# Influence of structural disorder on Raman scattering in amorphous porous silicon

N. N. Ovsyuk*

*Institute of Mineralogy and Petrology, Russian Academy of Sciences, Novosibirsk 630090, Russia*

V. N. Novikov

*Institute of Automation and Electrometry, Russian Academy of Sciences, Novosibirsk 630090, Russia*
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The Raman scattering spectra of amorphous porous silicon are investigated. It is found that the so-called boson peak in the acoustical part of the Raman spectra is more sensitive to the degree of structural disorder than the optical mode, which is normally used to determine the latter. This can be explained by the fact that the coupling coefficient of light to acoustical phonons has an additional factor in comparison with that of optical phonons: the square of inverse correlation length of vibrational excitations. This means that the Raman scattering intensity on acoustical phonons has an additional dependence on the degree of disorder in comparison with the scattering on optical phonons. [S0163-1829(98)13119-3]

The intensity of Raman scattering is sensitive to the degree of the structural disorder in solids, so this method can be used to measure relative fractions of the amorphous and the crystalline phases. However, there are problems in accurate estimation of such a fraction using experimental Raman spectra. For example, typically the ratio of the amorphous to the crystalline phase in thin silicon films is determined as a ratio of the integral area of a broad amorphouslike peak to a narrow crystalline peak of the transverse optical (TO) phonon.[1,2] We would like to point out that such a method is not quite accurate, since annealing of amorphous silicon microparticles and films differently influences the Raman spectra in the optical region. For example, in Ref. 3 it was shown that there were no sufficient changes of Raman spectra during annealing of small silicon particles at 800 °C. The spectra have demonstrated only a single amorphouslike TO peak while the films according to the Raman spectra have become totally crystalline. In addition, the Raman scattering on the optical phonon of microparticles ($<$10 nm) has always a very large contribution of the amorphous phase, while the high resolution electron microscopy indicates a crystalline structure.[4–6] In the present paper we show that the low-frequency Raman scattering on acoustical phonons is more sensitive to the degree of structural disorder than that on optical phonons, so the area of the acoustic peak corresponds more precisely to the amorphous phase volume.

In order to have more pronounced changes of the Raman scattering spectra in amorphous solids in increasing the degree of order one needs to have a sample of the size compared to the vibration correlation length. In this case the changes of the amorphous phase can be observed in the spectra more clearly than in large bulk samples since a larger volume quantity of the ordered phase will take part in the light scattering. From this point of view it is convenient to use either amorphous microparticles or microporous materials. We have selected the amorphous porous silicon since it yields intensive visible photoluminescence,[7,8] i.e., crystallinity is not a necessary condition for observation of the intensive visible photoluminescence under room temperature. In addition, using the micro-Raman spectroscopy it was found[9]

that areas of porous silicon, which produce the visible luminescence, besides the crystalline phase always contain the amorphous phase as well. This means that the porous silicon has always an amorphous component. These observations initiate us to look for more accurate determination of the ratio of the volumes of the amorphous to the crystalline phase in microstructures.

The porous silicon layers were formed by anodizing of silicon substrates of $p^+$-type with (100) orientation and resistivity 0.006 $\Omega$ cm in hydrofluoric acid solution (42.4% HF:$H_2$O:$C_3H_7$OH in proportion 2:1:2) at current density 100 mA cm$^{-2}$. This leads to formation of a silicon layer with 70% porosity and 2 $\mu$m thickness. To obtain an amorphous layer, irradiation by $^{10}$B$^+$ ions with the energy 100 keV was performed. For such ions the amorphization dose of the porous silicon was $5 \times 10^{15}$ cm$^{-2}$; this is one order of magnitude less than the same parameter for the ordinary silicon. The Raman spectra were recorded in 90° geometry of scattering using a double monochromator DFS-52 with the spectral slit of 2 cm$^{-1}$ and the light wavelength $\lambda = 488$ nm in doubly parallel polarization when both the incident and the scattered light beams were polarized in the scattering plane.

In Fig. 1 the Raman spectrum of the amorphous porous silicon is shown. It consists of the amorphouslike TO peak at 480 cm$^{-1}$ and the broad peak at 150 cm$^{-1}$. The latter peak is absent in the Raman spectrum of the crystalline silicon because the translation invariance leads to the selection rules, which forbid the light scattering by phonons in this spectral region. Traditionally such a peak in disordered materials is called the boson peak.[10] In glasses its frequency $\omega_b$ is typically equal to 1/5–1/7 of the Debye frequency; its nature is connected to the structure correlations on nanometer scale and the frequency—to the respective correlation length $l$, $\omega_b \sim v/l$ ($v$ is the sound velocity). The boson peak reflects the excess (in comparison with the sound waves) vibration density of states in the low-frequency region 20–100 cm$^{-1}$, which arises due to such structure correlations. In glasses the small value of the boson peak frequency in comparison with that of TA and LA modes is due to a comparatively large value of the structural correlation length. In tetragonal amor-
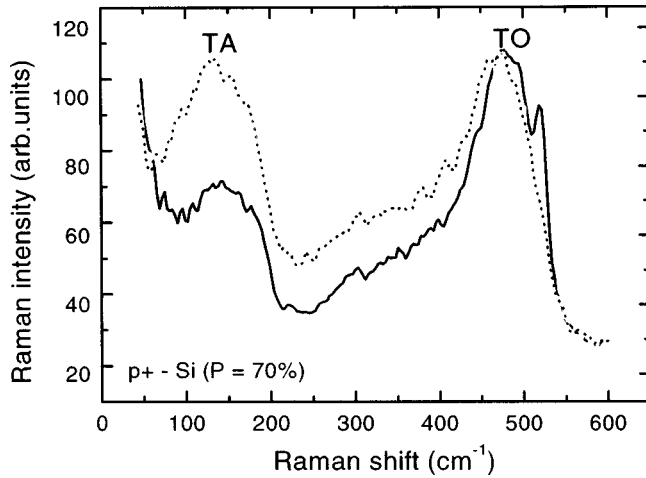
FIG. 1. Change of the Raman spectral shape of amorphous porous silicon after annealing in the nitrogen atmosphere during 30 min at $T=500$ °C. The dashed and the solid lines correspond to the spectra before and after annealing.

phous semiconductors the structure correlation length is less than in glasses and is comparable with the characteristic interatomic distance,[11] so the boson peak should be closer to the TA mode than in glasses. In particular, in amorphous silicon it is difficult to discriminate the boson peak and the transverse acoustic (TA) mode (see, e.g., Ref. 12); however, the discussion below is also applicable to the case of glasses when the boson peak is different from the TA mode. Let us note that a broad underlying spectral feature in $a$-Si:H with a maximum at 217 cm$^{-1}$ (i.e., higher than the frequency of the TA mode, 150 cm$^{-1}$) was found in Ref. 13 and interpreted by the authors as evidence that the boson peak does not correspond to the standard definition of the latter used above. Since the boson peak is absent in crystals its intensity, as well as the intensity of the amorphouslike TO peak, can also be a measure of the degree of disorder in solids.

After transformation of the porous silicon to the amorphous state we began to perform the stepwise isochronous annealing in the nitrogen atmosphere. The purpose was to investigate the influence of the decrease of the degree of disorder on the Raman spectra in the optical and the acoustical regions. When the temperature of annealing reached 500 °C we noticed the beginning of crystallization, which resulted in a small peak in the Raman spectrum at $\omega = 520$ cm$^{-1}$. This frequency corresponds to that of the TO phonon in crystalline silicon. Just at that temperature the boson peak amplitude abruptly decreased by a factor of 2 (Fig. 1). It is well known that the size of the critical nucleus in the bulk silicon is approximately 3–4 nm,[14] and the average size of the structure elements in the porous silicon with the porosity 70% (which is our case) is roughly equal to 4–5 nm.[15] Thus, the amorphous phase volume should sharply decrease at the moment when crystalline nuclei arise. However, in Fig. 1 one can see that a sharp change has occurred only in the boson peak amplitude, but no change has occurred in the amplitude and width of the amorphouslike TO peak, although it is known that the full width at half maximum (FWHM) of the latter peak after annealing should decrease down to approximately 30 cm$^{-1}$.[16] In our case the FWHM

of the TO peak is equal to 50 cm$^{-1}$, which indicates a high structure disorder in the region of layers that are close to the surface; also, the appearance of the sharp peak at 520 cm$^{-1}$ may partly mask possible shrinking if the TO peak.

It is known that the tendency to localization is stronger for optical vibrations than for the acoustical ones (see, e.g., Ref. 17), so a change in the degree of the structural disorder may result in different changes of the Raman scattering intensity by acoustical and optical vibrations due to a different degree of the violation of the wave vector selection rules. In the amorphous phase owing to the lack of translation invariance and as a consequence of the breakdown of the wave vector conservation rule, the total density of the vibrational state is observed in the Raman scattering spectra[18]:

$$I(\omega)=C(\omega)g(\omega)[n(\omega)+1]/\omega, \qquad (1)$$

where $C(\omega)$ is the coupling coefficient of light with vibrations; $g(\omega)$ is the density of vibrational states and $n(\omega)$ is the Bose factor. Let us consider first the case of the light scattering by the vibrations that form the boson peak. Since the vibrational density of states does not sufficiently change during the annealing[19] the observed decrease of the boson peak amplitude can be explained only by the decrease of the magnitude of the coupling coefficient of light with acoustic vibrations $C_{ac}(\omega)$ owing to the change of the degree of violation of the wave vector selection rule. We use the vibration correlation length $l_\omega$, which characterizes the size of the volume occupied by a vibrational eigenmode as a parameter that is sensitive to the degree of disorder and determines the magnitude of $C_{ac}(\omega)$.

The inelastic light scattering intensity is determined by the Fourier transform of the correlation function of the dielectric susceptibility tensor fluctuations $\delta\chi_{\alpha\beta}(\mathbf{r},t)$,[10,20]

$$I_{\alpha\beta\gamma\delta}(q,\omega)\propto \int dt d\mathbf{r}_1 d\mathbf{r}_2 e^{i\omega t - i\mathbf{q}(\mathbf{r}_1-\mathbf{r}_2)}$$
$$\times\langle \delta\chi_{\alpha\beta}^+(\mathbf{r}_1,t)\delta\chi_{\gamma\delta}(\mathbf{r}_2,0)\rangle, \qquad (2)$$

where $\mathbf{q}=\mathbf{q}_1-\mathbf{q}_2$ and $\mathbf{q}_1$ and $\mathbf{q}_2$ are the initial and the final photon wave vectors. Variations of the tensor $\chi_{\alpha\beta}(\mathbf{r},t)$ by acoustical phonons are proportional to the deformation tensor $\delta\chi_{\alpha\beta}\propto P_{\alpha\beta\gamma\delta}(\partial u_\gamma/\partial r_\delta + \partial u_\delta/\partial r_\gamma)$, where $P_{\alpha\beta\gamma\delta}$ is the tensor of elasto-optic constants and $u_\alpha(\mathbf{r},t)$ are the atomic displacements due to vibrations. Since the boson peak vibrations are in the acoustical region and have a typical length $l\gtrsim 1$ nm (Ref. 20) one can assume for them the same type of coupling with light via the deformation tensor. Taking into account the fact that $ql\ll 1$, where $q=2\pi/\lambda \sim 10^{-2}$ nm is the scattering wave vector ($\lambda\sim 500$ nm) one can set the exponential in integral (2) equal to one. Then for the Raman scattering intensity we have

$$I_{ac}(\omega)\propto \int d\mathbf{r}\langle\nabla u_\omega^+(\mathbf{r})\nabla u_\omega(0)\rangle g_{ac}(\omega) \qquad (3)$$

(the tensor indices are omitted for simplicity since here we are not interested in the polarization dependence of scattering). In Eq. (3) $g_{ac}(\omega)$ is the vibrational density of states in the region of the boson peak, and $u_\omega(\mathbf{r})$ is the amplitude of vibrations with frequency $\omega$. The brackets mean the spatial and the statistical averaging. The result of averaging depends

on the correlation of vibrational displacements at different points of a sample. It is convenient to express the vibration displacement gradients correlator with help of the normalized correlation function $F_\omega(r)$:

$$\langle \nabla u_\omega^+(\mathbf{r}) \nabla u_\omega(0) \rangle = F_\omega^{ac}(r) \langle |\nabla u_\omega(0)|^2 \rangle. \qquad (4)$$

$F_\omega^{ac}(r)$ satisfies the normalization condition $F_\omega^{ac}(r) \approx 1$ at $r \rightarrow a$, where $a$ is a characteristic interatomic distance. The exact form of the vibration correlation function in the spectral region of the boson peak in amorphous solids is unknown, since the nature of these vibrations is not well understood. It is commonly believed, however, that the characteristic size of these vibrations is of the order of a nanometer (see, e.g., Refs. 10,20–22). Averaging over an ensemble of such vibrations localized in spatial regions of an amorphous solid with different structural configurations leads to a correlation function that decreases spatially with a characteristic correlation length $l_\omega$ of the order of a nanometer. Inside the localization region a complementary decay of correlations is possible due to a specific geometry of the vibrational eigenmodes that are expected to have the effective spatial dimensionality less than 3 (Refs. 23 and 24) or to have the fractal properties.[25] This results in an additional factor $r^{-\alpha}$ in the correlation function. For example, correlations in the fractal structures are described by the function,[25,26]

$$F(r) \propto r^{d_f - 3} \exp(-r/\xi), \qquad (5)$$

where $d_f$ is the fractal dimensionality, which characterizes the internal geometry of the object and $\xi$ is a correlation length. We can use a more general form of the correlation function

$$F_\omega^{ac}(r) = (a/r)^\alpha f(r/l_{\omega ac}), \qquad (6)$$

where $l_{\omega ac}$ is a correlation length of the boson peak vibrations, $f(r/l_{\omega ac})$ is a decreasing function that reflects the spatial decay of correlations due to localization. As will be shown below, an exact form of the function $f(r/l_{\omega ac})$ is of no importance for the present paper; however, one can suggest that it corresponds to the exponential, $\exp(-r/l)$, or the Gaussian, $\exp(-r^2/l^2)$, decay. For example, in the case of the plane acoustic wave with the mean free path $l$ in an amorphous solid the correlation function (6) is equal to $\exp(i\mathbf{q}\cdot\mathbf{r} - r/l)(1 + r/l + r^2/3l^2)$. The oscillation factor is sure to disappear in the case of the boson peak vibrations owing to large variations in the form of the localized by disorder vibrational eigenfunctions and a broad band of the wave vectors needed for the localized mode formation.

Using a rough estimate $\nabla u_\omega \sim u_\omega/l_\omega$ and taking into account the fact that $\langle |u_\omega(0)|^2 \rangle \rightarrow [n(\omega)+1]/2\rho\omega$ ($\rho$ is the mass density) for the Stokes component of the Raman scattering we come to $\langle |\nabla u_\omega(0)|^2 \rangle \propto l_{\omega ac}^{-2}[n(\omega)+1]/\omega$. As a result, Eq. (4) looks like

$$\langle \nabla u_\omega^+(\mathbf{r}) \nabla u_\omega(0) \rangle \propto F_\omega^{ac}(r) l_{\omega ac}^{-2}[n(\omega)+1]/\omega. \qquad (7)$$

Substituting Eq. (7) in Eq. (3) and comparing the obtained expression with Eq. (1) we have

$$C_{ac}(\omega) \propto l_{\omega ac}^{-2} \int d\mathbf{r} F_\omega^{ac}(r). \qquad (8)$$

As opposed to Eq. (3), the Raman scattering intensity for optical vibrations is directly determined by the correlation of the atomic vibration displacements:

$$I_{opt}(\omega) \propto \int d\mathbf{r} \langle u_\omega^+(\mathbf{r}) u_\omega(0) \rangle g_{opt}(\omega). \qquad (9)$$

In this case there is no need to require that the Hamiltonian interaction of light with vibrations should be expressed by displacement derivatives as in the acoustical case, since the center of weight of an elementary cell does not change for optical vibrations. The optical vibration correlator will be characterized by the respective correlation function:

$$\langle u_\omega^+(\mathbf{r}) u_\omega(0) \rangle \propto F_\omega^{opt}(r)[n(\omega)+1]/\omega. \qquad (10)$$

From Eqs.(9) and (10) obtain

$$C_{opt}(\omega) \propto \int d\mathbf{r} F_\omega^{opt}(r). \qquad (11)$$

The comparison of Eqs. (8) and (11) shows that the coupling coefficient of light with vibrations for optical phonons has no additional length squared in the denominator, which arises owing to gradients of displacements in the case of acoustical phonons. Thus, when the correlation length increases during the annealing, the acoustical part of the spectrum decreases faster than the optical one, i.e., the former is more sensitive to the degree of disorder than the latter.

Let us return to the explanation of changes in the Raman spectrum during the annealing of amorphous porous silicon (Fig. 1). To this end we find the dependence of $C_{ac}(\omega)$ on the correlation length $l_{\omega ac}$. Using Eq. (6) it is easy to show that

$$\int d\mathbf{r} F_\omega^{ac}(r) = 4\pi b a^\alpha l_{\omega ac}^{3-\alpha}, \qquad (12)$$

where the dimensionless constant $b$ is of order 1; it is determined by the specific form of the function $f(r/l_{\omega ac})$:

$$b = \int_0^\infty x^{2-\alpha} f(x) dx. \qquad (13)$$

Then, from Eq. (8) it follows that $C_{ac}(\omega) \propto l_{\omega ac}^{1-\alpha}$. Since the vibrations in the boson peak region fulfill the Ioffe-Regel criterion,[21,27] $l_{\omega ac} \sim \lambda \propto \omega^{-1}$ where $\lambda$ is the wavelength of the acoustical phonon and the dependence of $C_{ac}(\omega)$ on the frequency is only via $l_{\omega ac}$, we have $C_{ac}(\omega) \propto \omega^{\alpha-1}$. The frequency dependence of $C_{ac}(\omega)$ in the boson peak region in amorphous solids is known from the comparison of the Raman spectra with the neutron ones[22,28] and from specific heat data.[29] Typically, $C(\omega) \propto \omega$. This corresponds to $\alpha = 2$ in the correlation function of the boson peak vibrations and $C_{ac}(\omega) \propto l_{\omega ac}^{-1}$. If inside an illuminated region the crystalline nuclei of diameter $D$ appear, then the free path length of the acoustic vibration should be equal to the diameter, $l_{\omega ac} \sim D$. This leads to a sharp change of the averaged over the sample inverse correlation length $l_{\omega ac}^{-1}$ since the correlation length for the amorphous silicon is not higher than 1.2–1.5 nm,[11] while the size of a critical nuclei is equal to 3–4 nm, so the Raman

intensity in the region of the boson peak sharply decreases approximately by a factor of 2.

In conclusion, to determine the volume fraction of the amorphous component in solids which contain the mixed phases by the Raman scattering it is more convenient to use the boson peak than the amorphouslike optical mode. This is explained by the higher sensitivity of the boson peak to the degree of the structural disorder on the nanometer scale.

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*Electronic address: ovsyuk@uiggm.nsc.ru

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