussed in the formation of optical fringes. A careful analysis of the Raman line-shape of nanocrystallites produced by laser-induced etching has been done in order to see the effect of possible stimulated Raman scattering (nonlinear phenomenon). Quantum confinement of phonons and electrons are invoked to analyze Raman and PL data of nanocrystallites, respectively. The mean size and size distribution were determined by using two-dimensional quantum confinement model from the Raman data. The photoluminescence (PL) spectrum is also reported to confirm the presence of nanocrystallites. We further show that the refractive index of nanocrystallites changes non-linearly with decrease in the size of nanocrystallites (<10 nm). Their influences on the optical fringe patterns are observed and analyzed by using the self-phase modulation of the exciting laser beam.

2. Experimental procedure

2.1. Fabrication process and optical fringe patterns

A commercially available n-type Si wafer with resistivity of 10 X cm was immersed in HF acid of 40% concentration. The immersed wafer was put on two teflon plates in such a way that current passes from the bottom surface to laser irradiated surface through the electrolyte. Laser-induced etching (LIE) [11,12] was done by using an argon ion laser beam (λ = 5145 Å) on a Si substrate. The
laser beam was focused to a circular spot of nearly 100 lm diameter and laser power of 50 mW was used during LIE and for recording the optical fringes. The samples were etched in this way for 30 and 10 min with the laser beam and were subsequently rinsed with ethanol and dried in air for recording Raman and PL spectra. The reflected beam was studied as the PS was formed on Si substrate during etching. A screen was placed at a distance 1.5 m from the surface of the crystal to observe the optical fringe patterns formed by the reflected beam in nearly back reflection geometry. Finally, the fringes were recorded by a CCD camera and stored in form of a motion picture. The fringes reported here are the stand-still photographs of the motion picture taken from the IBM computer using multimedia mode.

2.2. Experimental set-up for the Raman and PL spectroscopy

The PL and Raman spectra were recorded by employing a spectroscopic system which consisted of a RAMANOR double monochromator (HG 2S), a HAMAMATSU (R943-2) photomultiplier tube, an amplifier-discriminator assembly, a photon counter, a computer and an argon-ion laser (COHERENT, INNOVA 90-5) light source. The double monochromator included a holographic grating blazed for 5000 Å and was designed to produce a net dispersion of 2.5 Å/mm. The double monochromator was calibrated using a low pressure Cd-Hg lamp as well as by recording the known plasma lines from the discharge in the argon-ion plasma tube. The instrumental line width obtained by using a slit width of 100 lm was estimated to be better than 0.5 cm\(^{-1}\) (0.06 meV). The resolution of the spectrometer was also checked by recording the fine structure of the \(\text{CCl}_4\) line nearly at 459 cm\(^{-1}\) and the resolution was estimated to be \(\sim 0.5 \text{ cm}^{-1}\) for a slit width of 100 lm. The samples were excited by the 5145 Å line of a cw argon-ion laser beam. Raman and PL spectra were recorded with a slit width of 100 lm for the spectrometer mentioned above. In order to avoid thermal heating, the power of laser light on the sample surface was limited to 30 mW on a circular spot with a diameter of 100 lm.

3. Experimental results and discussion

3.1. Spatial confinement

3.1.1. Estimation of size of nanocrystallites by Raman spectroscopy

Fig. 1 displays the Raman spectra recorded with 30 mW for laser-etched Si substrates as a function of etching times for a fixed laser etching power. Fig. 1(a) shows the Raman spectrum of unetched Si substrate, included for comparison. This spectrum displays the usual optical phonon mode having a peak at 520 cm\(^{-1}\). For etching time of 10 min, the Raman peak position remains at 520 cm\(^{-1}\) and the line-shape becomes asymmetric with full-width at half maximum (FWHM) (4.5 cm\(^{-1}\)) as shown in Fig. 1(b). On increasing etching time to 30 min, the asymmetric broadening of the optical mode increases and optical-phonon mode shifts to 519 cm\(^{-1}\), as shown in Fig. 1(c). Furthermore, on increasing etching time more than 30
min, the peak position and asymmetry in broadening of optical mode remain the same.

It is well known [19-22] that the phonon confinement effect causes phonon softening of the Raman optic-mode in nanocrystallites. In our previous work [23,24] on LIE, the size distribution of nanocrystallites was calculated from the Raman spectra using a phonon confinement model (PCM) developed by Richter et al. [21] and modified by us for two-dimensional quantum confinement since the scanning electron microscopic images revealed column-like structures. In addition, a simple Gaussian distribution of size of nanocrystallites was assumed in this model to calculate the line-shape of Raman spectra. Therefore, the convoluted phonon Raman line-shape for a Gaussian distribution function of sizes is given by

\[ f' (\omega) \propto \int_{L_1}^{L_2} N dL \rho dL \times \int_{0}^{1} \exp \left( \frac{-q^2 L_2^2}{4\sigma^2} \right) \frac{1}{(\omega - \omega(q))^2 + \left( \frac{L_1}{2} \right)^2} d^2 q. \]  

(1)

Here \( q \) is expressed in the units of \( 2\pi/a \), where \( a \) \((-5.43 \text{ Å})\) is the lattice constant of Si. The \( L \) is the size of the nanocrystallites and \( C \) is the line width of the LO phonon in crystalline Si. The \( x_0 q \rho \) is the phonon dispersion of the optical-phonon of crystalline Si. The \( N(L) \exp[-(L-L_0)/\sigma^2] \) is the Gaussian distribution function of nanocrystallite sizes. The \( L_0 \) is the mean nanocrystallite size. The \( L_1 \) and \( L_2 \) are the minimum and maximum confinement dimensions of the nanocrystallites, respectively. The \( \sigma \) is the standard deviation of the Gaussian distribution. The Raman line position is mainly determined by \( L_0 \). Using the two-dimensional PCM, we are able to fit the experimental Raman data in Fig. 1. The parameters used in our calculations are given in Table 1. For etching time of 10 min, choosing \( L_0 = 8 \text{ nm}, L_1 = 10 \text{ nm}, L_2 = 15 \text{ nm} \) and \( r = 2 \text{ nm} \) provide a good fit to the observed Raman line-shape. For etching time of 30 min, \( L_0 = 5 \text{ nm}, L_1 = 3 \text{ nm}, L_2 = 8 \text{ nm} \) and \( <7 = 3 \text{ nm} \) and asymmetry ratio indicate that there is a preponderance of small nanocrystallites of sizes less than 8 nm.

It is found that the Raman intensity of optical phonon mode increases noticeably with etching time as shown in Fig. 1. In our result the Raman spectrum for etching time of 10 min in Fig. 1(b) shows the increase in Raman intensity, which indicates the onset of nonlinearity with the decrease in size of nanocrystallites. For etching time of 30 min, the Raman intensity of optical phonon-mode increases roughly threefold with significant change in the Raman line-shape in Fig. 1(c). Fig. 2 displays the Raman scattering efficiencies (ratio of Raman intensity to probe intensity) for two probing laser intensities on the sample having size distribution of 3-8 nm and mean size of 5 nm. As the probing intensity is increased from 6 to 30 mW for a focused spot diameter of 100 lm, in Fig. 2, there is a considerable enhancement of the Raman scattering efficiency by a factor of 2. A significant spectral narrowing is also observed from 12 cm\(^{-1}\) to 9.5 cm\(^{-1}\) at the FWHM. It is well known [25] that the scattered Raman intensity of a nonlinear medium (such as liquid crystal) increases nonlinearly with increase of intensity. The nonlinear increase in refractive index causes self-focusing of the probing laser beam. It enhances the number of

<table>
<thead>
<tr>
<th>Excitation photon energy (eV)</th>
<th>Etching time (min)</th>
<th>Experimentally measured</th>
<th>Theoretically calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Peak position (cm(^{-1}))</td>
<td>Asymmetry ratio ( r/j_b )</td>
</tr>
<tr>
<td>2.41</td>
<td>10</td>
<td>520</td>
<td>1.05</td>
</tr>
<tr>
<td>2.41</td>
<td>30</td>
<td>519</td>
<td>1.75</td>
</tr>
</tbody>
</table>
scattered photons per unit solid angle per unit frequency for a given laser power density. These are clear evidences of stimulated Raman effect in the nanocrystallites of Si as shown in Figs. 1 and 2. On the whole, Raman data reveal that the nonlinearity of refractive index enhances with the decreasing size of nanocrystallites.

3.1.2. Effect of size of nanocrystallites on photoluminescence and size estimation

Photoluminescence spectroscopy is the most often applied technique in the investigation of spatial confinement of electrons. For Si nanocrystals in the few nanometer range, observation of a broad band of PL in the visible region has been frequently reported [26-29]. Fig. 3 displays the PL spectrum of PS sample prepared by LIE when excited with photon energy of 2.41 eV. For etching time of 30 min, the PL peak position is observed at 1.84 eV with FWHM 250 meV. For etching time of 10 min, we do not observe any PL spectrum.

Quantum confinement model predicts that the radiative recombination of charge carriers should appear in the visible region for small nanocrystallites. In our earlier studies [23,24], it has been reported that bandgap or peak position of PL increases with the reduction of size of the nanocrystallites. In order to calculate the size of nanocrystallites present in the LIE sample, we have used Eq. (3) of [23]. For etching time of 30 min and excitation energy 2.41 eV, our calculations indicate that the sizes of nanocrystallites vary between 3 and 8 nm, and the mean nanocrystallite size is 5 nm. This is in agreement with Raman data, which reveal the existence of nonlinearity for the nanocrystallites of sizes less than 8 nm. No PL spectrum is observed for the sample etched for 10 min and the Raman data in this case indicate the presence of nanocrystallites of sizes greater than 8 nm as shown in Table 1. It is emphasized here that the quantum confinement of electron leads to increase in the band gap. The PL can only be observed for nanocrystallites, which have dimension less than 8 nm.

3.2. Optical fringes from nanocrystallites of silicon

Fig. 4 shows the intensity distribution of the reflected beam on the screen during etching. For the first 30 min of etching, a bright, reflected spot
without any fringe pattern is observed on the screen. Fig. 4(a) shows the intensity distribution of the reflected spot after 10 min of etching. On further etching for more than 30 min, fringes appear and the optical pattern is shown in Fig. 4(b). As etching proceeds, a fringe pattern is observed moving around the reflected spot on the screen and then disappears. After 30-45 s, the pattern again reappears and then disappears. This process gets repeated after every few seconds. Our Raman data have revealed gradual decrease of size of nanocrystallites as etching of Si substrate proceeds, as discussed in Section 3.1.1. It is observed that optical fringes are seen on the screen when etching time is more than 30 min and the nanocrystallite size calculated using Eq. (1) are less than 8 nm. It seems that the appearance and disappearance of fringes are related with the size of the nanocrystallites. Fringes will appear when the size of nanocrystallites is less than 8 nm and it will remain there unless the size is decreased to 3 nm. Fringes disappear when cluster of Si atoms (i.e., nanoparticles) collapses (i.e., short-range order) for size less than 3 nm. This is in accordance with the results of Iqbal et al. [30] and Shukla et al. [31], where they have shown that the instability of nanocrystallites of size less than 3 nm is due to the increase of free energy and lattice expansion. After a few seconds, appearance of fringes is observed again as a new layer of Si containing the nanocrystallites appear with etching. Nanocrystallites of larger size are formed in another layer and the size gradually decreases with etching time. We have observed that the optical fringes appear and then disappear faster for higher HF concentration and higher incident power densities.

The nonlinear characteristics of PS have been reported in literatures [6-10]. The optical fringe pattern formation in our experiment is mathematically analyzed as follows: when an intense laser beam passes through an optical material or nanocrystallites, the refractive index of the material can be altered by the intensity of the laser beam having a Gaussian profile. As the nanocrystallites of Si interact with a spatially varying laser beam, several nonlinear processes, e.g., self-focusing and self-phase modulation may occur. The change in the refractive index gives rise to a velocity distribution of the laser beam in the transverse plane. Thus, the beam propagates by varied optical paths and hence there occurs spatial phase variation. This leads to a visible optical fringe pattern in the transverse plane and the phenomenon is known to be the spatial analog of self-phase modulation in frequency domain [13]. A model of self-diffraction of propagation of light, in which self-phase modulation arising from nonlinear refractive index induced by the intensity of laser beam and the size effect of the nanocrystallites present in the sample, is utilized here. The far-field diffraction intensity distribution of the gaussian beam is given by [18]
\[ I(x) = I_0 \left( \frac{2\pi}{\lambda Z} \right)^2 \int_0^z r \, dr \, J_0 \left( \frac{k r x}{2Z} \right) \times \exp \left( \frac{r^2}{2W^2} \right) \left( -2W^2/T - \phi(r) \right)^2, \]  

where \( x \) is the distance from the center of the far field pattern to the observation point, \( I_0 \) the on-axis intensity of the laser beam having a Gaussian profile, \( k \) the wavelength of incident laser beam, \( Z \) the distance from the sample to the observation point, \( J_0(\cdot) \) the zero-order Bessel function of the first kind and \( k \) is the wave number in free space. Here, we have limited the integration up to the beam waist (\( w \)) beyond which no nanocrystallites are irradiated that can contribute to the self-phase modulation process. The phase factor, \( \phi(r) \), consists of the Gaussian phase depending on the wave front curvature and the phase shift of the beam reflected from the medium and it is given by

\[ \phi(r) = \phi_L(r) + \phi_{NL}(r), \]  

where \( \phi_L(r) \) is the intensity independent linear phase shift, given as

\[ \phi_L(r) = k \left( \frac{r^2}{2Z^2} \right) \simeq k \left( \frac{r^2}{2R^2} \right), \]  

where \( R \) is the radius of wave front curvature of the incident beam and can be taken as 1 at the focal point of the lens. The intensity-dependent nonlinear phase difference is

\[ \phi_{NL}(r) = kS A n(r), \]  

where \( k \) is the wave vector and \( <5 \approx 5 \) \( \text{nm} \) is the penetration depth of the incident laser light in the medium containing nanocrystallites of Si [32]. The \( Dn\delta rP \) is the distribution of change in the refractive index of the PS medium across the propagation of the beam. Light-induced electric dipoles, which are oscillating with frequency of light, are formed in the nanocrystallites of Si. It is expected that the oscillator strength of these dipoles increase with intensity of light \( I\delta rP \) (i.e., alignment of the dipoles along its electric field and increase in the dipole moment). It is well known that the dielectric constant as well as the refractive index arise from the electronic polarizability and can be coupled to optical frequency \( x \). Observation of optical fringes for nanocrystallites of size less than 8 nm invokes the increase of refractive index with the reduction of size of nanocrystallites. It seems that the intensity of the local electric field due to light-induced bound charges on the surface of nanocrystallites (polarization in atoms) increases rapidly as the size reduces below 8 nm. It further enhances the electronic polarizability inside the nanocrystallites resulting rapid nonlinear rise of refractive index. Therefore, the increase of refractive index \( Dn\delta rP \) across the beam inside the dielectric-like medium containing nanocrystallites is proposed as

\[ A^{\Pi W} = \left[ f \left( \frac{f}{L} \right) N(L) \, dL \right] I(r), \]  

where \( f \) is the coupling constant of light with the medium containing nanocrystallites and the integration takes care of the size distribution of the nanocrystallites. The \( N0LP \) is the Gaussian distribution of nanocrystallites. \( L1 \) and \( L2 \) are the minimum and maximum sizes of the nanocrystallites present in the Gaussian distribution and are taken from the Raman data of Table 1. When the sizes of nanocrystallites are large, we do not observe any fringe pattern. To confirm it, the values of \( L1 \) and \( L2 \) from Raman data in Table 1 for etching time of 10 min are used in Eq. (2) and theoretical calculation shows only a reflected spot without any fringes in Fig. 5(a). For etching time of 30 min, the values of \( L1 \) and \( L2 \) taken from Table 1 and theoretical simulation of Eq. (2) show multiple diffraction fringes in Fig. 5(b). The parameters used in Eq. (2) are given in Table 2. Using Eq. (2) the theoretically calculated curve seems to describe the experimental data fairly well. Multiple diffraction patterns will be observed for the sizes less than 8 nm. These results clearly indicate that the quantum confinement effect enhances the nonlinearity of the refractive index rapidly, for the mean crystallite sizes less than 8 nm. Nanocrystallites of Si constitute a dielectric like medium where nonlinear phenomena like self-focusing occurs. Therefore, our experiment shows that the nonlinearity of refractive index is related with the size of nanocrystallites. The theoretical plot of Fig. 5(b) is in agreement with the optical fringes of Fig. 4(b) observed during laser-induced etching of Si. The central fringe is brighter than the neighbouring ones because of reflection.
Fig. 5. The theoretically calculated plot of fringe pattern using Eq. (2) for two different size distributions taken from Table 1: (a) for nanocrystallites with sizes \( L_0 = 8 \) nm, \( L_1 = 10 \) nm and \( L_2 = 15 \) nm, (b) for nanocrystallites with sizes \( L_0 = 5 \) nm, \( L_1 = 3 \) nm and \( L_2 = 8 \) nm.

Table 2

<table>
<thead>
<tr>
<th>Parameters used in the calculation of Eqs. (2) and (6)</th>
<th>X (Å)</th>
<th>w (μm)</th>
<th>Z (m)</th>
<th>f (m^2/W)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5145</td>
<td>50</td>
<td>15</td>
<td>10^-7</td>
</tr>
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\( X \) is the laser wavelength used, \( w \) is the beam waist of focused light and \( f \) is the coupling constant.

from the interface of PS and bulk Si. The intensities of the side fringes are almost close to that of central fringe and do not decrease rapidly like a typical diffraction pattern of circular aperture. Fig. 6 shows the experimental results of intensity dependence of the optical fringe patterns. As the intensity of the laser beam is increased, the number of fringes gradually increases, as predicted by Eq. (6). Thus, it is concluded that nonlinearity exists in PS medium and the pattern formation can be explained by self-phase modulation process.

4. Conclusions

The nonlinear phenomenon appears when the size of nanocrystallites is decreased below 8 nm. Experimental results of the Raman scattering, photoluminescence and optical fringes are in excellent agreement with the theoretical results of self-phase modulation of laser beam. The intensity of local electric field due to light-induced bound charges on the surface of nanocrystallites increases appreciably with reduction in its size. It enhances
the polarizability, which is coupled to the optical frequency of laser beam. This leads to possible rapid enhancement of refractive index of the nanocrystallites. Evidence of stimulated Raman scattering and observation self-phase-modulated diffraction fringes reveal that self-focusing of laser beam is taking place in the dielectric-like medium of nanocrystallites. Nonlinearity increases as the size of the nanocrystallite is decreased below 8 nm. PL spectrum has also revealed the electronic states of confined electrons within the nanocrystallites. It also reveals almost the same size of nanocrystallites determined by the PL and Raman data, for which self-phase-modulated optical fringes are observed. However, the Raman data show the onset of stimulated Raman scattering for sample etched for 10 min when the size of the nanocrystallites lies between 10 and 15 nm. On the whole, nonlinearity exists in PS medium and formation of optical fringes due to nanocrystallites of Si is a nonlinear phenomenon.

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References