Influence of the degree of disorder of amorphous solids on the intensity of light scattering by acoustic phonons

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It is observed experimentally that in the low-frequency Raman light scattering spectrum of amorphous porous silicon the boson peak situated in the acoustic range is more sensitive to the structural order than the optical mode presently used to determine the degree of disorder. It is shown that this is because, unlike the coefficient of interaction with optical vibrations, the coefficient of interaction between light and acoustic vibrations contains an additional factor, the square of the reciprocal correlation length of the vibrational excitations, i.e., the intensity of light scattering by acoustic phonons has an additional dependence on the degree of disorder. © *1998 American Institute of Physics*. [S1063-7761(98)02107-6]

1. INTRODUCTION

Problems are currently being encountered in determining the ratio of the volumes of the amorphous and crystalline phases in solids using Raman scattering, which is highly sensitive to structural order. In the literature the ratio of the volumes of the amorphous and crystalline phases in thin silicon films has been determined using the Raman spectra from the ratio of the integrated areas below the broad amorphouslike and narrow crystalline peaks of the transverse optical (TO) phonon.^{1,2} However, this method is inaccurate because the annealing of amorphous silicon microparticles and films has a different influence on the Raman spectra in the optical range. In Ref. 3, for example, when small silicon particles were annealed to 800 °C, the Raman spectra revealed no appreciable changes and continued to show only one amorphous-like TO peak although the films, judging by the spectra, had become completely crystalline. In addition, the spectra of Raman scattering by optical phonons obtained for microparticles (<10 nm) also always contain a very large contribution of the amorphous component, although highresolution electron microscopy suggests that their structure is crystalline.⁴⁻⁶ We observed that light scattering by acoustic phonons is more sensitive to structural order than scattering in the optical range and thus, the area below the acoustic peak corresponds more accurately to the volume of the amorphous phase.

In order to ensure that the changes in the Raman spectra of amorphous solids are more noticeable as the degree of order increases, the sample must have dimensions comparable with the correlation length of the vibrational excitations. In this case, the changes in the volume of the amorphous phase will be more abrupt than in unbounded samples since a larger volume of the ordered phase will participate in the light scattering. From this point of view, it is convenient to use either amorphous microparticles or microporous media. We chose amorphous microporous silicon. This material has been attracting interest following the observation of photoluminescence similar to the luminescence from crystalline porous silicon,^{7,8} i.e., it was found that crystallinity is not a necessary condition for the observation of high-intensity visible luminescence at room temperature for microporous silicon. In another study of Raman scattering,⁹ observations with a microscope attachment revealed that the regions of porous silicon contributing to the visible luminescence necessarily always contain some amorphous phase, in addition to the crystalline, i.e., the amorphous phase is evidently always present in microporous silicon. These facts provided an additional stimulus for a more accurate determination of the ratio of the volumes of the amorphous and crystalline phases in microstructures.

2. SAMPLES AND EXPERIMENTAL SETUP

Layers of porous silicon were obtained by anodizing (100)-oriented p^+ -type silicon substrates with a resistivity of 0.006 $\Omega \cdot \text{cm}$ in a hydrofluoric acid solution (42.4% HF:H₂O:C₃H₇OH in the ratio 2:1:2) at a current density of 100 mA/cm². This produced a 2 μ m thick layer of silicon with 70% porosity. The samples were bombarded with 100 keV ¹⁰B⁺ ions to produce an amorphous layer. As a result of this ion implantation, the amorphization dose of the porous silicon was 5×10^{15} cm⁻², which is an order of magnitude lower than the similar value for ordinary silicon. The Raman spectra were recorded in a 90° scattering geometry using a DFS-52 double monochromator with a spectral slit of 2 cm⁻¹ width and λ = 488 nm exciting radiation under conditions of



FIG. 1. Variation of the Raman light scattering spectrum of p^+ -type amorphous porous (70% porosity) silicon as a result of annealing in a nitrogen atmosphere for 30 min at T=500 °C. The dashed and solid curves show the spectra before and after annealing, respectively.

doubly parallel polarization, i.e., when the exciting and scattered light beams were polarized in the scattering plane.

3. RESULTS AND DISCUSSION

It can be seen from Fig. 1 that the Raman spectrum of amorphous porous silicon consists of a broad TO mode at 480 cm^{-1} and a broadened peak at 150 cm^{-1} which is not observed for crystalline silicon. This type of peak in disordered materials is conventionally called a boson peak. In glasses it is usually observed at a frequency approximately 1/5 of the Debye frequency and is attributed to nanometerscale structural correlations, reflecting an excess density of vibrational states in the low-frequency range $(20-80 \text{ cm}^{-1})$ compared with the Debye density. In tetragonal amorphous semiconductors, the correlation length is shorter than in glasses and is comparable with the interatomic distances. In particular, in silicon the boson peak coincides with the transverse acoustic TA mode and the density of vibrations near the boson peak is thus simply the density of the TA vibrations, but the reasoning put forward below will also apply to cases when the boson peak does not coincide with the TA mode. Since the boson peak does not appear in the Raman spectra of crystals, its intensity (like that of the broad TO mode) may also serve as a measure of the amorphousness of the material.

After the porous silicon had been converted to the amorphous state, we commenced isochronous stepwise annealing in a nitrogen atmosphere to study the influence of an increase in the degree of order on the Raman spectra in the optical and acoustic ranges. When the annealing temperature reached 500 °C, crystallization was initiated, this being observed as a very small spike at 520 cm^{-1} , which corresponds to the transverse optical phonon frequency in crystalline silicon, and the amplitude of the boson peak unexpectedly dropped sharply, by approximately half (Fig. 1). It is known that the size of the critical nucleus in bulk silicon is approximately 3-4 nm and the average size of the structural elements of porous silicon with 70% porosity, such as that being studied, is approximately 4-5 nm. Thus, the volume of the amorphous phase should decrease sharply at the instant

when crystal nuclei appear. It can be seen from Fig. 1 that the Raman spectrum only revealed an abrupt change in the amplitude of the boson peak at the instant of nucleation, while the amplitude and half-width of the amorphous-like TO peak remained almost unchanged, although its half-width should be reduced to approximately 30 cm^{-1} as a result of annealing.¹⁰ In our case, the half-width of the TO peak is 50 cm^{-1} , which suggests a high degree of structural disorder in the layers near the interface.

It is well known that stronger localization is observed¹¹ for optical vibrations, and thus when the structural order of an amorphous medium changes, the intensities of the Raman scattering by acoustic and optical vibrations may behave differently as a result of the different degree of violation of the wave vector selection rule. In the amorphous phase, as a result of the absence of translational invariance and the consequent nonconservation of the wave vector, the light scattering spectrum reveals the complete density of the acoustic or optical phonons with a weight proportional to the interaction constant $C(\omega)$ between the light and these vibrations (Ref. 12):

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

where $n(\omega)$ is the Bose factor and $g(\omega)$ is the density of the acoustic or optical vibrational states.

We shall first analyze the case of scattering by acoustic vibrations. Since the density of the acoustic vibrations varies negligibly during annealing,¹³ the observed decrease in the amplitude of the boson peak can only be attributed to a decrease in $C_{\rm ac}(\omega)$ as a result of a change in the degree of violation of the wave vector selection rule. We shall use a method of analyzing the violation of the selection rule which is based on introducing a correlation length characterizing the spatial elongation of the normal vibrational mode and we shall show how $C_{\rm ac}(\omega)$ is related to the structural order.

In general, the Raman light scattering intensity is determined by the fluctuations of the permittivity tensor $\delta \chi_{\alpha\beta}(\mathbf{r})$ (Refs. 14 and 15):

$$I_{\alpha\beta\gamma\delta}(\mathbf{q},\omega) \propto \int dt \, d\mathbf{r}_1 d\mathbf{r}_2 \, \exp(i\omega t - i\mathbf{q} \cdot (\mathbf{r}_1 - \mathbf{r}_2))$$

$$\times \langle \delta \chi^+_{\alpha\beta}(\mathbf{r}_1, t) \, \delta \chi_{\delta\gamma}(\mathbf{r}_2, 0) \rangle, \tag{2}$$

where $\mathbf{q} = \mathbf{q}_1 - \mathbf{q}_2$ is the difference between the initial and final photon momenta. The variations of the tensor $\delta \chi_{\alpha\beta}(\mathbf{r},t)$ under the action of the acoustic phonons are proportional to the deformation tensor $\partial u_{\alpha}/\partial r_{\beta} + \partial u_{\beta}/\partial r_{\alpha}$, where $u_{\alpha}(\mathbf{r},t)$ is the displacement of the atoms induced by the vibrations. Since the vibrations determining the boson peak lie in the acoustic range, it may be assumed that they also interact with light by means of the deformation tensor. Bearing in mind that $q \ll l^{-1}$, where $q \sim 2\pi/\lambda \sim 10^{-2}$ nm is the momentum imparted by the light ($\lambda = 500$ nm) and l is the characteristic length of the vibrations near the boson peak, of the order of a nanometer,¹⁵ we can neglect the term $\mathbf{q} \cdot (\mathbf{r}_1 - \mathbf{r}_2)$ in the exponential function in Eq. (2) since this is much less than unity. For the Raman scattering intensity we then have

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

Here $u_{\omega}(\mathbf{r})$ is the amplitude of the vibrations at frequency ω and the angular brackets denote spatial and statistical averaging. The result of the averaging depends on how the vibrational displacements correlate at different spatial points. The correlation function of the gradients of the vibrational displacements at the frequency ω is conveniently expressed in terms of the normalized correlation function $F_{\omega,ac}(r)$:

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

The form of the correlation function near the boson peak in amorphous solids is not known exactly, since the nature of these vibrations is not sufficiently well understood: it is normalized using the condition $F_{\omega}(r) \rightarrow 1$ when $r \rightarrow 0$. However, it is generally acknowledged that these are quasilocal vibrational excitations with a characteristic dimension of nanometer order.14,15 When averaged over an ensemble of these vibrations localized in regions of a disordered solid having different configurations, the corresponding correlation function should decrease as a function of distance with a certain characteristic correlation length of nanometer order. In addition, an additional decay of the correlations may take place inside the region of localization as a result of the specific geometry of the vibrational modes which, as predicted, may have dimensions of less than three or fractal dimensions. This geometric factor leads to the appearance of an additional factor $r^{-\alpha}$ in the correlation function, where $\alpha < 3$, which reflects the power decrease in the correlation. As a result, the correlation function has the form

$$F_{\omega,\mathrm{ac}}(r) = (a/r)^{\alpha} f(r/l_{\omega,\mathrm{ac}}), \qquad (5)$$

where $l_{\omega,ac}$ is the correlation length of the acoustic vibrations, *a* is the interatomic distance, $f(r/l_{\omega,ac})$ is a decreasing function which reflects the decay of the correlations with distance as a result of localization of the vibrational modes, and the factor $r^{-\alpha}$ is associated with the internal geometry of the vibrations. The specific form of the function $f(r/l_{\omega,ac})$ is unimportant for the present study, as will become clear from the following analysis, although it may be postulated that this corresponds to exponential damping, $\exp(-r/l_{\omega,ac})$, or Gaussian damping, $\exp(-r^2/l_{\omega,ac}^2)$. For example, for a damped plane acoustic wave which describes long-wavelength acoustic vibrations in an amorphous solid, the correlation function (5) is given by

$$\exp(i\mathbf{q}\cdot\mathbf{r}-r/l_{\omega})(1+r/l_{\omega}+r^2/3l_{\omega}^2).$$

The oscillation factor naturally disappears from the boson peak for quasilocal vibrations because of the large variations in the form of the natural modes and the wide range of wave vectors required to form a localized mode. Bearing in mind that for harmonic vibrations and the Stokes component of the spectrum

$$\langle |u_{\omega}(0)|^2 \rangle \propto (n(\omega) + 1)/\omega,$$

and that

$$\nabla u_{\omega} \sim u_{\omega}/l_{\omega,\mathrm{ac}}$$

we have

$$\langle |\nabla u_{\omega}(0)|^2 \rangle \sim l_{\omega,\mathrm{ac}}^{-2} \langle |u_{\omega}(0)|^2 \rangle \propto l_{\omega,\mathrm{ac}}^{-2} (n(\omega)+1)/\omega$$

As a result, Eq. (4) has the form

$$\langle \nabla u_{\omega}^{+}(\mathbf{r}) \cdot \nabla u_{\omega}(0) \rangle \propto l_{\omega,\mathrm{ac}}^{-2} F_{\omega,\mathrm{ac}}(r)(n(\omega)+1)/\omega.$$
 (6)

Substituting Eq. (6) into Eq. (3) and comparing with Eq. (1), we obtain

$$C_{\rm ac}(\omega) \propto l_{\omega,\rm ac}^{-2} \int d\mathbf{r} \ F_{\omega,\rm ac}(r). \tag{7}$$

Unlike formula (3), for optical vibrations, the light scattering intensity is determined directly by the correlation function of the atomic vibrational displacements:

$$I_{\rm opt}(\omega) \propto \int d\mathbf{r} \langle u_{\omega}^{+}(\mathbf{r}) u_{\omega}(0) \rangle g_{\rm opt}(\omega).$$
(8)

In this case, there is no need to impose the constraint that the Hamiltonian of the interaction between the vibrations and light be expressed in terms of derivatives of the displacement components with respect to the coordinates, since for optical vibrations the center of gravity of a unit cell remains constant (see, for example, Ref. 16). Here the correlation function of the vibrational displacements has the form

$$\langle u_{\omega}^{+}(\mathbf{r})u_{\omega}(0)\rangle \propto F_{\omega,\text{opt}}(r)(n(\omega)+1)/\omega.$$
 (9)

Substituting Eq. (9) into Eq. (8) and comparing with Eq. (1), we obtain

$$C_{\text{opt}}(\omega) \propto \int d\mathbf{r} F_{\omega,\text{opt}}(r).$$
 (10)

It can be seen from a comparison of Eqs. (7) and (10) that the interaction coefficient between light and optical phonons does not contain the additional square of the correlation length in the denominator which appears as a result of the gradients of the displacements for the acoustic phonons. Thus, as the correlation length increases under annealing, the acoustic part of the spectrum decays more rapidly than the optical part, i.e., is more sensitive to the degree of disorder.

We shall now explain the changes in the Raman spectrum observed when amorphous porous silicon is annealed (Fig. 1). We shall first show how specific is the dependence of $C_{\rm ac}(\omega)$ on the correlation length. Using Eq. (5), it is easy to show that

$$\int d\mathbf{r} F_{\omega,\mathrm{ac}}(r) \propto b l_{\omega}^{3-\alpha},$$

where

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

is a certain constant which depends on the specific form of the correlation function. It then follows from Eq. (7) that

$$C_{\rm ac}(\omega) \propto l_{\omega,\rm ac}^{1-\alpha}$$

Since the vibrations near the boson peak are localized and satisfy the Ioffe–Regel criterion,¹⁷ $l_{\omega,ac} \sim \lambda \propto \omega^{-1}$, where $\lambda = 2\pi c/\omega$ is the wavelength of the acoustic excitation, *c* is the velocity of light, and assuming that near the boson peak $C_{ac}(\omega) \propto \omega$ (Ref. 18), we find that

$$l_{\omega,\mathrm{ac}}^{1-\alpha} = l_{\omega,\mathrm{ac}}^{-1},$$

i.e.,

$$C_{\rm ac}(\omega) \propto l_{\omega,\rm ac}^{-1}$$
.

If crystallites of diameter D appear within the illuminated region, the mean free path of an acoustic vibration in these crystallites should be equal to their size $l_{\omega,ac} \sim D$. In this case, the reciprocal correlation length averaged over the sample $l_{\omega,ac}^{-1}$ undergoes a jump since the upper limit of the correlation length for amorphous silicon is 1.2–1.5 nm and the size of a critical nucleus is 3–4 nm, and thus the intensity of the boson peak in Fig. 1 drops sharply, being approximately halved.

Thus, it can be concluded that when Raman scattering is used to determine the volume ratio of the amorphous component in solids consisting of mixed phases, the boson peak should be used in preference to the amorphous-like optical mode currently used since this peak is more sensitive to the order because the intensity of light scattering by acoustic phonons has an additional dependence on the degree of disorder.

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