RAMAN SCATTERING OF CdS MICROCRYSTALS IN ORGANIC MEDIA

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Raman scattering of CdS microcrystals in polymethyl methacrylate, polystrene and polyvinyl alcohol was observed. A comparison is made between the experimental results and values calculated from the microscopic dynamical theory.

1. Introduction

The optical properties of microcrystals have attracted much attention in the last few years. Raman scattering from GaP microcrystals was investigated by Hayashi et al. [1]. They pointed out that a new peak in the Raman scattering spectra can be identified with surface vibration modes. At nearly the same time a growth technique for semiconductor microcrystals in a glassy dielectric matrix was developed by Ekimov et al. [2]. They studied the absorption spectra of a number of II–VI compounds grown by this technique. Early in the seventies, Scott and Damen [3] reported Raman scattering from surface phonons in cylindrical CdS crystallites. Their samples consisted of polycrystalline films comprised of very small crystallites ($\ll 1$ μm). One of us has also reported on Raman scattering of CdS and CdS_xSe_{1-x} microcrystals in a glass medium [4].

In this paper, the Raman scattering of CdS microcrystals in organic media such as polymethyl methacrylate, polystyrene and polyvinyl alcohol are studied. A new strong scattering peak in these samples is observed which can be identified with surface vibration modes.

2. Sample preparation

A powder of cadmium sulfide can easily be made by chemical reaction of a solution of cadmium chloride with hydrogen sulfide. To prepare the CdS microcrystals in organic media, at first we prepared two sorts of solution: one was a solution of organic material in which about 5 g of organic material is dissolved in 100 ml of organic solvent (the polyvinyl alcohol is dissolved in the water); the other was a solution of cadmium chloride in which about 10 mg of pure cadium chloride is dissolved

in 100 ml of deionized water. Then, the samples are prepared using the following procedures:

a) A cleaned piece of glass is put into the solution of organic material for a little while. After the organic solvent has evaporated, a thin organic film is formed on the glass.

b) The glassy plate is placed in the solution of cadium chloride for a little while. After it is taken out of the solution, it is put in a container of gaseous hydrogen sulfide. A layer of CdS microcrystals is formed on the organic film.

c) In order to remove the residue of hydrogen chloride, the glass plate is put into deionized water, is slightly shaken several times, and is then put into an oven at 80°C for about one hour.

After the above procedures have been repeated many times, a thick layer of CdS microcrystals in the organic media can be obtained. Fig. 1 is a TEM photograph of CdS microcrystals in polymethyl methacrylate. From this photo one can see that the diameters of CdS microcrystals are less than 3×10^{-8} m. CdS micro-
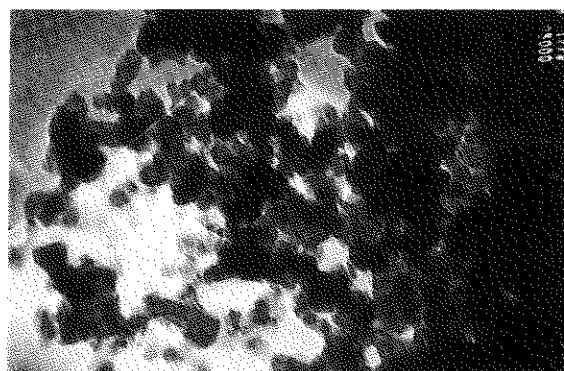

Fig. 1. TEM photograph of CdS microcrystals in polymethyl methacrylate, magnification $\times 10^5$.

crystals in polystyrene and polyvinyl alcohol give similar results.

3. Raman scattering spectra

Fig. 2 is the Raman scattering spectra of CdS microcrystals in polymethyl methacryslate, polystyene and polyvinyl alcohol. The peak located between the LO and TO vibrations can be identified with the surface vibration modes of CdS microcrystals. From this figure one can see that the frequency of the surface vibration depends on the dielectric constant of the medium in which the microcrystals are embedded.

The experimental results are interpreted using ref. [5] which gives the differential equation for the polarization vector for any uniformly shaped dielectric system as:

$$\chi_n^{-1}(\omega)\varepsilon_n\nabla \cdot P_n(r) = 0, \tag{1}$$

$$\chi_n^{-1}(\omega)\nabla \times P_n(r) = 0, \tag{2}$$

where the subscript n is the orderal of the dielectric layer, and $\chi(\omega)$ and $\varepsilon_n(\omega)$ are the dielectric susceptibil-
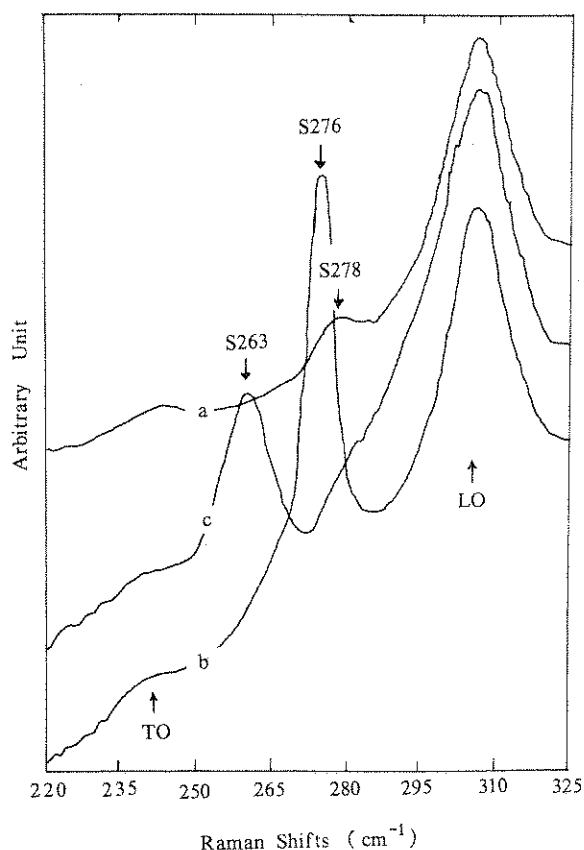

Fig. 2. Raman scattering spectra of CdS microcrystals in organic material: (a) in polystyrene; (b) in polyvinyl alcohol; (c) in polymethyl methacrylate.

ity and dielectric function of the dielectric layer n, respectively. Because the microcrystals distributed randomly in another dielectric can be approximately regarded as a dielectric sphere of radius R_1 embedded in a concentric dielectric spherical shell with outer radius R_2 ($R_2 \to \infty$), the equations (1) and (2) are also suitable for this spherical body. Because the polarization vector is irrotational, the vector of polarization P_n can be expressed in terms of the gradiant of a simple scalar potential $U_n(r)$. Then from eqs. (1) and (2) we have the Laplace equation:

$$\nabla^2 U_n(r) = 0. \tag{3}$$

Using spherical coordinates, the solution of this equation gives

$$P_1(r) = \nabla_r\left[\sum_{l,m} A_{lm}\frac{r^l}{R_s^{l+1}}Y_{lm}(\hat{r})\right], \qquad r < R_s, \tag{4}$$

$$P_2(r) = \nabla_r\left\{\sum_{l,m} B_{lm}\frac{R_s'}{r^{l+1}}Y_{lm}(\hat{r})\right\}, \qquad r > R_s, \tag{5}$$

where $Y_{lm}(\hat{r})$ are the spherical harmonics, the subscripts 1 and 2 refer to the CdS sphere and the outer concentric dielectric spherical shell respectively, and subscript s refers to the boundary of the CdS sphere. From the boundary condition $E_\parallel^1 = E_\parallel^2$, $D_\perp^1 = D_\perp^2$, we have

$$\left[\varepsilon_0\chi_2(\omega)\right]^{-1}P_{\parallel,1} = \left[\varepsilon_0\chi_2(\omega)\right]^{-1}P_{\parallel,2}, \tag{6}$$

$$\left[\varepsilon_0\chi_1(\omega)\right]^{-1}\varepsilon_1(\omega)P_{\perp,1} = \left[\varepsilon_0\chi_2(\omega)\right]^{-1}\varepsilon_2(\omega)P_{\perp,2}. \tag{7}$$

Applying the condition for the existence of a nontrivial solution we have the dispersion relation:

$$l\varepsilon_1(\omega) = -(l+1)\varepsilon_2(\omega), \tag{8}$$

where $l = 1, 2, 3$, etc. Because the outer dielectric is an organic material, $\varepsilon_2(\omega)$ is not the dielectric function, but is the real dielectric constant ε_2 of the organic material, and

$$\varepsilon_1(\omega) = \varepsilon_{\infty 1}\left(\omega_{L1}^2 - \omega_s^2\right)/\left(\omega_{T1}^2 - \omega_s^2\right), \tag{9}$$

where $\varepsilon_{\infty 1}$ is the high frequency dielectric constant of the microcrystals, ω_{L1}, ω_{T1} and ω_s are the vibration frequencies of LO, TO and surface phonons of the microcrystals, respectively. Inserting (9) into (8) gives

$$\omega_s = \left[\frac{\varepsilon_{\infty 1}l\omega_{L1}^2 + \varepsilon_2(l+1)\omega_{T1}^2}{l\varepsilon_{\infty 1} + \varepsilon_2(l+1)}\right]^{1/2}. \tag{10}$$

It is shown that there is only one frequency of surface vibration located between ω_{T1} and ω_{L1}. For the comparison with the experimental results the calculated values from eq. (10) are given in table 1 ($l = 1$ and l = very large).

One can see from table 1 that the calculated values basically agree with the experimental results. The small difference between the calculated values and the experi-

Table 1
The calculated va
microcrystal in org
cm^{-1}, $\varepsilon_{\infty 1}$ = 5.8

Organic material	D cc	ε_2
Silicate glass	2.	
Polystyrene	2.(	
PVA	3.(	
Polymethyl methacrylate	4.(	

[a] Taken from ref. taken to be n^2 (

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$$r < R_s, \qquad (4)$$

$$r > R_s, \qquad (5)$$

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Table 1
The calculated values and the experimental results for CdS microcrystal in organic media CdS: $\omega_{T1} = 239$ cm^{-1}, $\omega_{L1} = 306$ cm^{-1}, $\varepsilon_{\infty1} = 5.8$

Organic material	Dielectric constant ε_2	Experimental values ω_s (cm^{-1})	Calculated values ω_s (cm^{-1})
Silicate glass	2.1 [a]	292	283–290
Polystyrene	2.6	278	276–286
PVA	3.0	276	273–284
Polymethyl methacrylate	4.0	263	269–281

[a] Taken from ref. [4], the dielectric constant of the glass is taken to be n^2 (n = refractive index).

mental results may be attributed to the facts that the microcrystals are not completely spherical and that the dielectric constants ε_2 of the organic material are not exactly known.

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