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Raman scattering from the surface phonon mode in GaP microcrystals

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The Raman scattering from GaP microcrystals prepared by a gas-evaporation technique has been investigated. A new peak, which can be identified with the surface phonon mode, was found. The present results demonstrate that the surface phonon peak can be clearly observed only when the microcrystals are about one order of magnitude smaller than the wavelength of the incident laser radiation.

Effects of finite crystal size on long-wavelength optical phonons in ionic crystals have been investigated extensively by infrared absorption measurements. For a wide variety of ionic microcrystals, new absorption peaks, which can be assigned to surface phonon modes, have been observed and the observed features of surface mode absorption have been interpreted successfully by electromagnetic theories.[1] Theoretical discussions of Raman scattering from the surface phonon modes have been presented by several authors.[1–4] Evans *et al.*[5] and Ushioda *et al.*[6] have succeeded in observing the Raman scattering from surface phonon modes in two-dimensional surfaces (thin films). However, experimental results reported so far on microcrystalline samples are somewhat ambiguous. As far as the authors know, only two works made by Scott and Damen[7] on CdS crystallites in thin films and by Böckelmann and Schlecht[8] on MgO microcrystals seem to suggest positively the observation of surface phonon modes by Raman spectroscopy. However, it is still necessary to elucidate the effect of surrounding medium to judge whether the observed Raman peaks are truly attributable to the surface phonon modes or not. In other reports,[9,10] no positive indication of observing the surface phonon mode is found.

According to the electromagnetic theories,[1] the Raman peak due to the surface phonon mode should show the following three characteristic features: (i) The intensity of the peak increases as the size of microcrystals decreases. (ii) The peak is located between the bulk TO and LO phonon frequencies. (iii) The peak shifts to lower frequencies as the dielectric constant of surrounding medium increases. Raman results which demonstrate all these features have not been reported so far. In this paper, we report the first unambiguous observation of the surface phonon mode in GaP microcrystals by Raman spectroscopy. For GaP microcrystals prepared by the gas-evaporation technique, a new peak which shows the above three characteristic features of the surface phonon mode was found. The new peak can therefore be assigned to the surface phonon mode.

GaP microcrystals were prepared by means of the standard gas-evaporation technique.[11] We evaporated the single crystalline GaP from a tungsten basket in argon gas. Sootlike deposits were collected onto glass plates positioned above the basket. Evaporation temperature was kept at about 1700 °C. In order to obtain the particles of various sizes, the gas pressure and the height of particle collection (vertical distance between the basket and the glass substrate) were varied from 10 to 100 Torr and from 2 to 10 cm, respectively. We also prepared relatively large particles by grinding the bulk GaP crystals in a mortar. The Raman spectra were recorded by a JRS-400T(JEOL) spectrophotometer, equipped with a triple monochromator and a photon counting system. The spectra were excited with the 5145-Å line of an Ar-ion laser. The measurements were performed in a backscattering geometry. Laser power of 50 mW was used. Typical spectral slit width used was 1.5 cm^{-1}. After completing the Raman measurements, a part of sootlike deposit corresponding to a region sampled by the incident laser beam was scrapped off from the glass plate. The resulting powder was dispersed in ethyl alcohol, and a drop of it was put on Formvar-backed carbon thin film which was supported by an electron microscope grid. After the evaporation of alcohol, the grid was studied by a JEM-6A(JEOL) electron microscope.

In Fig. 1 we show typical transmission electron micrographs and diffraction patterns obtained for various samples. Hereafter, we denote the samples as A, B, C, and D. The sample A was prepared by grinding, and the others by the gas-evaporation technique. The average particle size was determined from these electron micrographs. Although the particles are not spherical, we adopted the following simple procedure to determine the average size, since the random orientation of particles can be assumed. We simply measured the linear dimension of particles along only one direction of micrographs. For every sample, such a measurement was made for more than a hun-

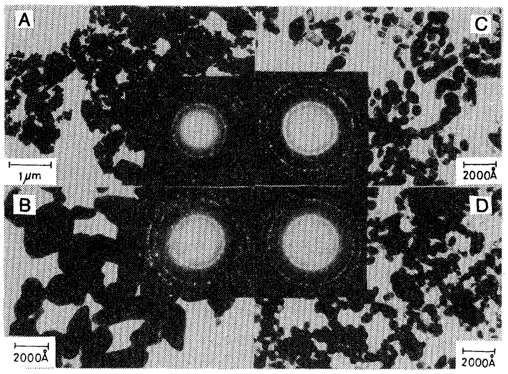

FIG. 1. Transmission electron micrographs and diffraction patterns of GaP microcrystals prepared.

dred particles and the results were averaged. The average determined by this procedure implies the rotational average as well as the average over the size distribution. The average sizes obtained for the samples A, B, C, and D are 4300, 990, 550, and 510 Å, respectively. As can be seen from Fig. 1, the diffraction patterns of all the samples are very similar, showing sharp rings. An analysis of these diffraction patterns revealed that the particles have the cubic zinc-blende structure.

The Raman spectra of the samples are presented in Fig. 2. Sample A shows two peaks at 366 and 402 cm^{-1}. These peaks can be assigned to TO and LO phonons of bulk GaP crystals.[12] It is clear that the finite-size effect is not apparent in the spectrum of sample A, which contains the particles as large as 4300 Å. However, as the particle size decreases further, new features in spectra can be observed. For sample B, which contains the particles as small as 990 Å, a shoulder appears at the low-frequency side of the LO phonon peak. When the particles are about one order of magnitude smaller than the wavelength of incident laser radiation (samples C and D), a distinct peak at 397 cm^{-1} splits off from the LO phonon peak and its intensity increases as the particle size decreases. Note that the new peak is stronger than the LO phonon peak for the sample D. It should be stressed here that the behavior of the new peak seen in Fig. 2 exactly corresponds to the first and the second characteristic features of the surface mode peak mentioned previously.

The spectra presented in Fig. 2 were recorded for the as-deposited samples. The surrounding medium for these samples is air, with the dielectric constant $\epsilon_m = 1.00$. In order to check the third characteristic feature of the surface mode peak, we examined the effects of surrounding medium. We first prepared several samples which show the spectra similar to the spectrum of the samples C or D in Fig. 2. Then drops of various liquids having different dielectric constants were put on the particle layers, and Raman spectra were recorded. In Fig. 3, we show the spectra obtained by such a procedure. The liquids used were nujol ($\epsilon_m = 2.00$), aniline ($\epsilon_m = 2.56$), and methylene iodide ($\epsilon_m = 3.10$). It is very clear from the figure that the new peak shifts to lower frequencies when the dielectric constant of the surrounding medium is increased. It can be noticed also that the new peak is significantly broadened when the drops of liquids are put on the particle layers.

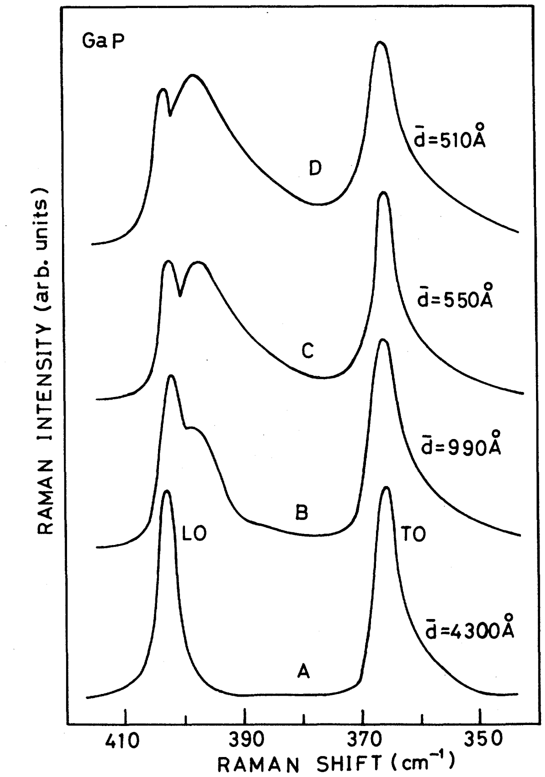

FIG. 2. Raman spectra of the samples from A to D. TO and LO are the bulk TO and LO phonon peaks. $\bar{d}$ is the average particle size.

The results presented in Figs. 2 and 3 demonstrate clearly that the new peak shows the three characteristic features of the surface phonon mode. We can therefore assign the new peak definitely to the surface phonon mode. Furthermore, the present results indicate that the surface mode peak can be clearly observed only when the microcrystals are about one order of magnitude smaller than the wavelength of the incident laser radiation. Failures in previous attempts to observe the surface phonon mode by Raman measurements[9,10] may be attributed to too large sizes of microcrystals used. It is also interesting to note that the surface mode peak in microcrystals appears to be more intense than that in thin films.[5,6] This can be

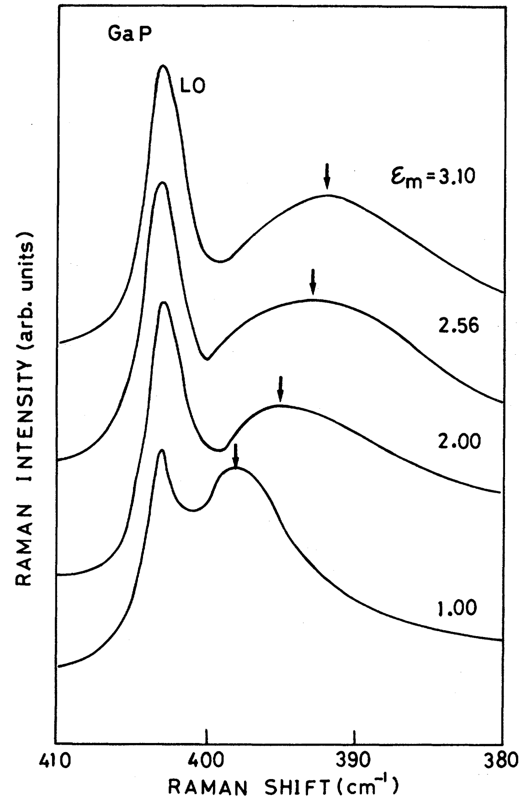

FIG. 3. Raman spectra recorded after putting drops of various liquids on particle layers. ϵ_m is the dielectric constant of the liquids. The arrows indicate the positions of the new peak.

understood by considering the larger surface to volume ratio in microcrystals.

For further analysis of the present results, we discuss here the shift of the surface phonon peak with respect to the dielectric constant of the surrounding medium. In Fig. 4, the observed dependence of the surface phonon frequency on the dielectric constant is plotted together with theoretical curves. The theoretical curves were calculated by using the following expression of the surface phonon frequency ω_s (Ref. 1):

$$\frac{\omega_s^2}{\omega_T^2}=\frac{\epsilon_0+\epsilon_m(1/L-1)}{\epsilon_\infty+\epsilon_m(1/L-1)}\ , \tag{1}$$

where ω_T is the frequency of the TO phonon mode, ϵ_0 and ϵ_∞ are the static and high-frequency dielectric constants, respectively, and L is the depolarization factor which depends on the particle shape. In the case of a sphere, L is equal to $\frac{1}{3}$. For an ellipsoid, three surface phonon frequencies can be derived from three different values of the depolarization factor corresponding to three major axes.

Using Eq. (1), we first calculated the dependence of ω_s on ϵ_m by assuming the spherical shape of particles and setting $L=\frac{1}{3}$. In the evaluation, the values $\epsilon_0=11.01$, $\epsilon_\infty=9.09$, and $\omega_T=366\ \mathrm{cm}^{-1}$, taken from Ref. 12, were used. The result is shown in Fig. 4 as a solid curve (a). It can be noted that the experimental points are always located at higher frequencies than the curve (a). The deviation of experimental points from the curve is relatively small in the case of air surrounding ($\epsilon_m=1.00$), but considerably large in the cases of the liquid surrounding ($\epsilon_m=2.00$, 2.56, and 3.10). Two reasons for this discrepancy between experiment and theory can be set forth: (i) the deviation of particle shape from the perfect spherical shape and (ii) the effect of particle aggregation. In effect, it is evident from the electron micrographs shown in Fig. 1 that the gas-evaporated particles are ellipsoidal rather than spherical. Thus the assumption of spherical shape is oversimplified. Furthermore, we have pointed out that, in addition to the shift, the surface phonon peak shows considerable broadening in the cases of liquid surrounding. This fact suggests strongly the formation of particle aggregation. As has been discussed theoretically by Clippe *et al.*,[13] if the particle aggregations are formed, the dipole-dipole interactions between particles give rise to many normal modes resulting in apparent broadening and shift of surface phonon peak. Therefore the effect of particle aggregation may explain the large deviation of experimental frequencies from the theoretical curve (a) and the considerable broadening

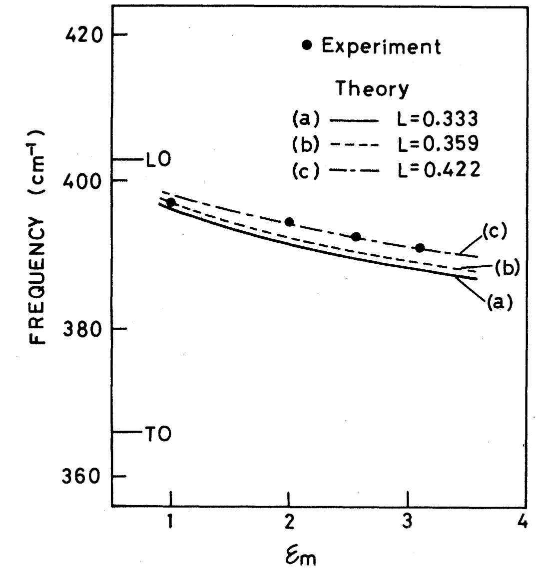

FIG. 4. Dependence of the surface phonon frequency on ϵ_m. Dots are experimental points. Curves (a), (b), and (c) were calculated from Eq. (1) by setting $L=0.333$, 0.359, and 0.422, respectively. Horizontal bars on the left-hand side indicate the bulk TO and LO phonon frequencies.

of the peak in the cases of liquid surrounding.

Although a proper account for the effect of particle shape and that of particle aggregation cannot be made within the framework of Eq. (1), we attempted tentatively to search values of L which can best fit the experimental points. The broken curve (b) and the chain curve (c) in Fig. 4 were calculated by setting $L = 0.359$ and 0.422, respectively. The experimental point for the air surrounding agrees fairly well with the curve (b), and the points for the liquid surrounding can be fitted well by the curve (c). Possible interpretations of the values of L obtained are as follows. The value $L = 0.359$, corresponding to the curve (b), is only slightly larger than the value for a sphere, $\frac{1}{3}$. This value may reflect the fact that the particles are not spherical. On the other hand, the relatively large value $L = 0.422$, corresponding to the curve (c), may result from the effect of particle aggregation superposed on the effect of nonspherical particle shape. This last interpretation of L is equivalent to the idea of the effective depolarization factor introduced by Granqvist and Hunderi.[14] For a more quantitative analysis of the present data, it is necessary to develop a theory which describes the Raman intensity of surface phonon modes in nonspherical particles. It is also helpful if experimental methods of knowing the geometry of particle aggregation are invented.

In conclusion, we measured Raman spectra of GaP microcrystals prepared by the gas-evaporation technique. A new peak which can be identified with the surface phonon mode was found. It was shown that the effects of particle shape and particle aggregation should be taken into account to explain the observed shift of surface mode peak with respect to the dielectric constant of the surrounding medium. Our results suggest strongly that the Raman spectroscopy is successful in investigating the surface phonon modes in microcrystals, provided that the microcrystals are small enough. Extension of the present study to other materials including II-VI and III-V semiconductors is straightforward.

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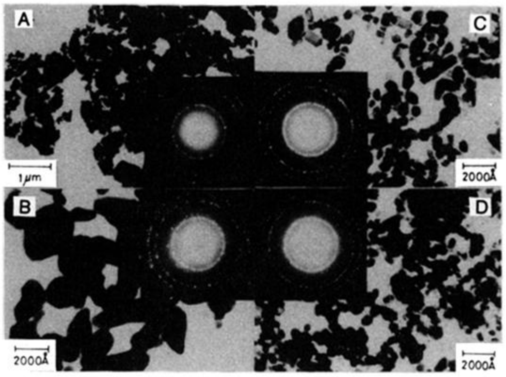

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