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Photoluminescence from microcrystalline CuCl films grown from the amorphous phase

S Kondo, M Kakuchi and T Saito

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

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Abstract

In situ demonstration of confinement-induced enhancement of CuCl free-exciton photoluminescence has been carried out for microcrystalline films (extremely densely dispersed microcrystals compared to those dispersed in bulk materials), grown from the amorphous phase using shot-like IR laser light irradiation. There is an optimum crystallite size level at which the films show the strongest free-exciton emission band. Its integrated intensity is 2.5–4 times larger than that for the polycrystalline state of the same films. Excitonic superradiance is suggested as a possible cause of the enhanced free-exciton luminescence.

1. Introduction

Semiconductor microcrystals have attracted much attention over the last two or three decades owing to the mesoscopic enhancement of linear and nonlinear optical properties. Various efforts have been made to obtain microcrystals or nanodimensional particles, according to the object of the investigation. In the study of the quantum size effect on excitons, which is one of the most attractive mesoscopic properties exhibited by nanodimensional particles, the particles are usually embedded in a glass or crystal matrix. Such a specimen has mostly been prepared by means of quenching from thermal equilibrium for phase separation of a eutectic mixture. The mole fraction of the particles is generally very small, typically of the order of 0.1 mol% or less. On the other hand, many metal halide semiconductors including CuCl can be rendered amorphous by quench deposition, yielding film samples. By appropriate heat treatment of the amorphous films, it is possible to obtain microcrystalline films. The microcrystalline films provide alternative, extremely densely dispersed nanoparticles useful for studying mesoscopic enhancement of optical properties. Such films are not merely desirable for basic research, but also for application studies.

For obtaining microcrystalline films from the amorphous films of metal halides, we have employed two different methods of heat treatment: the resistive-heater method and the shot-like

IR light irradiation method. The former method was applied to CuCl [1], where blue-shifted exciton absorption bands due to quantum size effects on the excitons were clearly observed, indicating that microcrystalline films at various mean crystallite size levels were attainable from the amorphous phase. Recently, the latter method was shown to be very effective for achieving high-quality CsPbCl₃ films [2], leading to the result that the microcrystalline state exhibits much stronger free-exciton emission than the polycrystalline state. A possible explanation for the result was given in terms of excitonic superradiance occurring in the microcrystallites.

In the present work, *in situ* measurements of exciton absorption and photoluminescence spectra were performed for microcrystalline films of CuCl, a typical metal halide whose quantum size effects on excitons have been extensively studied for dispersed microcrystals, but not for microcrystalline films. The microcrystalline CuCl films were achieved in a controlled manner by the shot-like IR light irradiation method, which will be described in some detail in connection with the associated optical configuration for the *in situ* exciton absorption and luminescence spectroscopy (in [2], only a brief description is given of the method). The photoluminescence of the films was dominated by free-exciton emission, whose intensity was strongly dependent on the mean microcrystallite size of the films. There was an optimum microcrystallite size level at which the films show a maximal integrated luminescence intensity for the free-exciton recombination.

2. Experimental details

We first prepared amorphous CuCl films by quench deposition onto silica-glass substrates attached to a copper block cooled to 77 K [3]. The deposition was carried out in a vacuum of about 9×10^{-6} Pa using a tungsten basket heating element placed 8 cm in front of the substrate. Then the films were subjected to rapid heating/cooling cycles to achieve various mean sizes of CuCl crystallites in the films. This procedure was performed by means of shot-like IR light irradiation of the films using a cw CO₂ laser (USA Synrad, Model 48-1-SW; wavelength, 10.6 μ m; power, 10 W), with the substrate kept in contact with the 77 K copper block. The spot size of the CO₂ laser beam (Gaussian beam) was about 3 mm in diameter at the film surfaces. One shot caused one cycle of the rapid heating/cooling. The irradiation time per shot was in the range 10–1000 ms, depending on the desired crystallite size. The ON/OFF switching for the predetermined irradiation time was achieved using a universal controller (USA Synrad, Model UC-1000, an optional unit for 48-1-SW; since 48-1-SW employs an RF excited plasma tube whose standby state is maintained in an ignited state by a pre-ionizing 1 μ s tickle signal of frequency 5 kHz, the use of UC-1000 enables one to produce output laser light of a predetermined time duration, a multiple of the period 0.2 ms of the tickle signal). To monitor the current state of the film during the repeated heating/cooling cycles, photoluminescence and absorption spectra were intermittently measured (at 77 K) using a liquid nitrogen-cooled CCD spectrometer equipped with a 0.47 m grating monochromator, using a fibre optic as a light guide. The measuring time per spectrum is 1 s and 20 ms for the luminescence and absorption spectrum, respectively. A 500 W xenon lamp in combination with a 0.5 m grating monochromator was used as the light source for the measurements of the photoluminescence, and a 30 W deuterium lamp was employed for measuring absorption spectra. The light irradiating the films, with the help of mechanical shutters, was focused at the centre of the CO₂ laser-irradiated spot of the films, with the irradiation area of about 1×0.5 mm² for the luminescence measurements and about 0.5 mm in diameter for the absorption measurements. The luminescence was recorded in the configuration of back-scattering normal to the film surface in order to minimize reabsorption (the incident angle of the exciting light is 45°).

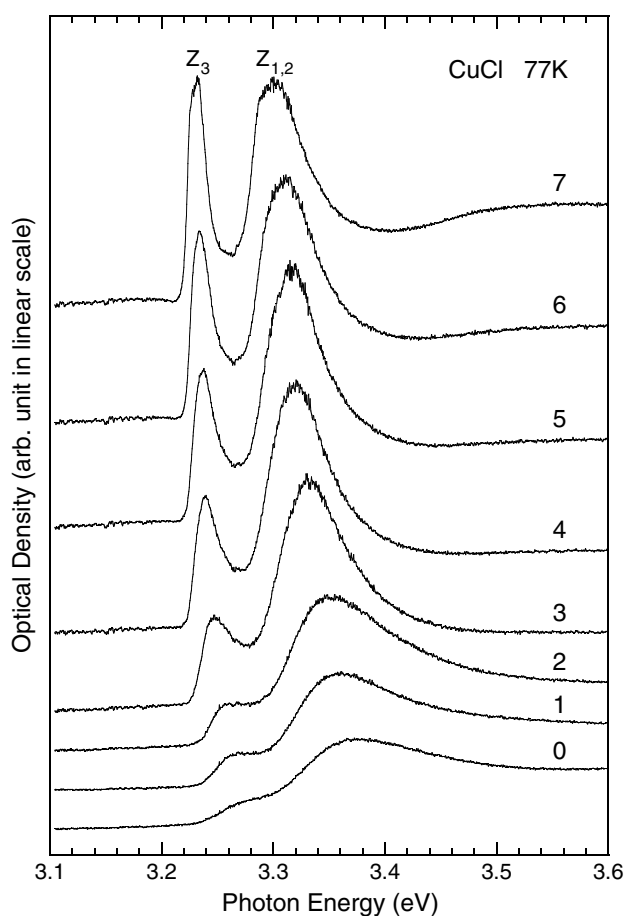


Figure 1. Sequential change of the exciton absorption spectrum of a CuCl film (thickness, ~ 95 nm) during heat treatment by repeated heating/cooling operations starting from the amorphous phase (see the text). The spectra are shifted along the Y axis for clarity.

3. Results

Figures 1 and 2 show an example of the sequential changes of the absorption spectrum measured in the Z_3 and $Z_{1,2}$ exciton absorption regions and of the photoluminescence spectrum excited at 3.54 eV (350 nm), respectively, for a CuCl film (thickness, ~ 95 nm). The numbers, 0–7, in the figures indicate the extent of the heat treatment to which the film was subjected: the larger the number (heat treatment number, HTN), the film heavier the heat treatment as regards repetition of the heating/cooling operation, where HTN for the as-deposited film was denoted as '0'. With the increase of HTN, both the absorption and the luminescence spectra shift to lower energies. On the other hand, although the absorption intensity monotonically increases with HTN, the luminescence is maximum in intensity for HTN 3, after which the luminescence intensity decreases with increasing HTN. We note that, in both the absorption and luminescence measurements, the spectral profile (peak energies, peak intensities, and full width at half-maximum, FWHM) for the last HTN, 7, was unchanged by further repetition of the heating/cooling cycles with the longest heating duration of 1000 ms.

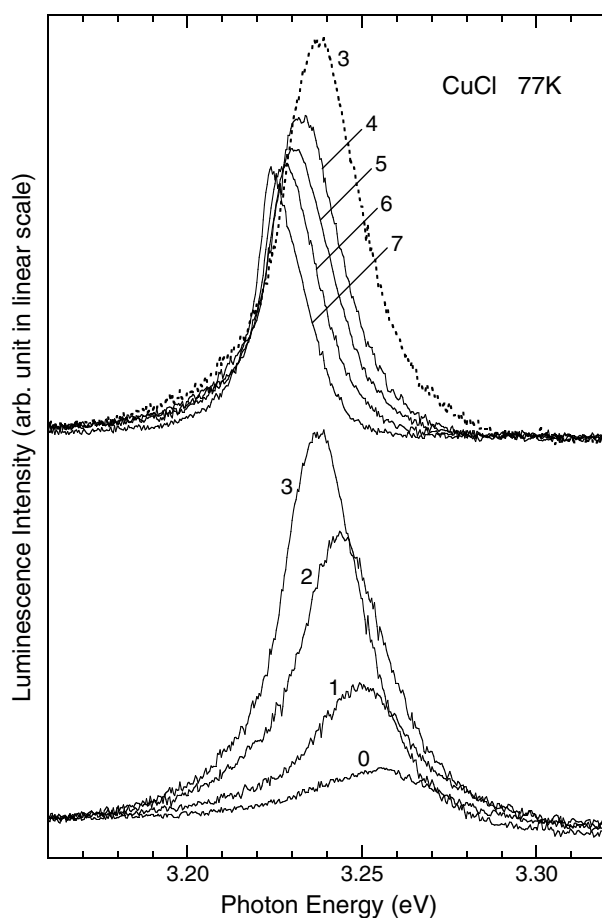


Figure 2. Sequential change of the exciton luminescence spectrum (of the film whose absorption spectra are shown in figure 1) during heat treatment by repeated heating/cooling operations starting from the amorphous phase (see the text), excited at 3.54 eV (350 nm). The spectra are shifted along the *Y* axis, differently for curves 0–3 and 3–7, for clarity.

The absorption spectra shown in figure 1 reproduce well the previous results [1]. In [1], the quantum size effect on the excitons, i.e., the blue shift of the exciton absorption energies, was exhibited in both the amorphous and crystalline states, with the confinement size being increased with increasing annealing temperature (the extent of the short-range order in the amorphous state increased with increasing annealing temperature below the crystallization temperature, 177 K). In the amorphous state (HTN 0–1), the excitons are confined within a size defined by the short-range order, whereas grain boundaries in the crystalline state (HTN 2–7) provide (incomplete) confinement potential barriers. We note that the strain effects on the CuCl films, and thus on the CuCl exciton energies, thermally induced by the substrates are not considerable, since such effects have been ruled out for CuCl films with thickness larger than 10 nm [4].

The quantum size effect on the excitons is more clearly exhibited in the luminescence spectra shown in figure 2. All the spectra are composed of single bands with well-definable peak energies depending on the HTN. The peak energy (3.225 eV) and FWHM (14 meV) of

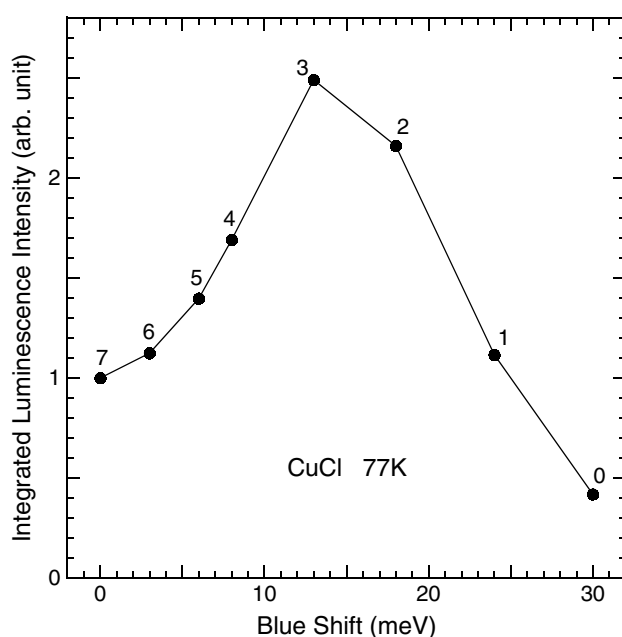


Figure 3. The integrated luminescence intensities, plotted against the blue shift in peak energy relative to the peak energy for the polycrystalline state.

the luminescence spectrum for HTN 7 are almost the same as those of the Z_3 free-exciton emission band observed (at 80 K) for crystalline CuCl films [5], which were grown along the $\langle 111 \rangle$ direction on (0001) Al_2O_3 substrates (in [5], luminescence spectra measured as a function of temperature for a film of 100 nm thickness are presented in the temperature range 10–70 K with the spacing of 10 K, whose extrapolation carried out for the Z_3 free-exciton band yields a peak energy of about 3.225 eV and FWHM of about 13 meV at 80 K). Therefore, the present film for HTN 7 is considered to be in the polycrystalline state. With the decrease of HTN, the peak energy of the Z_3 free-exciton band shifts to high energies, thus clearly demonstrating the effect of quantum confinement on the Z_3 free excitons. We note that a trace from the I_1 bound-exciton band due to a neutral acceptor (Cu^+ vacancy [6]) was by no means detected for all the HTN values (in [5], the same trace is evidently detected at 3.20 eV at 70 K). All the spectra are composed of only single, Z_3 free-exciton bands without exhibiting any other emission band, suggesting high quality of the film. It is notable that excitons even in the microcrystalline film are free from being trapped, despite the expectation [7] of a high density of surface states; such high quality of the film, prepared from the amorphous phase, was also shown for the microcrystalline CsPbCl_3 films [2]. On the other hand, the line broadening of the free-exciton band with decreasing HTN is considered to be due to a size distribution of the crystallites in the film.

Figure 3 shows the integrated intensities of the luminescence spectra versus the blue shifts in peak energies relative to the peak energy for the polycrystalline state; all the data points are indicated by HTN values, with the solid curve being a guide for the eyes. The X axis of the plot can be viewed as a measure of the size of the confinement of the Z_3 free exciton; that is, the larger the X value, the smaller the size. The largest blue shift, 30 meV, which is observed for HTN 0, corresponds to an effective radius for the exciton confinement (which will be referred to as EREC) of 2.3 nm, if we assume the effective-mass approximation in the

weak confinement regime [8] using the Z_3 free-exciton mass, $2.3 m_0$ (m_0 is the electron mass). It is seen from the figure that the luminescence efficiency for the microcrystalline state with the blue shift of 17 meV (EREC, 3.1 nm) is 2.5 times larger than that for the polycrystalline state.

In all the films studied, there was an optimum value of EREC for which the free-exciton luminescence was maximized in intensity (as suggested by figure 3). The maximum luminescence and the corresponding blue shift were carefully measured for several films with thickness in the range 80–100 nm, together with the luminescence for the polycrystalline state. The measurement was carried out by annealing the films step by step in the blue-shift range of 10–20 meV (see figure 3) and simultaneously monitoring the luminescence spectrum for each step, with one step including only one cycle of the heating/cooling operation with the heating duration of 50 ms. All the films showed a maximum of the integrated luminescence intensity at the steps where the blue shift of the spectrum (relative to the peak energy, 3.225 eV, of the spectrum for the polycrystalline state) reached a particular value of about 15 meV (EREC, 3.3 nm). In the measurement of the luminescence for the polycrystalline state, on the other hand, the films were subjected to the heating/cooling cycles with the longest heating duration of 1000 ms; the luminescence spectrum whose intensity no longer varied with further repetition of the heating/cooling operation was taken as the luminescence spectrum for the polycrystalline state. It was shown from these measurements that the ratio of the largest integrated luminescence intensity (at the optimum EREC) to that at the polycrystalline state (i.e., at the final film state) varied from film to film, but always lay in the range from 2.5 to 4.

4. Discussion

It is notable that the free-exciton luminescence efficiency is strongly enhanced (by a factor of 2.5–4) for the microcrystalline state (with the optimum EREC, 3.3 nm) as compared to that for the polycrystalline state. There are two possible candidates for being the physical origin of the enhanced luminescence. One is the occurrence of new radiative decay processes resulting from ballistic collisions of the free excitons at the boundaries of the microcrystallites, a microcrystalline counterpart of so-called wall collisions. The wall collisions, i.e., ballistic collisions of free excitons at the *film surfaces*, were proposed by Shuh *et al* [9] to explain their first observation, i.e., extremely shortened free-exciton lifetimes in CuCl thin films (as compared with that in bulk CuCl crystals) without simultaneous reduction of the free-exciton luminescence efficiency. Indeed, Nakayama *et al* [10] found that the intensity of the free-exciton luminescence relative to the bound-exciton luminescence in CuCl thin films increases remarkably with decrease of the thickness; for example, in a CuCl film with a thickness of 3.5 nm (which is comparable to the optimum EREC, 3.3 nm, in the present films), the photoluminescence was completely dominated by the free-exciton emission even at a very low temperature of 12 K. They attributed the enhanced free-exciton luminescence to wall collisions (according to them, the wall collisions result in enhancement of the conversion efficiency from the exciton polaritons to photons around the polariton bottleneck regions). It should be noted, however, that, although the wall collision-enhanced free-exciton emission band is asymmetric in shape [10] exhibiting a tail to the high-energy side due to an exciton temperature much higher than the lattice temperature, such asymmetry is by no means recognized for the present films as exemplified by the spectra shown in figure 2. It is, therefore, insufficient to explain the enhanced free-exciton luminescence in the present microcrystalline films in terms of the microcrystalline counterpart of the wall collisions.

The more likely explanation may be concerned with excitonic superradiance, to which the enhanced free-exciton luminescence observed for microcrystalline CsPbCl₃ films was

reasonably attributed in the previous work [2]. In terms of the previous explanation under the assumption of excitonic superradiance, the increase of the luminescence intensity from HTN 0 to 3 in figure 2 corresponds to an increase of the superradiance-enhanced radiative decay rate due to crystal growth (or due to relaxed short-range order for HTN 0–1). The subsequent decrease of the luminescence intensity with increasing HTN, i.e., increasing size of the microcrystals in the film, is considered to be due to dephasing-induced quenching of the excitonic superradiance. The main cause of the dephasing in the excitonic superradiance may be exciton–phonon scatterings rather than lattice imperfections in the microcrystals.

Measurements of the decay time of the free excitons are expected to be very useful, because the two origins under consideration should give rise to opposite results for the decay time versus crystallite size, thus leading to a conclusion as regards the above discussion. It is also worth measuring the luminescence under high-density excitation. In the latter measurement, excitonic superradiance-induced stimulated emission is expected to occur under relatively weak excitation power, as was indeed the case for microcrystalline CsPbCl₃ films [11] (excitonic superradiance, being a cooperative radiation process, favours the occurrence of stimulated emission).

5. Conclusion

Photoluminescence spectra have been measured for microcrystalline CuCl films (extremely densely dispersed microcrystals compared to those dispersed in bulk materials) with thicknesses in the range 80–100 nm, crystallized and grown step by step from the amorphous phase by the shot-like IR laser light irradiation method. The spectra are dominated by a free-exciton emission band without showing any other trace of emission, suggesting high quality of the films. There is an optimum microcrystallite size level at which the films show a maximal integrated luminescence intensity for the free-exciton recombination. The peak energy of the corresponding emission band is characterized by a confinement-induced blue shift of 15 meV of exciton energy, which corresponds to an effective radius for the exciton confinement, 3.3 nm, under the assumption of the effective-mass approximation. The maximal integrated luminescence intensity is 2.5–4 times larger than the integrated luminescence intensity for the final, polycrystalline state of the films. A possible cause of the enhanced free-exciton luminescence is suggested: the occurrence of excitonic superradiance, although further experimental investigations are necessary for reaching a decisive conclusion. The quantum yield of the free-exciton emission in the CuCl microcrystalline films with the optimum microcrystallite size is expected to be very high compared to that in bulk CuCl, because even the polycrystalline films (with thickness of the order of 100 nm) exhibit much stronger free-exciton luminescence than bulk crystals due to wall collisions [10]. The present work is the first straightforward demonstration of confinement-induced enhancement (mesoscopic enhancement) of CuCl free-exciton luminescence using the same starting specimens, i.e. the same quantities, or numbers, of CuCl molecules—such a direct demonstration is difficult to carry out for CuCl microcrystals dispersed in bulk matrices because of thermal decomposition/generation of CuCl molecules during heat treatments [12].

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