Dielectric confinement effect on excitons in PbI4-based layered semiconductors

X. Hong, T. Ishihara,* and A. V. Nurmikko

Division of Engineering and Department of Physics, Brown University, Providence, Rhode Island 02912
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By varying the dielectric environment in new PbI4-based layer-type perovskite compounds, we have demonstrated directly the contribution by dielectric confinement to the exciton binding energy in three such "natural-quantum-well" semiconductors. With different dielectric environment, exciton binding energies of 320, 220, and 170 meV have been observed, dominated by the dielectric confinement. In terms of the conventional size-related electronic confinement, two of the materials represent monolayer PbI4 quantum wells while the third corresponds to a bilayer case, with a corresponding reduction in the electronic confinement. From theory, including the dielectric confinement effect, the effective mass of the exciton in a PbI4-based dielectric quantum well has been determined to be $0.09m_e$; the corresponding quasi-two-dimensional exciton Bohr radii were 15.5, 17.0, and 20.5 Å for the three cases, respectively.

Optical properties of excitons in conventional semiconductor quantum-well structures have been the subject of extensive studies. In addition to the usual spatial confinement of electrons and holes by variations in the electronic potential across the barrier and the well layers, the choice of a barrier layer with a smaller dielectric constant can further increase the binding energy of excitons in the well. When the dielectric constant in the barrier layer is sizably smaller than that in the well layer ($\epsilon_b < \epsilon_w$), theory suggests that the binding energy of excitons in the well can substantially exceed the value of four exciton Rydbergs, the ideal limit of the conventional two-dimensional (2D) system. This large enhancement of the exciton binding energy has been referred to as "dielectric confinement," a physical circumstance which induces a "dielectric quantum well" (DQW).[1-3]

In order to synthesize such DQW structures epitaxially, one is immediately faced with the difficulty of artificial layering either highly lattice mismatched and/or heterovalent materials to provide a suitably large dielectric constant difference. However, as an alternative, there exist layered materials which are naturally arranged so that the possibility for exciton dielectric confinement exists. Ishihara, Takahashi, and Goto[4,5] reported the discovery of strong excitonic effects with an estimated exciton binding energy $E_x = 320$ meV in the layered perovskite-type compound $(C_nH_{2n+1}NH_3)_2PbI_4$ (abbreviated below as C_n-PbI4 with $n = 4,8,9,10,12$), where the 2D atomic monolayers of the inorganic semiconductor base PbI4 are sandwiched between the organic alkylammonium insulating spacers.[6] Also recently, the electroabsorption, magnetoabsorption, and third-harmonic generation effects were observed in C_{10}-PbI4.[7-9] The high-frequency dielectric constant of the alkylammonium spacers is much smaller than that of PbI4 well layers, typically $\epsilon_b = 2.4$ and $\epsilon_w = 6.1$. After comparison with the generally accepted exciton binding energy $E_x = 30$ meV for the equivalent 3D case of PbI2, it was suggested that the large exciton binding energy in C_{10}-PbI4 could hence be attributed to the dielectric confinement effect.[4] However, as the local configuration for Pb ions in C_{10}-PbI4 is not the same as in PbI2, direct proof for dielectric confinement in this case

remained elusive since it requires some variation in the dielectric environment for the PbI4-based layered structures themselves. In this paper, we have chemically introduced such changes without changing the well structure and demonstrate that this does indeed "tune" the exciton binding energy. In the process we have also been able to vary the excitonic band gap itself by the normal quantum confinement (size) effect, based on quantum-well thickness.

In our experiments we used the compound C_{10}-PbI4 as a starting reference. The first example of the dielectric modification is $(C_6H_5\text{-}C_2H_4NH_3)_2PbI_4$ [bis(phenethyl-ammonium)tetraiodoplumbate], abbreviated here as PhE-PbI4, where the decylammonium barrier layer in C_{10}-PbI4 is replaced by $C_6H_5\text{-}C_2H_4NH_3$, whose high-frequency dielectric constant is expected to be larger than alkylammonium due to its aromatic ring. Hence smaller binding energy of the exciton is expected.[10] Very recently, Calabrese et al.[11] have synthesized generic compounds $(RNH_3)_2(CH_3NH_3)_{m-1}Pb_mI_{3m+1}$, where R can label an alkyl group, for example, and m is the number of Pb-ion monolayer sheets within a well layer. Both compounds C_{10}-PbI4 and PhE-PbI4 belong to this generic class. As the second example of the modification, we have employed $(C_6H_5\text{-}C_2H_4NH_3)_2(CH_3NH_3)Pb_2I_7$ (abbreviated as PhE-Pb2I7 below), where in addition to the dielectric changes, the PbI4 quantum-well thickness of PhE-PbI4 is doubled.

The single crystals of PhE-PbI4 were synthesized from PbI2 in an acetone and nitromethane solution with phenethylammoniumiodide $C_6H_5\text{-}C_2H_4NH_3I$, which was obtained from reacting $C_6H_5\text{-}C_2H_4NH_2$ and HI. The PhE-PbI4 single crystals can be grown from its own solution into two different forms. The growth temperature was kept at 30°C. A fast growth (in one day) gives yellow needlelike crystals. These crystals do not give any luminescence under any laser excitation. In contrast, a slower growth (in one week) gives orange, rectangularlike platelets with a typical size of $1.0 \times 5.0 \times 0.3$ mm^3 which can be easily cleaved along the ab (basal) plane with excellent optical properties, including strong photoluminescence. The single crystals of PhE-Pb2I7 were grown simi-

larly with CH_3NH_3I added to C_6H_5-$C_2H_4NH_3I$ and were dark red.

Figure 1 shows the optical-absorption spectra for the three materials at room temperature and $T = 10$ K. The detailed temperature dependence will be published elsewhere. The spectra are dominated by a very strong exciton absorption which persists at room temperature, where the ground-state exciton is measured at a photon energy of 2.4, 2.4, and 2.2 eV for C_{10}-PbI_4, PhE-PbI_4, and PhE-Pb_2I_7, respectively. This interpretation of the ground-state exciton has been further verified from reflectance data (a low-temperature example of which is shown in Fig. 2). When the temperature is decreased to 10 K, the exciton absorption becomes sharper with a peak absorption coefficient measured typically on the order of $\alpha \approx 10^6$ cm^{-1}. Furthermore, the electron-hole free particle band gap is identified above the exciton absorption. This band gap, indicated in the figure as E_g, is especially clear for PhE-PbI_4 samples of high quality, displaying a clear 2D-like step at 2.58 eV. Analogous features are also seen for C_{10}-PbI_4 and PhE-Pb_2I_7 in the figure, with the latter (bilayer) material showing also a feature which we tentatively identify as an $n = 2$ confined particle exciton (at 2.62 eV). From such data, an exciton binding energy of $E_x = 320$, 220, and 170 meV for the three materials, respectively, is obtained. In comparing the photon energies of the excitonic resonance and the band gap of C_{10}-PbI_4 between $T = 10$ K and room temperature, it should be noted that this particular material undergoes a structural phase transition at $T \approx 273$ K, as a consequence of which its band gap increases by about 0.1 eV.[4,5] This aspect does not influence the dielectric confinement problem at hand. For PhE-PbI_4 and PhE-Pb_2I_7, both the band edge and the exciton peak blueshift continuously with temperature at a rate of approximately 20 meV/100 K. The energies of the exciton and the band gap in PhE-Pb_2I_7 are lower than those in PhE-PbI_4, as expected from the weaker quantum (size) confinement effect in the bilayer PhE-Pb_2I_7, which has twice the monolayer well thickness. The quantum confinement effects will be described separately elsewhere. We also point out that we have seen no clear evidence for excited exciton states in the absorption spec-
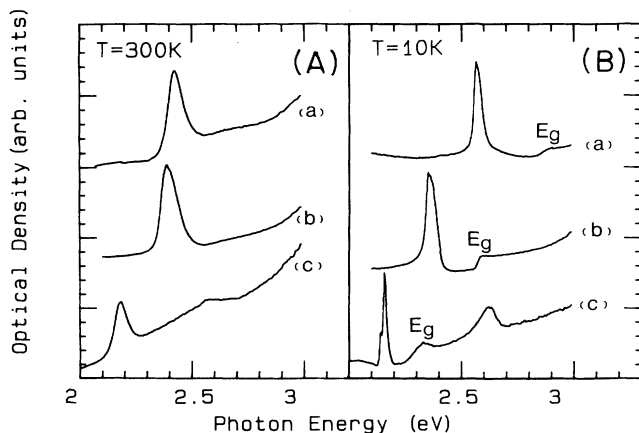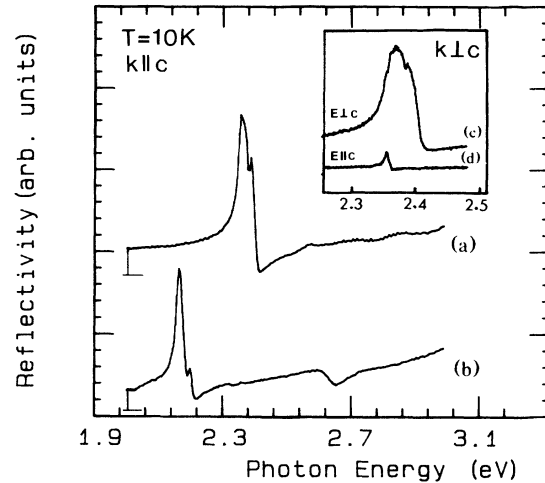

FIG. 2. Reflection spectra for (a) PhE-PbI_4 and (b) PhE-Pb_2I_7 at $T = 10$ K. The short horizontal lines identify zero baseline reflectance. The inset shows polarized reflection spectra in $k \perp c$ configuration with (c) $E \perp c$ and (d) $E \| c$ for PhE-PbI_4 at $T = 10$ K.

tra so far. Considerable reduction is, of course, expected in their corresponding absorption cross sections generally for the 2D exciton case.

The unpolarized reflection spectra of PhE-PbI_4 and PhE-Pb_2I_7 with $k \| c$ at $T = 10$ K is shown in Fig. 2, with the inset displaying the polarization dependence for $k \perp c$ for PhE-PbI_4 (as expected for an anisotropic layered material). The reflectance spectra of C_{10}-PbI_4 can be found in Refs. 4 and 5. For PhE-PbI_4, the spectrum shows a reflection peak at about 2.36 eV where the maximum of the intensity reflection coefficient exceeds 0.75. From Kramers-Kronig analysis of the spectra, the energy of the transverse exciton and the longitudinal exciton are obtained as 2.354 and 2.404 eV, respectively, yielding for the longitudinal-transverse (LT) energy splitting $\Delta E_{LT} = 50$ meV. Then the oscillator strength per formula unit is 0.5, which while very large, is approximately 30% smaller than that in C_n-PbI_4. In the configuration where the optical field E is parallel to c axis, we measured the maximum of the reflection to be 5 times weaker than that for the $E \perp c$ configuration. Comparable conclusions have been obtained for PhE-Pb_2I_7, with the LT splitting $\Delta E_{LT} = 46$ meV and the oscillator strength per formula unit of ≈ 0.62. Normalized to monolayer thickness (as PhE-Pb_2I_7 includes two Pb ions in its formula unit), this indicates an equivalent oscillator strength of about 0.3 when compared with C_{10}-PbI_4 and PhE-PbI_4.

Very efficient photoluminescence was obtained from all three materials at low temperatures, in our experience easily comparable with or in excess to that, e.g., in wide band-gap II-VI and III-V quantum-well structures. The details of the photoluminescence (PL) spectra will be published elsewhere; as an example the inset in Fig. 3 shows the PL traces for PhE-PbI_4 single crystals at low and room temperatures. While some extrinsic as well as phonon-related features are seen in the PL spectra, they are generally dominated by intrinsic (free) exciton recombination, as seen from the spectral proximity to the corre-

FIG. 1. Absorption spectra at (A) $T = 300$ and (B) 10 K for (a) C_{10}-PbI_4, (b) PhE-PbI_4, and (c) PhE-Pb_2I_7.

sponding absorption peak (energy separation $\Delta E \leq 10$ meV). We attribute this emission to free-exciton recombination. Figure 3 displays the integrated intensity of the free-exciton luminescence as an inverse function of temperature for the PhE-PbI$_4$ samples. The PL efficiency remains almost constant up to $T = 250$ K beyond which it decreases approximately as $\exp(E_a/k_b T)$ with $E_a = 220 \pm 30$ meV. This thermal activation energy is in agreement with the 220 meV exciton binding energy obtained from the absorption spectra. Similar data was obtained for C$_{10}$-PbI$_4$ and PhE-Pb$_2$I$_7$, also in agreement with the assignment of the exciton binding energy from absorption data. The temperature dependence of the PL shows that, following phonon-intermediated excitation of the ground-state exciton into the free particle states, the probability of nonradiative recombination from free-electron–hole pairs is very large.

In order to obtain the effective dielectric constants for the barrier layers in our quantum wells, we measured the dielectric constants independently for PhE-PbI$_4$ and C$_{12}$-PbI$_4$ (Ref. 12) to be $\epsilon_\infty = 4.41$ and 3.39, respectively (obtained by the interference fringe technique at about 1.5 eV, well below all electronic resonances but above vibrational resonances). These values thus represent the average dielectric constants of the barrier and the well materials. That is $\epsilon_\infty = (\epsilon_w L_w + \epsilon_b L_b)/(L_w + L_b)$ or $\epsilon_b = [\epsilon_\infty(L_w + L_b) - \epsilon_w L_w]/L_b$, where L_w and L_b are the layer thicknesses for the well and barrier layers, respectively. Values for L_w and L_b are obtained from information available about the corresponding crystal structures. Taking $L_w = 6.36$ Å, the distance between two iodine "sheets" in a well, we obtain $L_b = 9.82$ Å for PhE-PbI$_4$ and $L_b = 18.15$ Å for C$_{12}$-PbI$_4$ from the lattice constants. We also take $\epsilon_w = 6.1$ by using the value for the high-frequency dielectric constant of PbI$_2$. This leads to $\epsilon_b = 3.32$ for PhE-PbI$_4$ and PhE-Pb$_2$I$_7$, and to $\epsilon_b = 2.44$ for C$_n$-PbI$_4$. Following

FIG. 3. Integrated exciton luminescence intensity in PhE-PbI$_4$ (natural log scale), as a function of inverse temperature. The inset shows luminescence spectra of PhE-PbI$_4$ at (a) $T = 2$ and (b) 300 K.

the variational method used by Hanamura et al.,[2] where the dielectric confinement effect was treated explicitly, we performed the calculation of the exciton binding energy for C$_{10}$-PbI$_4$, PhE-PbI$_4$, and PhE-Pb$_2$I$_7$. The Coulomb attraction between an electron at (r_e, z_e) and a hole at (r_h, z_h) is evaluated by the image charge method as

$$V_{eh} = -\frac{e^2}{\epsilon_w} \sum \frac{[(\epsilon_w - \epsilon_b)/(\epsilon_w + \epsilon_b)]^{|n|}}{\{(r_e - r_h)^2 + [z_e - (-1)^{|n|} z_h - 2nl]^2\}^{1/2}},$$
(1)

where the integer summation index n runs from $-\infty$ to ∞. The Hamiltonian H of an electron and a hole in the well of thickness $2l$ is written (with respect to an energy gap E_g) as

$$H = -\frac{\hbar^2}{2M}\nabla_R^2 - \frac{\hbar^2}{2\mu}\nabla_r^2 - \frac{\hbar^2}{2m_e}\frac{\partial^2}{\partial z_e^2} - \frac{\hbar^2}{2m_h}\frac{\partial^2}{\partial z_h^2} + V_{eh}$$

$$+ \frac{e^2}{2\epsilon_w} \sum_{n \neq 0} \left(\frac{\epsilon_w - \epsilon_b}{\epsilon_w + \epsilon_b}\right)^{|n|} [|z_e - (-1)^{|n|} z_e - 2nl|^{-1} + |z_h - (-1)^{|n|} z_h - 2nl|^{-1}],$$
(2)

where μ is the reduced in-plane electron-hole mass. The corresponding trial wave function is

$$\Psi = \frac{1}{la}\left[\frac{2}{\pi}\right]^{1/2} \cos\left[\frac{\pi z_e}{2l}\right] \cos\left[\frac{\pi z_h}{2l}\right] \exp\left[-\frac{r}{a}\right].$$
(3)

The variational parameter a was determined by minimizing the expectation value of the Hamiltonian in the trial wave function, $E = \langle \Psi | H | \Psi \rangle$. Then the exciton binding energy was calculated from

$$E_x = -\left\langle \Psi \left| -\left[\frac{\hbar^2}{2\mu}\right]\nabla^2 + V_{eh} \right| \Psi \right\rangle.$$
(4)

The reduced effective mass was employed as the only fitting parameter in the calculation and was assigned the value $\mu = 0.09 m_e$. This compares with a reduced mass of
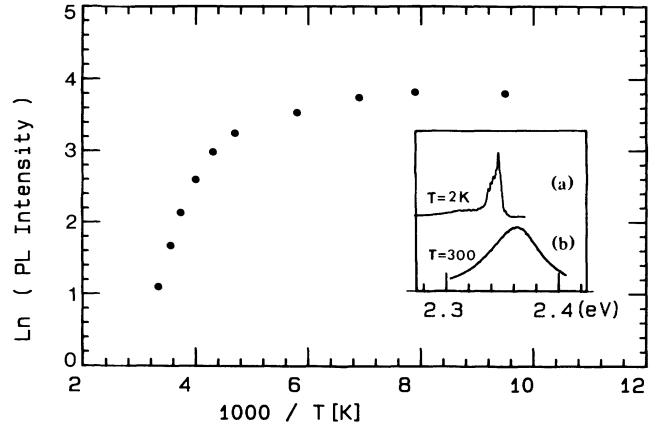
$\mu = 0.08 m_0$ for bulk PbI$_2$, obtained from adopting the binding energy of 30 meV and dielectric constant of 6.1. The calculated exciton binding energies are 315, 230, and 175 meV for C$_{10}$-PbI$_4$, PhE-PbI$_4$, and PhE-Pb$_2$I$_7$, respectively, in very good agreement with the experiment. Note that the binding energy in PhE-Pb$_2$I$_7$ is smaller than that in PhE-PbI$_4$, because the well thickness of the former is twice as much as the latter. Thus the dielectric confinement is also reduced. The corresponding quasi-2D exciton Bohr radii are 15.5, 17.0, and 20.5 Å, respectively. Note that they are substantially larger than the nearest-neighbor distance of Pb ions, 6.24 Å. These results are summarized in Table I with relevant material parameters. The table also includes a comparison of oscillator strengths; the experimental value of C$_{10}$-PbI$_4$ was used to normalize the calculated ones.

TABLE I. Comparison between experimentally and theoretically determined exciton binding energies and oscillator strengths per formula unit for the three compounds, together with relevant material parameters.

	L_w (Å)	a_B (theor) ϵ_b	E_b (theor) (Å)	E_b (expt.) (meV)	(meV)	f_{expt}	f_{theor}
C_{10}-PbI_4	6.36	2.44	15.5	315	320	0.7	(0.7)
PhE-PbI_4	6.36	3.32	17.0	230	220	0.5	0.58
PhE-Pb_2I_7	12.72	3.32	20.5	175	170	0.3	0.40

In conclusion, we have directly demonstrated the dielectric confinement effect on excitons by varying the dielectric constant of the barrier material in PbI_4-based layered structures. In these materials, we find that the dielectric confinement dominates the exciton binding energy, in contrast with conventional semiconductor quantum wells. Using a variational method, with the dielectric confinement effect included, we find very good agreement with our experimental observations of the exciton binding energy and obtain also a value for the in-plane effective mass of the exciton in the PbI_4-based DQWs.

*On leave from Tohoku University, Sendai, Japan.

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