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SIZE QUANTIZATION OF EXCITONS IN PbI_2 MICROCRYSTALLITES

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PbI_2 microcrystallites are embedded into E-MAA copolymer by ion exchange method. Platelet shaped microcrystallites with different thicknesses are prepared for the subsequent heat treatment procedures. In the absorption spectra of these samples, exciton structures due to size quantization appear in the visible and near ultraviolet regions. For the crystallites with more than three layers, the layer thickness dependence of the exciton energy is well explained by the exciton confinement model.

For one and two layer crystallites, however, exciton energies deviate to the lower energy from the theoretical value, and its origin is discussed.

QUANTUM wells, wires and dots in semiconductors have been studied very extensively in recent years under abrupt development of crystal growth techniques. For studying size quantization, a PbI_2 crystal is one of the excellent candidates, since it has a layer type structure and the ultra thin film can be grown. In 1987, absorption spectra of the PbI_2 ultra-thin film evaporated on a cleaved KCl crystal were measured by Goto and Maeda [1], and it was reported that the energies of exciton bands depend on the layer number of the evaporated crystal. Unfortunately, they could not find any structure of the excited states due to the size quantization. Sandroff *et al.* [2] have found three absorption bands in the ultraviolet region of PbI_2 colloids in solutions and concluded that these bands are associated with size quantization within unit layer. Wang and Herron [3] have noticed, however, that these bands are found in I_3^- solutions not containing Pb^{2+} ions, and hence, there is another possibility for the origin.

We have prepared platelet type microcrystallites embedded into organic polymers for the first time, with use of the similar method to that of PbS particles [4] and studied quantum size effect on exciton absorption bands of these microcrystallites with different thicknesses. The polymer used in the present experiments is ethylene methacrylic acid copolymer (E-MAA) supplied from Mitsui du Pont Polychemical Co. The ball-shaped polymer was kept in a vacuum sealed glass ampoule at 170°C for a week with 0.3 mol.% lead acetate tryhydrate Pb $(CH_3COO)_2 3H_2O$. The resultant polymer was a film with the thickness of the order of 0.1 mm. By this procedure, two hydrogen ions in this polymer were exchanged into a lead ion Pb^{2+}. Thus treated polymer films were exposed to HI gas for one hour at 50°C. As a result, the film became yellow which is colour of PbI_2 microparticles. To grow the crystallites, the polymer film was heated up to 80°C in air or immersed into hot water at 80°C, and kept for the time up to 180 min. The crystal size was measured with a transmission electron microscope TEM. For the measurement with TEM, the film was cut into a 100 nm thick one. The photograph was taken at 100 K to avoid heating effect by the electron beam, and one example is shown in Fig. 1. The absorption spectrum of this sample is shown in curve *d* of Figs. 2 and 3, as stated later. One can grow an ultra thin platelet like crystal, of which the *c*-axis is perpendicular to the surface, on a carbon film [1]. In general, the crystal is known to be easy to grow in the stretching direction of the polymer film. From these facts, one may be able to see the edge of the crystal plate in the microphotograph. Hence, the thickness and the lateral diameter of the platelet-like crystallites are directly measured from the photograph. A number indicated in this figure is a layer number of the crystallites. Here, the thickness of the unit layer is 0.7 nm.

For measuring the absorption spectrum, the sample was cooled at 4.2 K and the transmitted light was detected using the combination system of a

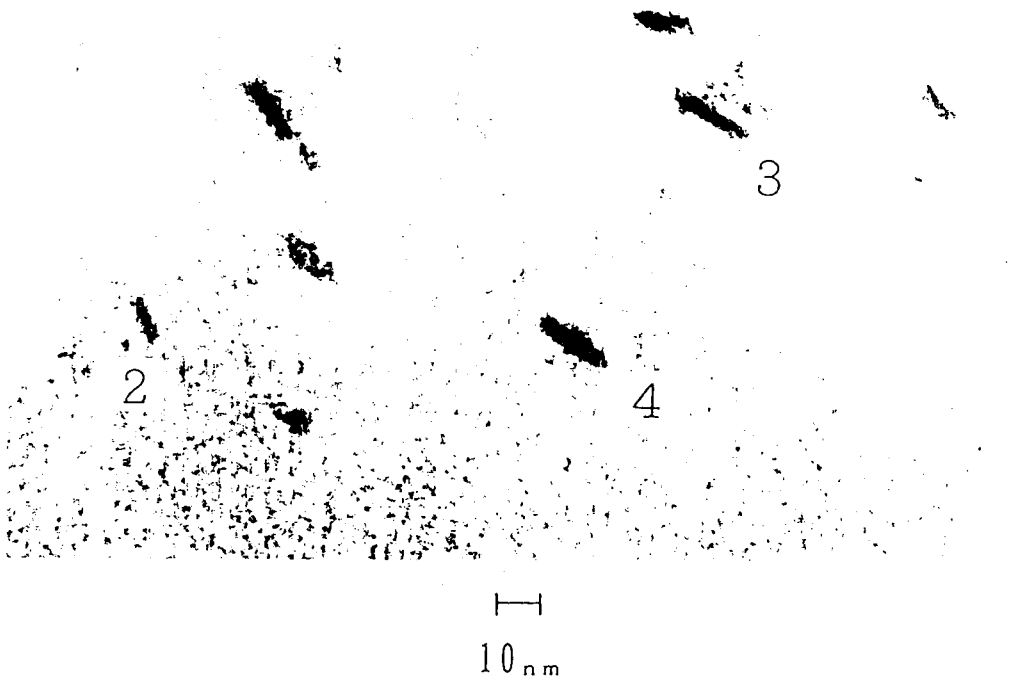

Fig. 1. An electron transmission micrograph of PbI_2 crystallites embedded into an E-MAA polymer at 100 K. The *c*-axes of the PbI_2 microcrystallites are parallel to the photograph. A marked number is that of the layer in the platelet type microcrystallite.

candescent lamp, a Jobin–Yvon U-1000 double monochromator and a picoammeter.

Figure 2 shows the absorption spectra of the PbI_2 crystallites with different heat treatments at 4.2 K. Samples of curves a and b are kept in dry air at 80°C for 20 and 180 min, respectively. Sample c is kept in water vapour at 80°C for 7 min. Samples d, e and f are immersed in hot water kept at 80°C for 20, 60 and 80 min, respectively. It is known from the micrograph that the lateral diameters of samples a and b are 4–6 nm and the thicknesses seem to be one layer. In order from curve b to f, the crystal thickness becomes larger. In the spectrum f, an absorption band appears at 2.54 eV which is close to the energy 2.48 eV of the bulk exciton consisting of the A_4^- conduction electron with the lowest energy and the uppermost A_4^+ valence hole, as assigned by Schlüter and Schlüter [5]. The small energy difference may be caused by the different polytypism or the interaction between the microcrystallite and the surrounding polymer. Another sharp band apears at 3.37 eV which is close to the energy 3.3 eV of the bulk exciton composed of the A_5^-, A_6^- electron and the A_4^+ hole. Hence, it is concluded that both the bands correspond to these excitons in the bulk crystal. A broad band near 3.1 eV is assigned as due to a dipole transition between the lowest conduction and the highest valence bands in general points of the Brillouin zone from the correspondence to the bulk spectrum. The absorption bands at 2.75 eV and 3.48 eV in curves a and b may be exciton bands generated in the thinnest crystallite with unit layer. Bands at 2.63 and 2.59 eV in curves c and d, and a band at 2.56 eV in curve d may be associated with

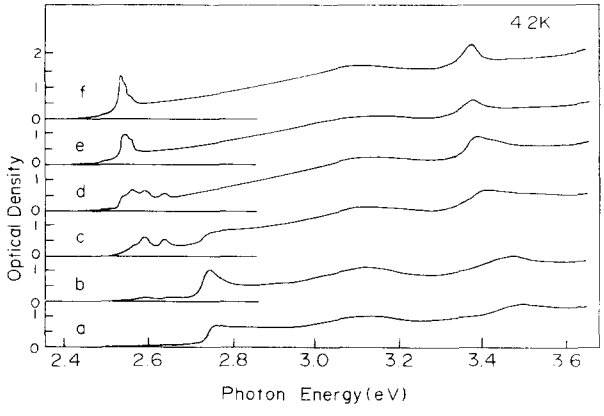

Fig. 2. Absorption spectra of PbI_2 embedded E-MAA polymer films after different heat treatments at 4.2 K. Average crystal thickness increases in order of curves a, b, c, . . . , f.

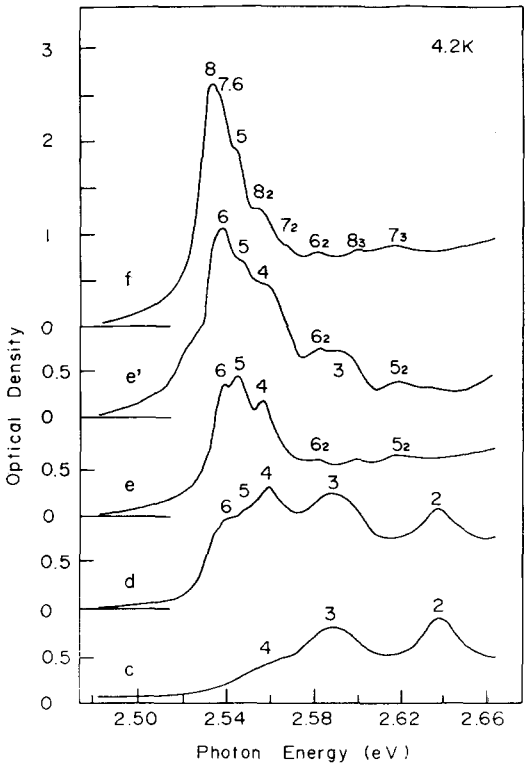

Fig. 3. Detailed spectra of curves c, d, e and f in Fig. 2. Spectrum e' is added to those ones. A layer number of the microplatelet corresponding to the absorption peak is indicated in the spectrum.

excitons in crystallites with two, three and four layers, respectively, from the comparison with the TEM photographs. As seen in this figure, the exciton energy shifts clearly to the higher energy side as the layer number decreases. The exciton band at 3.37 eV in the spectrum of the thickest crystallites also shifts to the higher energy side when the crystal thickness decreases. On the contrary, the broad band near 3.1 eV does not seem to shift. The exciton peak energy due to one or two layers changes by up to 5 meV, sample by sample. The change is probably, caused by the difference in the lateral dimension.

Figure 3 shows detailed absorption spectra of thicker samples around the first exciton band. The second highest curve is a spectrum of a new sample which has a crystal size between samples e and f. A peak indicated by a single number is assigned as due to the ground state exciton of the microcrystallite from the correspondence to exciton bands of the ultra thin film in Ref. [1]. The indicated number is the layer number of the crystallite in which its exciton peak appears. The peak energies of the ground state exciton in Figs. 2 and 3 are plotted in Fig. 4 as a function of L^{-2}, where L is the crystal thickness.

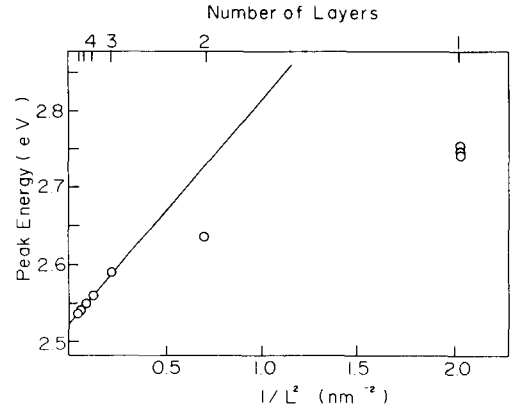

Fig. 4. Peak energies of the absorption bands in Figs. 2 and 3 vs $1/L^2$, where L is the thickness of the microcrystallite. Circles show the experimental points, and a straight line the equation (1) with $p = 1$.

Here, if the exciton is confined in the platelet like crystal and the translational motion is restricted inside the infinite potential well at the crystal boundary in the direction of the c-axis, the exciton energy E is quantized in the effective mass approximation as

$$E = E_B + \frac{\hbar^2}{2M}\frac{\pi^2 p^2}{L^2}, \quad p = 1, 2, 3, \ldots, \qquad (1)$$

where M is the exciton total mass in the direction of the c axis and E_B the exciton energy in the bulk. A straight line in Fig. 4 represents equation (1) when $M = 1.3\,m_0$ as an adjustable parameter, where m_0 is a free electron mass. This mass value is close to that of the evaporated film $1.0\,m_0$ [1], and to the exciton total mass $1.0\,m_0$ in the direction of the c axis of a 4H-type single crystal [6]. However, it is very different from the exciton reduced mass which is smaller than the isotropic hole mass $0.195\,m_0$ estimated from the diamagnetic shift of the bound exciton by Skolnick and Bimberg [7]. For the crystallites of more than three layers, the straight line of $p = 1$ gives a good fit to the experimental points. This coincidence clearly indicates that it is not the motion of the electron and hole, but the translational motion of the free exciton that can be quantized in the crystallites with more than three layers. On the other hand, the exciton energies of the one and two layer crystallites deviate extremely from the theoretical solid line. This large discrepancy suggests breakdown of the effective mass approximation in the wave vector region far distant from the Brillouin zone center. Moreover, it might be suggested that the electronic band structures of these microcrystallites deviate from that of the bulk.

Other smaller peaks in Fig. 3 are assumed to originate from the higher exciton states due to size quantization. Moreover, it is assumed that there

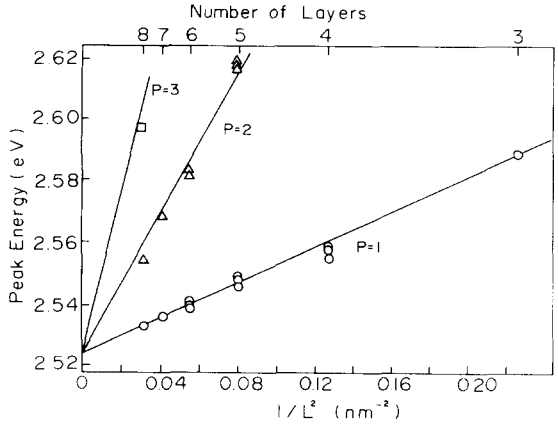

Fig. 5. Peak energies of the absorption bands in Fig. 3 vs $1/L^2$ for the platelets with more than three layers. Three straight lines represent the equation (1) with $p = 1$, 2 and 3.

appear only peaks due to the size-quantized excited state associated with the larger absorption bands to the ground state exciton. Under these assumptions, the assigned peaks are indicated by a number with a subscript. The subscript number shows a value of p in equation (1). However, only a peak at 2.59 eV in curve e cannot be assigned yet. The energies of all peaks assigned in Fig. 3 are plotted in Fig. 5 as a function of L^{-2}. Straight line indicate equation (1) with $p = 1$, 2, 3. These calculated lines agree well with the measured points within the experimental errors. From the good fit, it is concluded that the translational energy of the exciton is quantized and the effective mass approximation is valid for this exciton system.

In summary, ultra thin platelets of PbI_2 crystal are grown inside an organic polymer. One observes the discrete exciton absorption bands due to size quantization and their energies depend on the layer number of the PbI_2 platelets.

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