PbBr-Based Layered Perovskite Containing Chromophore-Linked Ammonium Molecule as an Organic Layer

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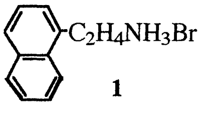
Oriented thin films of new organic-inorganic layered perovskites having a quantum-well structure combined with PbBr-based semiconductor layer and a chromophore-linked ammonium molecule layer were formed in a self-organizing manner by a simple spin-coating from the solutions of stoichiometric amounts of lead bromide $PbBr_2$ and an ammonium bromide linked with a chromophore such as naphthalene and azobenzene.

Lead halide-based layered perovskites, $(RNH_3)_2PbX_4$, are a family of attractive low-dimensional semiconductor materials; they self-organize a quantum-well structure consisting of a lead halide (PbX_4) semiconductor layer and an organic ammonium (RNH_3) barrier layer.[1-11] Because of their quantum confinement effect, they form a stable exciton with a large binding energy of several hundred meV, and exhibit attractive optical properties due to the stable exciton: strong and sharp photoluminescence[1-3] and electroluminescence,[4-6] and highly efficient nonlinear optical effect.[7,8]

In the layered perovskites, inorganic semiconductor layers of a two-dimensional network of PbX_6 octahedra and organic layers of an ammonium molecule form an alternate layered-structure, where the inorganic semiconductor layers are isolated each other at a distance of a few nanometers by a bimolecular layer of the organic ammonium molecules. So far, simple alkyl ammonium molecules have been used as the organic layer in the layered perovskite, in which they play only the role of a barrier layer with both a low dielectric constant and a large band gap in the quantum-wells.[11]

From the standpoint of the material design in organic-inorganic quantum-wells, however, it is very attractive to employ not only alkylammonium molecules but various ammonium molecules as the organic layer of the layered perovskites. If functionalized ammonium molecules (e.g. chromophore-linked ones) are employed as the organic layer, for example, one can construct a variety of novel organic-inorganic quantum-wells assembled with a functionalized organic layer and an inorganic semiconductor layer at a molecular scale. Here, as the first example of this approach, we report the preparation of oriented thin films of PbBr-based layered perovskites containing an organic layer of chromophore-linked ammonium molecules through a simple spin-coating.

Two functionalized organic ammonium molecules containing naphthalene or azobenzene chromophore (**1** and **2**) were employed as an organic layer. Stoichiometric amounts of lead bromide and the ammonium bromide were dissolved in dimethylformamide. Then, thin films of PbBr-based layered perovskites with a chromophore-linked ammonium molecule as an organic layer were prepared on fused quartz substrates by a spin-coating from the solutions.



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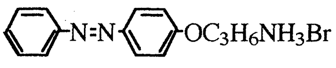

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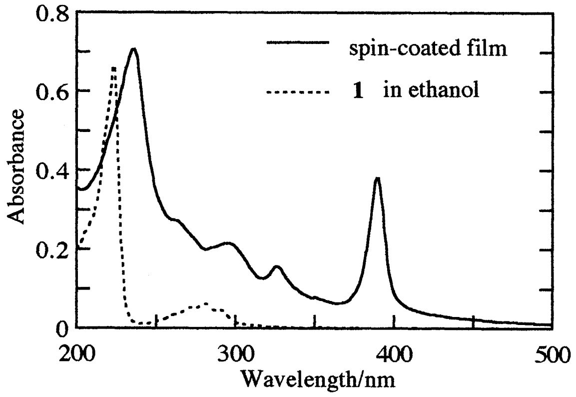

Figure 1. Absorption spectrum of a film spin-coated from the mixed solution of $PbBr_2$ and ammonium bromide **1** ($PbBr_2$: **1** = 1 : 2 in molar ratio). Dotted line shows absorption spectrum of ammonium bromide **1** in ethanol.

Figure 1 shows absorption spectrum of a film spin-coated from the mixed solution of $PbBr_2$ and naphthylethylammonium bromide (**1**). The film exhibits strong and sharp absorption at 390 nm which is assigned to exciton absorption of PbBr-based layered perovskite.[8,9,11] Appearance of the exciton absorption demonstrates that layered perovskite structure was surely formed in the spin-coated film. Another strong absorption is observed at 235 nm, which is not observed in conventional PbBr-based perovskites with an alkyl ammonium layer. The absorption is assigned to the absorption band of naphthalene-chromophore from the comparison with the absorption spectrum of **1** in ethanol (dotted line in Figure 1).

In Figure 2, Xray diffraction from the spin-coated film is compared with that from powdered crystals of PbBr-based layered perovskite with naphthylethylammonium layer. Only diffraction peaks correspond to (0 0 2n) plane (n=1-6) are observed in the spin-coated film. The diffraction profile clearly demonstrated that the spin-coated film was oriented; the c-axis, which is along the stacking direction of the layered structure, is normal to the film plane. In other words, the layer plane is parallel to the film plane. From the diffraction peaks, the layer spacing was calculated to be 2.05 nm.

We have also succeeded in preparing oriented thin films of a layered perovskite containing an azobenzene-linked ammonium molecule as an organic layer. Figure 3 shows absorption spectra of a film spin-coated from the mixed solution of PbBr and azobenzene-linked ammonium bromide (**2**). Absorptions due to exciton of PbBr-based layered perovskite and the H-aggregate of azobenzene-chromophore[12] are observed at 390 nm and 300 nm respectively, demonstrating the formation of a layered perovskite quantum well containing the azobenzene-linked ammonium layer.

Orientational structure of the layered perovskite film was evaluated by the polarized absorption measurement.[13,14] Inset in

Figure 3 shows the incident angle dependencies of dichroic ratio Ap/As derived from the polarized absorption measurement, where Ap and As are absorbances measured with p- and s-polarized light, respectively. The value of Ap/As at 390 nm due to the exciton band was decreased from 1.0 to 0.7 with increase of incident angle from 0 to 50 degrees. The decreasing dependence of Ap/As demonstrates that transition moment of the exciton is parallel to the film plane, namely, the layer structure is oriented parallel to the film plane.

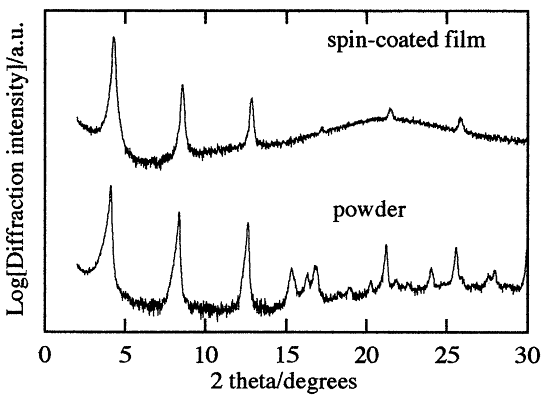

Figure 2. Comparison between Xray diffractions from a film spin-coated from the mixed solution of $PbBr_2$ and ammonium bromide **1** and powdered crystals of PbBr-based layered perovskite with naphthylethyl ammonium layer.

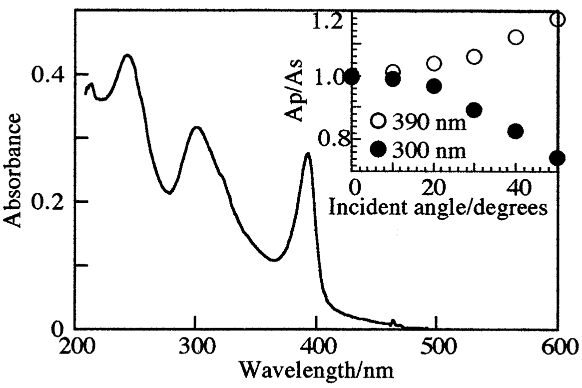

Figure 3. Absorption spectra of a film spin-coated from the mixed solution of $PbBr_2$ and ammonium bromide **1** ($PbBr_2$:**1** = 1 : 2 in molar ratio). Inset shows the incident angle dependencies of dichroic ration Ap/As in the spin-coated film: open circles at 390 nm and solid circles at 300 nm.

Meanwhile, azobenzene-chromophore was demonstrated to be oriented with the long axis nearly vertical to the film plane; the dichroic ratio Ap/As at 300 nm due to H-aggregate of azobenzene-chromophore is increased from 1.0 to 1.2 as increasing the incident angle of polarized lights from 0 to 50 degrees (open circles in the inset). It is likely that the relatively bulky and rod-like shape azobenzene-chromophore has a tendency to have its long axis vertical to the layer plane for occupying in the limited space of organic layer in the layered perovskite. This result also suggests that the layered perovskites possess a possibility to control chromophore-orientation in the layered perovskite by molecular design of the ammonium molecule, in particular, design in molecular shape.

In addition, the exciton absorption of the new layered perovskites was gradually decreased under irradiation of UV light in the air, suggesting gradual degradation of the layered peroskites. For the practical application of the layered perovskites to optical devices, improvement of their stability is necessary.

In this study, we successfully demonstrated that oriented film of layered perovskite containing a chromophore-linked ammonium molecules as an organic layer were formed in a self-organizing manner through a simple spin-coating. This success represents that the approach to construct quantum-well materials containing a functionalized organic layer based on the self-organization of the layered perovskites is promising. The introduction of a functionalized organic layer into quantum-well materials makes it possible to utilize the organic layer not only as a simple barrier layer but as an active layer which modifies optical and electronic properties of the quantum-well. Therefore, we believe, this approach provides a variety of material design in organic-inorganic quantum-wells and contributes greatly to the development of study on organic-inorganic quantum-well.

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