Exciton switching and Peierls transitions in hybrid inorganic-organic self-assembled quantum wells

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The switching behavior of exciton absorption and photoluminescence is systematically explored in hybrid inorganic-organic multiple quantum well structures, based on $(C_{12}H_{25}NH_3)_2PbI_4$ thin films and single crystals. Two structural phases found between 15 and 75 °C, based on orthorhombic and monoclinic unit cells, show different optical excitons which are demonstrated to arise from the reversible crumpling of the quantum well layers. Structural flips can be controlled by annealing or film thickness, with different thermal hysteresis behavior observed for single crystals and thin films. © *2009 American Institute of Physics.* [doi:10.1063/1.3257725]

Hybrid organic-inorganic perovskite semiconductors provide significant opportunities as multifunctional materials for many electronic and optoelectronic applications. These include organic-inorganic light emitting diodes, organic-inorganic field-effect transistors, and nonlinear optical switches based on strong exciton-photon coupling in microcavity photonic architectures.[1–4] The basic structure of these lead (II) halide-based two-dimensional (2D) pervoskites takes the general form $(R\text{-}NH_3)_2PbI_4$ (where R is organic) consisting of layers of corner-sharing lead iodide octahedra with bilayers of organic cations stacked between the inorganic layers.[5–7] These form 'natural' multiple quantum well structures, where wells of the 2D inorganic semiconducting layer are clad by barriers of the wider bandgap organic layers. Typical layer thicknesses of well and barrier are ~6 and ~10 Å, respectively. The low dimensionality of carriers confined within the inorganic layers (by quantum confinement) combined with the large dielectric mismatch (giving dielectric confinement) between the layers, enables formation of stable excitons with large binding energy even at room temperatures.[8,9] These hybrids are thermally stable up to 200 °C and exhibit narrow and strong excitonic absorption and emission features favorable for optoelectronics applications. Of particular focus here is the observation of reversible structural phase transitions at easily accessible device temperatures in a special class of hybrid materials.[10,11] Although the crystal structures and optical features of many 2D layered perovskites are known,[12] the evolution of excitonic characteristics through a phase transition is unstudied. Understanding thermo-optic switching of these hybrids is essential for applications in photonic architectures.

Here we systematically explore the behavior of excitons in one such phase-change hybrid inorganic-organic multiple quantum well (IO-MQW) structure, $(C_{12}H_{25}NH_3)_2$ PbI_4 (hereafter C12PI), both in thin film and single crystal form. Yellow single-crystal platelets of $1 \times 2 \times 0.1$ mm^3 dimensions of C12PI were harvested from chemical synthesis, as

previously reported.[7,13,14] Several other 2D IO-MQW hybrids were also prepared by similar methods. Thin films were obtained by spin-coating a solution of crystals dissolved in acetonitrile. Both single crystal and thin film x-ray diffraction (XRD) studies were performed at room temperature. Photoluminescence (PL) and transmission measurements were carried out using a modified confocal microscope with a temperature-controlled scanning stage, which locally collects from a 3 μm spot the emitted PL (excited by a 447 nm cw diode laser) and the white light transmission over $\lambda = 300 - 1000$ nm. This system allows simultaneous recording of high-resolution images as well as PL and absorption spectra for 1 mm^2 areas with 1 μm resolution.

Single-crystal XRD analysis[11] shows that this phase transition at ~60 °C in C12PI separates low-temperature (hereafter phase-I) and high-temperature (hereafter phase-II) schematic crystal structures shown in Fig. 1(a). In both cases, side-linked PbI$_6$ octahedra are extended as 2D planar sheets over (100) planes while, between PbI$_6$ octahedra, two organic moieties are coupled via N-H$\cdots$I weak hydrogen
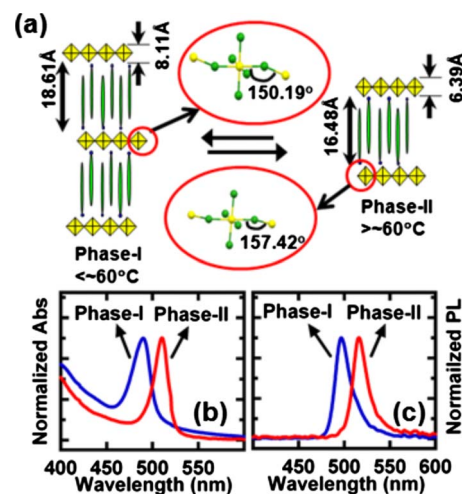

FIG. 1. (Color online) (a) Schematic crystal structure of C12PI phase-I and II. Inset shows the Pb and I atomic bonds in the inorganic network. [(b) and (c)] Exciton absorption (b) and PL (c) of above crystal phases. Phase-I and Phase-II were recorded at 25 and 70 °C, respectively.

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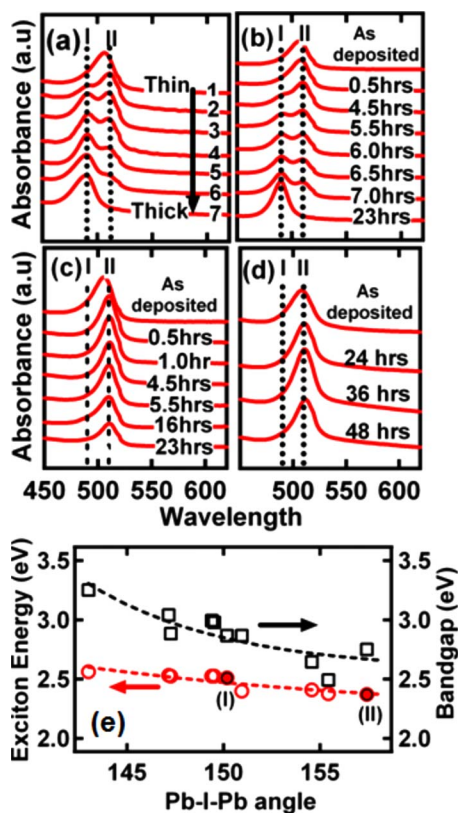
FIG. 2. (Color online) Exciton absorption of C12PI for effects of (a) film thickness and (b) aging (c) after annealing and (d) after PMMA capping of ~50 nm thickness films. (e) plot of Exciton PL peak position and lowest bandgap vs Pb-I-Pb in-plane bond angle of various 2D hybrids (see text). Opaque circles are for PL maxima of C12PI phase-I and II. Dashed lines are guide to eye.

bonds through the NH₃ ligands of the organic cation. Though both the phases have similar layered structures, the crystal packing of the phase-I is an orthorhombic unit cell while the phase-II is monoclinic with space groups (P*bca*) and (P2₁/*a*), respectively. The PbI network layers are not completely planar but possess in-plane Pb-I-Pb angles of 150.19° and 157.42°, respectively. This increased crumpling of the QW sheets in phase-I produces ~20 nm blueshifts in the exciton energies observed in both absorption and emission [Figs. 1(b) and 1(c)]. The room-temperature-stable phase-I exhibits exciton absorption at ~490 nm and PL at ~500 nm, while phase-II excitons absorb at ~510 nm and emit at ~520 nm. Nevertheless, both phases preserve strong excitons with narrow bandwidths below 15nm.

These hybrids also show exciton switching with increasing film thickness and aging of the film. To systematically investigate such environmental influences we present absorption spectra of thin films at room temperature, of increasing thicknesses 50, 60, 70, 80, 100, 120, and 350 nm [curves 1 to 7 in Fig. 2(a), respectively]. For films below ~50 nm thickness, the exciton absorption observed at 510 nm is associated with phase-II. However as the film thickness increases, two exciton peaks are observed at 510 and 490 nm and for thicker films (>350 nm) the exciton completely switches to the 490 nm phase-I. In addition, the films show noticeable aging effects, with 50 nm thick films gradually switching over from phase-II (510 nm) to phase-I (490 nm) within 24 h [Fig. 2(b)]. However, this phase transformation can be prevented (for >50 hours) by annealing the films at 50 °C for

an hour [Fig. 2(c)] or by overcoating the film with a polymer such as polymethyl methacrylate (PMMA) [Fig. 2(d)].

According to recent[11] and previous[13] structural, thermal and spectroscopic studies, the change from phase I to II leads to the following: (1) increased disorder in the orientation of alkyl chains in the organic moiety, (2) changes in the crystal structure between orthorhombic and monoclinic, (3) arrangement of inorganic layers, and (4) spatial shifts in the coupling between the ammonium group in the organic moiety and the PbI network.[15,16] Despite some understanding of how exciton energies in these hybrids depend on the 2D QW structure (both the inorganic *well* width and organic *barrier* separation), the dielectric contrast,[8] and the inorganic layer geometrical arrangement,[15] quantitative calculations of exciton binding energies remain out of reach. Thus we have synthesized[14] and studied a number of similar 2D layered hybrids with different organic moieties and have established a systematic correlation between the exciton energies and a specific structural feature, the Pb-I-Pb in-plane bonding angle [Fig. 2(e)]. The exciton PL energy monotonically increases with decreasing Pb-I-Pb in-plane bending angle, with the observed trend matching both phase I and II of the C12PI structure. Extended Hückel tight-binding calculations [CAESAR™ V2.0] (Ref. 17) were used to evaluate band structures of a series of 2D hybrids using available single-crystal structural data.[5–7,10,11] Though this method underestimates the bandgap, it accounts well for the observed correlation between sheet crumpling and electronic energy levels. This confirms the key relationship between crumpling of the QW layers and the bandgap (and hence exciton energies) apart from other influencing factors such as dielectric confinement and barrier/well widths. Previous calculations in related systems imply that phase transitions in layered perovskites are driven by distortion-induced mixing between degenerate electronic bands allowing the system to reduce its energy by crumpling the QW layers.[18] The connection between layer corrugation and bandgap suggests that this energy reduction is less effective in thin films due to the buildup of high strain, thus favoring the flatter phase-I PbI QWs.

The temperature dependence of the exciton PL and absorption is compared between thin films and single crystals to explore the environmental control of this layer crumpling. Cycling single crystals through the phase transition shows the yellow-orange color transition directly [Fig. 3(a)]. Spectral scanning of PL and absorption across 1 mm² areas with 20 μm resolution is performed at each 3 °C temperature step between 15 °C and 75 °C. The phase transition is clearly seen in the images [Figs. 3(b) and 3(c)] for selected wavelengths highlighting phase-I and phase-II demonstrating complete switching of the exciton peak PL.

Comparing the temperature-dependent PL spectra of both thin films and single crystals [Fig. 4] reveals identical phase transition temperatures of ~57 °C on heating.[11,13] Besides the exciton energy shifts, different PL intensity ratios are observed, ~40 for crystals and ~3 for thin films. Extracting the maximum PL wavelength through a full temperature cycle reveals full reversibility of the phase transition as well as distinct hysteresis [Fig. 4(c)] with differences between thin film and crystal on the cooling cycle. On cooling, single crystals show the phase-change at 45 °C, while in thin films the phase-II (523nm exciton) persists metastably even at room-temperature and remains for several hours. However when films are further cooled to 15 °C, phase-I appears
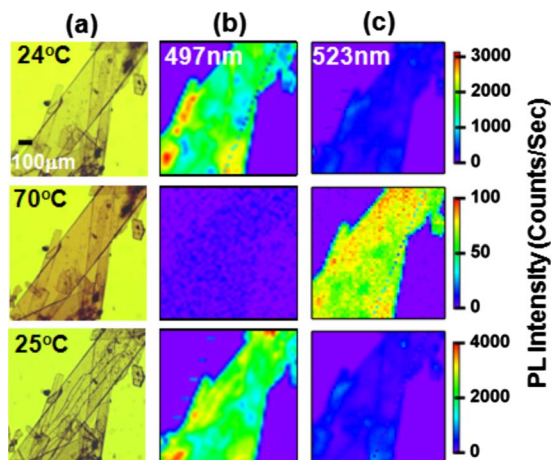
FIG. 3. (Color online) (a) Confocal transmission images of C12PI single crystals recorded at 24 °C, heated to 70 °C and cooled down to 25 °C. [(b) and (c)] PL images at each temperature for (b) λ=497 nm phase-I and (c) λ=523 nm phase-II excitons.

along with phase-II and complete recovery of phase-I only happens after several hours. Once again, the layer crumpling is energetically favorable once many tens of QW layers have built up. Below this, the Peierls distortion is hampered by strain, leading to the metastable behavior in thin films. Hence the exciton switching can be modified by the local nanoscale environment, providing innovative opportunities for device application.
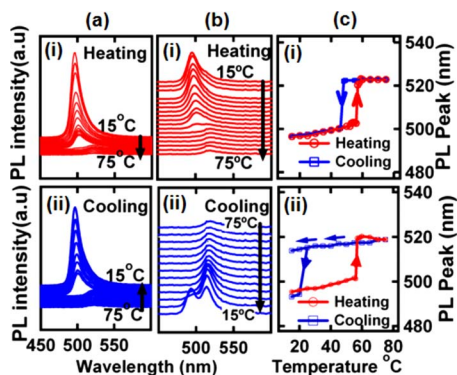

FIG. 4. (Color online) (a) C12PI crystal and (b) thin film (of thickness ~50 nm) PL spectra during (i) heating and (ii) cooling between temperatures 15 to 75 °C and (c) Peak PL wavelength vs temperature on heating and cooling for (i) single crystal and (ii) thin film.

In conclusion, the switching behavior of exciton optical absorption and PL in a phase-change hybrid $(C_{12}H_{25}NH_3)_2PbI_4$ was systematically explored both in thin films and single crystals. Both these phases show strong, narrow excitonic spectra. To exploit these phase-change hybrids in optoelectronic devices, such detailed understanding of the exciton behavior is essential. For example, incorporating these hybrids in strong-coupling microcavities[19] dramatically enhances the nonlinear optical switching. Such experiments are in progress.

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