In situ intercalation strategies for device-quality hybrid inorganic-organic self-assembled quantum wells

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AQ: #1

Thin films of self-organized quantum wells of inorganic-organic hybrid perovskites of $(C_6H_9C_2H_4NH_3)_2PbI_4$ are formed from a simple intercalation strategy to yield well-ordered uniform films over centimeter-size scales. These films compare favorably with traditional solution-chemistry-synthesized thin films. The hybrid films show strong room-temperature exciton-related absorption and photoluminescence, which shift with fabrication protocol. We demonstrate the potential of this method for electronic and photonic device applications. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3186639]

The large family of metal halide-based inorganic-organic hybrid perovskite crystals has attracted much attention because of their unique flexibility in structure and electro/optical properties.[1–3] Especially of interest are two-dimensional (2D) layered perovskites, generally in the form of $(R{-}NH_3)_2MX_4$ (R is organic group, M=Pb, Sn, and Ge, and X=Br, Cl and I), regarded as a naturally self-assembled multiple quantum-well (QW) structure where sheets of extended $[MX_6]$ octahedra and organic spacer layers are alternately stacked. These hybrids show large exciton binding energies enabling QW excitons to be observed even at room temperature due to quantum mechanical as well as dielectric confinement effects.[1–4] However, usage of these QW hybrids in electronic and optoelectronic devices is limited by the lack of appropriate methodologies to generate uniform and highly ordered thin films.[5] This is challenging since solution processing and spin-coating techniques are constrained in obtaining well-ordered films with good uniformity. Although methods such as layer-by-layer deposition[6] and Langmuir–Blodgett techniques[7] have been explored, potential applications demand much simpler and more reliable techniques.

Here we establish a much simpler but efficient technique to prepare highly ordered and strongly emitting lead iodide-based self-assembled QW sheets, formed of cyclohexenyl ethyl ammonium lead iodide $(C_6H_9C_2H_4NH_3)_2PbI_4$ (CHPI). A very general method is adopted to intercalate organic guest moieties into the vacuum deposited host, lead iodide (PbI_2), [Fig. 1(a)]. The evolution of the intercalation process is directly tracked both structurally and optically, showing improved performance over thin films produced from CHPI single crystals. We demonstrate this technique for potential applications in photonic/electronic device fabrication.

The 2-(1-cyclohexenyl) ethyl ammonium iodide, $C_6H_9C_2H_4NH_3I$ (CHI) organic moiety is dissolved in a 1:6 mixture of isopropyl alcohol:toluene. PbI_2 thin films of variable thickness are thermally evaporated onto glass/silicon substrates and the resulting films are dipped for controlled times into CHI solution to obtain intercalated CHPI films. For comparison, we also prepare thin films from single crystals of CHPI, according to the procedure reported in Ref. 8 by redissolving the crystals in acetonitrile solution and spin coating thin films onto glass/silicon substrates. Films are characterized both structurally by x-ray diffraction (XRD) and atomic force microscopy (AFM), and optically by absorption and photoluminescence (PL).

AQ: #2

The intercalation process inserts appropriately sized guest moieties into the empty spaces within a crystalline host. This is most favorably achieved for layered structures since there is greater flexibility in adjusting the interlayer separations. The kinetics and layer formation during intercalation are typically dependent on the nature and shape of the guest moiety, the concentration of guest molecules, and the solvent used.[9] The CHPI thin films processed from both intercalation as well as spin coating are subjected to extensive optical and structural characterization to ascertain the dependence on fabrication parameters.

The XRD patterns imply that the bulk polycrystalline PbI_2 2D layers appears to be weakly organized with the c axis orientated perpendicular to the substrate, and plane separation d=6.78 Å [Fig. 1(b) (i)]. We track the intercalation process through XRD of the films for increasing inter-

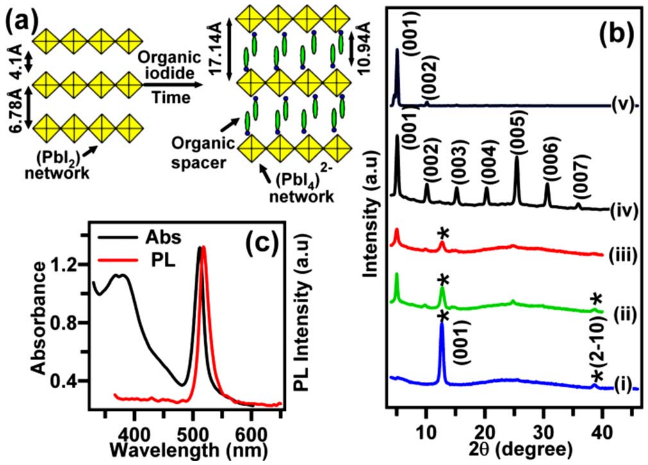

FIG. 1. (Color online) (a) Schematic intercalation process for CHPI. (b) XRD diffraction patterns of (i) pure PbI_2 film, (ii)–(iv) intercalated CHPI films for intercalation durations of 1, 2, and 10 s, respectively, and (v) spin-coated CHPI film. $*$ indicates PbI_2 diffraction peaks. (c) UV-visible absorption and PL of the intercalated thin CHPI film.

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calation times up to 10 s [Fig. 1(b) (ii)–(iv)]. Within 1 s of intercalation time, the XRD pattern starts to show a new (001) diffraction peak at $2\theta=5.075°$, indicating the substantial enhancement in layer-to-layer distance, with $d_{(001)}=17.4$ Å. Here the edge-sharing layered PbI_3 octahedra turn into layers of corner-sharing PbI_6 octahedra separated by bilayers of organic moieties [Fig. 1(a)].[10,11] However, the presence of host PbI_2 [Fig. 1(b) (ii) and (iii)] suggests that the intercalation process is not fully complete. After 10 s of intercalation time, the XRD pattern shows narrow peaks of higher diffraction orders, related to $(00l)$ $(l=2,3,4,\ldots)$ CHPI crystal planes, with no traces of host PbI_2. Therefore, these XRD studies clearly show that PbI_2 molecules completely react with the organic moieties, which penetrate from the solution, and the resultant hybrid is self-organized and highly crystalline in nature. Measurements by AFM of the top film surface (not shown here) show that intercalation has little or no effect on the surface quality. Comparable thin films from resuspension of CHPI crystals were also fabricated by spin coating giving the XRD in Fig. 1(b) (v). The weaker higher-order diffraction peaks observed for this spin-cast film, as well as their rougher surfaces, indicate that the intercalated films are indeed of much higher quality. Hence this intercalation process is an effective strategy to form uniform and highly oriented CHPI films from PbI_2 and should be more generally applicable for all inorganic-organic hybrid perovskites, provided that the intercalation time, concentration of the organic solution, and the film thickness are optimized.

Optical properties also reveal the structural organization of these hybrid layered structures for different fabrication conditions. In general, these compounds are self-organized "quantum-well" structures, in which a 2D lead iodide semiconductor layer and an organic moiety layer are alternately stacked. Due to the low dimensionality of the semiconductor PbI network, these hybrids exhibit strong room-temperature excitons with large binding energies of about 200 meV, resulting from quantum confinement and enhanced dielectric confinement effects.[1–5] Figure 1(c) shows typical absorption and PL spectra of intercalated CHPI films. Both spin coated as well as intercalated CHPI films show relatively narrow (full width at half maximum ∼16 nm) and strong excitonic absorption (at 512 nm) and PL (at 517 nm) at room temperature. Figures 2(a) and 2(b) show the absorption and PL spectra of intercalated films of various thicknesses, with constant intercalation time of 10 s. Both absorption and PL spectra show significant thickness dependence, with the spectral peaks shifting in *opposite* directions. The spectral separation between maximum absorption and PL (the Stokes shift) increases from 5 to 18 nm as the thickness increases from 40 to 350 nm. The XRD patterns of these samples [Fig. 2(c)] show the persistent presence of higher-order $(00l)$ diffraction peaks indicating that the layer stacking along the *c* axis is uniform throughout the film. However for films more than 130 nm thick, the appearance of a weak diffraction peak at 12.5° related to PbI_2 suggests that the intercalation process does not fully complete within 10 s. Since further structural developments are not observed, possibilities such as formation of bilayers of inorganic/organic entities[12] and/or distortion of the 2D network can be ruled out. The extra Stokes shift could thus be due to either distorted bond angles within $(PbI_6)^{4-}$ octahedra[13] or due to the low-level presence of unreacted lead iodide impurities.

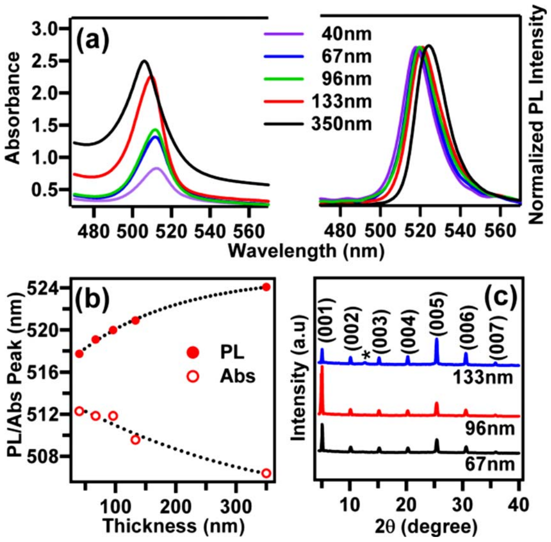

FIG. 2. (Color online) (a) Absorption and normalized PL spectra of intercalated CHPI films of different thicknesses. Intercalation time is 10 s for all the films. (b) PL and absorption spectral peaks vs film thickness. (c) XRD of CHPI intercalated films of different thickness. * indicates PbI_2 diffraction peaks.

AQ: #7

To examine the intercalation process in real time, we perform *in situ* transmission measurements [Fig. 3(a)] with a time interval of 70 ms. We extract here the transmission at the CHPI excitonic absorption peak (510 nm) for two films of thicknesses 67 and 350 nm. Imaging the transmission spectra versus time [Fig. 3(b)] shows the smooth evolution of the process. As seen from Fig. 3(a), the intercalation process follows a double exponential behavior independent of thickness: a fast initial process (0.1–0.4 s) producing attenuation of up to 40%, followed by a slower (5–8 s) saturation of the intercalation. The initial drop in transmission is ascribed to the immediate increase in reflectivity of the upper

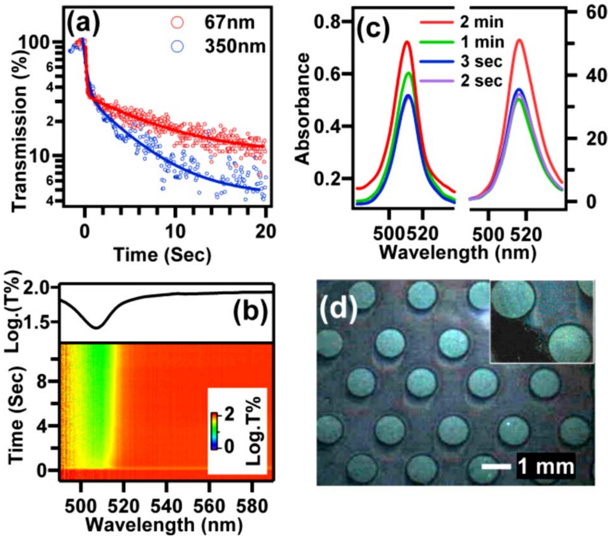

FIG. 3. (Color online) (a) Transmission vs intercalation time of CHPI films, monitored at 510 nm absorption maximum. Solid lines are double exponential fits. (b) Transmission spectra vs intercalation time of 67-nm-thick CHPI film. (c) Absorption and PL spectra of 67-nm-thick intercalated CHPI film for increasing intercalation time, and (d) microscope reflection image of patterned CHPI films on Si substrate. Inset is magnified view.

surface on commencement of intercalation, while the slower changes tracks the progression of the intercalation front through the sample. This agrees with the high optical density per layer of the CHPI which, in order to observe strong excitonic features, needs only tens of self-assembled layers[6] to saturate the optical features. This is further evident from the absorption and PL spectra plots of a 67-nm-thick film, displayed at selected intercalation times [Fig. 3(c)].

For practical application, it is essential to establish the suitability of this technique for potential use in fabricating microscale photonic/electronic devices, compatible with lithographic techniques[14] and focused ion/laser beam writing. Currently such experiments are ongoing. We exemplify the templated growth of millimeter-scale structures [Fig. 3(d)], where a template comprised of circular apertures was used as a mask to deposit PbI_2 pillars for intercalation. As seen from the microscopic images, these structures are uniform over a large scale and are highly luminescent and with less than 5 nm roughness (which was confirmed from AFM results, not shown here). Efforts are currently underway in our laboratories to fabricate micron-scale pillar structures.

In conclusion, we demonstrate a simple approach to fabricating high-quality and highly luminescent hybrid inorganic-organic self-assembled QW structures. We show how the optical and structural properties are robust, and that the intercalation process is efficient for further potential usage in optoelectronic applications. These hybrid films have highly ordered stacking over the substrate with good uniformity over large areas, and show strong and narrow excitonic absorption and photoluminescence. We establish the potential of this method for fabricating micron-scale devices. Further progress using this simple effective technique is aimed toward device applications such as strongly coupled microcavities.[15]

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