Uniaxial Stress Effects on Exciton Spectra in PbI_2 Thin Film and $\text{PbI}_2/\text{CdI}_2$ Superlattice

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Uniaxial stress effects on exciton spectra in PbI_2 thin film and $\text{PbI}_2/\text{CdI}_2$ superlattice at 77K are investigated for the first time. In PbI_2 thin film the observed exciton absorption peaks are found to have a pressure coefficient of $-150 \pm 5 \text{ meV/GPa}$. This value is different from that under hydrostatic pressure in bulk material and the difference reflects the smaller volume compression by the uniaxial stress. In $\text{PbI}_2/\text{CdI}_2$ superlattice the uniaxial stress gives a large reduction of the well width and then yields a pressure coefficient of the exciton peak, $-125 \pm 10 \text{ meV/GPa}$, being smaller in magnitude than that in thin film.
 [$\text{PbI}_2/\text{CdI}_2$ superlattice, quantum well, exciton energy, uniaxial stress]

1. Introduction

Optical measurements in semiconductors under uniaxial stress as well as hydrostatic pressure yield much information on electron and phonon states. For layered materials, the application of a uniaxial stress causes a sample damage easily and then the investigation of optical properties in these materials under a uniaxial stress is difficult and has been done very little.

In layered metal iodide crystals of PbI_2 and CdI_2 , an interaction between layers arises from a van der Waals force, and then lattice constants are easily compressed by applied pressure.[1] This brings about the large change of the optical transition energy due to an exciton (exciton energy) in PbI_2 under hydrostatic pressure.[2] The different pressure dependence is expected to appear, if the uniaxial stress is applied to the material.

Recently we have prepared $\text{PbI}_2/\text{CdI}_2$ superlattices. In this system, quantum confinement effects of an exciton appear clearly: an exciton energy becomes higher with a decrease in the well width.[3] When the uniaxial stress is applied to this system the large change for confinement states may occur because of the large compression to the c -axis direction. In this paper we present results of optical absorption measurements in PbI_2 thin film and $\text{PbI}_2/\text{CdI}_2$ superlattice under the uniaxial stress for the first time. The pressure dependence of the exciton energy in these systems under the uniaxial stress is discussed.

2. Experimental Procedure

Figure 1 shows a schematic illustration of a sapphire anvil system for optical measurements under a uniaxial stress. In order to perform uniaxial stress experiments, a PbI_2 thin film with $\sim 1000\text{\AA}$ thickness and a $\text{PbI}_2/\text{CdI}_2$ superlattice were evaporated on the inner face of a sapphire anvil by using the hot wall epitaxy. Because of the large elastic stiffness of a sapphire the pressure on the evaporated films remains uniaxial.[4] The sapphire anvil with the flat of 1.0mm ϕ in a diameter and the phosphor bronze gasket with 0.5mm thickness were used. The stray light, caused by cracks in samples under pressure, is

necessary to be removed and thus we devised the gasket to have the two-step hole with different sizes: 0.2 and 0.6mm ϕ in diameters.

To perform optical absorption measurements under the uniaxial stress at 77K, the anvil cell with a coaxial bellows device is set into a cryostat.[5] In this apparatus, the uniaxial stress to the c -axis direction in samples can be obtained by the high-pressure helium gas, introduced to the bellows device. Liquid nitrogen was used as a pressure medium. The uniaxial stress was monitored by the spectral shift of the ruby R_1 luminescence line by Ar laser excitation.[6] There is little distribution of pressure in the gasket hole, since the width (FWHM) of R_1 luminescence of $0.7\text{\AA}$ changes little under the uniaxial stress, though some pieces of ruby are set in the center and the end position in the gasket hole. The optical transmission measurements were performed with a halogen lamp and a Jobin Yvon monochromator provided with a photomultiplier. In our experimental set up optical measurements can be performed under the uniaxial stress up to 1.5GPa .

Fig. 1. Schematic illustration of a sapphire anvil system for optical measurements under the uniaxial stress. In order to perform uniaxial experiments, samples are evaporated on the inner face of a sapphire anvil.

3. Results and Discussions

Figure 2 shows typical optical transmission spectra under the uniaxial stress in the PbI_2 thin film. In the spectrum at ambient pressure we see the optical absorption peak due to an exciton transition at 2.550 eV. Upon the application of the uniaxial stress the absorption peak goes to lower energies and its intensity slightly decreases. Only a small intensity reduction under the uniaxial stress shows our pressure experimental system works very well for optical measurements under a uniaxial stress.

Exciton energies in the PbI_2 thin film and the $\text{PbI}_2/\text{CdI}_2$ superlattice as a function of pressure are plotted in Fig. 3. Firstly, we discuss the result of the PbI_2 thin film. The pressure coefficient of the exciton energy in the PbI_2 thin film is obtained to be -150 ± 5 meV/GPa; this value is smaller in magnitude than the value -168 meV/GPa under hydrostatic pressure in bulk PbI_2 [2]. The negative pressure shift of the exciton energy originates from an expansion of valence (cation 6s state) and conduction (cation 6p state) bands width by pressure. This comes from the increase in the overlap of wave functions in valence and conduction states by a decrease in the volume of samples under pressure. From the values of the elastic moduli in PbI_2 [1], we estimate the values of volume compressibilities, 3.51×10^{-2} /GPa under the uniaxial stress and 6.46×10^{-2} /GPa under the hydrostatic pressure, respectively. Thus it is considered that the smaller volume compression in PbI_2 under the uniaxial stress yields smaller pressure shift of the exciton energy than that under the hydrostatic pressure.

Next $\text{PbI}_2/\text{CdI}_2$ superlattice is discussed: the system belongs to the type-I superlattice, where PbI_2 and CdI_2 constitute the well and barrier layers, respectively, as seen in Fig. 4. In superlattices with the well width less than 50 Å, the large higher energy shift of the exciton energy appears because of the large change of electron and hole subband energies. In the well width larger than 100 Å the energy change for the subband states are much smaller and then the exciton energy becomes closer to that in PbI_2 thin film.

In the present $\text{PbI}_2/\text{CdI}_2$ superlattice the exciton energy appears at 2.590 eV under atmospheric pressure, as seen in open circle in Fig. 3. From this energy position and the curve of the exciton energy as a function the well width in $\text{PbI}_2/\text{CdI}_2$ superlattices [3], the well width of the present superlattice is assigned to be 49 Å thickness.

The uniaxial stress dependence of the exciton energy in $\text{PbI}_2/\text{CdI}_2$ superlattice is shown in Fig. 3. The exciton energy goes to lower energies with the increase in the uniaxial stress, being similar to that in PbI_2 thin film. The pressure coefficient of the exciton energy, -125 ± 10 meV/GPa, is obtained. This value is smaller in magnitude than the value of -150 ± 5 meV/GPa in the thin film. The difference between two pressure coefficients in the superlattice and the thin film is $+25$ meV/GPa; the positive energy shift of the exciton energy in superlattice occurs under the uniaxial stress. This shift is considered to reflect characteristic pressure dependence in $\text{PbI}_2/\text{CdI}_2$ quantum well system. The uniaxial stress produces the

Fig. 2. Optical transmission spectra in PbI_2 thin film under the uniaxial stress of 0.1MPa, 0.24 and 0.67GPa at 77K. The exciton absorption peak shifts to lower energies with the increase in pressure.

Fig. 3. Uniaxial stress dependence of the exciton energies in PbI_2 thin film and $\text{PbI}_2/\text{CdI}_2$ superlattice. The pressure coefficients of the exciton energy are obtained to be -150 ± 5 meV/GPa in PbI_2 and -125 ± 10 meV/GPa in $\text{PbI}_2/\text{CdI}_2$ superlattice, respectively.

Fig. 4. Schematic illustration of an energy profile of the quantum well in $\text{PbI}_2/\text{CdI}_2$ superlattice at an ambient pressure and a uniaxial stress. The decrease in the well width by the uniaxial stress produces the change of the electron and the hole subband energies in the superlattice.

decrease in the well width and the large change of the electron and the hole subband energies, resulting in the positive pressure shift of the exciton energy in superlattice.

Here we briefly discuss this positive pressure shift in more details. The positive shift of the exciton energy in superlattice under the uniaxial stress can be roughly estimated from the data of elastic moduli. In the uniaxial stress condition, the compressibility to the c -axis in PbI_2 is calculated to be $7.5 \times 10^{-2}/\text{GPa}$. The well layer of PbI_2 in the superlattice is considered to be compressed in the same way as in bulk PbI_2 . For instance, the well width 49 Å at ambient pressure becomes 45.3 Å at 1 GPa uniaxial stress. An exciton energy becomes higher with the decrease in the well width at ambient pressure in the superlattice: when the well width changes from 49 Å to 42 Å, i.e., the well width in PbI_2 decreases by one monolayer, the exciton energy is estimated to increase by 22 meV from the curve of the exciton energy versus the well width[3]. Then the value of the positive energy shift by the uniaxial stress of 1 GPa in superlattice with the 49 Å well width at ambient pressure is estimated to be 12 meV. This value roughly agrees with the experimental result of 25 meV. Thus we conclude that the application of the uniaxial stress to $\text{PbI}_2/\text{CdI}_2$ quantum wells yields the decrease in the well width and then the increase in energy separation between an electron and a hole subband states, as seen in Fig. 4. This produces the smaller pressure coefficient of the exciton energy in magnitude in the superlattice than that in the PbI_2 thin film.

In summary, for the first time, we performed optical measurements in PbI_2 thin film and $\text{PbI}_2/\text{CdI}_2$ superlattice under the uniaxial stress by using a direct evaporation on the inner face of a sapphire anvil. In the PbI_2 thin film the pressure coefficient of the exciton energy, $-150 \pm 5 \text{ meV/GPa}$, is obtained. In the $\text{PbI}_2/\text{CdI}_2$ superlattice the application of the uniaxial stress to the c -axis produces the smaller pressure shift in the exciton energy: large decrease in the well width brings the change of the

electron and the hole subband energies and the exciton energy in superlattice.

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