

Studying the initial stage of nucleation with low-frequency Raman scattering

N. N. OVSYUK^(a)

The Institute of Geology and Mineralogy, Russian Academy of Sciences - Novosibirsk, 630090, Russia

received 20 April 2010; accepted in final form 4 July 2010
published online 3 August 2010

PACS 63.22.-m – Phonons or vibrational states in low-dimensional structures and nanoscale materials

PACS 78.30.Ly – Infrared and Raman spectra: Disordered solids

PACS 63.50.-x – Vibrational states in disordered systems

Abstract – The objective of this paper is to show that low-frequency Raman scattering appears to be a sensitive method for the investigation of the initial stage of nucleation in multi- and mono-component systems. In the case of the mono-component systems, when the crystalline nuclei do not have an acoustic mismatch as compared to the amorphous matrix, we cannot observe their surface vibrations, but we can make use of the fact that in nucleation there is a jump in a structure correlation length. This results in a sharp decrease in contribution to the density of the acoustic vibration states because of decreasing the concentration of structural correlations on which acoustic phonons are localized. In addition, low-frequency Raman spectroscopy may be useful in the research into the phase transformation in materials for phase-change memories.

Copyright © EPLA, 2010

Introduction. – The low-frequency Raman scattering caused by interaction of light with acoustic vibration modes of nanoparticles is an effective method of their research. This is because of the fact that in nanoparticles due to violation of the wave vector conservation rule, the total density of vibration states is observed in Raman scattering spectra. Just this feature allows studying the initial stage of crystallization since the occurrence of crystal nuclei in a matrix of glass results in an additional contribution to density of the acoustic vibration states associated with the surface vibration modes of nanocrystals. The surface vibrations of a homogenous spherical elastic body under stress-free boundary conditions was first theoretically analyzed by Lamb [1]. These vibration modes can be classified as either spheroidal or torsional. The torsional mode frequencies depend on the transverse acoustic phonon velocity v_t , while the spheroidal mode frequencies depend on both the longitudinal acoustic phonon velocity v_l and the transverse acoustic phonon velocity. These modes observations require polarization measurements, since spherical vibrations lead to a polarized scattering, while the torsional vibrations bring about a depolarized scattering. It has been experimentally established [2] that only the lowest-energy

spheroidal vibrational modes are active in Raman scattering. The frequencies of such modes calculated according to the Lamb theory are $\omega_0 = 0.7 \cdot v_l/d$ (where d is the size of a crystal nucleus) and $\omega_2 = 0.85 \cdot v_t/d$. It was previously shown [3] that the matrix of glass has also an influence on eigenfrequencies of the surface vibrational modes of nanocrystals, and the above formulas can be written down as

$$\omega = k \cdot v/d, \quad (1)$$

where v is the average longitudinal or transverse sound velocity, k is the fractional factor, which depends on the light polarization and on the stiffness of a glass matrix, in which the microcrystals are imbedded. Low-frequency Raman spectra give information about the sizes, form and concentration of nuclei formed in a glass matrix. As compared to conventional methods, such as small-angle X-ray scattering, this method is more sensitive when the sizes of nuclei ≤ 2 nm.

Results and discussion. –

Multi-component system. For the first time, low-frequency Raman scattering was found on nuclei formed after annealing the ceramic glass by Champagnon *et al.* [4] (fig. 1(a)). This figure shows the appearance of a narrow peak at 26 cm^{-1} before a broad boson peak (to be discussed below), which is associated with acoustic

^(a)E-mail: ovsyuk@uiggm.nsc.ru

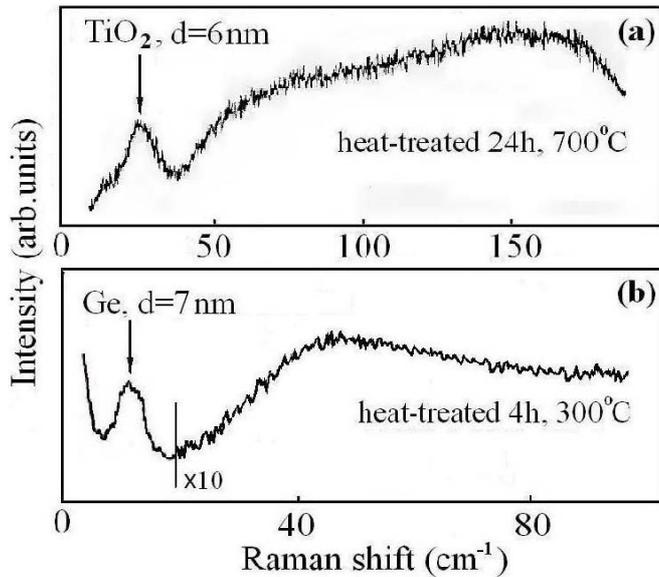


Fig. 1: Low-frequency Raman scattering (a) on TiO_2 nuclei formed after annealing ceramic glass $\text{Li}_2\text{O-MgO-ZnO-P}_2\text{O}_5\text{-Al}_2\text{O}_3\text{-SiO}_2$ with a nucleating component TiO_2 (spectrum is taken from ref. [4]); (b) on Ge nuclei formed after annealing dielectric film GeO in a helium flow.

vibration modes of TiO_2 nanoparticles with diameter of 6 nm. We, also, have observed a similar low-frequency Raman peak after annealing dielectric film GeO in a helium flow (fig. 1(b)). In the resulting heterophase film, Ge microcrystals were dispersed inside an amorphous dielectric GeO_2 matrix according to the disproportionation reaction $2\text{GeO} \rightarrow \text{Ge} + \text{GeO}_2$. Varying the synthesis conditions, we could control the size of microcrystals. Raman measurements were carried out in a conventional 90° scattering geometry at room temperature. The spectra were excited by the 514.5 nm line of Ar-ion laser and recorded by Jobin Yvon U-1000 spectrophotometer equipped with a double monochromator and photon-counting system. In fig. 1, a low-frequency peak in Ge sample appears at a smaller Raman shift than in TiO_2 sample, because the sound velocities in these microcrystals as well as stiffness of the surrounding matrices are different. Figure 2 shows that maxima of low-frequency peaks are shifted to higher frequencies with decreasing the sizes of nanoparticles according to eq. (1). We determined the sizes of nuclei by a transmitting electron microscope with an error of 30%. When determining the size of microcrystals with the use of maxima of a low-frequency peak, it appears possible to decrease an error up to 5%, but in this case, it is necessary to know the mass densities and Lamé's constants for microcrystals and the matrix in which they are embedded as well as polarization of light.

We have considered the low-frequency Raman spectra for multicomponent systems with annealing of which there occur crystal nuclei with a high density inside a glass matrix of another chemical compound with a lower

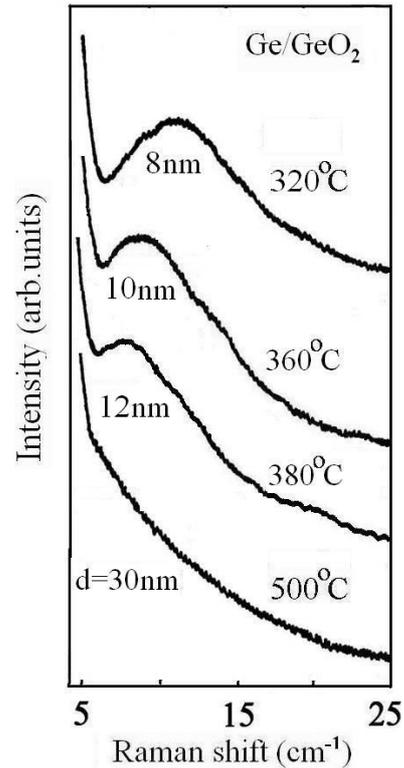


Fig. 2: Low-frequency Raman spectra of Ge microcrystals embedded in GeO_2 matrix at different annealing temperatures.

density. Then, because of a large acoustic mismatch between a glass matrix and microcrystals $\rho_1 v_1 / \rho_2 v_2$ (ρ is density of material, v is sound velocity) there occurs a reflection of sound at the microcrystals interfaces resulting in localization of phonons.

Mono-component system. If nucleation occurs in a mono-component system, for example, in crystallization of amorphous Si, then phonons will not be localized inside microcrystals, and the above-discussed low-frequency Raman peaks will not appear. However in amorphous materials, even without crystal nuclei, there is also present an excess vibration density of states in a low-frequency range ($20\text{--}100\text{ cm}^{-1}$) as compared to the Debye density, which arises due to structure correlations. Generally, a peak in low-frequency Raman spectra associated with phonons localization on the structure correlations of disordered materials is called the boson peak. In glasses, its frequency ω_b is typically equal to $1/5\text{--}1/7$ of the Debye frequency and is connected with a structure correlation length l_ω as $\omega_b \sim v/l_\omega$ (v is average longitudinal or transverse sound velocity), which is the same as in eq. (1) for acoustic vibrations of nanocrystals. Only in the latter case, the size of a nanoparticle is replaced by a correlation length. Taking into account the fact that in nucleation there is a change in a correlation length, this, in turn, should change parameters of a boson peak. It is necessary to note that the above change will take place as in the case of first-order transition as a jump because there

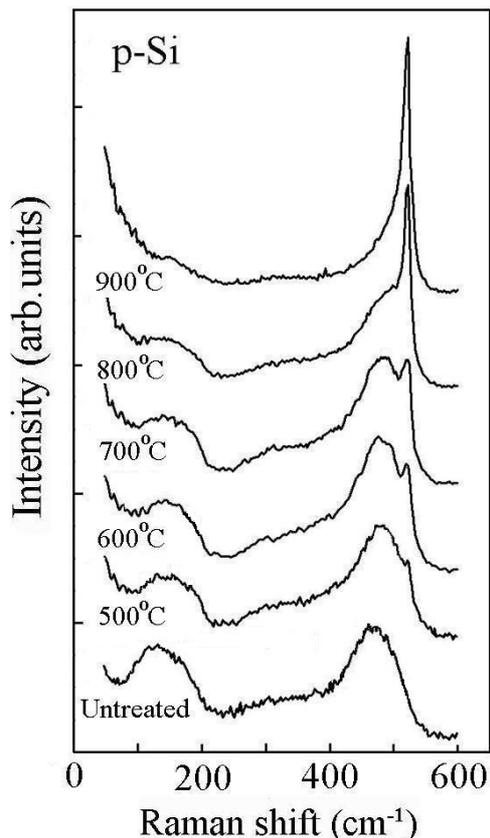


Fig. 3: Change of Raman spectral shape of amorphous porous silicon after the stepwise isochronous annealing in nitrogen atmosphere.

is no continuous gradation in the correlation length over all values from single-atom spacings to the crystal dimensions. In other words, there appears to be the lowest limit on the crystallite size (about 3–4 nm for Si) and the upper limit on the correlation length in amorphous materials (1.2–1.5 nm for Si) [5]. We do not expect to observe a frequency shift of a boson peak ω_b , since the low-frequency velocity of sound for Young's modulus mode in amorphous Si is found to be only 55–60% of the value expected for the crystalline state [6].

For carrying out the experiment, we have prepared a porous silicon with 70% porosity and 2 μm thickness. To obtain an amorphous layer, irradiation by $^{10}\text{B}^+$ ions with energy 100 keV was performed. For such ions, the amorphization dose of the porous silicon was $5 \cdot 10^{15} \text{ cm}^{-2}$. After transformation of the porous silicon to the amorphous state we began to perform the stepwise isochronous annealing in the nitrogen atmosphere in order to observe the crystallization process (fig. 3). Let us consider the two lower spectra in fig. 3 in greater detail. In fig. 4, the lower Raman spectrum of amorphous porous silicon consists of an amorphous-like TO peak at 480 cm^{-1} and a broad peak at 150 cm^{-1} , which is called the boson peak. In glasses, a small value of the boson peak frequency in comparison with that of TA and LA modes is due to a comparatively

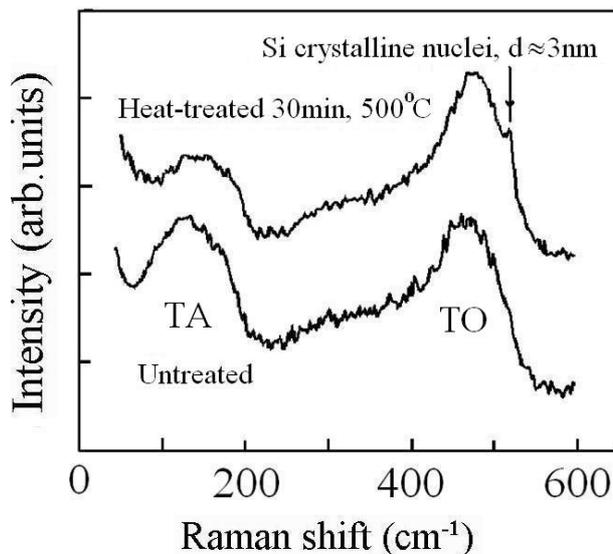


Fig. 4: Change of Raman spectral shape of amorphous porous silicon after the appearance of crystalline nuclei in the course of annealing in nitrogen atmosphere during 30 min at $T = 500 \text{ }^\circ\text{C}$.

large value of the structural correlation length. In tetragonal amorphous semiconductors, the structure correlation length is less than in glasses and is comparable with a characteristic interatomic distance, so the boson peak can coincide with the transverse acoustic TA mode. On the upper spectrum it is well seen that when the temperature of annealing reached $500 \text{ }^\circ\text{C}$, a small peak has appeared in the Raman spectrum at 520 cm^{-1} . This frequency corresponds to that of TO phonon in crystalline silicon. Just at that temperature, the boson peak amplitude abruptly decreased by a factor of 2. It is well known that the size of the critical nucleus in the bulk silicon is approximately 3–4 nm [7], and the average size of the structure elements in the porous silicon with porosity 70% (which is our case) is roughly equal to 4–5 nm [8]. Thus, the amorphous phase volume should sharply decrease at the moment when crystalline nuclei arise.

In the amorphous phase owing to the lack of translation invariance and, as consequence, of violation of the wave vector conservation rule, the total density of the vibrational state is observed in Raman scattering spectra [9]:

$$I(\omega) = C(\omega)g(\omega)[n(\omega) + 1]/\omega, \quad (2)$$

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. Since the vibrational density of states does not sufficiently change in the course of annealing [10], an observed decrease in the boson peak amplitude can be explained only by a decrease in magnitude of the coupling coefficient of light with the acoustic vibrations $C_{ac}(\omega)$ owing to a change of the degree of violation of the wave vector selection rule. We make use of the vibration correlation length l_ω , 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 $C_{ac}(\omega)$. To show the connection $C(\omega)$ with a structural order, we express Raman intensity for acoustic and optical vibrations with the help of the normalized correlation function $F_{\omega}(r)$. Taking into account the fact that the center of weight of an elementary cell does not change for optical vibrations, for the coupling coefficients of light with vibrations, the following formulas are obtained [11]:

$$C_{ac}(\omega) \propto l_{\omega,ac}^{-2} \int dr F_{\omega,ac}(r), \quad (3)$$

$$C_{opt}(\omega) \propto \int dr F_{\omega,opt}(r), \quad (4)$$

where $F_{\omega}(r)$ are normalized correlation functions, whose exact form is of no importance for the present case. The comparison of eqs. (3) and (4) shows that the coupling coefficient of light with vibrations for optical phonons has no additional length squared in the denominator. Thus, when the correlation length increases in the course of annealing, the acoustical part of the spectrum decreases faster than the optical one, *i.e.*, acoustics is more sensitive to the degree of disorder than optics.

Let us return to the explanation of changes in Raman spectrum when annealing amorphous porous Si (fig. 3). Analyzing possible kinds of correlation functions, from eq. (3) we obtain that in the boson peak region:

$$C_{ac}(\omega) \propto l_{\omega,ac}^{-1}. \quad (5)$$

If inside an illuminated region the crystalline nuclei of diameter D appear, then a free path length of the acoustic vibration should be equal to the diameter, $l_{\omega,ac} \sim D$. This leads to a sharp change in the average of the inverse correlation length $l_{\omega,ac}^{-1}$, since the correlation length for amorphous silicon is not higher than 1.2–1.5 nm, while the size of critical nuclei is equal to 3–4 nm, so Raman intensity in the region of the boson peak sharply decreases approximately by a factor of 2.

Conclusions. – To conclude, it may be said that low-frequency Raman scattering of light in the acoustic range is a sensitive method for investigation of the initial stage of nucleation. It is necessary to note that in multi-component glasses, phonons are localized on the crystalline nuclei which have the mass density distinguished from that of

a matrix. This results in an additional contribution to the density of the acoustic vibration states associated with the surface vibration modes of nanocrystals. In the case of mono-component systems, when the crystalline nuclei do not have an acoustic mismatch between the amorphous matrix and microcrystals, we make use of the fact that in nucleation there is a jump in the correlation length. This results in a sharp reduction in the additional contribution to the density of the acoustic vibration states because of decreasing the concentration of structural correlations on which phonons are localized in the energy range of the boson peak. In addition, low-frequency Raman spectroscopy may be useful to study phase transformation in materials for phase-change memories, because the phase transformation generally begins with nucleation, in which a small aggregate of atoms organizes into a different structural symmetry.

This work was supported by the Russian Foundation for Basic Research (Grant No. 08-05-01025).

REFERENCES

- [1] LAMB H., *Proc. London Math. Soc.*, **13** (1882) 187.
- [2] DUVAL E., BOUKENTER A. and CHAMPAGNON B., *Phys. Rev. Lett.*, **56** (1986) 2052.
- [3] OVSYUK N. N. and NOVIKOV V. N., *Phys. Rev. B*, **53** (1996) 3113.
- [4] CHAMPAGNON B., BOUKENTER A. and DUVAL E., *J. Non-Cryst. Solids*, **94** (1987) 216.
- [5] BRODSKY M. H., in *Light Scattering in Solids*, edited by CARDONA M. (Springer, New York) 1975, p. 208.
- [6] TESTARDI L. R. and HAUSER J. J., *Solid State Commun.*, **21** (1977) 1039.
- [7] VEPREK S., IQBAL Z. and SAROTT F.-A., *Philos. Mag. B*, **45** (1982) 137.
- [8] GREGORA I., CHAMPAGNON B. and HALIMAONI A., *J. Appl. Phys.*, **75** (1994) 3034.
- [9] SHUCKER R. and GAMMON R. W., *Phys. Rev. Lett.*, **25** (1970) 222.
- [10] SHIMADA T., KATAYAMA Y., NAKAGAWA K., MATSUHARA H., MIGITAKA M. and MURUYAMA E., *J. Non-Cryst. Solids*, **59-60** (1983) 783.
- [11] OVSYUK N. N. and NOVIKOV V. N., *Phys. Rev. B*, **57** (1998) 14615.