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Exciton spectroscopy and assessment of crystallization of amorphous $(PbBr_2)_{0.9}(CuBr)_{0.1}$ films

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Abstract
Amorphous $(PbBr_2)_{0.9}(CuBr)_{0.1}$ films have been obtained by quench deposition of the mixture of $PbBr_2$ and CuBr. Upon crystallization of the films, Cu^+ ions aggregate to form very small CuBr crystallites, which are uniformly embedded in the crystalline $PbBr_2$ matrix, exhibiting blue-shifted CuBr exciton absorption. Despite the precipitation of the CuBr crystallites, the resulting films retain a relatively flat surface (rms roughness, ~15 nm for films with ~800 nm thickness).

1. Introduction

Many metal halides such as silver [1], thallium [2], copper [3], lead [4] or cadmium [5] halides have been shown to be amorphized by quench deposition yielding film samples. The amorphous films exhibit excellent transmittance below the absorption edge and have a well defined, characteristic crystallization temperature at which the optical absorption spectrum changes drastically. Many of the crystalline films produced via the amorphous phase show very high transmittance compared with (crystalline) films deposited onto hot substrates. This is particularly the case for lead halides.

Previously we reported an ion-glass model [6] of the amorphous state of lead halides. The model, which was applied to amorphous PbX_2 with X = F, Cl and Br, proposed that each Pb^{2+} ion in amorphous PbX_2 was surrounded by nine neighbouring X^- ions without any well defined site symmetry around it. By using an effective Pb^{2+}–X^- distance d for the superionic assembly $[PbX_9]^{7-}$, the logarithmic fluctuation $\Delta d/d$ was shown to have a Gaussian distribution with a full-width at half-maximum of about 0.05. Such a large fluctuation was considered to be favourable for replacing the Pb^{2+} ion by a pair of small monovalent cations up to a considerable concentration. Indeed, we recently showed [7] that heavily Cu^+-doped amorphous $PbCl_2$ and CuCl were obtainable by quench deposition of the mixture of $PbCl_2$ and CuCl. The amorphous state was explained in terms of quasicomplexes, that is, the Pb^{2+} ion in the superionic assembly $[PbCl_9]^{7-}$ with a large Pb^{2+}–Cl^- distance in the amorphous environment was replaced by a pair of Cu^+ ions, forming a quasicomplex $[Cu_2Cl_9]^{7-}$. Upon crystallization of the films, the Cu^+ ions aggregated to form CuCl precipitates embedded in the crystalline $PbCl_2$ matrix, exhibiting exciton absorption slightly blue-shifted in energy (by a few milli-electron volts) due to the size effect on the exciton. The experiment opened up the possibility of producing densely dispersed CuCl clusters in a controlled manner in $PbCl_2$ films.

The above study on the $PbCl_2$–CuCl system was based on *in situ* UV exciton spectroscopy, which was shown to provide a powerful means of studying the growth of copper halide nanocrystals in a lead halide matrix (similar to the case of CuCl nanocrystal growth in alkali halide bulk-crystal matrix [8]). However, film assessment such as surface morphology and compositional analysis was not carried out due to the low crystallization temperature (260–270 K) of the films. In the present work a similar experiment was carried out on the $PbBr_2$–CuBr system, and film assessment was performed on both amorphous and crystalline phases so that they could be compared (the crystallization temperature of amorphous $PbBr_2$ films lies above room temperature, 335 K [9]).

2. Results and discussion

Figure 1 shows optical absorption spectra at 77 K of an amorphous $PbBr_2$–CuBr film quench deposited [7] by vacuum evaporation of a melt-quenched mixture of the two compounds onto a silica-glass substrate (EDH grade from Nippon Sekiei Garasu Co.) cooled to 77 K. The nominal molar ratio of the mixture was $PbBr_2$:CuCl = 9:1, and the thickness of the film, which was determined by an interference method [10], was

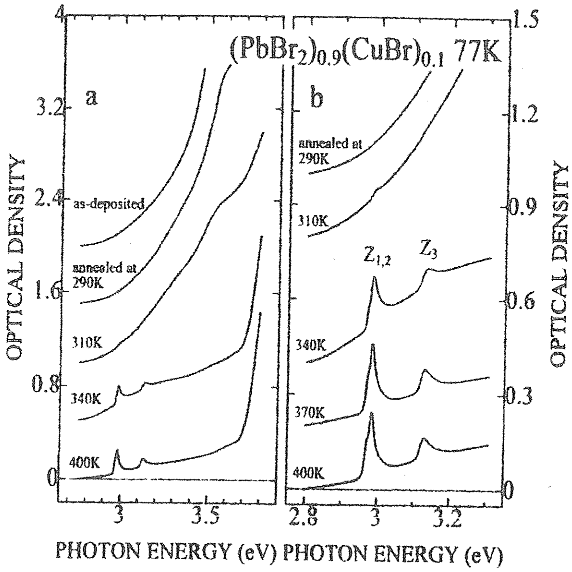

Figure 1. (a) The effect of annealing on the absorption spectrum of a quench-deposited amorphous $(PbBr_2)_{0.9}(CuBr)_{0.1}$ film with a thickness about 450 nm. All the spectra were measured at 77 K for the increasing annealing temperatures indicated. The scale on the ordinate is given only for the lowermost spectrum. (b) The magnified spectra of the same film showing the occurrence and growth of CuBr $Z_{1,2}$ and Z_3 exciton absorptions with the rise of the annealing temperature.

about 450 nm. A spectrum was first measured *in situ* on the as-deposited film. The film was then subjected to *in situ* annealing cycles to measure spectra (at 77 K) for increasing annealing temperatures (T_a). Each annealing cycle involves heating at a rate of 1 K min^{-1}, annealing for 10 min and cooling at a rate of 10 K min^{-1}.

The overall spectral behaviour is similar to the previous results on the $PbCl_2$–CuCl system [7]. However, to read the present results, it is relevant to recall the transient spectra of amorphous $PbBr_2$ films during crystallization. The absorption spectrum of amorphous $PbBr_2$ films is characterized by a non-excitonic, prominent first band peaking at 3.700 eV (absorption edge, about 3.4 eV) [6]. On slow heating (0.4 K min^{-1}), the films show sharp crystallization in a narrow temperature range of 2.5 K near 335 K [9], with the first band transformed to a sharp excitonic peak located at 3.929 eV (absorption edge, about 3.7 eV). A detailed measurement [11] achieved at a very slow heating rate of 0.05 K min^{-1} in the range 334–338 K revealed that threee competing spectral structures showed up during crystallization. Of the three, the lowest-energy (about 3.55 eV) structure, A, which was associated with nucleation in the films, was observed at the initial stage of crystallization. With the progress of crystallization, structure A became weaker and finally disappeared, leaving behind the excitonic peak.

In the present film, the absorption edge changes from about 3.4 eV for $T_a = 77$ K (as-deposited film) to about 3.7 eV for $T_a \geqslant 340$ K, as seen from figure 1(a). This reflects crystallization of the film. The structure appearing around 3.5 eV for 290 K $\leqslant T_a \leqslant$ 310 K corresponds to structure A of the $PbBr_2$ film (note that the optical density at the peak of the first band for $T_a = 77$ K amounts to about 10 when calculated for a $PbBr_2$ film of 450 nm thickness). Therefore, we can conclude that the crystallization of the present film starts to occur at about 290 K and is completed at about 340 K. The Cu^+ ions in the film have the effect of lowering the crystallization temperature and widening the temperature range where the crystallization proceeds. After completion of crystallization there arise new structures at energies in the range 2.9–3.2 eV due to $Z_{1,2}$ and Z_3 exciton absorption of crystalline CuBr. This indicates that the Cu^+ ions aggregate to form CuBr clusters during the final stage of crystallization of the host, as in the case of $PbCl_2$–CuCl system. The growth process of the CuBr clusters is seen from the magnified spectra

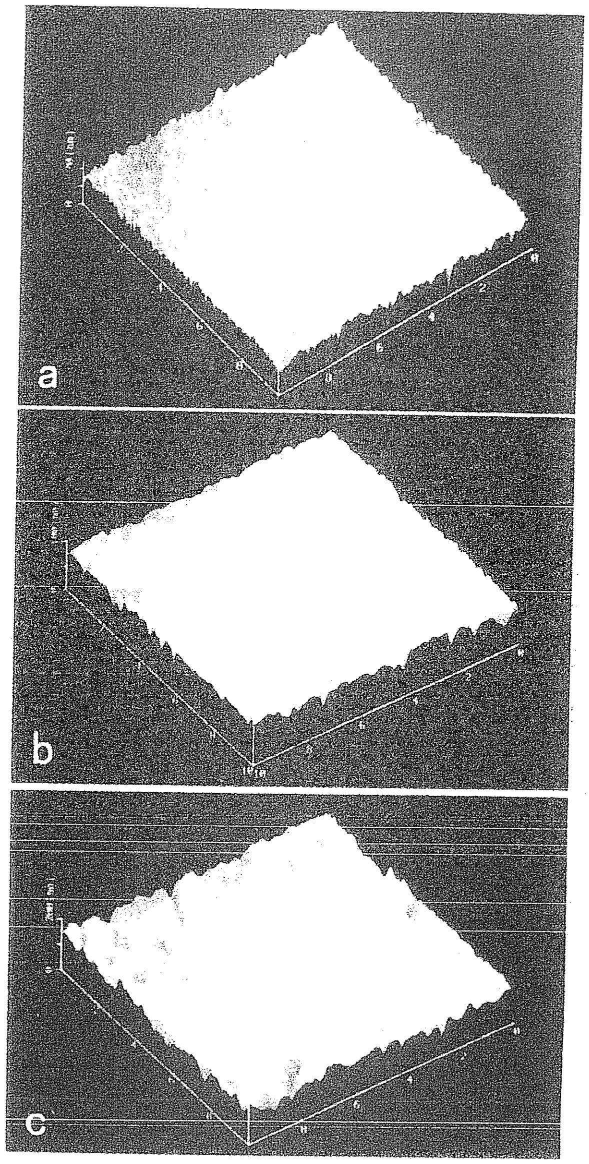

Figure 2. Large-scale (10 μm × 10 μm) AFM images of quench-deposited $(PbBr_2)_{0.9}(CuBr)_{0.1}$ films annealed at (a) ~290 K (Z:10 nm/div), (b) ~400 K (Z:50 nm/div) and (c) ~500 K (Z:100 nm/div), for a duration of 10 min. All the films have nearly the same thickness, about 800 nm.

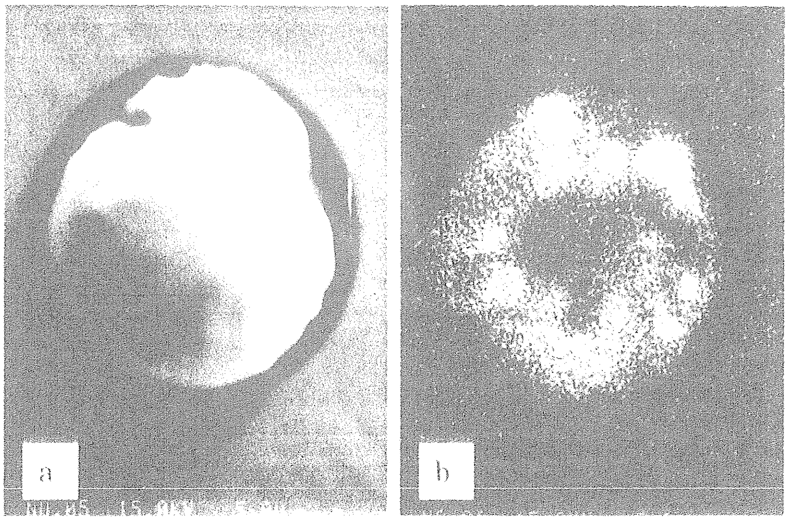

Figure 3. An example of (a) SEM and (b) EPMA images of one of the small particles found for the film annealed at 500 K for 10 min. The EPMA image represents the distribution of copper (white region).

in figure 1(b). Although there is no trace of exciton absorption for T_a = 290 K, clear peaks due to $Z_{1,2}$ and Z_3 exciton transitions are observed for T_a = 340 K. Upon further annealing, they sharpen in shape and become strong in intensity accompanying a small red shift of the peak energies (by a few milli-electron volts), similar to the $PbCl_2$–CuCl case. The red shift reflects the growth of the CuBr clusters, i.e. relaxation of the quantum confinement effect on the excitons. We note that the exciton peaks for T_a = 400 K were still blue-shifted by a few milli-electron volts relative to those of CuBr films vacuum evaporated onto hot substrates.

We assessed surface morphology differences between the films annealed at different temperatures *ex situ* using an atomic force microscope (AFM). Figure 2 shows large-scale (10 μm × 10 μm) AFM images of the films annealed at (a) ~290 K (room temperature), (b) ~400 K and (c) ~500 K, for a duration of 10 min (the individual films were deposited to thicknesses of about 800 nm onto separate substrates using the same source material (a mixture with nominal molar ratio, $PbBr_2$:CuBr = 9:1) as that used for preparing the film whose spectra are shown in figure 1. The first film (T_a = 290 K) was in the amorphous phase and the others were in the crystalline phase. The rms roughnesses obtained from these figures were (a) ~4 nm, (b) ~15 nm and (c) ~70 nm, respectively. The amorphous film is found to retain a relatively flat surface at room temperature. The crystalline film annealed at 400 K results in surface roughening. The roughening due to crystallization is, despite the precipitation of CuBr crystallites, comparable to those occurring for covalent semiconductors such as Se (for example, it is reported in [12] that (undoped) amorphous Se films (thickness, about 850 nm) deposited by vacuum evaporation on Corning glasses at room temperature, though having a very flat surface with an rms roughness of about 0.8 nm, result in a surface roughness of about 13 nm when crystallized by annealing at 100 °C). On the other hand, in the film annealed at 500 K (figure 2(c)), for which the exciton absorption due to CuBr crystallites was not longer observed, there occurs pronounced surface roughening. Observation of this film under an optical microscope found several small particles (black in colour) existing in the images. Therefore, we further investigated the film with a scanning electron microscope (SEM) and an electron probe x-ray micro-analyser (EPMA). Figure 3 is a comparison between (a) the SEM and (b) the EPMA images of one of the small particles. It was found from the SEM observation that the size of the particle in the figure was about 30 μm in diameter and 4 μm in height. The analysis with EPMA disclosed that copper existed only inside the particle but not outside; the particle was mainly composed of copper and lead (see below).

Table 1. The elemental composition of the three films whose AFM images are shown in figure 2. For the 500 K annealed film, the composition is listed both for the regions inside and outside the particle whose SEM and EPMA images are shown in figure 3.

Annealing temperature (K)	Element	Number ratio of atoms
290	Pb	0.338
	Cu	0.038
	Br	0.623
400	Pb	0.353
	Cu	0.048
	Br	0.598
500		
Inside the particle	Pb	0.771
	Cu	0.201
	Br	0.028
Outside the particle	Pb	0.461
	Cu	0.000
	Br	0.539

We analysed the elemental composition of the three films using EPMA. The results are shown in table 1. The spatial resolution of the EPMA measurement was 1 μm × 1 μm (probing depth, 1 μm). The nominal molar ratio, $PbBr_2$:CuBr = 9:1, of the mixture (used as a source material to deposit the films) corresponds to the number ratio Pb:Cu:Br = 0.31:0.034:0.65. The measurement results are close to this ratio for the two films annealed at 290 and 400 K, respectively. In particular, the nominal ratio of the metals, Pb:Cu = 9:1, is well reproduced in the films (0.90:0.10 and 0.88:0.12 for the films annealed at 290 and 400 K, respectively). In addition, there was little scatter (less than a few per cent) in the measurement values from region to region in the films. In view of the spatial resolution, 1 μm, of the EPMA measurements, therefore, it can be inferred that a uniform amorphous $(PbBr_2)_{1-x}(CuBr)_x$ solid solution with predetermined nominal CuBr concentration, $x = 0.1$, was attained by the present method and the crystallization of the obtained amorphous solid solutions yielded very small CuBr crystallites (see next paragraph) uniformly embedded in the $PbBr_2$ polycrystalline matrix. On the other hand, concerning the film annealed at 500 K, whose EPMA result is presented both for the film regions inside and outside the above-mentioned particle, a clear segregation occurs. That is to say, the particle is mainly composed of Pb and Cu forming an alloy, while outside the particle there is no trace of Cu.

The volume fraction of the CuBr crystallites in the film annealed at 400 K amounts to 0.05 (under the assumption of the same density ratio of CuBr and $PbBr_2$ as that of the bulk crystals). If we assume spherical CuBr crystallites of radius a are embedded in the film, then the mean distance between nearest-neighbour crystallites is calculated to be, for example, about 220 nm for $a = 50$ nm, which corresponds to the film in which only four or five crystallites of radius 50 nm are embedded along the length of 1 μm (spatial resolution of EPMA). The EPMA measurements with resolution of 1 μm, if carried out on such a film, would result in a large scatter in the measurement values from region to region in the film, due to a random (but uniform) distribution of the crystallites. Therefore, the very low scatter (less than a few per cent) in the EPMA measurement values for the actual film annealed at 400 K suggests a very small effective radius (presumably, less than 50 nm) of the CuBr crystallites embedded therein. In favour of this suggestion, exciton spectroscopy indeed detected the blue shifts of $Z_{1,2}$ and Z_3 exciton transitions due to the effect of confinement on the excitons, although a direct measurement of the crystallite size using a method such as electron microscopy or x-ray diffraction is necessary for a quantitative consideration.

3. Conclusion

Amorphous $(PbBr_2)_{0.9}(CuBr)_{0.1}$ films were obtained by quench deposition of the mixture of $PbBr_2$ and CuBr. Similar to the previous experiment on the $PbCl_2$–CuCl system, Cu^+ ions are considered to be incorporated into the amorphous matrix of the lead halide base, with the $PbBr^{+2}$ ion in the superionic assembly $[PbBr_9]^{7-}$ of a large Pb^{2+}–Br^- distance being replaced by two Cu^+ ions, thus forming a quasicomplex $[Cu_2Br_9]^{7-}$. Crystallization of the host environment due to annealing gave rise to aggregation of Cu^+ ions, yielding very small CuBr crystallites uniformly embedded in the crystalline $PbBr_2$ matrix. Surface roughening of the films due to crystallization was comparable to that occurring for covalent semiconductors such as Se, despite the precipitation of the CuBr crystallites. Studies aimed at achieving densely and uniformly dispersed clusters (nanocrystals) with a specified size distribution are in progress on the PbX_2–CuX (X = Cl, Br) systems (the results will be reported in the near future). Such films are not merely desirable for the basic research of particle confinement problems and related mesoscoptic enhancement of linear and nonlinear optical properties, but for their application studies.

Acknowledgments

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