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Amorphous $Tl_{1-x}Cu_xCl$ solid solution and their crystallization studied by optical absorption spectroscopy

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Abstract

Amorphous solid solutions are obtainable for the binary $Tl_{1-x}Cu_xCl$ system by means of two-sources evaporation onto 77 K substrates. Their annealing behavior has been studied for a film with $x \sim 0.4$ by optical absorption spectroscopy. In the as-prepared film an appreciable amount of Cu 3d states is localized with the energies lying above the upper valence bands. On annealing the film, Cu^+ ions migrate to form clusters in the amorphous environment, with their size depending on the annealing temperature. The lowest annealing temperature at which the clusters are formed lies near the crystallization temperature of amorphous CuCl. On further annealing at higher temperatures, the clusters grow until the amorphous environment has a particular atomic composition ratio suggestive of a new, novel compound, which exhibits a well defined crystallization temperature, 300 K.

Keywords: $Tl_{1-x}Cu_xCl$; Crystalization; Optical absorption spectroscopy

1. Introduction

A lot of metal halides such as silver [1], copper [2], thallium [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 well-defined, characteristic crystallization temperature at which the optical absorption spectrum changes distinctly. In particular, crystallization of the amorphous films of mixed metal halides produces small clusters or nanocrystals. For instance, we recently obtained [6] CdI_2 films in which stable two-molecule BiI_3 clusters were densely monodispersed up to 10 mol% of BiI_3 concentration. The clusters were stoichiometrically embedded in the CdI_2 crystal matrix. It was also possible to disperse CuCl clusters in crystalline $PbCl_2$ films at high density ($\sim$3 mol%) [7]. In these studies the amorphous films of the metal halides heavily doped with foreign metal ions were obtainable by evaporating the mixture of two metal halides (host and guest metal halides) onto cooled substrates; in the amorphous surroundings the cations of the metal halides were replaceable by foreign metal ions up to appreciable concentrations despite the difference in the valency between the guest and host cations. The crystallization of the amorphous films yielded small clusters or nanocrystals of the guest-metal halide embedded in the crystalline matrix of the host-metal halide. These results suggest that amorphization and subsequent crystallization of the mixture of metal halides provide a new method for obtaining small clusters or nanocrystals.

In the present work a similar study was carried out on the binary TlCl–CuCl system to investigate the properties of amorphization and crystallization in the mixed system of equal cation valencies. The amorphization was achieved by using an improved setup, which was developed to prepare amorphous films of various mixed systems. It was shown that TlCl and CuCl can be made amorphous solid solution up to a significant concentration ratio because of their equal cation valencies. The annealing of the amorphous solid solution yielded CuCl clusters densely dispersed in a new, amorphous or crystalline environment with their size depending on the annealing temperature.

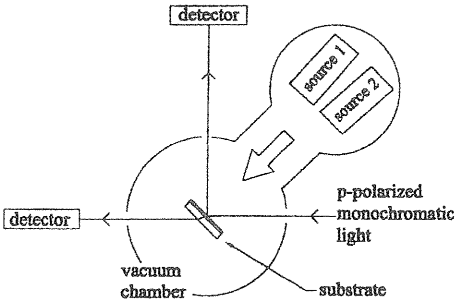

Fig. 1. A schematic view of experimental configuration illustrating preparation of two-sources evaporated amorphous films of mixed metal halides and in situ UV absorption measurement of the films.

2. Experimentals

Fig. 1 shows a geometrical and optical configuration of the experimental setup used. It is equipped for preparing quench-deposited amorphous films of mixed metal halides and for studying their crystallization behavior in situ by optical absorption spectroscopy. Amorphous films of the binary TlCl–CuCl system were obtained by means of a two-sources (source 1 and source 2) evaporation onto a silica–glass substrate cooled to 77 K in a vacuum of about 9×10^{-6} Pa, using a pair of evaporators. The body of the evaporators was made up of a copper block, in which a cylindrical cell and two cartridge heaters were embedded. A powder reagent put in the cell was vaporized by the heaters in a controlled manner. The use of the two evaporators in a pair enabled us to obtain amorphous films of mixed TlCl–CuCl films with any composition ratios. Details including the construction of the evaporators will be reported elsewhere. Optical properties of amorphous films and their crystallization behavior were investigated in situ by UV absorption spectroscopy, using an improved double beam method described in [6]. The method is based on simultaneous measurements of transmittance and reflectance from which accurate optical densities of the films can be determined.

3. Results

Fig. 2 shows the absorption spectra at 77 K of a quench-deposited $Tl_{1-x}Cu_xCl$ film with $x \sim 0.4$. Spectrum 1 was first measured for the as-prepared film. Then the film was subjected to various annealing cycles to observe irreducible change in the spectrum at 77 K with increasing annealing temperature. Heating and cooling in each annealing cycle were performed at rates of 1 and 10 K min^{-1}, respectively. The annealing temperature, T_a (K), and annealing time, t_a (min), for each spectrum labeled with the number, n, in the figure are, in terms of n (T_a, t_a), as follows: 2 (100, 1), 3 (120, 1), 4 (140, 1), 5 (160, 1), 6 (180, 1), 7 (200, 1), 8 (220, 1), 9 (240, 1), 10 (260, 1), 11 (280, 1), 12 (300, 1), 13 (300, 10), 14 (300, 180) and 15 (360, 1).

The spectra labeled 1 to 12 in Fig. 2 are all characterized by nearly the same spectral feature in the photon energy region above 4 eV exhibiting a monotonous broad band around 5.5 eV; annealing of the film up to $T_a = 300$ K results in almost no spectral change in this photon energy region. On annealing for 10 min at 300 K, however, an abrupt change occurred in the spectral shape as seen from spectrum 13, giving rise to several fine, but weak, structures (at 4.1, 4.6, 5.5 and 5.8 eV). These structures were stable and unchanged during a further annealing period, $t_a = 180$ min, at $T_a = 300$ K (spectrum 14) and even for a higher annealing temperature $T_a = 360$ K (spectrum 15).

In the photon energy region below 4 eV, on the other hand, there occurs gradual change in the spectral structure with increasing annealing temperature even below 300 K. Fig. 3 illustrates this photon energy region in a

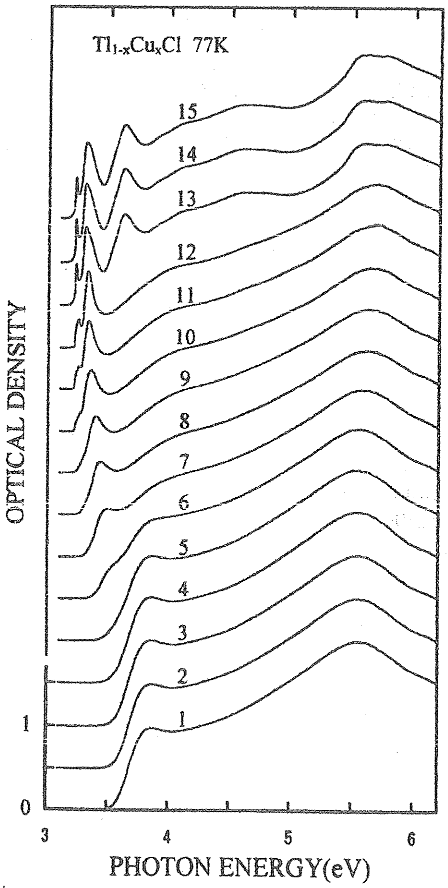

Fig. 2. The effect of annealing on optical absorption of a $Tl_{1-x}Cu_xCl$ ($x \sim 0.4$) film prepared by means of two-sources evaporation onto 77 K substrate. The absorption spectra are measured at 77 k for increasing annealing temperatures.

magnified scale, where spectra 1–4 and spectra 14 and 15 are omitted because their shapes are entirely the same as spectrum 5 and spectrum 13, respectively. As seen from the figure, a new absorption band shows up around 3.5 eV for $T_a = 180$ K (spectrum 6). As the annealing temperature is increased, it becomes prominent and shifts to low energies exhibiting two absorption bands, around 3.24 and 3.32 eV for $T_a = 300$ K ($t_a = 1$ min, spectrum 12), which correspond to the CuCl Z_3 and $Z_{1,2}$ excitons [8], respectively. As compared with this gradual change in the spectrum with increasing T_a up to 300 K, further annealing at 300 K, but only for 10 min, of the film (spectrum 13) gave rise to an abrupt spectral change characterized by the sharpened Z_3 exciton peak and a new, strong absorption band appearing around 3.6 eV with a weak shoulder at about 3.53 eV. These features of spectrum 13 were shown to remain unchanged for further annealings (spectra 14 and 15 in Fig. 2).

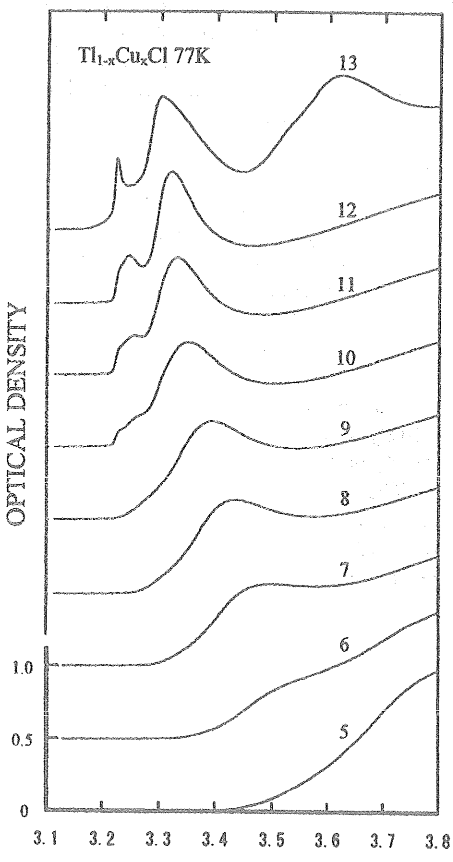

Fig. 3. Spectra 5–13 in Fig. 2 are replotted in a magnified scale in the region near the fundamental edges.

4. Discussion

As mentioned in Section 1, amorphous films of metal halides including TlCl and CuCl have well-defined crystallization temperatures (98 K for TlCl [3], 177 K for CuCl [2]), at which there occurs distinct change in their absorption spectrum. In the present experiments, we found that such a characteristic change of spectrum also occurs in the $Tl_{1-x}Cu_xCl$ film for $T_a = 300$ K, seen from the distinct difference between spectra 12 and 13 Fig. 2. It may be supposed, therefore, that the film is in amorphous state below 300 K and crystallization of the film starts to occur at $T_a = 300$ K and is completed within 10 min at that temperature. The crystalline nature for spectrum 13 is read by the fine structures appearing above 4 eV, which are reminiscent of van Hove singularities of the associated energy band. The completion of the crystallization (within 10 min at 300 K) is evidenced by the fact that no further spectral change occurred during further annealing at 300 K or even at higher annealing temperatures (≤ 360 K).

To elucidate characteristics of the 'amorphous' $Tl_{1-x}Cu_xCl$ film, we will first mention the absorption spectra of TlCl [3] and CuCl [2] films in terms of amorphous versus crystalline. Curves a and c in Fig. 4a (TlCl) and Fig. 4b (CuCl) are the spectra of the amorphous and crystalline (crystallized) films in the exciton energy region, respectively. For comparison spectra, 1 and 12 of the $Tl_{1-x}Cu_xCl$ film are also plotted in Fig. 4c. The crystalline films exhibit a sharp exciton peak at 3.49 eV for TlCl and two very sharp ones at 3.224 (Z_3) and 3.29 eV (Z_{12}) for CuCl (the non-zero optical densities in CuCl in the otherwise transparent region below 3.2 eV are due to devitrification during crystallization and subsequent crystal growth). Although there is no indication of exciton transitions in the amorphous film of TlCl, discernible exciton bands are observed for the amorphous CuCl film due to a very small exciton radius (0.68 nm for Z_3 [9], which is so small that the exciton is able to exist within the extent of the short-range order [2]). Spectrum 1 of the $Tl_{1-x}Cu_xCl$ film is very similar in feature near the absorption edge to curve a of TlCl but with the somewhat red-shifted (by about 0.3 eV) optical energy gap and exhibits no sign of CuCl exciton absorption despite the considerable CuCl concentration in the film. This suggests that the Cu atoms in the as-prepared $Tl_{1-x}Cu_xCl$ film are substituted for Tl atoms in the TlCl amorphous network, thus forming amorphous solid solution of a TlCl base.

It is well known that in amorphous semiconductors a certain amount of extended states near the band edges is localized due to amorphization-induced structural disorder. As to amorphous TlCl, whose absorption spectrum near the fundamental edge is characterized by the missing excitonic absorption and blue-shifted (by about 0.4 eV) optical energy gap as shown in Fig. 4a, it

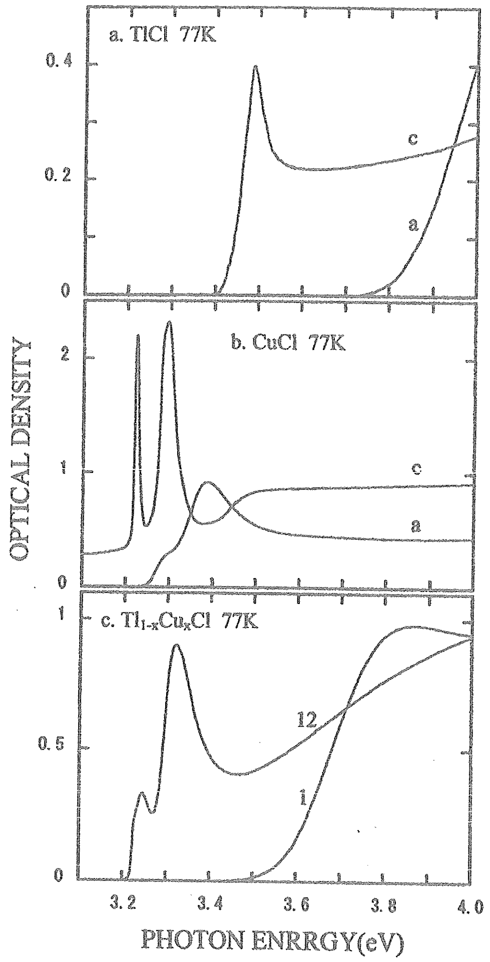

Fig. 4. Absorption spectra of (a) TlCl, and (b) CuCl measured at 77 K for the amorphous (curves a) and crystalline (curves c) films. For comparison, spectra 1 and 12 of (c) $Tl_{1-x}Cu_xCl$ ($x \sim 0.4$) are also presented.

was necessary to assume that a considerable amount of the uppermost valence band coming from the Tl-6s state and the lowermost conduction band from the Tl-$6p_{1/2}$ states were localized by amorphization [10], in order to explain the characteristic absorption spectrum. In the case of amorphous $Tl_{1-x}Cu_xCl$ solid solution, further localization of electronic states is expected to occur due to the effect of chemical disorder. If Cu atoms are substituted for Tl atoms at a high density in the TlCl crystal matrix, the Cu-3d states may contribute to upper valence bands (in CuCl, the Cu-3d states indeed contribute to upper valence bands [11]). It is probable, therefore, that an appreciable amount of the Cu-3d states are localized in the amorphous $Tl_{1-x}Cu_xCl$ solid solution. This may account for the smaller optical energy gap for the amorphous $Tl_{1-x}Cu_xCl$ solid solution than for amorphous TlCl. The strong absorption appearing as a broad band around 3.8 eV for the former may be due to a high density of the localized Cu-3d states.

The crystallization temperature of the amorphous $Tl_{1-x}Cu_xCl$ solid solution, 300 K, is much higher than those of both amorphous films of TlCl (98 K) and CuCl (177 K). This exemplifies that the chemical disorder has the effect of increasing the crystallization temperature. Such increased crystallization temperatures due to chemical disorder were previously observed for amorphous $TlCl_{1-x}Br_x$ solid solution (e.g. 137 K for $x = 0.4$ as compared with 98 and 95 K for amorphous TlCl and TlBr, respectively [12]). In the present experiment, however, the situation is somewhat different. As seen from Fig. 3, on annealing the amorphous $Tl_{1-x}Cu_xCl$ solid solution, a new absorption band begins to show up around 3.5 eV for $T_a = 180$ K (spectrum 6). The band may be due to formation of CuCl clusters because it grows to the CuCl Z_3 and $Z_{1,2}$ exciton peaks with increasing T_a (e.g. spectrum 12). It can be stated, therefore, that the Cu^+ ions begin to migrate to form clusters in the amorphous environment at annealing temperatures near the crystallization temperature of amorphous CuCl. Such a clustering behavior is in great contrast to that observed in the system of heavily Cu^+-doped amorphous $PbCl_2$, where crystallization of the host $PbCl_2$ accompanies the formation of CuCl clusters, which are necessarily embedded in the crystalline matrix of $PbCl_2$. In the present $Tl_{1-x}Cu_xCl$ system, however, the CuCl clusters are considered to be embedded in the amorphous matrix.

It was shown in [2] that the excitons in amorphous CuCl are 'confined' within a size defined by the short-range order in the amorphous network. The corresponding exciton energies (3.28 and 3.38 eV for Z_3 and $Z_{1,2}$, respectively as shown in Fig. 4b) were nearly equal to those of Z_3 and $Z_{1,2}$ of spectrum 9 ($T_a = 240$ K) in Fig. 3. Therefore, annealing of the amorphous $Tl_{1-x}Cu_xCl$ solid solution at temperatures below 240 K (but above 177 K) yielded CuCl clusters of a size smaller than the extent of the short-range order of the CuCl amorphous network, as suggested by the corresponding blue-shifted absorption band observed for spectra 6–8. Further annealings at temperatures above 240 K resulted in the growth of the CuCl clusters (spectra 10 ($T_a = 260$ K) to 12 ($T_a = 300$ K)) which were embedded in the $Tl_{1-x}Cu_xCl$ amorphous matrix, and the crystallization of the amorphous matrix occurred for annealing at 300 K and is completed within 10 min (spectrum 13) as mentioned above. After the crystallization, the Z_3 exciton absorption exhibited a sharp peak at 3.224 eV, which coincided with the Z_3 exciton peak energy of the crystalline CuCl film in Fig. 4b.

Spectrum 13 exhibited neither discernible structure reminiscent of TlCl exciton absorption (at 3.49 eV) nor enhanced absorption of the CuCl Z_3 and $Z_{1,2}$ excitons (compared with that of spectrum 12); instead, the spectrum was characterized by a prominent absorption band around 3.6 eV (with a shoulder at about 3.53 eV). This suggests that the crystalline matrix in which the CuCl clusters were embedded was made of a new, novel compound, and negated the possibility of an eutectic product (mixture of TlCl and CuCl crystallites) for the crystalline matrix. The absorption intensity of the CuCl Z_3 and $Z_{1,2}$ excitons seems to be saturated before the crystallization of the amorphous matrix. In fact, the integrated absorption intensity in the region 3.2–3.55 eV was shown to be entirely the same (within the experimental errors) for spectra 11 ($T_a = 280$ K) and 12. This indicates that a certain concentration ratio of the Cu atoms to the Tl atoms, appropriate to the molecular formula of the new compound, is reached in the amorphous matrix at $T_a = 280$ K, owing to the decrease of the Cu atoms due to the growth of the CuCl clusters (the somewhat smaller band widths for Z_3 and $Z_{1,2}$ of spectrum 12 than of spectrum 11 may be due to a narrowed size-distribution of the CuCl clusters due to annealing). Therefore, the annealing temperature '300 K' for spectrum 13 is considered to be the crystallization temperature for the amorphous phase of the new compound — the amorphous film of the new compound has a well-defined, characteristic crystallization temperature, 300 K, at which the absorption spectrum changes distinctly, similar to other metal halides mentioned in the first paragraph in Section 1.

It is noted that the CuCl microcrystals embedded in the amorphous matrix exhibit the much larger band width for Z_3 excitons than the case of the crystalline matrix, as seen from the comparison of spectra 12 and 13. A plausible explanation for this might be given in terms of a size distribution of the CuCl microcrystals. If this is the case, however, the band width for $Z_{1,2}$ relative to the enhanced band width for Z_3 in spectrum 12 would be too large to be favorably compared with the observed $Z_{1,2}$ band width of spectrum 12, since the size effect on exciton energies should be stronger for $Z_{1,2}$ than for Z_3 because of the larger exciton radius for the former. Therefore, another explanation should be given. One of the possible explanations may be in terms of 'effective strains'. It is considered that the boundaries between the amorphous matrix and the individual CuCl microcrystals embedded therein are less well-defined than the case of the crystalline matrix. Therefore, the exciton wave functions for the former may be under 'effective strains' near the boundaries. Such strains may cause various magnitudes of the shift of the exciton energy according to the different modes and different magnitudes of the strains. According to [13], the effect of strains on bulk CuCl excitons is stronger for Z_3 than for $Z_{1,2}$ as far as the shift of the exciton energies are concerned. These considerations are favorable for explaining the enhanced Z_3 band width under consideration.

5. Conclusion

The two compounds TlCl and CuCl, though crystallize in different crystal structures, can be rendered amorphous solid solution with high mixing ratios by means of two-sources evaporation onto 77 K substrates, yielding film samples. Annealing behaviors of a representative film of the amorphous solid solution, $Tl_{1-x}Cu_xCl$ with $x \sim 0.4$, was studied by optical absorption spectroscopy. The absorption spectrum of the as-prepared (before annealing) film was characterized by enhanced, non-excitonic absorption near the fundamental edge, due to contribution of localized Cu 3d-states. When the film was annealed at temperatures near the crystallization temperature (177 K) of amorphous CuCl, a new absorption band appeared around 3.5 eV due to formation of CuCl clusters in the amorphous environment. On further annealing at higher temperatures, the band grew to well resolved Z_3 and $Z_{1,2}$ bands indicating the formation of CuCl microcrystals, with their total integrated absorption intensity showing the tendency to saturate at the annealing temperature about 280 K. As a result, the amorphous environment had a particular atomic composition of Tl and Cu suggestive of a novel compound which had a well defined, characteristic crystallization temperature, 300 K. The CuCl microcrystals, embedded in the amorphous matrix of the novel compound exhibited a large band width for Z_3, probably due to ' effective strains' near the microcrystal surfaces.

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