

Raman scattering from quantum dots of Ge embedded in SiO₂ thin films

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Raman measurements were carried out on Ge quantum dots from 6.1 to 15 nm in size embedded in SiO₂ thin films. The samples were prepared by rf co-sputtering and post-annealing. In contrast to the amorphous-like broad spectra previously obtained for gas-evaporated Ge microcrystals of comparable sizes, relatively sharp lines around 300 cm⁻¹ were observed, because the present dots satisfy the fixed boundary condition. The increase in the linewidth observed with decreasing the size is in good agreement with the results of the calculation based on the phonon confinement model. However, the downward shift of the line predicted from the calculation was not observed presumably due to the compressive stress exerted on the dots.

The optical properties of semiconductor microcrystals as small as a few nanometers (usually called quantum dots) embedded in solid matrices are currently attracting much interest, because they are expected to show very large optical nonlinearity^{1,2} and offer the possibility of fabricating novel optical devices. Until now much experimental work based on the linear and nonlinear optical spectroscopy has been made in order to clarify the size-quantized electronic states in these dots and explore new optical phenomena related with the size quantization (quantum size effects).³⁻⁵ However, to our knowledge no systematic measurement on the vibrational states of the quantum dots embedded in solid matrices has been made so far. Information on the phonons is indispensable for the discussion of electron-phonon interactions in the dots.

Very recently, we have succeeded in producing Ge quantum dots ranging from 3 to 10 nm in size embedded in thin films of pure SiO₂ by applying an rf co-sputtering technique.⁶ In our previous paper,⁶ we reported the results of optical transmission measurements which demonstrate the quantum size effects. This work is an extension of the previous work and we report here results of Raman measurements. The Raman lines observed are relatively sharp in contrast to the broad amorphous-like bands previously observed for gas-evaporated Ge and Si microcrystals.^{7,8} The size dependence of the Raman line is discussed on the basis of the phonon confinement model.

The samples were prepared by the rf co-sputtering method similar to that used in our previous work.⁶ Small pieces of Ge wafers ($\sim 0.5 \times 5 \times 15$ mm³) were placed on a pure SiO₂ target 10 cm in diameter and they were co-sputtered in Ar gas. Thin films of the mixture of Ge and SiO₂ were first deposited onto Si wafers, then they were annealed at 800 °C for 30 min in vacuum of the order of 10⁻⁵ Pa. In the present sample preparation method, the size of Ge microcrystals is controllable by varying the vol-

ume ratio of Ge to SiO₂, i.e., the number of Ge targets at the moment of sputtering. Raman measurements were carried out in a conventional 90° scattering configuration. The spectra were excited by the 514.5 nm line of an Ar ion laser and recorded by a Spex Ramalog 5M spectrophotometer. After completing the Raman measurements, samples for cross-sectional transmission electron microscopy (TEM) were prepared following a standard thinning procedure including mechanical and ion thinning techniques. High-resolution electron microscopic (HREM) images were obtained by operating a JEM-200CX electron microscope at 200 kV.

Figure 1 shows a HREM image of a film obtained by placing two Ge targets on the SiO₂ target. Lattice fringes corresponding to Ge microcrystals grown in the SiO₂ matrix are clearly seen. The microcrystals are spherical and well dispersed in the matrix. From the distance between the fringes (0.33 nm) and the angle between crossed fringes (70.5°), we can identify these fringes with the {111} planes of the diamond structure. In this work, the average size d (diameter) of the Ge microcrystals was determined directly from TEM images. For the sample shown in Fig. 1 we obtained $d = 6.1$ nm with a standard deviation of the distribution equal to 1.7 nm. The ratio of the standard deviation to the average size was roughly the same (~ 0.28) for all the samples prepared.

Figure 2 displays the results of Raman measurements. We see that the sample with $d = 15$ nm exhibits a sharp Raman peak at about 300 cm⁻¹, which is essentially the same as that observed for bulk Ge crystals. The peak can thus be attributed to the $\Gamma_{25'}$ phonon at the center of the Brillouin zone. As the average size decreases from 15 to 6.1 nm, the Raman peak broadens and shifts slightly to higher frequencies. Furthermore, the peak becomes weaker and asymmetric accompanying a tail at the low-frequency side. The tail is very pronounced for the sample with $d = 6.1$ nm. Results of a precise measurement of the full width at half maximum (FWHM) and peak frequency are plotted in Fig. 3 together with theoretical curves explained later.

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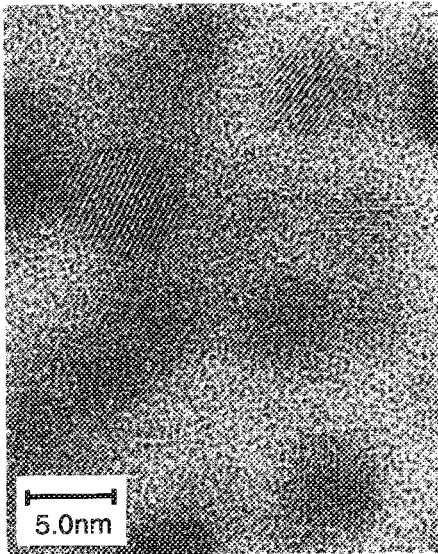


FIG. 1. HREM image of quantum dots of Ge embedded in a SiO₂ thin film. We can clearly see lattice fringes corresponding to the {111} planes of the diamond structure.

The FWHM for the sample with $d = 15$ nm is slightly larger than that of the bulk Ge (~ 3.5 cm⁻¹), but as the size decreases to 6.1 nm, the FWHM increases up to 10 cm⁻¹, which is about three times larger than the bulk value. In contrast to the strong size dependence of the FWHM, the size dependence of the peak frequency is very weak. The peak tended to shift to higher frequencies but less than 2 cm⁻¹.

It should be noted here that the Raman peaks presently observed for the Ge quantum dots are relatively sharp in good agreement with previous Raman data for so-called microcrystalline Si films,⁹⁻¹¹ in which Si grains smaller than 10 nm are contained. However, the present data completely disagree with our previous data for gas-

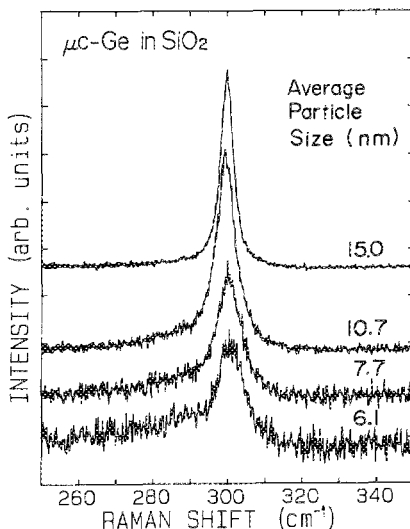


FIG. 2. Size dependence of Raman spectrum for quantum dots of Ge embedded in SiO₂ thin films. The average particle size d was determined from electron micrographs.

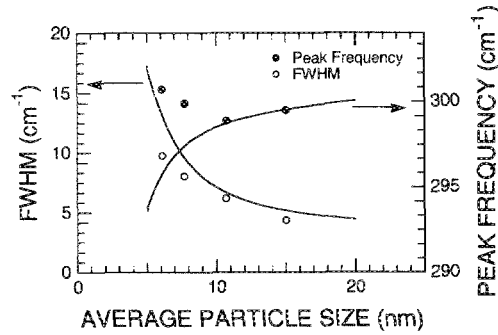


FIG. 3. Plot of the FWHM and peak frequency as a function of the particle size. Open and closed circles are experimental FWHM and peak frequencies, respectively. Solid curves represent the results of calculation based on the phonon confinement model.

evaporated Ge microcrystals.^{7,8} In fact, we have shown that gas-evaporated Ge microcrystals about 8 nm in size exhibit very broad amorphous-like spectra, although they are crystalline judged from HREM images. The great difference in the Raman spectra is thought to arise from the difference in the surface boundary condition.

Since the Ge microcrystals in the gas-evaporated samples are only loosely packed, they satisfy the free-boundary condition resulting in strong surface effects.^{7,8} The amorphous-like Raman signals are thought to come from the surface layers of the microcrystals, whose atomic arrangement is more or less in disorder. Furthermore, the signals are believed to be enhanced by several surface enhancement mechanisms. On the other hand, the present Ge microcrystals are embedded in the SiO₂ matrix and similarly Si microcrystals in the microcrystalline films are tightly stacked. The surfaces of these microcrystals are not free and the surface effects are weak. The Raman spectra of the present samples as well as those of the microcrystalline Si films thus conserve the bulk character and the signals are thought to come mainly from the interior of the microcrystals. Although the surface effects are weak in the present samples, a tail appearing at the low-frequency side of the Raman peak for smaller microcrystals may be attributed to the surface layers. It is natural that the tail becomes stronger as the size decreases, because the surface to volume ratio increases.

For a semiconductor quantum dot as small as a few nanometers, one would expect changes in the Raman spectrum caused by the confinement of phonon in a finite volume. Using expressions of the Raman intensity and phonon confinement function given by Campbell and Fauchet [Eqs. (6) and (9) in Ref. 11], we have calculated the size dependence of the Raman line. The phonon dispersion curves given by Nilsson and Nelin¹² were used in the calculation. The solid lines in Fig. 3 represent the calculated size dependence of the FWHM and peak frequency. Because of the size-dependent breakdown of the $k = 0$ selection rule in the Raman scattering process, the calculated FWHM increases with decreasing size, while the peak frequency decreases. Although the experimental points for the FWHM are slightly lower than the calculated curve,

the agreement between experiment and calculation is satisfactory. In contrast to this, the present samples do not show the large downward shifts predicted by the calculation. We note here that for the microcrystalline Si films, the downward shifts of the Raman peak have been observed with decreasing the grain size.⁹⁻¹¹

The reason for the discrepancy in the experimental and calculated size dependence of the peak frequency is not clear at present. However, a possible explanation is the compressive stress exerted on Ge microcrystals due to the existence of the SiO₂ matrix. The nearest neighbor distance in α -SiO₂ is of the order of 0.16 nm and that in Ge crystals is 0.24 nm. The mismatch in the nearest neighbor distances may result in the compressive stress on the Ge microcrystals, similar to the cases of strained superlattices and epitaxial layers on various substrates. The compressive stress leads to upward shifts of the Raman line thereby compensating the downward shifts caused by the phonon confinement. The stress may also affect the linewidth of the Raman line. However, discussion of the effects of the stress on the linewidth is extremely difficult at present, because detailed information about the stress is not available. For example, we do not know to what extent the stress is uniaxial or hydrostatic. If the stress is uniaxial, it may induce the splitting of the phonon branch and result in an apparent broadening of the Raman line. Further detailed studies are required to clarify the effects of the stress on both the peak position and the linewidth.

In the above discussion we did not take into account the effects of size distribution. If there is a strong size dependence of the peak position, the size distribution will cause a non-negligible inhomogeneous broadening of the Raman line. However, we did not observe the strong size dependence of the peak position. Therefore, the inhomogeneous broadening is thought to be much less important compared to the broadening caused by the phonon confinement.

In summary, we have demonstrated that Ge quantum dots embedded in thin SiO₂ films show sharp Raman lines in severe disagreement with amorphous-like broad bands previously observed for gas-evaporated Ge microcrystals of comparable sizes. The present Raman lines are sharp, because the present dots satisfy the fixed boundary condition. The increase in the linewidth observed with decreasing size is in good agreement with the calculation based on the phonon confinement model. However, the downward shift predicted from the calculation was not observed presumably due to the compressive stress exerted on the dots. The present results together with those on gas-evaporated Ge microcrystals clearly demonstrate that the surface boundary condition plays a crucial role in determining the Raman spectra.

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- ¹S. Schmitt-Rink, D. A. B. Miller, and D. S. Chemla, *Phys. Rev. B* **15**, 8113 (1987).
- ²E. Hanamura, *Phys. Rev. B* **37**, 1273 (1988).
- ³D. W. Hall and N. F. Borrelli, *J. Opt. Soc. Am. B* **5**, 1650 (1988).
- ⁴A. Nakamura, H. Yamada, and T. Tokizaki, *Phys. Rev. B* **40**, 8585 (1989).
- ⁵T. Itoh, M. Furumiya, T. Ikehara, and C. Gourdon, *Solid State Commun.* **73**, 271 (1990).
- ⁶S. Hayashi, M. Fujii, and K. Yamamoto, *Jpn. J. Appl. Phys.* **28**, L1464 (1989).
- ⁷S. Hayashi and K. Yamamoto, *Superlatt. Microstruct.* **2**, 581 (1986).
- ⁸S. Hayashi, H. Wakayama, T. Okada, S. S. Kim, and K. Yamamoto, *J. Phys. Soc. Jpn.* **56**, 243 (1987).
- ⁹Z. Iqbal, S. Veprek, A. P. Webb, and P. Capezzuto, *Solid State Commun.* **37**, 993 (1981).
- ¹⁰J. Gonzalez-Hernandez, G. H. Azarbayejani, and R. Tsu, *Appl. Phys. Lett.* **47**, 1350 (1985).
- ¹¹I. H. Campbell and P. M. Fauchet, *Solid State Commun.* **58**, 739 (1986).
- ¹²G. Nilsson and G. Nefin, *Phys. Rev. B* **15**, 364 (1971).