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Structure and optical properties of CdTe microcrystallites in CaF₂

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Abstract. Using a pulsed-laser-beam and electron beam coevaporation method, we have embedded CdTe microcrystallites into a CaF₂ thin film in a high-vacuum chamber. Nanometre-scale CdTe particles embedded in the CaF₂ thin film are observed in transmission electron micrographs. The blue shifts of the absorption bands and in particular the corresponding photoluminescence bands are easily obtained in the CdTe-microcrystallite-doped CaF₂ thin film. A broadened optical phonon Raman structure and low-wavenumber acoustic phonon structure are also obtained. These results are considered to be a size effect of the CdTe microcrystallites.

1. Introduction

Many investigations [1–16] on mesoscopic semiconductor crystallites have been carried out because of their unusual physical properties, e.g. the large non-linear susceptibility with fast response expected according to theoretical work. In this research, we use the coevaporation growth technique to embed semiconductor microcrystallites into a matrix. This growth technique may have great advantages over other techniques.

(1) The material selection for the semiconductor and matrix has no special limitations, which may be good for finding favourable interfaces between semiconductor microcrystallites and matrix.

(2) We can obtain a high concentration of semiconductor microcrystallites and hence a large $\chi^{(3)}$ is expected.

(3) In the form of thin films, these materials may be easy to develop into devices.

In our present research, we choose CdTe as a semiconductor microcrystallite material. CdTe has a cubic zinc sulphide crystal structure. Its band gap E_g is 1.60 eV at liquid-nitrogen temperature, and its exciton Bohr radius a_B is 73 Å. CdTe has the largest exciton Bohr radius of the II–VI semiconductors already grown as microcrystallites, hence, quantum confinement effects can occur even when the microcrystallite is of a larger size. We chose CaF₂ as the matrix material. CaF₂ has a cubic fluorite crystal structure. Its band gap E_g is 12 eV which is much larger than that of CdTe. The wide transmission band of CaF₂ leads to a multitude of optical applications.

We know from the references that it is not easy to observe the photoluminescence of CdTe microcrystallites which are usually embedded in glass. However, in our present research, we obtain the photoluminescence of CdTe microcrystallites in CaF₂ without much difficulty.

The present paper is organized as follows. First, in section 2, we describe the sample preparation. Then, in section 3, we show a transmission electron micrograph and an electron diffraction pattern of a sample. These data demonstrate that we can successfully obtain nanometre semiconductor particles using our sample preparation system. In section 4, we give the optical absorption and photoluminescence spectra of some samples. In section 5, we give the Raman spectra and draw conclusions in section 6.

2. Sample preparation

The sample growth chamber is shown in figure 1. A powerful turbomolecular pump was used to generate a vacuum in the growth chamber (base pressure, about 10^{-9} Torr). The CdTe target was evaporated using a pulsed excimer KrF laser with a maximum pulse energy of 50 J cm^{-2} , and the CaF_2 target was evaporated by an electron beam. The film growth rate and the thickness were controlled with a quartz crystal monitor. The substrate was heated with a halogen lamp, and the temperature was maintained with a temperature controller. The pulsed-laser evaporation technique is a good method for thin film growth. For example, the pulsed-laser evaporation technique has been used to grow good-quality II-VI compound superlattices [17]. To grow a good-quality thin film, a high-vacuum chamber was needed. In the work of Bujor and Vook [18], it was found that, only when the vacuum pressure was less than 10^{-6} Torr can a CaF_2 epitaxial single-crystal film be produced on a NaCl substrate. In our experiments, the residual gas pressure during evaporation was about 5×10^{-7} Torr; the evaporation rate was controlled at about 10 \AA s^{-1} ; the thickness was controlled at about $1 \text{ }\mu\text{m}$; the substrate temperature was controlled at 300°C , and the substrates were a CaF_2 single crystal or glass.

3. Transmission electron microscopy and electron diffraction

Using transmission electron microscopy (TEM), we can directly observe whether we can embed CdTe microcrystallites into CaF_2 . A special thin film was prepared on a KCl single-crystal substrate for TEM measurement. The film was separated from the KCl substrate in water for the measurement. The bright-field electron micrograph and the electron diffraction pattern of the CdTe-doped CaF_2 thin film are shown in figures 2(c) and 2(a), respectively. The diffraction pattern shows that the CaF_2 thin film is a (100) epitaxial single-crystal film. The diffraction spots of CdTe and CaF_2 are indicated by small and large circles, respectively, in figure 2(b). In the diffraction pattern, we can see, even though not very obviously, the diffraction spots of CdTe, and they have a zincblende-type structure. In figure 2(c) the small particle of CdTe cannot be clearly distinguished. However, in the dark-field electron micrograph (shown in figure 3) taken with the arrowed diffraction spot of CdTe in figure 2, we can see many white nanometre spots which are ascribed to CdTe particles of diameter about $50\text{--}100 \text{ \AA}$. On comparison with materials such as CuCl, CdTe has a small effective electron mass, and the $50\text{--}100 \text{ \AA}$ size is small enough to investigate their quantum size effects, e.g. the blue shift of the absorption band will be about $0.1\text{--}0.5 \text{ eV}$. Nanometre CdTe microcrystallites in CaF_2 are observed in TEM photographs. Thus, we can use our system and the coevaporation method to grow nanometre semiconductor particles into the matrix.

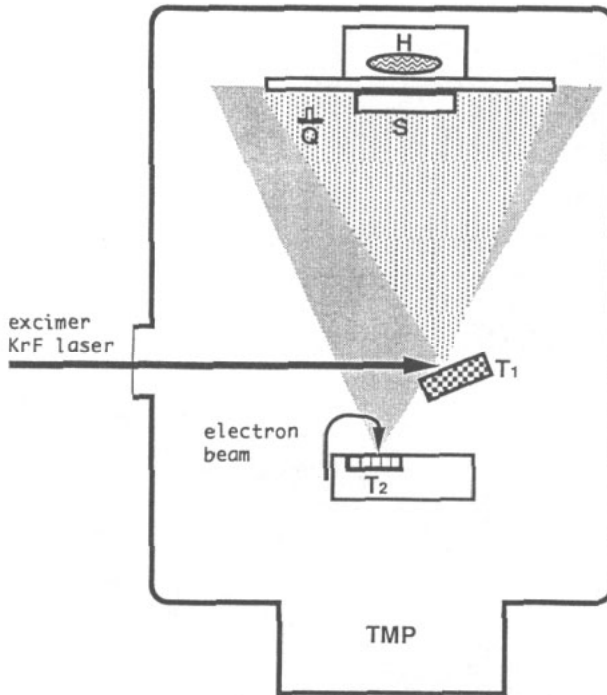


Figure 1. The sample growth chamber system: TMP, turbomolecular pump; T₁, CdTe target evaporated by excimer KrF laser technique; T₂, CaF₂ target evaporated by the electron beam method; Q, quartz sensor; S, substrate; H, halogen lamp heater controlled with a temperature controller.

4. Absorption and photoluminescence spectra

The optical properties of the semiconductor microcrystallites are of interest. To investigate the optical absorption, a film several thousand ångströms thick which is much thicker than the film prepared for TEM measurement is necessary. The blue shift of the optical absorption band and its corresponding blue shift of photoluminescence are used to identify small semiconductor microcrystallites. In the following, we shall describe the optical absorption and photoluminescence of the CdTe-doped CaF₂ thin films.

In figure 4 the optical absorption and photoluminescence spectra of some samples at 77 K are shown. Here the excitation light for photoluminescence is the 4579 Å line of an Ar⁺ laser. Figure 4(a) shows the absorption and photoluminescence spectra of a CdTe thin film grown on a glass substrate. In figure 4(a), a clear exciton luminescent peak and an absorption band edge are observed at 1.6 eV. On the lower-energy side of the exciton luminescence peak, there is a very broad and strong luminescence structure, which is considered to be the luminescence coming from crystal defects and impurities. The other spectra in figure 4 are spectra of the CdTe-doped CaF₂ thin film grown on CaF₂ single-crystal substrates. In figures 4(b)–(d), the blue shift of the absorption band from that of the CdTe thin film and the corresponding blue shift of the photoluminescence band are clearly shown. The growth conditions of the samples whose spectra are given in figures 4(b)–(d) have different excimer laser powers. That is, the laser power increases in the order of figures 4(b), 4(c) and 4(d). The laser power may be important for the size of the CdTe

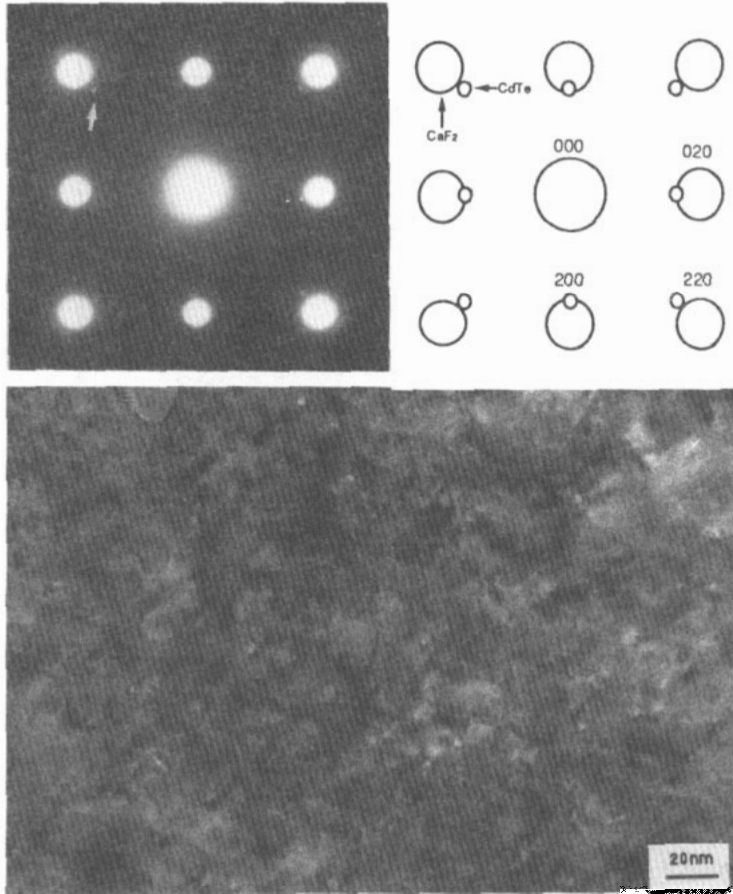


Figure 2. (c) The bright-field electron micrograph and (a) the electron diffraction pattern of a CdTe-doped CaF_2 thin film. (b) The diffraction spots of CdTe and CaF_2 are indicated by small and large circles, respectively.

microcrystallites. The stronger the laser power, the larger are the CdTe microcrystallites. From figures 4(b)–4(d), we note the following points. In figure 4(b), the photoluminescence peak is at 5695 \AA ; the absorption peak is at about 5690 \AA . Photoluminescence has almost no Stokes shift. In figure 4(c), the photoluminescence peak is at about 6920 \AA ; the absorption peak is at about 6530 \AA . In this case, the Stokes shift is about 110 meV . In figure 4(d), the photoluminescence peak is at about 7320 \AA ; the absorption peak is at about 6700 \AA . The Stokes shift is about 155 meV . The blue shift of the absorption band relative to that of bulk CdTe shown in figure 4(a) is given in the effective-mass approximation by [4]

$$E = \hbar^2/2\mu R^2 - 1.786q^2/2\pi\epsilon R - 0.248E_x$$

where E is the blue shift of the exciton formation energy, μ the reduced mass, R the radius of particles, q the charge of electron, ϵ the dielectric constant and E_x the binding energy of the exciton of bulk CdTe. The average radii of CdTe microcrystallites for figures 4(b), 4(c) and 4(d) are estimated to be 27 \AA , 36 \AA and 40 \AA , respectively. Here we assume the microcrystallites to be spherical.

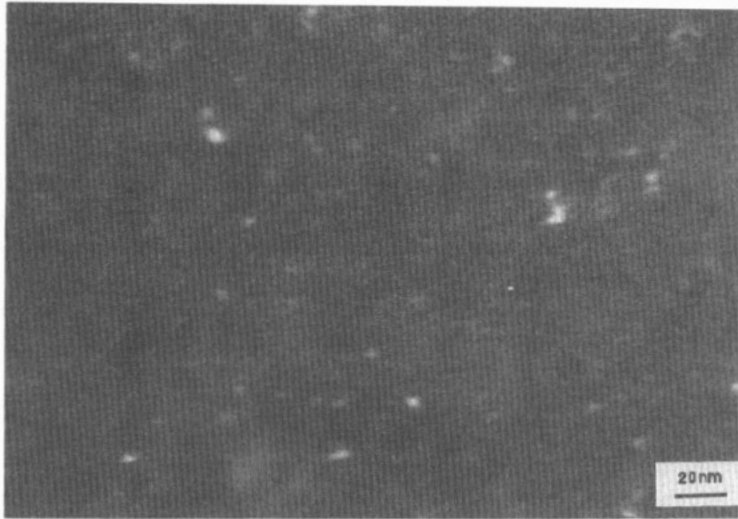


Figure 3. The dark-field electron micrograph of the arrowed diffraction spot of CdTe in figure 2.

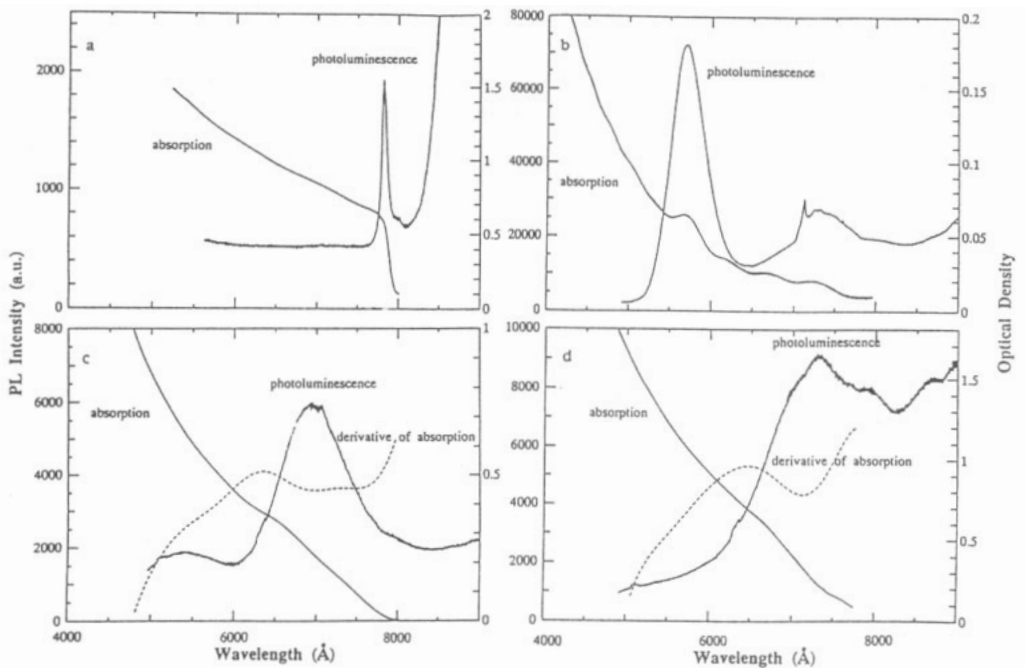


Figure 4. The photoluminescence and absorption spectra of some samples. (a) The absorption and photoluminescence spectra of a CdTe thin film grown on a glass substrate. The other spectra are from a CdTe-doped CaF₂ thin film grown on CaF₂ single-crystal substrates. (b)–(d) Spectra for increasing excimer laser power. The broken curves in (c) and (d) are the wavelength derivative of the absorption spectra.

For the semiconductor microcrystallites, the optical absorption properties are dominated

by quantum size effects. The luminescence properties are particularly sensitive to the surface defects which are associated with the surface atom situation. These surface defects result in Stokes shifts, which can be controlled by surface chemistry [7, 9]. On the other hand, when the concentration of the microcrystallites is high, the larger microcrystallites can reabsorb the photoluminescence of smaller microcrystallites, which also results in Stokes shifts.

The Stokes shift may give some information about the surface of low-concentration CdTe microcrystallites. For the sample in figure 4(b), there is almost no Stokes shift, which may indicate that the surface ions of CdTe microcrystallites are passivated by CaF₂, just as those of CdS microcrystallites are passivated by ammonia in the work of Wang *et al* [9].

For the samples in figures 4(c) and 4(d), the ablation laser power is much higher than that for the sample in figure 4(b). When the laser power is high, the concentration of the CdTe particles may also be high, and these high-concentration small particles may join together to form larger particles in the atmosphere of CaF₂. In the joined larger particles, the interfaces between these small particles may have some defects which cannot be passivated by the matrix CaF₂. The high concentration of microcrystallites will increase the larger microcrystallite reabsorption of photoluminescence of smaller microcrystallites. In figures 4(c) and 4(d) the reabsorption may result in the Stokes shifts because the defects result in larger Stokes shifts. The defects which cannot be passivated by the matrix CaF₂ may contribute to the luminescence above 8000 Å in figure 4(d). Thus, considering the reabsorption effect, we may understand that, when the laser power is higher, we have a larger Stokes shift.

In figure 4(b), the absorption spectra have some oscillations, which may result from interference. In order to show the absorption structure clearly, the wavelength derivative of the absorption spectra are shown in figures 4(c) and 4(d). The oscillations in figures 4(c) and 4(d) are not caused by the interference because the interval in the oscillations is larger than that in figure 4(b) and is inversely proportional to the film thickness which in the samples in figures 4(c) and 4(d) is three times that in figure 4(b); because the optical densities of the samples in figures 4(c) and 4(d) are very large (much larger than that of the sample in figure 4(b)), this makes it difficult for interference to occur. Therefore the shoulder structures at about 6530 Å and 6700 Å in the absorption spectra in figures 4(c) and 4(d), respectively, result from the quantum size confinement effect.

In the photoluminescence experiment, it is found that the films grown on the CaF₂ single-crystal substrates give stronger photoluminescence than those grown on glass substrates. This may be reflected by the influence of the CaF₂ matrix on the CdTe microcrystallites. The CaF₂ grown on a CaF₂ single-crystal substrate may be epitaxial, while those grown on glass may be random. The former film has a special CaF₂ crystalline orientation. As we know from the references, it is not easy to observe the photoluminescence of CdTe microcrystallites. The CdTe microcrystallites are usually embedded in glass. The condition of the surface of the microcrystallite is very important for photoluminescence [7, 9]. The surface of the CdTe microcrystallites in glass may be too poor to give photoluminescence. The CdTe microcrystallite in CaF₂ grown on the CaF₂ single-crystal substrate may have a 'better' surface than that grown on the glass substrate. It is very important to improve the surface of the microcrystallite for the realization of the potential applications of microcrystallites.

5. Raman spectra

Raman spectra have been used to investigate semiconductor microcrystallites. So far, the following characteristics of Raman spectra of semiconductor microcrystallite have been

reported: broadened Raman peaks due to LO phonons [15] and Raman scattering structure at low wavenumbers less than 20 cm⁻¹ because of acoustic phonons [8]. In our samples, we have also observed these phenomena.

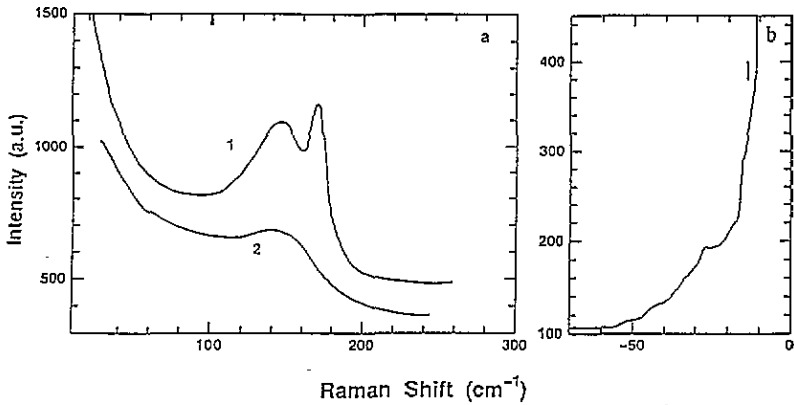


Figure 5. Raman spectra of the sample in figure 4(c). (a) The optical phonon Raman structure: curve 1, spectrum of the sample at liquid-nitrogen temperature; curve 2, spectrum at room temperature. (b) The low-wavenumber anti-Stokes Raman spectrum of the sample at room temperature.

Figure 5 shows the Raman spectra of the sample in figure 4(c). In figure 5, curve 1 is the Stokes Raman spectrum at liquid-nitrogen temperature, and curve 2 is that at room temperature. For the Raman experiment, the excitation light is the 5145 Å laser line of an Ar⁺ laser. In curve 1, two broad peaks are clearly seen. One is at about 150 cm⁻¹, and the other at about 170 cm⁻¹. The peak at 170 cm⁻¹ may originate from the CdTe LO phonon. The width of the peak is about 20 cm⁻¹ which is much wider than that (4 cm⁻¹) of the bulk CdTe LO phonon. The other broad peak at 150 cm⁻¹ may result from TO phonons. The width is about 50 cm⁻¹, which is much wider than that of the bulk crystal. In curve 2, at room temperature, the two-peak structure due to LO and TO phonons cannot be clearly resolved because the LO-phonon signal is weak. The reason that the width of the CdTe TO phonon is much wider than that of the CdTe LO phonon is not clear and needs further research.

In figure 5(b), the anti-Stokes Raman spectrum in the low-wavenumber region at room temperature is shown. The structure at 25 cm⁻¹ may result from some lattice dislocation on the surface of microcrystallites as there is a strong peak at 25 cm⁻¹ in the Raman spectra of amorphous CdTe [19]. Our optical phonon Raman spectrum is very different from that of the amorphous CdTe. At room temperature, in curve 2 of figure 5(a), our Raman peak is at about 145 cm⁻¹, but the Raman peak of amorphous CdTe [19] is at about 165 cm⁻¹. The crystallinity of CdTe microcrystallites is different from that of amorphous CdTe.

There are two effects which influence the width of the LO phonon Raman peaks. One is the size effect [15], and the other is the lattice dislocation effect [20]. Both effects may contribute to the widths of the LO-phonon Raman peaks. The size effect is perhaps more important because in our photoluminescence experiment we see that our CdTe microcrystallites are of good quality.

In figure 5(b), there is a structure at about 15 cm⁻¹ which may result from the acoustic phonons of small CdTe microcrystallites. The average size of CdTe microcrystallites can

be estimated from the relation [8, 21]

$$r \simeq v/2\omega c$$

where r is the radius, v the velocity of sound, c the velocity of light and ω the acoustic phonon Raman shift. Using $v \simeq 3000 \text{ m s}^{-1}$, we obtain $r \simeq 33 \text{ \AA}$ which is nearly equal to the value (36 \AA) obtained by the effective-mass approximation.

6. Conclusion

Using pulsed-laser ablation techniques, we have doped CdTe into electron-evaporated CaF_2 thin films in a high-vacuum chamber. Using TEM, we directly observed nanometre CdTe microcrystallites in CaF_2 . As a result, we succeeded in growing nanometre-sized crystals of CdTe in the CaF_2 matrix. The blue shifts of the absorption band and the corresponding blue shifts of photoluminescence which is usually difficult to observe are obtained. The broadened optical phonon structures and an acoustic phonon structure near 15 cm^{-1} are also found in the Raman spectrum. We consider that these optical properties are associated with the size effect of the CdTe microcrystallites.

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