Heavily Cu+-doped amorphous PbCl2 films and aggregation of Cu+ions due to crystallization observed by UV spectroscopy

Heavily Cu^+-doped amorphous $PbCl_2$ films and aggregation of Cu^+ ions due to crystallization observed by UV spectroscopy

S Kondo, N Tanaka and T Saito

Research Centre for Development of Far-Infrared Region, Fukui University, Bunkyo, Fukui 910-8507, Japan

Abstract. Heavily Cu^+-doped amorphous $PbCl_2$ has been obtained by quench deposition of the mixture of $PbCl_2$ and CuCl. Upon crystallization, the large majority of Cu^+ ions aggregate to form CuCl precipitates embedded in the crystalline $PbCl_2$ matrix. The present experiment opens up the possibility of producing densely dispersed CuCl clusters in a controlled manner in $PbCl_2$ films.

1. Introduction

One of the interests in producing film material rather than growing single crystals is the possibility of introducing high concentration impurities. For example, Cu^+-doped KCl films with the Cu^+ concentration ranging from 10^{20} to 10^{21} cm^{-3} have been attained (for the purpose of device application such as ultraviolet (UV) optical filters) by resistive co-evaporation of KCl–CuCl mixed powders with nominally 1–15 mol% CuCl concentration [1]. Recently, we doped CdI_2 films with trivalent Bi^{3+} ions up to 10 mol% of cation concentration [2], despite the different valencies between the host and guest cations. The heavy doping was achieved in the amorphous form of the films by quench deposition of the mixture of CdI_2 and BiI_3. Crystallization of the films resulted in well defined two-molecule BiI_3 clusters densely monodispersed in the CdI_2 polycrystalline matrix. In the present work we investigated $PbCl_2$ films heavily doped with Cu^+ ions, to study the opposite case of non-stoichiometric impurity, i.e. the impurity having smaller valency than the host cation.

Both $PbCl_2$ [3] and CuCl [4] can be rendered amorphous by quench deposition. The two compounds have similar vapour pressure; for instance the temperature at which the vapour pressure becomes 1 Torr (130 Pa) is 547 °C for $PbCl_2$ and 546 °C for CuCl. This may provide a good condition for preparing an amorphous solid solution by the co-evaporation of their mixture. Furthermore, the small ionic radius of the Cu^+ ion (0.96 Å [5]) compared to the Pb^{2+} ion radius (1.24–1.28 Å [5]) makes it favourable for the Pb^{2+} ions to be substituted by the Cu^+ ions in the amorphous environment. Aggregation of the substituted Cu^+ ions may be observed by exciton spectroscopy, as indeed demonstrated for CuCl nanocrystal growth in alkali halide single crystals [6]. These considerations motivated the present work.

2. Experimental details

For the preparation of the heavily Cu^+-doped $PbCl_2$ films, mixed powders of $PbCl_2$ and CuCl were put into silica-tube containers. The containers were evacuated to 5×10^{-4} Pa at 200 °C for 24 h and sealed to get vacuum-sealed ampoules of the mixtures. The ampoules were heated to 555 °C, held at that temperature for 1 h, and then quenched in ice water to achieve homogeneity in the concentration of the mixtures.

Amorphous films of the thus-prepared mixtures were obtained by quench-deposition described in [7]. In brief, the deposition was carried out on a fused-silica substrate cooled to 77 K in a vacuum of about 9×10^{-6} Pa using a tungsten basket heating element placed 8 cm in front of the substrate; the deposition rate was about 20 nm min^{-1}. Such a high deposition rate was considered to be favourable for achieving the nominal composition ratio of $PbCl_2$ and CuCl in the films, although the resulting composition ratio was not analysed. The thicknesses of the films were determined by an interference method [8].

The doped $PbCl_2$ films were investigated by an improved UV absorption spectroscopy, described in [2]. The method is based on simultaneous measurements of transmittance and reflectance from which accurate optical densities of weakly-absorbing films can be determined. The measurements were made *in situ* on a film annealed at various temperatures.

3. Results

Figure 1 illustrates the effect of annealing on the absorption spectra of a quench-deposited amorphous $PbCl_2$:CuCl film. The nominal concentration of CuCl is 10 mol%. The thickness of the film is about 850 nm. Spectral

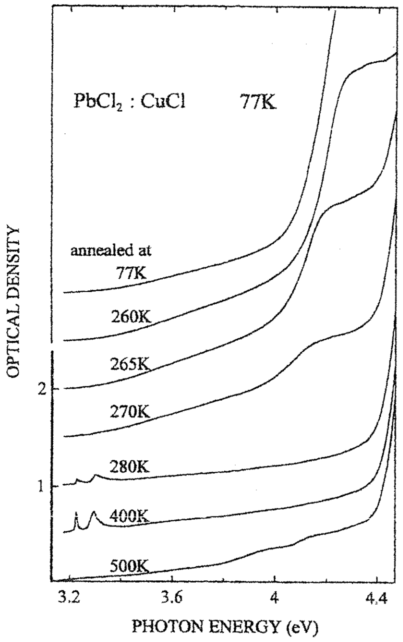

Figure 1. The effect of annealing on the absorption spectrum of a quench-deposited amorphous $PbCl_2$:CuCl film of nominal 10 mol% CuCl concentration. All the spectra are measured at 77 K for the increasing annealing temperatures indicated. The scale on the ordinate is given only for the lowermost spectrum. The film thickness is about 850 nm.

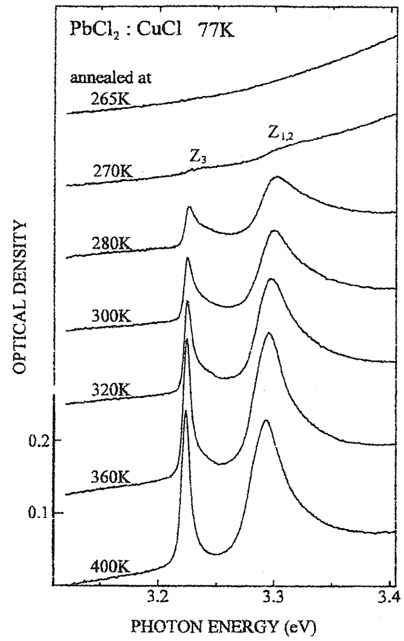

Figure 2. Details of the effect of annealing ($T_a \geqslant 265$ K) on the absorption spectra at 77 K in the region of CuCl exciton absorption, measured for the same film as that for the spectra in figure 1.

measurements were carried out at 77 K for increasing annealing temperatures (T_a). Heating and cooling in each annealing cycle were performed at rates of 1 and 10 K min^{-1}, respectively.

In order to explain the annealing behaviour, it is convenient to briefly describe the transient spectra during crystallization of undoped amorphous $PbCl_2$ films. The absorption spectrum of undoped amorphous $PbCl_2$ films is characterized by a non-excitonic, prominent first band peaking at 4.418 eV (absorption edge, about 4.0 eV) [9]. On slow heating (1 K min^{-1}), they show sharp crystallization in a narrow temperature range of 1.5 K near 282 K [3], with the first band transformed to a sharp excitonic peak located at 4.66 eV (absorption edge, about 4.4 eV). A detailed measurement [10] achieved at a very slow heating rate of 0.05 K min^{-1} in the range 281.5–283 K revealed that three competing spectral structures showed up during crystallization. Of the three, the lowest-energy structure (about 4.2 eV), 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.

As seen from figure 1 the absorption edge of the present film changes from about 4.0 eV for $T_a = 77$ K (as-deposited film) to about 4.4 eV for $T_a \geqslant 280$ K, reflecting crystallization of the film. The structure appearing around 4.2 eV for 260 K $\leqslant T_a \leqslant$ 270 K corresponds to structure A of the undoped $PbCl_2$ film (note that the optical density at the peak (4.418 eV) of the first band for $T_a = 77$ K amounts to 22 when calculated for an undoped film of 850 nm thickness). Therefore, we can conclude that the crystallization of the present film starts to occur at about 260 K and is completed at about 280 K. The Cu^+ ions in the film have the effect of lowering the crystallization temperature and widen the temperature range where the crystallization proceeds.

After completion of crystallization there arise new structures at energies in the range 3.2–3.3 eV due to exciton absorption of crystalline CuCl. This indicates that the Cu^+ ions aggregate to form CuCl clusters during the final state of crystallization of the host. It is interesting to note that the temperature at which crystalline CuCl is precipitated in the $PbCl_2$ matrix is much (by about 100 K) higher than the crystallization temperature (177 K [4]) of amorphous CuCl.

Figure 2 presents magnified spectra of the same film in the region of CuCl exciton absorption to show the growth process of crystalline CuCl. Although there is no trace of exciton absorption for $T_a = 265$ K, weak structures reminiscent of Z_3 and $Z_{1,2}$ excitons are observed for $T_a = 270$ K and they grow to clear peaks at $T_a = 280$ K. Upon further annealing, they sharpen in shape and become strong in intensity (by about 20%), accompanying a small red shift of the peak energies (by a few milli-electron volts) (as evaluated by a lineshape analysis [11]). The integrated exciton-absorption intensity for $T_a = 400$ K corresponds to a 13 nm thickness of a CuCl film. From this, the CuCl concentration with which the CuCl precipitates are embedded in the $PbCl_2$ polycrystalline matrix is calculated to be 3.1 mol%.

Further annealing at temperatures above 400 K gave rise to an abrupt reduction in the absorption intensity of the excitons. In fact, the exciton absorption decreased 10 times for $T_a = 440$ K and completely disappeared for $T_a = 500$ K; instead, new weak structures appeared around 3.95 and 4.15 eV, as seen from the lowermost curve in figure 1. The precipitated CuCl is considered to be dissociated, yielding new absorption centres responsible for the structures.

4. Discussion

In situ absorption spectroscopy has been shown to provide a powerful means of studying the growth of copper halide nanocrystals in alkali halides [6]. Exciton lines are used as a signature of crystallinity and a broad absorption peak measures the number of Cu^+ ions. The present study demonstrates that a similar method is also useful to trace CuCl in $PbCl_2$.

Previously we reported [4] that exciton absorption in CuCl was observed even in the amorphous state because of the very small radius of the exciton (the Bohr radius is 6.8 Å for the Z_3 exciton [12]), which is so small that the exciton was able to exist within the short-range order. In the amorphous $PbCl_2$:CuCl film, however, no trace of CuCl exciton transitions is discernible, as shown in section 3. Presumably, Cu^+ ions are dispersed as dimers in the amorphous environment; the dimerization is due to the necessity of electrical neutrality, i.e. Pb^{2+} ion can only be replaced by two Cu^+ ions.

The assumption may be accessible based on an ion-glass model [9] of amorphous lead halides. The model proposed that each Pb^{2+} ion in amorphous PbX_2 (X = Br, Cl, F) 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 the full-width at half-maximum of about 0.05. Therefore, there may be a possibility of having a large enough d for the superionic assembly $[PbX_9]^{7-}$ to be replaced by a quasicomplex of $[Cu_2X_9]^{7-}$. The small ionic radius of the Cu^+ ion compared to the Pb^{2+} ion radius is considered to be favourable for heavily doping amorphous $PbCl_2$ with Cu^+ ions in such a manner.

Since crystallization of the film requires $\Delta d/d \to 0$, it is expected that the large majority of the densely dispersed Cu^+ dimers aggregate to form CuCl clusters during crystallization, yielding CuCl crystallites. This is evidenced by the appearance of exciton absorption for $T_a = 280$ K (figure 2). Other Cu^+ dimers which still occupy Pb^{2+} ion sites may contribute to the growth of the crystallites at higher annealing temperatures (280 K $< T_a \leqslant$ 400 K). The growth of the crystallites leads to the small increase of the exciton absorption intensity (by about 20%) and the small red shift of the exciton peak (by a few milli-electron volts). The red shift is attributable to relaxation of the quantum size effect on the exciton due to the growth of the crystallites.

It is instructive to compare the present result with previous work on heavily Bi^{3+}-doped CdI_2 films [2]. The heavy doping was achieved by quench-deposition, yielding amorphous films with three Cd^{2+} ions replaced by two Bi^{3+} ions up to 10 mol% of BiI_3 concentration. After crystallization of the films, stable Bi^{3+} dimers existed without forming higher-order clusters. In the case of the present result for $PbCl_2$:CuCl, however, larger clusters were already observed for the film just after crystallization. The difference in the clustering behaviour between the two systems may be explained in terms of dimensionality. In the CdI_2:BiI_3 system, where both CdI_2 and BiI_3 are layer compounds, clustering of Bi^{3+} ions is considered to occur in two dimensions, i.e. within single cation layers. Therefore, it is difficult to yield larger clusters, unlike in the case of the $PbCl_2$:CuCl system where a three-dimensional process proceeds.

In [6], the growth of CuCl nanocrystals was studied by UV spectroscopy for a Cu^+-doped single crystal of NaCl with the nominal 0.2 mol% fraction of CuCl. Although the CuCl concentration is very small, aggregation and dissociation of CuCl are similar in behaviour to the present $PbCl_2$:CuCl case. The growth of CuCl nanocrystals in the NaCl crystal occurred for annealing temperatures T_a above 275 K, with the Z_3 and $Z_{1,2}$ exciton absorption enhanced and with their peak positions redshifted with increasing T_a up to 450 K. For $T_a > 450$ K the exciton absorption decreased, and at $T_a = 600$ K all clusters were destroyed, exhibiting a broad absorption band at 4.86 eV due to single Cu^+ ions. In the present $PbCl_2$:CuCl system the grown CuCl crystallites started to decrease at nearly the same T_a (above 400 K), despite the much higher CuCl concentration. The weak structures observed at 3.95 and 4.15 eV for the lowest curve in figure 1 are attributed to absorption due to destroyed CuCl crystallites, i.e. Cu^+ dimers. (Cu^+ dimers in the amorphous $PbCl_2$:CuCl film may also absorb light of similar photon energies; however, such absorption, being considered to be hidden by the strong absorption for the host $PbCl_2$, is not observed in figure 1.)

5. Conclusion

Heavily Cu^+-doped amorphous $PbCl_2$ was obtained by quench deposition of the mixture of $PbCl_2$ and CuCl, despite the different valencies between the cations of the two compounds. The Pb^{2+} ion in the superionic assembly $[PbCl_9]^{7-}$ with a large Pb^{2+}–Cl^- distance in the amorphous environment has a possibility of being replaced by two Cu^+ ions, forming a quasicomplex $[Cu_2Cl_9]^{7-}$. Upon crystallization of the host environment, the large majority of Cu^+ ions aggregate to form CuCl precipitates embedded in the crystalline $PbCl_2$ matrix. The present experiment opens up the possibility of producing densely dispersed CuCl clusters in a controlled manner in $PbCl_2$ films. For example, the size of the clusters is expected to be controllable by developing annealing performance as well as by varying the CuCl mole fraction. Studies on achieving densely dispersed small clusters (nanocrystals) with a specified size distribution are in progress and the results will be reported later.

Acknowledgments

This work was partly supported by the Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, and also partly by the Hokuriku Industrial Advancement Centre.

References

[1] Oliveira L, Cruz C M G S, Silva M A P and Siu Li M 1994 *Thin Solid Films* **250** 273

[2] Kondo S, Suzuki T and Saito T 1988 *J. Phys. D: Appl. Phys.* **31** 2733

[3] Kondo S, Maruyama H and Saito T 1995 *Phys. Status Solidi* a **147** 453

[4] Kondo S and Seki T 1992 *Mater. Sci. Eng.* B **15** 133

[5] Kittel C 1986 *Introduction to Solid State Physics* 6th edn (New York: Wiley) p 76

[6] Haselhoff M and Weber H-J 1988 *Phys. Rev.* B **58** 5052

[7] Kondo S, Itoh T, Saito T and Mekata M 1991 *J. Phys. Soc. Japan* **60** 2764

[8] Kondo S and Matsumoto H 1981 *J. Phys. Soc. Japan* **50** 3047

[9] Kondo S 1996 *Phys. Status Solidi* a **153** 529

[10] Kondo S, Maruyama H and Saito T 1996 *Phys. Status Solidi* a **156** 151

[11] Kondo S and Seki T 1993 *Phys. Status Solidi* b **178** K113

[12] Honerlage B, Klingshirn C and Grun J B 1976 *Phys. Status Solidi* b **78** 599