Optical properties of PbI_2 microcrystallites in E-MAA co-polymer

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Abstract

Chapter I. Introduction

Electronic properties in low-dimensional semiconductors, such as quantum wells, wires and dots, have been studied by various methods. With development of sample preparation methods in recent years, electron confinement in a quasi two-dimensional system has been studied using superlatices of GaAs, ultrathin films of CuCl and so on. In addition to these materials, ultrathin films of layer semiconductors, such as MoS_2, WSe_2, and PbI_2 have been utilized for studying the optical properties of quantum confinement. PbI_2 crystal is one of the typical layer semiconductors and shows phonon which is one of the rigid layer mode in the Raman spectrum.

The optical properties in the visible region of the PbI_2 ultrathin film have been investigated by some groups and in our laboratory, but estimations of the film thickness were not very clear. And the rigid layer mode has not been studied yet, to our knowledge in the ultrathin crystal.

We have prepared PbI_2 ultrathin microcrystallites with various thicknesses in organic polymer, E-MAA. In the resonant Raman spectra, a new line is observed in the acoustic phonon energy region, which is intimately related to the exciton absorption band in the ultrathin microcrystallite with finite number of layers. The phonon energy as a function of the crystal thickness is explained on the basis of a finite chain model. From this analysis, the relationship between the exciton absorption band and the number of layers is confirmed.

Chapter II. Experiment

Microcrystallites of PbI_2 were prepared by exchange of a hydrogen ion of E-MAA copolymer for a Pb^{2+} ion, followed by a reaction with HI gas. The thickness of the crystallites was controlled by heat treatment of the stretched polymer film.

Chapter III. Results and Discussion

From measurement using a transmission electron microscope, the PbI_2 microcrystallite shows platelet-shape. The lateral diameter ranges from 2 to 80 nm, depending on the thickness.

Optical absorption spectra of samples which have different size distribution are observed at 4.2K. Discrete absorption bands are observed around the energy region where the lowest exciton absorption band of bulk PbI_2 appears. As the crystal thickness increases, the highest energy band disappears and new absorption bands appear on the lower energy side. These discrete absorption bands are considered to be due to layer thickness.

In the resonant Raman spectra, a new line is observed in the acoustic phonon energy region, which is intimately related to the exciton absorption band in the ultrathin microcrystallite with finite number of layers. The phonon energy as a function of the crystal thickness is explained on the basis of a finite chain model. From this analysis, the relationship between the exciton absorption band and the number of layers is confirmed. Raman scattering of bulk PbI_2 is forbidden for the compressional mode but allowed for the shear mode from group analysis. However, the Raman line in this experiment is considered to be due to the compressional mode phonon. PbI_2 microcrystallites have symmetry different from that of the bulk crystal because of the finite layers. Hence, the selection rule for Raman scattering of the bulk cannot be applied. Furthermore, both the spatially confined exciton and the deformation potential induced by the lowest energy phonon are expressed by a standing wave with the same length and phase. Therefore, a deformation potential type interaction may be strong.

Using this relation, we interpret the dependence of exciton energy on the layer thickness. Consequently, the thickness dependence of the exciton energy is well explained by the quantum confinement model of the exciton translational motion in the crystallites with more than five layers. In crystallites with thinner layers, however, the exciton energies deviate from the theoretical values.

Chapter IV. Conclusion

In the resonant Raman spectra of PbI_2 microcrystallites in polymer, a new Raman line is observed in the low energy region. This Raman line is considered to be due to the compressional mode phonon. The relationship between the Raman shift and the layer thickness corresponding to the resonant excitation is well described by a linear chain model. From this relation, we obtain the correspondence between the exciton absorption band and the layer number and conclude that the energy shift of the exciton confined in crystallites with more than five layers is well explained by an effective mass approximation. However, the exciton energies in thinner crystallites deviate from the theoretical value. This discrepancy may be mainly caused by transfer from exciton confinement to electron-hole confinement.