Self-Organized Growth of PbI-Based Layered Perovskite Quantum Well by Dual-Source Vapor Deposition

Masanao Era, Toshihiko Hattori, Takahiro Taira, and Tetsuo Tsutsui*

Department of Materials Science and Technology Graduate School of Engineering Sciences Kyushu University, Kasuga-shi, Fukuoka 816, Japan

Received August 12, 1996
Revised Manuscript Received November 19, 1996

Families of the layered perovskite, $(RNH_3)_2PbI_4$ and their analogues, naturally form a quantum-well structure where a two-dimensional semiconductor layer of lead iodide PbI_4 and an organic ammonium dielectric layer of RNH_3 are alternately piled up.[1−10] Owing to the low-dimensional semiconductor nature, the perovskite compounds form a stable exciton with a large binding energy of several hundred millielectronvolts and exhibit strong exciton absorption and sharp exciton emission even at room temperature. In addition, electroluminescence due to the exciton emission[11−13] and large third-order optical nonlinearity due to the large oscillator strength of the exciton[14,15] were observed in some layered perovskites. The attractive excitonic properties promote much interest in the application of these materials for optical devices such as emissive devices and optical signal processing devices.

Two different morphologies of the layered perovskites, single crystals and spin-coated thin films, have been employed for the studies on optical and electronic devices. When one attempts to use single crystals, the preparation of high-quality single crystals with a large size and high purity is required. For the preparation of such high-quality single crystals, the crystal growth technique from the melt phase which has been well-developed in the present semiconductor technology is preferable. Unfortunately, the crystal growth from the melt phase is not applicable here because the layered perovskites decompose before melting. Therefore, layered perovskite single crystals are usually prepared by crystal growth from a solution phase.[9,10,16,17]

In the solution method, stoichiometric amounts of metal halide (PbI_2, SnI_2, etc.) and organic ammonium halide are dissolved in water or organic solvents such as acetone and methanol. Then, layered perovskite crystals are allowed to grow through slow evaporation of solvents or slow cooling. Resultant crystals from the solution methods are too small (typical $2 \times 2 \times 0.1$ mm^3), and their optical quality is not sufficient for optical device applications. A silica gel method which is a useful crystal growth technique to obtain large size crystals from a solution phase has also been shown to be applicable to the layered perovskites.[16,17] Even in the cases when the silica gel method is used, however, the growth of layered perovskite crystals with large-area flat surfaces is difficult. It should be noted that this method also has a problem of contamination of ionic impurities from the gel medium. Thus, layered perovskite crystals with high optical quality and a large flat surface satisfactory for device applications have not been prepared as yet.

The layered perovskites are easily spin-coated from solutions, because they are soluble in conventional organic solvents such as acetone, acetonitrile, and dimethylformamide. By spin-casting from solutions, one can prepare thin films of the layered perovskites with good optical quality and an oriented layered structure.[6,7,12,13,14] This excellent film processability has been used for the fabrication of high-quality layered perovskite thin films useful for electronic and optical devices. However, the spin-coating technique has difficulty in the precise control of film thicknesses and film structures. In addition, the technique is not compatible with dry processing for the preparation of semiconductor films and devices in vacuum. Therefore, a new film-preparation technique which not only provides precise control of film thicknesses but also has good compatibility with dry processing is needed.

In this study, we succeeded in growing oriented thin films of the layered perovskites from the vapor phase by using a rather simple vacuum vapor deposition process. This new preparation technique is promising in not only making it possible to prepare precisely controlled layered perovskite thin films but also offering much flexibility in the material design of quantum-well materials based on the layered perovskites. Here, we report the new self-organized growth method of the layered perovskite thin films which, we believe, is promising for the development of the layered perovskite compounds as optical device materials.

Layered perovskite films were grown by a simple dual-source vapor deposition of lead iodide PbI_2 and organic ammonium iodide RNH_3I (Figure 1). Initially, 2-phenylethylammonium iodide $C_6H_5C_2H_4NH_3I$ (PhEI) was used as RNH_3I. Both PbI_2 and PhEI were evaporated and deposited simultaneously on fused quartz substrates under a pressure of about 10^{-6} Torr. The deposition rate and the deposited amount were monitored with a quartz oscillator balance. The deposition

(1) Ishihara, T.; Takahashi, J.; Goto, T. *Solid State Commun.* **1989**, *69*, 933.
(2) Ishihara, T.; Takahashi, J.; Goto, T. *Phys. Rev. B* **1990**, *42*, 11099.
(3) Hong, X.; Ishihara, T.; Nurmikko, A. V. *Phys. Rev. B* **1992**, *45*, 6961.
(4) Ishihara, T.; Hong, X.; Ding, J.; Nurmikko, A. V. *Surf. Sci.* **1992**, *267*, 323.
(5) Kataoka, T.; Kondo, T.; Ito, R.; Sasaki, S.; Uchida, K.; Miura, N. *Phys. Rev. B* **1993**, *47*, 2010.
(6) Xu, C.-Q.; Fukuta, S.; Sakakura, H.; Kondo, T.; Ito, R.; Takahashi, Y.; Kumata, K. *Solid State Commun.* **1991**, *77*, 923.
(7) Papavassiliou, G. C.; Patsis, A. P.; Jagouvardos, D. J.; Koutselas, I. B. *Synth. Met.* **1993**, *57*, 3889.
(8) Papavassiliou, G. C.; Koutselas, I. B.; Terzis, A.; Whangbo, M.-H. *Solid State Commun.* **1994**, *91*, 695.
(9) Mitzi, D. B.; Feild, C. A.; Harrison, W. T. A.; Guloy, A. M. *Nature* **1994**, *369*, 467.
(10) Mitzi, D. B.; Wang, S.; Feild, C. A.; Chess, C. A.; Guloy, A. M. *Science* **1995**, *267*, 1473.
(11) Hong, X.; Ishihara, T.; Nurmikko, A. V. *Solid State Commun.* **1992**, *84*, 657.
(12) Era, M.; Morimoto, S.; Tsutsui, T.; Saito, S. *Appl. Phys. Lett.* **1994**, *65*, 676.
(13) Hattori, T.; Taira, T.; Era, M.; Tsutsui, T.; Saito, S. *Chem. Phys. Lett.* **1996**, *254*, 103.
(14) Xu, C.-Q.; Fukuta, S.; Sakakura, H.; Kondo, T.; Ito, R.; Takahashi, Y.; Kumata, K. *Solid State Commun.* **1991**, *79*, 249.
(15) Calabrese, J.; Jones, N. L.; Harlow, R. L.; Herron, N.; Thorn, D. L.; Wang, Y. *J. Am. Chem. Soc.* **1991**, *113*, 2328.
(16) Dolzhenko, Y. I.; Inabe, T.; Maruyama, Y. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 563.
(17) Henish, H. K. *Crystal growth in Gels*; Pennsylvania University Press: Pennsylvania, 1970.

S0897-4756(96)00434-6 CCC: $14.00

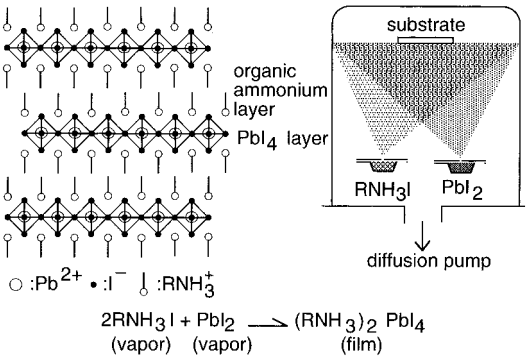

Figure 1. Schematic representation of the structure of layered perovskites $(RNH_3)_2PbI_4$ and preparation process of layered perovskites using the dual-source vapor deposition.

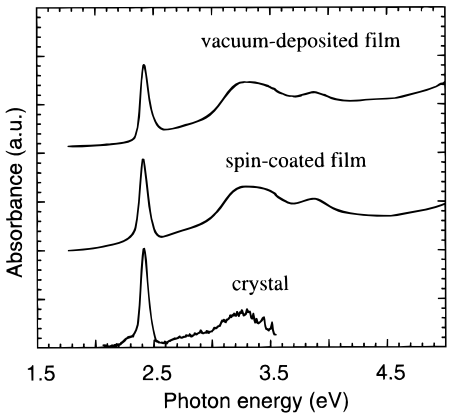

Figure 2. The absorption spectrum of the co-deposited film of PbI_2 and phenethylammonium iodide. The absorption spectra of the spin-coated film and the crystal of the layered perovskite with phenethylammonium layer are also shown.

rates of PbI_2 and PhEI were adjusted to be 7.1 and 21 ng cm^{-2} s^{-1}, respectively. The total amount deposited was 11.4 μg cm^{-2}. In the preparation, the substrates were allowed to stand at room temperature. The crucible temperatures of PbI_2 and PhEI were about 570 and about 520 K, respectively.

The vacuum-deposited films were uniform and transparent with a dim orange color. Figure 2 shows the absorption spectrum of the vacuum-deposited film when PhEI was used as RNH_3I. The spectrum of the vacuum-deposited film corresponds well to those of single crystal and spin-cast film forms of the layered perovskite with the (phenylethyl)ammonium layer, $(C_6H_5C_2H_4NH_3)_2PbI_4$ (referred to as PhEPbI4). A strong exciton absorption is observed at 2.42 eV and a sharp exciton emission peak at 2.37 eV. Appearance of the strong exciton absorption and sharp exciton emission proves that the layered perovskite structure was organized in the vacuum-deposited film.

Figure 3 shows a comparison of the X-ray diffraction profile for the vacuum-deposited film of PbI_2 and $C_6H_5C_2H_4NH_3I$ with that of a spin-coated film of PhEPbI4. Thin plastic films were used as the substrate, and X-ray irradiation was at a grazing angle with respect to the film plane. The broad diffraction at around 2θ of 19° in the profiles is due to the substrate plastic films. The appearance of the diffraction peak at 5.6° in the vacuum-deposited film, which corresponds to the interlayer spacing of the PhEPbI4 crystal (1.6 nm), demonstrates that the layered structure of the films was oriented parallel to the film plane.[15] However, higher

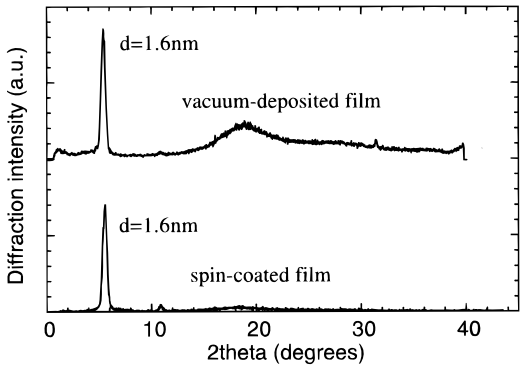

Figure 3. X-ray diffraction profile of the co-deposited film of PbI_2 and phenethylammonium iodide. The profile of the spin-coated film of the layered perovskite with phenethylammonium layer is also shown.

order diffraction peaks were not observed. The lack of higher order peaks suggests that the vacuum-deposited film is defective and disordered. For the preparation of high-quality vacuum-deposited films of the layered perovskite with less defects and a higher degree of order, a further exploration of the deposition conditions will be required.

When other organic ammonium iodides, i.e., the alkylammonium iodides $C_nH_{2n+1}NH_3I$ ($n = 4, 6, 10$) and 2-(1-cyclohexenyl)ethylammonium iodide ($C_6H_9C_2H_4NH_3I$), were used as the RNH_3I, layered perovskite thin films were also successfully prepared. All of the vacuum-deposited films showed strong exciton absorption. The exciton bands were located at 2.41 eV for $C_4H_9NH_3I$, 2.42 eV for $C_6H_{13}NH_3I$, 2.48 eV for $C_{10}H_{21}NH_3I$, and 2.45 eV for $C_6H_9C_2H_4NH_3I$, respectively. The exciton bands were in good agreement with those of spin-coated films of the corresponding layered perovskites. The results demonstrate that wide variety of organic amines can be applied in the dual-source vacuum-deposition technique. In other words, this technique provides a potential method to prepare a variety of perovskite films with tailored structures, because their optical and electronic characteristics are expected to be modulated by changing organic amine components.

Two possible growth mechanisms for the formation of layered perovskite structures via our dual-source vapor deposition method have been considered: one is that the layered perovskite structure is formed in vapor phase followed by adhering to a substrate, and the other is that the growth of the layered perovskite structure occurs in the solid phase on the substrate. The following experiment clearly demonstrated that the latter growth mechanism is more plausible.

First, a thin film of PbI_2 (thickness $\approx$ 20 nm) was deposited on a fused quartz substrate, and then the deposited PbI_2 film was exposed to PhEI vapor under a base pressure of about 10^{-6} Torr. During the exposure, the weight of the PbI_2 film continued to increase at a rate of 14.3 ng cm^{-2} s^{-1}. The PhEI-exposed PbI_2 film was found to have the layered perovskite structure, because it has the strong exciton absorption at 2.42 eV and the sharp exciton emission at 2.37 eV. This experiment clearly indicates that the layered perovskite structure is formed by the intercalation of organic ammonium iodide into the PbI_2 solid film. Further, it is plausible that the self-organizing intercalation of RNH_3I into the PbI_2 film promotes rearrangement of

the aggregated structure of PbI_2 and the formation of an oriented layered perovskite film in the dual vapor deposition of RNH_3I and PbI_2.

A film of the cubic perovskites was also fabricated by using the dual-source vapor deposition technique; by the co-vacuum-deposition of PbI_2 and methylammonium iodide, we succeeded in preparing thin films of the cubic perovskite $(CH_3NH_3)PbI_3$, $C1PbI_3$. In the absorption spectrum of the vacuum-deposited film, a step-shaped absorption with the absorption edge at around 1.6 eV was observed. This absorption edge is in good agreement with the reported bandgap of $C1PbI_3$.[18]

In conclusion, we have successfully demonstrated that thin films of layered perovskites $(RNH_3)_2PbI_4$ and a cubic perovskite $(CH_3NH_3)PbI_3$ were grown in a self-organizing manner through the simple dual-source vapor deposition of lead iodide and organic ammonium iodide. High self-organizing capability of the layered perovskites is assumed to be the origin of the formation of layered perovskite films. This unique preparation technique of layered perovskite films, we believe, surely contributes to the future development of high-performance electronic and optical devices using the layered perovskites. Further studies on the preparation of precisely controlled perovskite thin films and application of the vacuum-deposited thin films to emissive devices are now in progress.

Acknowledgment. This work was partly supported by NEDO International Joint Research Grant, Japan, and Grant-in-Aid for Scientific Research on Priority Areas "Molecular Superstructure—Design and Creation", the Ministry of Education, Science, Sports and Culture, Japan.

CM960434M

(18) Ishihara, T. *J. Lumin.* **1994**, *60/61*, 269.