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Optical properties of organic–inorganic hybrid films prepared by the two-step growth process

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ABSTRACT

Thin films of microcrystalline $(C_8H_{17}NH_3)_2PbBr_4$ have been prepared by the two-step growth process as follows: (1) precipitation of nanometer-sized $PbBr_2$ particles on substrates by vapor deposition and then (2) growth of $(C_8H_{17}NH_3)_2PbBr_4$ films by exposing $PbBr_2$ particles to $C_8H_{17}NH_3Br$ vapor. Atomic force microscope observations reveal that the substrate is fully covered with nanometer-sized rodlike precipitates. X-ray diffraction studies suggest that $(C_8H_{17}NH_3)_2PbBr_4$ films are found to be microcrystalline form, single phase and highly oriented with the *c*-axis perpendicular to the substrate surface. $(C_8H_{17}NH_3)_2PbBr_4$ films show a clear exciton absorption and free-exciton emission even at room temperature. At low temperatures below 40 K, the emission band separates into three bands at 3.07 (A-band), 3.14 (B-band) and 3.20 (C-band) eV, respectively. Both A- and C-bands correspond to the free-exciton emission with large binding energies. On the contrary, time-resolved PL spectra indicate that the B-band is attributed to phosphorescence formed by the intersystem crossing.

1. Introduction

In recent years, self-assembly of molecules, ions and amphiphilic polymers has attracted considerable interest due to the possibility of creating interesting low-dimensional materials [1,2]. Lead-halide-based layered perovskite compounds, with the general formula of $(C_nH_{2n+1}NH_3)_2PbX_4$ (X: halogen), can be regarded as one of the self-assembled materials consisting of organic $(C_nH_{2n+1}NH_3^+)$ and inorganic (PbX_4^{2-}) layers [3,4]. In these compounds, the PbX_4^{2-} and $C_nH_{2n+1}NH_3^+$ layers are alternatively stacked with each other. The PbX_4^{2-} layer has a smaller band gap and a higher dielectric constant than those of the $C_nH_{2n+1}NH_3^+$ layer [5,6]. As a result, the exciton binding energy is amplified due to the quantum and dielectric confinement effects [7]. In addition, lead halides are well known as an ionic crystal with large exciton binding energy (30 meV for PbI_2 [5,6]). Stable excitons, with substantially large binding energy as large as a few hundreds meV, exist in $(C_nH_{2n+1}NH_3)_2PbX_4$ even at room temperature [8]. The large exciton binding energy offers interesting opportunities for use in novel optical and electrical devices [9–14]. From the viewpoint of materials design, $(C_nH_{2n+1}NH_3)_2PbBr_4$ can be expected to be interesting optical devices operated at the near-ultraviolet region because the optical band gap of $PbBr_2$ locates at 4.1 eV.

So far, $(C_nH_{2n+1}NH_3)_2PbI_4$ has been prepared as microcrystalline thin films and as single crystals by solution processes [6,15,16]. On the contrary, the solution process is often limited due to the poor solubility of raw materials. Vapor phase deposition techniques are one of the promising candidates to overcome the difficulty [17–19]. By a single-source thermal ablation technique, $(C_6H_5C_2H_4NH_3)_2PbX_4$ films (X = Br and I) have been prepared within a very short periods (<1 s) [18]. Precise control of the film thickness should be difficult due to its rapid ablation process. It is reasonable that organic components $(C_nH_{2n+1}NH_3X)$ evaporate at much lower temperatures compared to inorganic components (PbX_2). Therefore, a dual-source vapor deposition technique may require new synthetic parameters for each composition to balance the evaporation rates between organic and inorganic sources. Recently, a two-step growth technique has been proposed by the authors as follows: (1) precipitation of $PbBr_2$ particles on substrates by vapor deposition and then (2) growth of $(C_8H_{17}NH_3)_2PbBr_4$ by exposing $PbBr_2$ particles to $C_8H_{17}NH_3Br$ vapor [20]. Exposure time probably plays an important role in the formation of $(C_nH_{2n+1}NH_3)_2PbBr_4$ because the synthetic approach is based on the layer-by-layer technique. However, the effect of exposure time on some properties of $(C_8H_{17}NH_3)_2PbBr_4$ films was still unclear. In this article, $(C_8H_{17}NH_3)_2PbBr_4$ films have been prepared by the two-step growth process and their surface morphology, absorption and luminescence properties have been investigated.

2. Experimental procedures

Samples were prepared using the two-step growth process [20]. Commercially available $PbBr_2$ (99.9%) and $C_8H_{17}NH_3Br$

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(95.0%) were used as raw materials. $C_8H_{17}NH_3Br$ was washed with diethyl ether to remove impurities. A simple vacuum chamber was used as a deposition apparatus. The chamber is attached to a vacuum system, two-independent thermal evaporation sources, a shutter and a substrate holder. Background pressure of the vacuum chamber was about 8×10^{-6} Torr. The thermal evaporation source consists of a quartz cell ($10 \times 10 \times 40\,mm^3$ in size) coiled with a tantalum wire. First of all, $PbBr_2$ particles were deposited on SiO_2 glass and on Si (1 0 0) substrates by vapor deposition. The chamber pressure was adjusted to about 1.5×10^{-5} Torr. Deposition time of $PbBr_2$ (denoted as t_1 hereafter) was fixed at 60 s. Next, $PbBr_2$ particles were exposed to $C_8H_{17}NH_3Br$ vapor for growing of $(C_8H_{17}NH_3)_2PbBr_4$ films. Exposure time (denoted as t_2 hereafter) was varied from 0 to 600 s. The crucible temperature and chamber pressure was adjusted to about 130 °C and 5.0×10^{-5} Torr, respectively. It should be noted that the substrate temperature was kept at room temperature during deposition.

The film thickness was measured using a surface profiler (Veeco, Dektak 3). The film thickness depends on the deposition time of $PbBr_2$. The film thickness was approximately 20 nm when t_1 was 60 s.

Samples were characterized with X-ray diffraction (XRD, Rigaku RINT-2500 X-ray diffractometer) with a monochromatic CrKα radiation (20 kV, 10 mA). Surface morphology of the sample was observed with an atomic force microscope (AFM, Nanoscope III, Digital Instruments) in atmospheric pressure. Temperature dependence visible–UV optical absorption, photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured with spectrophotometers (JASCO V-570 Spectrophotometer and Perkin-Elmer LS-50B Spectrophotometer) equipped with a liquid helium cryostat. Time-resolved PL spectra of the sample were measured with a streak camera (Hamamatsu C4334 Streakscope) by a single photon counting technique at 6 K. A N_2 laser (USHO, KEC-160) was used as an excitation source. The repetition rate was 10 Hz and the full-width at half-maximum of the laser pulse was approximately 800 ps.

3. Results

3.1. Thin film formation

Fig. 1 shows AFM images of as-synthesized samples. Exposure time (t_2) was (a) 0, (b) 120 and (c) 600 s, respectively. Deposition time of $PbBr_2$ (t_1) was fixed at 60 s. Marked difference is observed for the samples depending on the period of t_2. The unexposed sample (a) shows a large number of $PbBr_2$ particles throughout the substrate surface. The average particle size was about 100 nm in diameter. When the period of t_2 was 120 s, the substrate surface of the sample (b) is fully covered with nanometer-sized rodlike particles. The sample (c) is composed of submicron-sized particles with distinct shape.

X-ray diffraction patterns of the samples are shown in Fig. 2. The period of t_1 was 60 s and that of t_2 was (a) 60, (b) 120, (c) 240 and (d) 600 s, respectively. The samples (a) and (b) show an intense and narrow Bragg reflection and much weaker ones with d-spacing of 20.9, 10.5, 7.0, 5.3, 4.2 and 3.5Å, respectively. The corresponding peaks can be indexed as $(0\,0\,2\,l)$ ($l = 1$–6) reflections of $(C_8H_{17}NH_3)_2PbBr_4$ with a unit cell parameter, $c = 42.1$Å. The estimated value was the same as our previous data ($c = 42.1$Å, $t_1 = 150$ s, $t_2 = 600$ s) [20]. No diffuse scattering associated with an amorphous phase is observed. These results lead us to an important suggestion that the film fabricated by the two-step growth process is a single phase and highly oriented, with the c-axis perpendicular to the substrate surface. However, the samples (c) and (d) show other Bragg reflections with d-spacing of 24.6, 12.3 and 8.3Å, respectively. These peaks can be indexed as $(0\,0\,l)$ ($l = 1$–3) reflections of $C_8H_{17}NH_3Br$ with the unit cell parameter, $c = 24.7$Å.

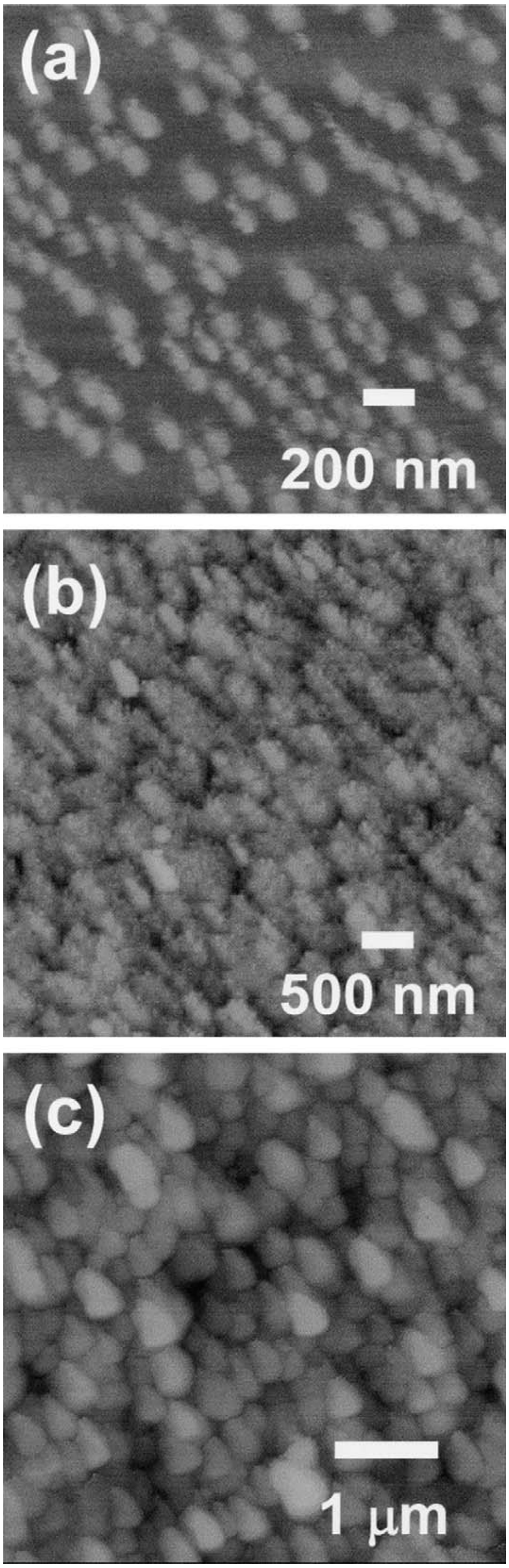

Fig. 1. AFM images of as-synthesized samples. Exposure time (t_2) is (a) 0, (b) 120 and (c) 600 s, respectively.