JOURNAL OF MATERIALS SCIENCE **37** (2002) 4845–4848

Preparation and stability of nanocrystalline $(C_6H_5C_2H_4NH_3)_2PbI_4$-doped PMMA films

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Preparation and stability of nanocrystalline $(C_6H_5C_2H_4NH_3)_2PbI_4$-doped PMMA films were investigated. By using spin-coating and subsequent annealing technique, nanometer-sized $(C_6H_5C_2H_4NH_3)_2PbI_4$ precipitates were successfully formed into a PMMA matrix. These films showed clear exciton absorption and free exciton emission at room temperature. Comparing with $(C_6H_5C_2H_4NH_3)_2PbI_4$ film, marked improvement of thermal- and photo-stability was observed for nanocrystalline $(C_6H_5C_2H_4NH_3)_2PbI_4$-doped PMMA films. The thermal-stability of these films correlates with the decomposition of the organic part. As for photo-stability, photo-irradiation induced oxidation is one of the possible reasons for the degradation of the films. © *2002 Kluwer Academic Publishers*

1. Introduction

During the past decade, low-dimensional materials with quantum functions have attracted attention due to the possibility of creating interesting optical and electrical materials. The lead halide-based layered perovskite compounds, with the chemical formula $(RNH_3)_2PbX_4$ (R: C_nH_{2n+1}, C_6H_5-C_nH_{2n}-, X: halogen), have been extensively studied owing to their substantially large exciton binding energy (as large as a few hundreds meV), unique crystal structure and highly self-organizing ability [1–3]. In these compounds, $[PbX_6]^{4-}$ octahedral inorganic layers act as a semiconductor (well) layer and organic layers act as an insulator (barrier) layer. Furthermore, the exciton binding energy is significantly enhanced by both the dielectric and quantum confinement effects because the inorganic well layer has higher dielectric constant and smaller band-gap than the organic barrier layer [4]. As a result, these compounds exhibit pronounced excitonic effects such as photoluminescence (PL), electroluminescence (EL) and large third-order optical nonlinearity [5–7]. Recently, heterostructure EL devices, bi-exciton laser and thin film field-effect transistors (TFT) made by using these compounds have been reported [8–10].

From the viewpoint of the material design for optical applications, it is quite important to fabricate stable materials. However, one difficulty in the practical application of these compounds is the poor stability (i.e., photo-stability, thermal-stability) because these compounds are composed of organic compounds and lead halide. Therefore, to overcome this difficulty, the stability should be clarified and improved. Here, we report the preparation, optical properties and stability of nanocrystalline $(C_6H_5C_2H_4NH_3)_2PbI_4$-doped PMMA [poly(methyl methacrylate)] films as the first example for making "stable materials".

2. Experimental procedure

2.1. Sample preparation

Nanocrystalline $(C_6H_5C_2H_4NH_3)_2PbI_4$-doped PMMA films (about 1 μm in thickness) were fabricated on a SiO_2 glass substrate by a conventional spin-coating technique as reported in ref [11]. Poly(methyl methacrylate) (PMMA), stoichiometric amounts of $C_6H_5C_2H_4NH_3I$ and PbI_2 were dissolved in N, N-dimethyl formamide (DMF). The concentration of PMMA in DMF was 20 wt% and the weight ratio of $(C_6H_5C_2H_4NH_3)_2PbI_4$/PMMA fixed at 0.1 in this study. Using these solutions, spin coating was carried out at 2000 rpm for 60 sec. After spin coating, these films were then annealed at various temperatures for various times. Thin films, about 20 nm in thickness, of $(C_6H_5C_2H_4NH_3)_2PbI_4$ (denoted as PhE-PbI_4 hereafter) were also fabricated. A 2 wt% acetonitrile solution, dissolved stoichiometric amounts of $C_6H_5C_2H_4NH_3I$ and PbI_2, was used for depositing PhE-PbI_4 films.

2.2. Stability measurements

The photo-stability of the samples was estimated from the relative exciton absorption intensity (I_t/I_o) as a function of photo-irradiation time. Exciton absorption intensity of the samples before and after irradiation was measured using a conventional Vis-UV spectrophotometer (JASCO V-570 Spectrophotometer) at room temperature. Note that I_o means an exciton absorption intensity of the as-prepared film and I_t means that of a film irradiated for t min. The samples were irradiated by using a high pressure mercury lamp (500 W) with a band-pass filter (U-34) as an UV-irradiation source, and focused to 1 mm in diameter. The photo-irradiation was carried out at atmospheric pressure or in a vacuum (approximately 0.1 Pa) at room temperature.

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The thermal-stability of the samples was also investigated from the relative exciton absorption intensity (I_t/I_o) as a function of annealing time at various temperatures. The thermal-stability measurements were carried out at atmospheric pressure.

2.3. Characterization of nanocrystalline $(C_6H_5C_2H_4NH_3)_2PbI_4$-doped PMMA films

The crystallinity and orientation of the samples before and after irradiation were characterized by X-ray diffraction (XRD, Rigaku, RINT2500 X-ray diffractometer) using monochromated CuKα radiation (30 kV, 20 mA). $(C_6H_5C_2H_4NH_3)_2PbI_4$ precipitates formed in a PMMA matrix were observed with a field emission type transmission electron microscope (FE-TEM, Hitach HF-2000). The near-surface composition of the samples was estimated by using X-ray photoelectron spectroscopy (XPS, PHI Model-1600) using non-monochromated MgKα radiation (15 kV, 26 mA). Room temperature photoluminescence (PL) and photoluminescence excitation (PLE) spectra of the films were recorded (Perkin Elmer, LS-50B).

3. Results and discussion

3.1. Formation of nanocrystalline $(C_6H_5C_2H_4NH_3)_2PbI_4$-doped PMMA films

X-ray diffraction (XRD) spectra of nanocrystalline $(C_6H_5C_2H_4NH_3)_2PbI_4$-doped PMMA films showed diffraction peaks corresponding to the (0 0 1) plane of the PhE-PbI_4 crystal, which revealed that PhE-PbI_4 precipitates were formed in the PMMA matrix.

Fig. 1 shows a typical FE-TEM photograph for the film annealed at 125°C for 30 min. As seen in the picture, $(C_6H_5C_2H_4NH_3)_2PbI_4$ precipitates with particle size of a few nanometers were clearly observed within the film. The evidence led us to strongly support the fact that nanometer-sized $(C_6H_5C_2H_4NH_3)_2PbI_4$ crystals were successfully precipitated into the PMMA matrix by using spin-coating and subsequent annealing technique from their DMF solutions.

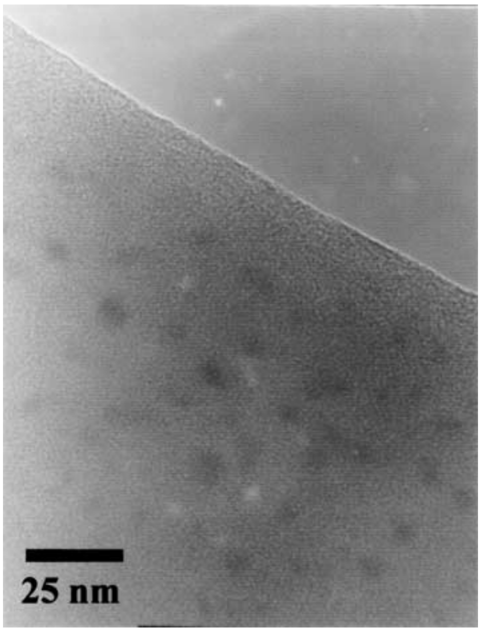

Figure 1 FE-TEM photograph of nanocrystalline $(C_6H_5C_2H_4NH_3)_2PbI_4$-doped PMMA film annealed at 125°C for 30 min.

Vis-UV optical absorption spectra of nanocrystalline $(C_6H_5C_2H_4NH_3)_2PbI_4$-doped PMMA films annealed at (a) 60, (b) 100, (c) 125 and (d) 150°C for various times are shown in Fig. 2. When the films were annealed above 100°C (see Fig. 2b–d), the films showed a strong absorption band with narrow bandwidth ($\sim$70 meV) at around 518 nm. This absorption band has been attributed to the exciton of PhE-PbI_4 crystal formed in the $[PbI_6]^{4-}$ layer by the transition from Pb^{2+} (6s) to Pb^{2+} (6p) orbital [12]. The fundamental transition from Pb^{2+} (6s) to Pb^{2+} (6p) orbital was also observed at around 360 nm. On the other hand, when the films were annealed at low temperature below 60°C as shown in (a), the film showed a broad absorption band at around 380 nm owing to the formation of PbI_2 precipitates. Note that the absorption band due to PbI_2 precipitates was also observed for the films annealed at 125°C for 60 min (see Fig. 2d).

Fig. 3 shows room temperature photoluminescence (PL) and photoluminescence excitation (PLE) spectra of nanocrystalline $(C_6H_5C_2H_4NH_3)_2PbI_4$-doped PMMA films annealed at 125°C for 10 min. As seen in this figure, pronounced PL from the sample with narrow bandwidth was also observed at 520 nm. Note that this PL is easily seen with the naked eye. Comparing with the exciton absorption and PL bands, the PL from the samples is consistent with free exciton emission due to its very small (8 meV) Stokes shift [13].

3.2. Stability of nanocrystalline $(C_6H_5C_2H_4NH_3)_2PbI_4$-doped PMMA films

Changes in the relative exciton absorption intensity (I_t/I_o) of nanocrystalline $(C_6H_5C_2H_4NH_3)_2PbI_4$ -doped PMMA films as a function of annealing time are shown in Fig. 4. In the case of PhE-PbI_4 film, the I_t/I_o ratio decreased rapidly even at 100°C due to its poor thermal-stability. On the contrary, $(C_6H_5C_2H_4NH_3)_2PbI_4$-doped PMMA films showed good thermal-stability when the film was annealed at 100°C. In this case, the I_t/I_o decreased slightly with the irradiation time up to 240 min. However, when the film was annealed at 125°C, the I_t/I_o gradually decreased with increasing annealing time. From the X-ray diffraction and optical absorption spectra of the films annealed at high temperatures above 125°C for long times, more than 240 min, formation of PbI_2 precipitates was observed. Therefore the decrease in the I_t/I_o ratio during annealing, that is, thermal-stability correlated with the decomposition of the organic part, $C_6H_5C_2H_4NH_3I$.

Fig. 5 shows the changes in the relative exciton absorption intensity (I_t/I_o) of nanocrystalline $(C_6H_5C_2H_4NH_3)_2PbI_4$-doped PMMA films as a function of photo-irradiation time. In PhE-PbI_4 films, continuous decrease in the relative exciton absorption intensity was observed. For nanocrystalline $(C_6H_5C_2H_4NH_3)_2PbI_4$-doped PMMA

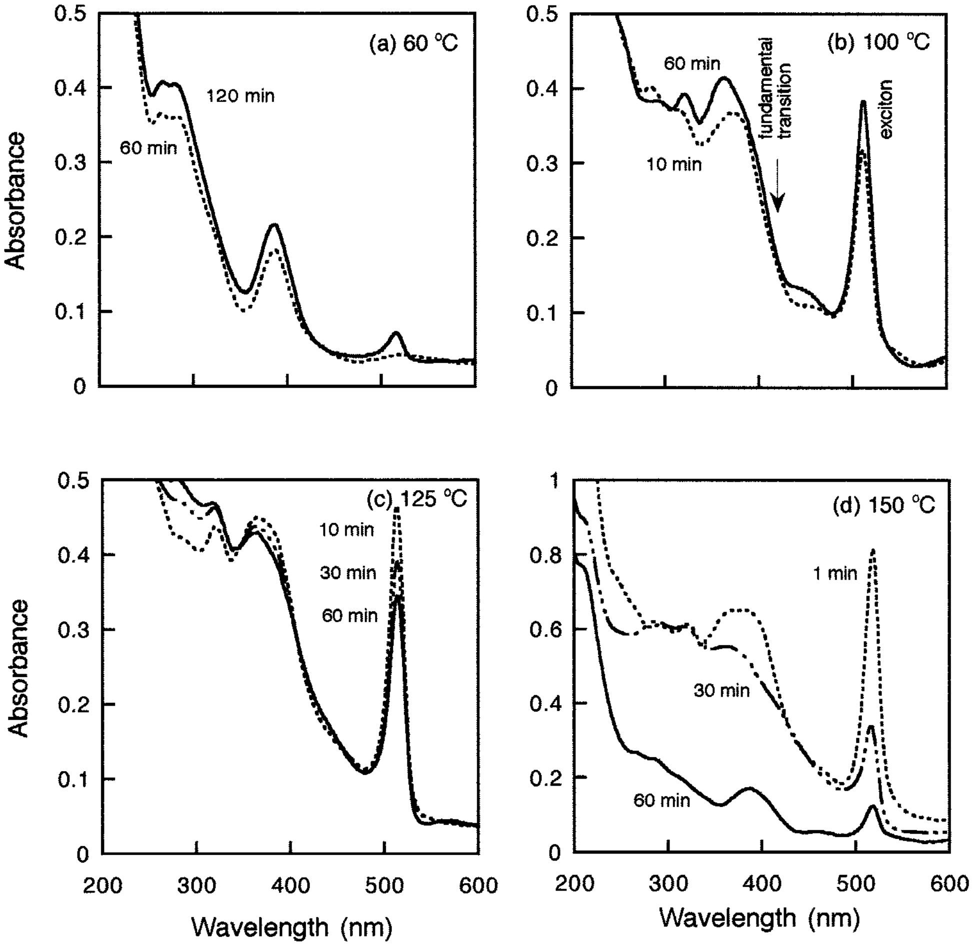

Figure 2 Vis-UV optical absorption spectra of nanocrystalline $(C_6H_5C_2H_4NH_3)_2PbI_4$-doped PMMA films annealed at (a) 60, (b) 100, (c) 125 and (d) 150°C for various times.

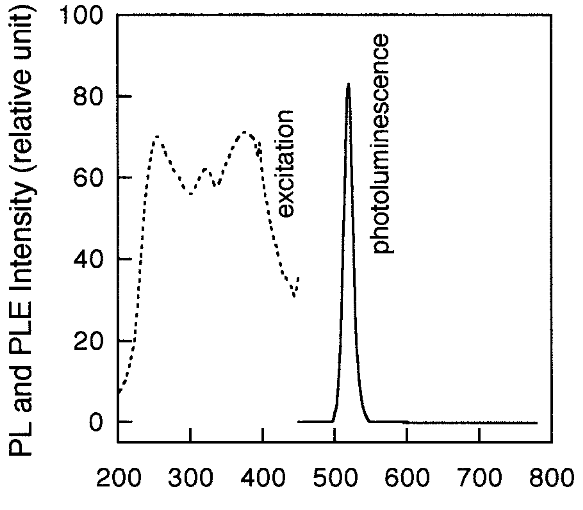

Figure 3 Room temperature photoluminescence (PL, solid line) and photoluminescence excitation (PLE, dotted line) spectra of nanocrystalline $(C_6H_5C_2H_4NH_3)_2PbI_4$-doped PMMA films annealed at 125°C for 10 min.

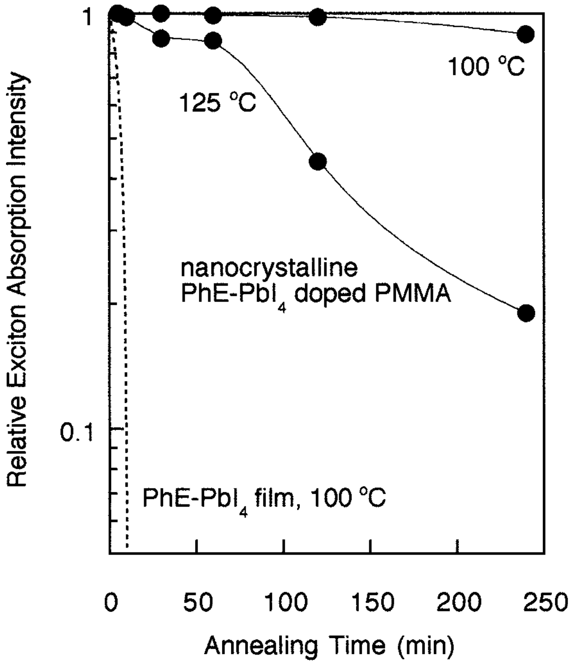

Figure 4 Changes in the relative exciton absorption intensity (I_t/I_o) of nanocrystalline $(C_6H_5C_2H_4NH_3)_2PbI_4$-doped PMMA films as a function of annealing time.

films, improvement of the photo-stability was observed. This result suggested that the degradation of $(C_6H_5C_2H_4NH_3)_2PbI_4$ crystals doped in PMMA induced by the photo-irradiation could be suppressed by the present technique. Therefore, $(C_6H_5C_2H_4NH_3)_2PbI_4$-doped PMMA films can be promising candidates for use in interesting optical materials, especially for use in third-order nonlinear optical materials because of the substantially large exciton binding energy.

In this paragraph, degradation mechanism of $(C_6H_5C_2H_4NH_3)_2PbI_4$-doped PMMA films is discussed. As mentioned before, degradation of

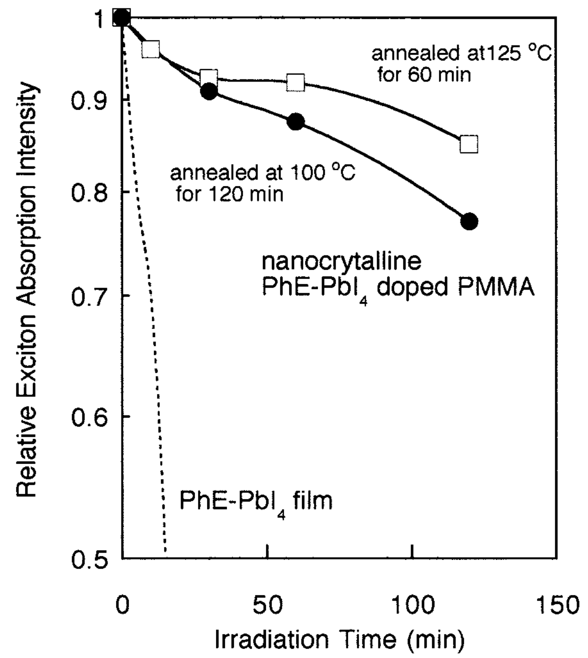

Figure 5 Changes in the relative exciton absorption intensity (I_t/I_o) of nanocrystalline $(C_6H_5C_2H_4NH_3)_2PbI_4$-doped PMMA films as a function of photo-irradiation time.

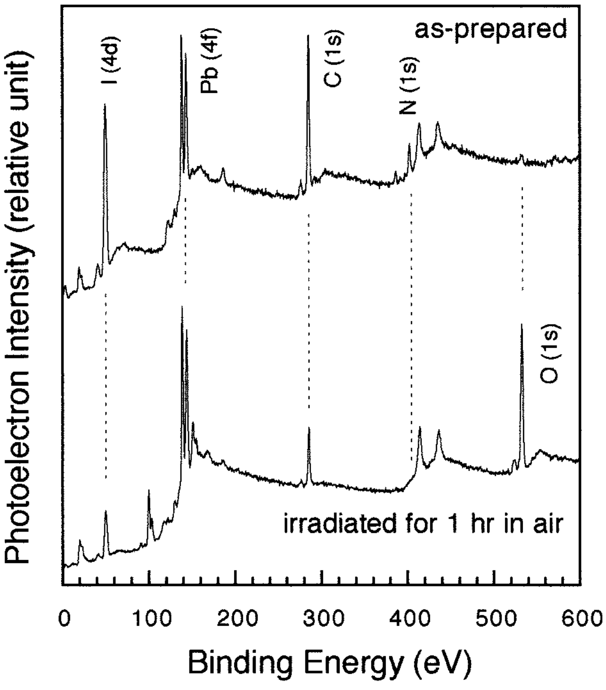

Figure 6 XPS spectra of PhE-PbI$_4$ films before and after photo-irradiation.

$(C_6H_5C_2H_4NH_3)_2PbI_4$-doped PMMA films caused by the thermal-annealing correlates with the decomposition of the organic part. However, the degradation mechanism due to photo-irradiation is still unknown. Fig. 6 shows typical XPS wide-scan spectra of PhE-PbI$_4$ films before and after photo-irradiation. After irradiation in air, decreases in the photoelectron intensity of I(4d) and C(1s) orbital were observed compared with that of Pb(4f) orbital, and the XPS spectrum showed a clear O(1s) signal. From these results, photo-irradiation induced oxidation is one of the possible reasons for the degradation of the films. Further, elimination of the halogen species should occur as well as oxidation in the films because the intensity of the I(4d) signal also decreased when the sample was irradiated in vacuum. Consequently, the permeability of oxygen and halogen species through the PMMA matrix becomes a dominant factor of the photo-stability of $(C_6H_5C_2H_4NH_3)_2PbI_4$-doped PMMA films.

More detailed studies on the stability of $(C_6H_5C_2H_4NH_3)_2PbX_4$-doped PMMA films (X; halogen) and the measurement of their optical properties are being carried out.

4. Conclusions

In this study, preparation, optical properties and stability of nanocrystalline $(C_6H_5C_2H_4NH_3)_2PbI_4$-doped PMMA films were investigated. The following conclusions were drawn.

1. Nanocrystalline $(C_6H_5C_2H_4NH_3)_2PbI_4$-doped PMMA films were successfully fabricated on glass substrates from its DMF solutions by using spin-coating and subsequent annealing.
2. The films showed clear exciton absorption and free exciton emission at room temperature owing to the substantially large exciton binding energy.
3. Improvement of thermal- and photo-stability was observed by doping nanometer sized $(C_6H_5C_2H_4NH_3)_2PbI_4$ crystals into PMMA matrix.
4. Thermal-stability of nanocrystalline $(C_6H_5C_2H_4NH_3)_2PbI_4$-doped PMMA films correlates with the decomposition of the organic part.
5. Photo-irradiation induced oxidation is one of the possible reasons for the degradation of the films.

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Received 5 February
and accepted 26 March 2002