Magneto-optical study of quantum confinement in Cd(S,Se) quantum dots

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A well-distinguished excitonic structure of the absorption spectrum of Cd(S,Se) quantum dots (QD) was obtained using magnetic-circular-dichroism measurements. This method enabled us to observe at least four distinct excitonic absorption peaks, which were successfully assigned to heavy-hole and light-hole exciton levels. The assignment was made for the QD with infinite confining barrier, but taking into account electrostatic electron-hole interaction as well as their interactions with the charge polarized at the surface of the QD. The effective radius of the QD estimated from the theoretical calculation was confirmed by the transmission-electron microscopy.

In nanometer-sized semiconducting spheres, also called quantum dots (QD's), electronic states are strongly modified by the three-dimensional confinement of electrons and holes.[1,2] Although the absorption-edge shift has usually been used as evidence of the confinement effect in QD's for a variety of semiconducting materials, observation of plural optical transitions between quantum eigenstates as distinct peaks is needed to confirm the existence of the confinement effect. However, by ordinary optical absorption, photoluminescence (PL), and photoluminescence excitation spectroscopies, it is difficult to observe the optical transitions to higher excited states in the QD. This sometimes causes significant controversy concerning the existence of quantum-confined electronic states. CdS_xSe_{1-x}[Cd(S,Se)] microcrystallites in glass have received specific attention with regard to their extraordinary large and fast nonlinear optical effects,[3] which can be used for optical information and signal processors,[4] and the commercial colored filters containing Cd(S,Se) crystallites have been extensively studied. These optical properties are believed to arise from the quantum confinement of the excitons. Warnock and Awscahlom[5] reported the quantum-size effect in Cd(S,Se) crystallites in commercially available Corning 2-61 colored filter glasses. They observed a large energy shift of the photoluminescence peak relative to bulk energy levels and attributed it to the quantum confinement. Borrelli *et al.*[6] also investigated the optical properties of the Corning colored filter glasses by optical absorption and photoluminescence. They denied the confinement effect in the Cd(S,Se) filter glass and attributed the variations in their optical properties to changes in stoichiometry of the Cd(S,Se) mixed-anion system. Recently, Shum *et al.*[7] observed a distinct infrared-absorption peak of the Cd(S,Se) QD induced with a subpicosecond visible-pump laser pulse, and attributed it to the excitonic transition between the $1S$(hh) (heavy-hole) and $1P$(hh) quantum states. Nomura and Kobayashi[8] applied the modulation electroabsorption spectroscopy to observe resolved exciton peaks in the Cd(S,Se) QD, and attributed two observed peaks to transitions from the highest valence subband and from the spin-orbit splitoff band to the conduction band. In this paper, magneto-optic spectra of the Cd(S,Se) microcrystallites are reported, and the existence of three-dimensionally confined quantum states is discussed.

The band diagram of the bulk Cd(S,Se) crystal is schematically shown in Fig. 1(a). External magnetic field H splits the A, B, and C hole bands as well as the conduction band by the Zeeman effect. The Zeeman splitting energy of each band is given as $g\mu_B m_J H$, where μ_B is the Bohr magneton, m_J is the spin projection quantum number, and g is the respective g value of the conduction band (g_c), the heavy-hole band (g_{hh}), the light-hole band (g_{lh}) and the splitoff hole band (g_{sh}). The g value of the Cd(S,Se) crystal is anisotropic because of its wurtzite structure. Since the c axes of Cd(S,Se) microcrystallites embedded in glass are randomly oriented, their effective g values must be considered to be averaged over the c-axis orientation. When the magnetic field is applied along the light propagation direction (Faraday geometry with $H>0$), the allowed transitions are two circularly polarized σ_+ and σ_- transitions. The σ_+ polarization is

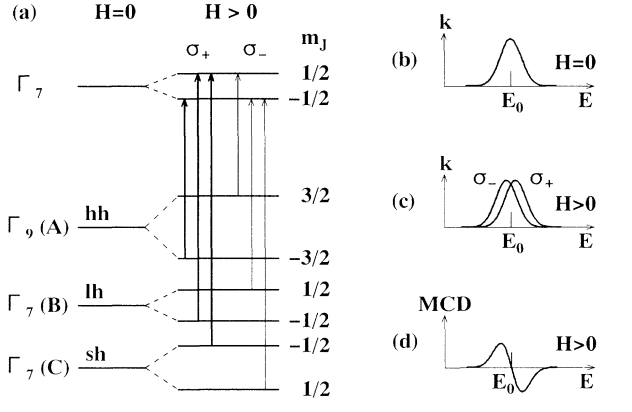


FIG. 1. (a) A schematic energy-band diagram for the Cd(S,Se) bulk crystal under magnetic field. (b) and (c) The optical-absorption coefficient k splits into k_+ and k_- for the two circular polarization σ_+ and σ_- under external magnetic field. (d) The schematic form of the MCD ($=k_- - k_+$) spectrum.

defined so that the electric vector of the light rotates to the left at the time the observer looks at the light source. The optical-absorption spectrum $k(E)$ is split into the spectrum $k_+(E)$ for σ_+ polarization and $k_-(E)$ for σ_- polarization, respectively [Figs. 1(b) and 1(c)]. The splitting energies are $(g_c-3g_{hh})\mu_B H$, $(-g_c-g_{lh})\mu_B H$, and $(-g_c+g_{sh})\mu_B H$ for the transitions between the conduction band and the hh, lh, and sh bands, respectively. In a case where all of the g values are typical values of 2, the splittings are $-4\mu_B H$, $-4\mu_B H$, and 0 for the hh, lh, and sh transitions, respectively. Then the magnetic circular dichroism (MCD), defined as $k_-(E)-k_+(E)$, should show a dispersion-type curve centered at the optical transition energy E_0 for the hh and lh transitions [Fig. 1(d)], and the MCD signal from the sh transition is much smaller than others. The g value depends on the material: $g_c=1.75$, $g_{hh\parallel}=+1.25$ for CdS,[9] and $g_c=0.52$, $g_{hh\parallel}=1.41$, $g_{lh\perp}=0$ for CdSe.[10] The values of g_{lh} and g_{sh} are not available for CdS and CdSe. Furthermore, the possible different oscillator strengths for each optical transition and/or the overlap of plural optical transitions modify the actual MCD spectrum. However, under a reasonable assumption that the g values are not so much different from 2 for nonmagnetic materials, the above simple discussion is useful for interpreting the MCD spectra. Because the modulation technique is applicable to the MCD measurement as described below, the MCD is a sensitive tool for investigating the energy levels in semiconductors.[11]

We measured the MCD spectra of Corning 2-61 filter glass. The sample was ground and polished down to 340-μm thickness. The state of the polarization of monochromatic light from a Xe lamp in a spectrum range from 300 to 730 nm was modulated between the σ_+ and σ_- polarizations with 50 kHz by a photoelastic modulator. The transmitted light was detected by a photomultiplier tube and a lock-in amplifier. A magnetic field up to 1.2 T was applied along the light propagation directions. The photoluminescence spectra of the sample was also investigated by using cw Ar^+ 515-nm laser light. The samples were cooled down to 15 K by using a closed-cycle He-gas refrigerator. A piece from the same filter glass was examined by the transmission electron microscope to measure the diameters of Cd(S,Se) crystallites.

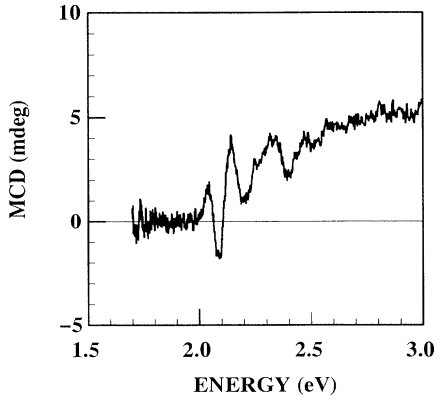


FIG. 2. The MCD spectrum of the 340-μm-thick Corning 2-61 colored filter under magnetic field $H=1$ T at 300 K.

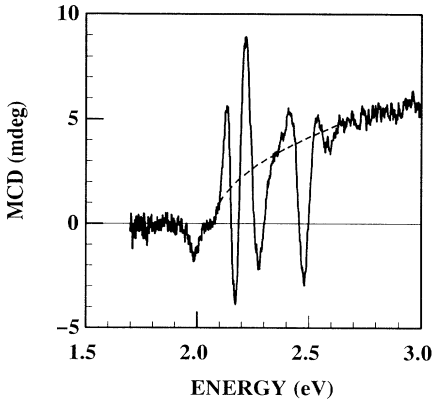


FIG. 3. The MCD spectrum of the 340-μm-thick Corning 2-61 colored filter under magnetic field $H=1$ T at 15 K. The energy dependence of the positive broad background is approximated by the $E^{1/2}$ dependence, as shown by a dashed line.

The MCD spectra at 300 and 15 K are shown in Figs. 2 and 3, respectively. The MCD intensity linearly increases with the magnetic field. Plural peaks on the broad background are observed. The negative peak near 2 eV at 15 K is not observed at 300 K. The other peaks can be observed at 15 and 300 K. These results imply that the origin of the negative peak near 2 eV is different from those of the other peaks. It is certain that the positive broad background comes from the Cd(S,Se) crystal in the glass, but its origin is not understood as of now. We arbitrarily assume a $E^{1/2}$ dependence for the background, as shown by a dashed line in Fig. 3. From the cross points of the MCD curve with the background curve, we determine the optical transition energies at 15 K, as shown in Table I. One more optical transition energy was determined to be 1.94 eV, although the positive wing of the MCD dispersion curve was not clearly observed.

We attribute the optical transition at 2.153 eV to the transition in the microcrystallites, whereas the transition near 1.94 eV arises from the larger bulklike fragments which can exist in the glass.[5] The bulk band gap of 1.94 eV corresponds to the composition of $CdS_{0.28}Se_{0.72}$. These attributions are supported by the photoluminescence spectrum of the sample (Fig. 4). On the broad background due to the deep trap levels, there is a peak at 2.106 eV and a smaller peak at 1.888 eV, which were attributed to the luminescences from the microcrystallites and from the larger bulklike fragments, respectively, by

TABLE I. A comparison of experimental and calculated values for the optical transition energies in Cd(S,Se) crystallites in glass at 15 K.

Experimental	Assignment	Calculated
2.153 eV	hh	2.154 eV
2.247 eV	lh	2.238 eV
2.441 eV	hh	2.450 eV
2.561 eV	lh	2.621 eV

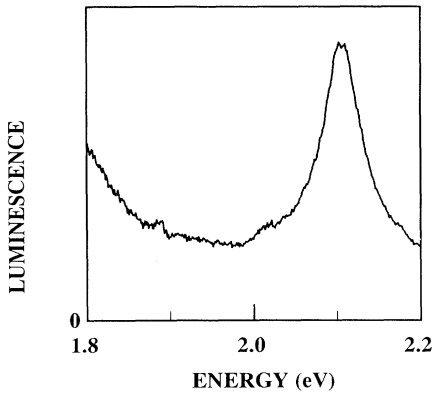


FIG. 4. The photoluminescence spectrum of the 340-μm-thick Corning 2-61 colored filter excited by cw Ar^+ 515-nm laser light at 15 K.

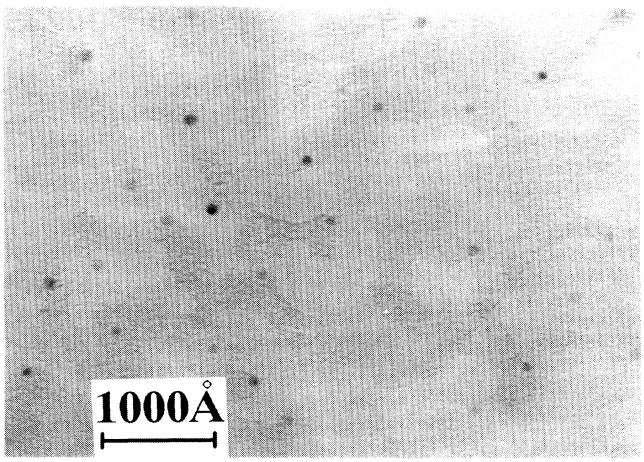
Warnock and Awschalom.[5] It has been reported that in Cd(S,Se)-doped glasses, the usually observed PL peaks under low optical excitation intensity as in this study are redshifted by several tens of meV from the direct electron-hole recombination.[12,13] Each PL peak position of our sample is redshifted by ~ 50 meV from the corresponding energy positions of the MCD spectrum.

The other optical transitions were attributed to the microcrystallites. To avoid excess theoretical problems related to the finiteness of the confining barrier and a coupling of the valence hh and lh bands, we have used for the assignment a well-established model of the spherical QD with an infinite confining potential barrier, but taking into account electrostatic interactions between the electron, the hole, and the charge polarized at the surface of the QD.[14] The excitonic energy levels were calculated independently for hh and lh excitons. We believe that such a simplified model is sufficient to demonstrate the validity of the assignment made.

The calculations were made by the numerical matrix diagonalization method.[15] Twenty-four basis functions were enough to obtain the lowest two optically active exciton levels with an accuracy within some meV. The dielectric constants of Cd(S,Se) and the glass matrix were fixed to be 8.8 (Ref. 5) and 2.55, respectively. As can be seen from Table I, the satisfactory agreement between the experimental and theoretical values has been obtained for the values of the bulk band gap $E_g = 1.96$ eV, the effective radius of the quantum dot $a = 33$ Å, the electron effective mass $m_e^* = 0.145 m_0$, the hh effective mass $m_{\rm hh}^* = 0.95 m_0$, and the lh effective mass $m_{\rm lh}^* = 0.30 m_0$, where m_0 is the electron mass. The values of the effective masses used reasonably agree with the interpolated values of $m_e^* = 0.15 m_0$, $m_{\rm hh}^* = [m_{{\rm hh}(l)} m_{{\rm hh}(t)}^2]^{1/3} = 0.91 m_0$, and $m_{\rm lh}^* = [m_{{\rm lh}(l)} m_{{\rm lh}(t)}^2]^{1/3} = 0.58 m_0$ for $CdS_{0.28}Se_{0.72}$ from the reported values for CdS and CdSe.[7,16,17] A not so good agreement for lh exciton levels in comparison with the hh exciton can be explained by using the idealization of the infinite confining barrier, to which the positions of lh exciton levels are more sensitive than that of hh excitons.

The estimated effective radius has to be compared with the directly measured radius by TEM observation. As shown in Fig. 5, the Cd(S,Se) QD's appear in the TEM micrograph as dark spheres on the background patterns of the density fluctuation and the compositional variation of the matrix glass.[6] The distribution of the radii of 68 dots is well approximated by a Gaussian distribution function with a mean radius of 38 Å and a variance of 7.5 Å. Bearing in mind the large distribution of the radius, the good agreement of the calculated effective radius with the TEM data strongly supports our assignments of the MCD peaks to the transitions between the quantum-sized eigenstates.

It is interesting to note that the MCD peaks from the QD can be clearly observable at both 300 and 15 K, whereas the peak attributed to the bulklike fragments disappears at 300 K. It is well known that the exciton is stabilized in the low-dimensional system. In fact, the enhancement of the MCD intensity is observed in $CdTe/Cd_{1-x}Mn_xTe$ multiple quantum wells.[18] Then the clearly observed MCD signal in the QD implies the



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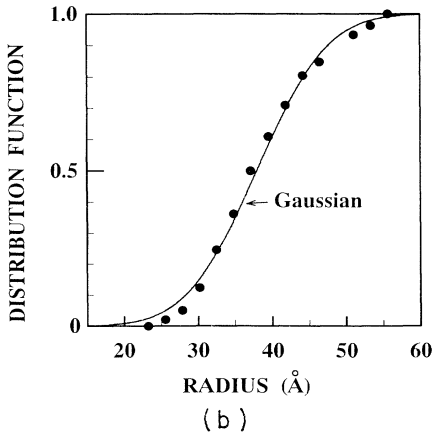

(b)

FIG. 5. (a) A transmission electron micrograph of the Corning 2-61 colored filter. (b) The distribution of the radii of Cd(S,Se) quantum dots, determined from the transmission electron microscope observation.

enhancement of the magneto-optic effect in the QD by the exciton confinement.

In conclusion, the magneto-optic effects of the Cd(S,Se) quantum dots in colored glass are measured. The spectra clearly show the positions of at least the four lowest exciton levels in Cd(S,Se) microcrystallites. The optical transition energies determined from the MCD spectra were compared with the theoretical calculation. The estimated effective radius of the quantum dot was confirmed by the transmission electron microscopy. The above analyses show the usefulness of magneto-optical spectroscopy for investigating the electronic state in quantum dots.

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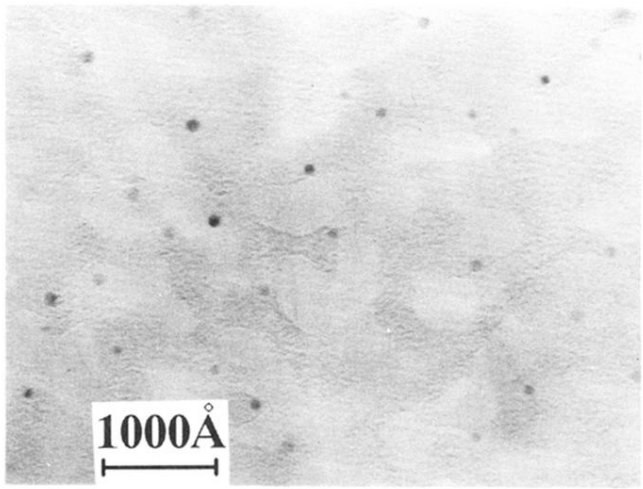

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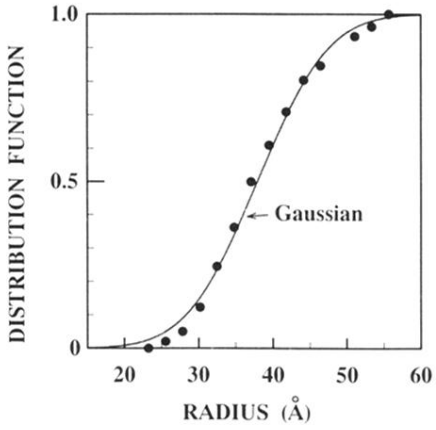

(b)

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