Hot excitons in CuCl and CuBr crystalline thin films grown by vacuum deposition

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We report on the luminescence properties of CuCl and CuBr thin films with layer thickness of 3.5–100 nm from the viewpoint of hot excitons. Crystalline thin films preferentially oriented along the $\langle 111 \rangle$ crystal axis were grown on (0001) Al_2O_3 substrates by vacuum deposition. The relative intensity of the free-exciton luminescence to the bound-exciton one in the CuCl and CuBr thin films remarkably increases with a decrease in the film thickness. The excitation spectra of the free-exciton luminescence clearly exhibits oscillatory structures with the period of the LO-phonon energy in all of the thin films. The profiles of the excitation spectra, which reflect the relaxation processes of the hot excitons, hardly depend on the film thickness. It is concluded that the enhancement of the radiative efficiency of the free excitons results from nonequilibrium at the final stage of the relaxation in the polariton bottleneck region. Furthermore, it has been found that the energy of the free-exciton luminescence in the CuBr thin films has an oscillatory dependence on the excitation energy with the period and amplitude of the LO-phonon energy. This indicates the intense nonequilibrium of the free excitons. [S0163-1829(97)01016-3]

I. INTRODUCTION

Under the condition that photogenerated excitons have very short lifetimes, thermal equilibrium in the relaxation process is not achieved. A nonequilibrium exciton called a hot exciton has been extensively investigated in semiconductors and ionic crystals.[1] In the relaxation process of hot excitons, the emission of longitudinal-optical (LO) phonons is remarkable, so that the excitation spectrum of its luminescence exhibits an oscillatory structure with the period of the LO-phonon energy. Cuprous-halide crystals are typical materials for such an oscillatory structure of the excitation spectrum.[2] Recently, optical properties of CuCl thin films grown by molecular-beam epitaxy (MBE) in ultrahigh vacuum were investigated from the viewpoint of the exciton confinement.[3–5] Shuh *et al.*[4] reported that the free-exciton lifetimes of CuCl thin films with thickness of 3–120 nm were much shorter than that of a bulk CuCl crystal. Since the radiative efficiency of the free excitons in the CuCl thin films was not reduced, they concluded that the very short lifetime did not result from nonradiative processes, but from new radiative processes peculiar to thin films. One of the possible explanations is that the conversion from the exciton polaritons to photons results from the ballistic collisions at the film boundaries, so-called wall collisions. The wall-collision time is estimated to be of the order of ps in a ~10-nm thin film from the group velocity of the exciton polariton in the bottleneck region.[4] This mechanism leads to a new type of hot excitons in thin films; however, the excitation spectra reflecting the hot-exciton properties in CuCl thin films have not been reported until now. In addition, there has been no report on such a hot-exciton phenomenon in thin films of other cuprous halides.

In the present work, we have investigated the luminescence properties of CuCl and CuBr thin films with layer thickness of 3.5–100 nm from the viewpoint of hot excitons. We prepared the thin films on (0001) Al_2O_3 (sapphire) substrates by using a vacuum deposition method in high vacuum (order of 10^{-6} Torr), and confirmed that crystalline thin films grew preferentially along the $\langle 111 \rangle$ crystal axis from the x-ray diffraction patterns. The relative intensity of the free-exciton luminescence to the bound-exciton luminescence in the CuCl and CuBr thin films remarkably increases with the decrease of the thickness. This is consistent with the results of crystalline CuCl thin films grown by MBE.[4] Furthermore, we measured the excitation-energy dependence of the free-exciton luminescence and the bound-exciton one. The excitation spectra of the free-exciton luminescence clearly exhibit oscillatory structures with the period of the LO-phonon energy in all of the thin films. In addition, it has been found that the energy of the free-exciton luminescence in the CuBr thin films has an oscillatory dependence on the excitation energy: The period and amplitude of the oscillation are the same as the LO-phonon energy. On the other hand, such an excitation-energy dependence has not been observed in the CuCl thin films. This paper presents the details of the above hot-exciton properties.

II. EXPERIMENTAL PROCEDURE

The CuCl and CuBr thin films with layer thickness of 3.5–200 nm were grown on (0001) Al_2O_3 substrates at ~60 °C using a vacuum deposition method in high vacuum ($\sim 3\times 10^{-6}$ Torr). The substrates were heated to ~100 °C in the vacuum chamber before the thin-film growth. Commercially supplied powders of CuCl and CuBr with a purity of 99.9% were heated in a crucible, and the deposition rate, which was controlled by monitoring the frequency of a crystal oscillator, was about 0.15 nm/s. The deposition rate was calibrated by measuring the thickness of some thin films with a profilometer. The uncertainty of the layer thickness is estimated to be around 10%. We performed no thermal treatment after the deposition. At present, the optimum substrate temperature for the deposition is not clear. We note that the sticking coefficient of CuCl to the (0001) Al_2O_3 substrate remarkably decreases above ~100 °C. Similar results were

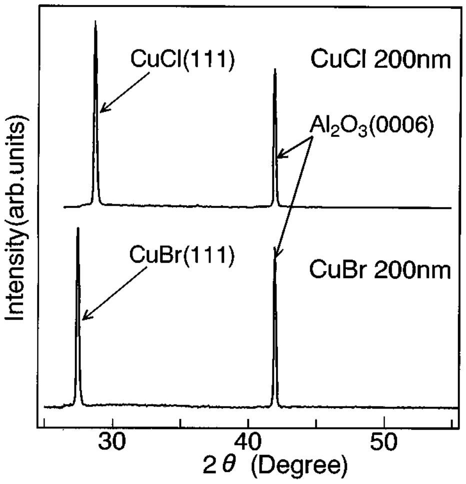

FIG. 1. θ-2θ x-ray diffraction patterns of the CuCl and CuBr thin films with thickness of 200 nm.

obtained in the case of a CaF_2 substrate.[6]

All the optical measurements were performed at 12 K using a closed-cycle helium-gas cryostat. In luminescence measurements, the excitation light was produced by combination of a 150-W Xe lamp and a 32-cm single monochromator with a resolution of 0.5 nm. The excitation-light power was of the order of $\mu W/cm^2$. The emitted light was dispersed by a 25-cm double monochromator with a resolution of 0.3 nm and detected by a conventional photon-counting system with a cooled photomultiplier. The absorption spectra of thin films were measured by a double-beam spectrometer with a resolution of 0.1 nm.

III. RESULTS AND DISCUSSION

Figure 1 shows the θ-2θ x-ray diffraction patterns of the CuCl and CuBr thin films with a thickness of 200 nm. The radiation source is a Cu-$K\alpha$ line through a Ni filter. Since the 2θ angle of the (111) spacing of a CuCl (CuBr) crystal is estimated to be 28.6° (27.1°) from the lattice constant of a bulk crystal,[7] the diffraction patterns clearly indicate the growth of crystalline thin films preferentially oriented along the $\langle 111 \rangle$ crystal axis. The resolution and accuracy of the diffractometer are not sufficient to discuss the crystal quality and strain effects. In the thin-film growth, the choice of substrates is very important. In recent works on CuCl thin films,[3–6,8,9] crystalline substrates of (111) Si,[3] $(1\bar{1}02)$ Al_2O_3,[4] (001) MgO,[5,9] (111) CaF_2,[6] and (001) NaCl (Ref. 8) were used. It was confirmed that CuCl thin films grown on (001) MgO (Refs. 5 and 9) and (001) NaCl (Ref. 8) substrates were oriented along the $\langle 111 \rangle$ and $\langle 001 \rangle$ crystal axes, respectively. To our knowledge, there has been no report on a CuBr thin film grown on a crystalline substrate. A few works on the optical properties of CuBr thin films grown on fused quartz substrates were reported;[10,11] however, the crystal orientation of thin films was not clear. The present results indicate that we can easily prepare $\langle 111 \rangle$-oriented crystalline thin films of CuCl and CuBr on the (0001) Al_2O_3 substrate.

Hereafter, we discuss the luminescence properties of the CuCl and CuBr thin films. Figure 2 shows the luminescence spectra of the CuCl thin films with thicknesses of 100, 24, 18, 12, and 3.5 nm and the absorption spectrum of the 12-nm thin film, where the energy of the excitation light corresponds to that of the $Z_{1,2}$ free-exciton energy, ~3.27 eV, and the maximum absorbance of the Z_3 free-exciton band is 0.45. The high-energy luminescence band originates from the Z_3 free exciton because its energy just agrees with that of the Z_3 absorption peak in all of the thin films. The observed energy of the Z_3 free-exciton luminescence is 3.204 eV in the 12-nm thin film. The luminescence band whose energy is 25-meV lower than that of the Z_3 free exciton is due to an exciton bound to a neutral acceptor which is called the I_1 bound exciton.[12] The differences between the observed exciton energies in the thin films and those in a bulk crystal[12] are within 3 meV.

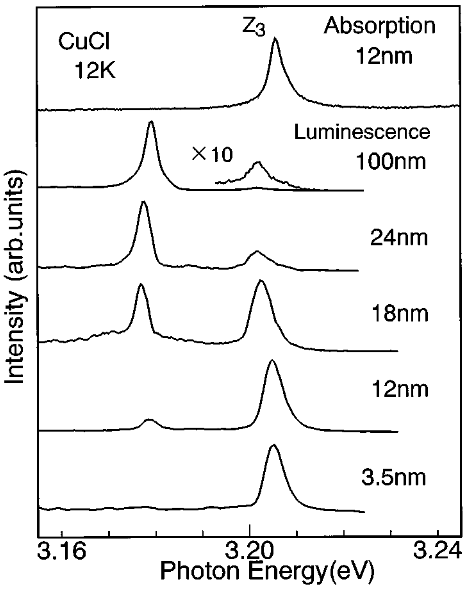

FIG. 2. Luminescence spectra of the CuCl thin films with thicknesses of 100, 24, 18, 12, and 3.5 nm, and the absorption spectrum of the 12-nm thin film, where the excitation energy corresponds to the $Z_{1,2}$ exciton one, ~3.27 eV.

Figure 3 shows the luminescence spectra of the CuBr thin films with layer thicknesses of 100, 24, 12, and 6 nm, and the absorption spectrum of the 12-nm thin film, where the energy of the excitation light corresponds to that of the Z_3 free-exciton energy, ~3.12 eV, and the maximum absorbance of the $Z_{1,2}$ free-exciton band is 0.38. We could not grow a high-quality CuBr thin film with thickness less than 5 nm. From the comparison between the luminescence and absorption spectra of the 12-nm thin film, we find that the peak energy (2.962 eV) of the high-energy luminescence band agrees with the energy of the low-energy shoulder of the $Z_{1,2}$ absorption band. This feature is observed in all the CuBr thin films. It has been revealed that the free-exciton luminescence in a CuBr bulk crystal is attributed to the lowest-energy triplet exciton, called the Z_f one, whose energy is slightly lower than that of the $Z_{1,2}$ free exciton because of the exchange interaction.[2] Although the dipole transition of the triplet exciton is forbidden in principle, it is allowed in the CuBr crystal owing to mixing between the singlet and triplet exciton states resulting from the so-called k-linear term.[13] Thus the high-energy luminescence band originates from the

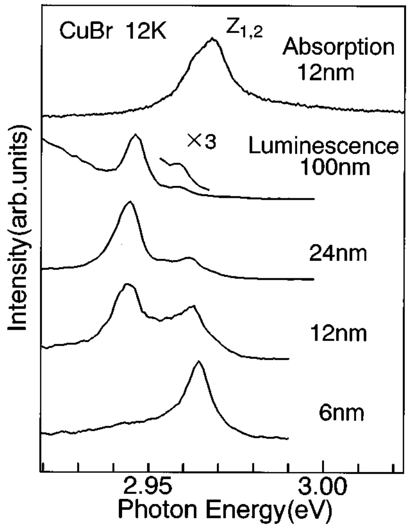

FIG. 3. Luminescence spectra of the CuBr thin films with thicknesses of 100, 24, 12, and 6 nm, and the absorption spectrum of the 12-nm thin film, where the excitation energy corresponds to the Z_3 exciton one, ~3.12 eV.

Z_f free exciton. The luminescence band whose energy is 18 meV lower than that of the Z_f free exciton is due to the I_1 bound exciton. Although the 1LO- and 2LO-phonon replicas of the Z_f free-exciton luminescence are observed in a CuBr bulk crystal,[12] they are not detected in the thin films. The broad luminescence band on the low-energy side of the I_1 bound-exciton band is observed only in the 100-nm thin film. The differences between the observed exciton energies in the CuBr thin films and those in a bulk crystal[12] are within 3 meV, which is consistent with the results of the CuCl thin films. This indicates that strain effects on the CuCl and CuBr thin films induced by the substrates are not considerable; however, only the 3.5-nm CuCl thin film seems to be slightly strained, as discussed below.

From the viewpoint of quantum confinement effects, we expect an increase of the free-exciton energy with a decrease of the film thickness. In Figs. 2 and 3 we observe slight blueshifts of the free-exciton luminescence energies in the CuCl and CuBr thin films as the thickness decreases. The confinement energy is estimated to be 13 meV in the 3.5-nm CuCl thin film from a simple effective-mass approximation with the exciton mass of $2.3m_0$,[2] where m_0 is the free-electron mass. The difference between the observed Z_3 free-exciton energies of the 3.5-nm and 100-nm thin films is about 3 meV, which is much smaller than the expected value of the confinement-induced energy shift. It is expected generally in the thin-film growth that the film strain due to the substrate increases with the decrease of the thickness; therefore it seems that the strain-induced energy shift, which might be slightly negative, hides the confinement effect. For the CuBr thin films, it is difficult to discuss quantitatively the confinement effect on the Z_f free exciton because of the complicated dispersion of the triplet exciton.[14] It is noted that we observe the blueshifts of the $Z_{1,2}$ and Z_3 free-exciton bands of the absorption spectra with the decrease of the thickness. The details of the absorption spectra are beyond the scope of this paper.

It is obvious from Figs. 2 and 3 that the relative intensity of the free-exciton luminescence to the bound-exciton one in the CuCl and CuBr thin films remarkably increases with the decrease of the film thickness. The radiative efficiency of the free-exciton luminescence tends to increase as the thickness decreases: The efficiency in the 12-nm CuCl and CuBr thin films is estimated to be one order of magnitude over that in the 100-nm thin films. Similar results were obtained in CuCl thin films grown by MBE.[4] According to Ref. 4, the lifetimes of the Z_3 free excitons in the CuCl thin films are less than the detection limit of 40 ps, which is much shorter than the lifetime in a bulk crystal, 850 ps. The above results of the radiative efficiency and lifetime indicate the existence of a radiative decay mechanism peculiar to thin films. A possible explanation was proposed: ballistic collisions of the free excitons at the film boundaries, so-called wall collisions, open a new radiative decay channel.[4] This mechanism produces the nonequilibrium of excitons in the radiative decay process.

The shape of the Z_3 free-exciton luminescence band in every CuCl thin film shown in Fig. 2 is asymmetric and exhibits the tail to the high-energy side. From the viewpoint of hot excitons, the high-energy tail reflects the thermal distribution of the Z_3 free excitons due to an effective temperature higher than the lattice temperature.[15] For the Z_f free-exciton luminescence in the CuBr thin films shown in Fig. 3, the asymmetric line shape is not clear because of the broader band shape and narrower spacing to the I_1 bound-exciton band than those in the CuCl thin films. We estimate the effective temperature of the Z_3 free-exciton luminescence in the CuCl thin films according to Ref. 15. In the estimation, we assume a three-dimensional density of states and a two-dimensional one for the 100-nm thin film and for the thinner films, respectively. The estimated values, 26±3 K, are almost independent of the layer thickness. Since the excitation-light power of the order of μW/cm^2 in the present work should cause no high-density excitation, such a high effective temperature indicates the nonequilibrium in the radiative decay process of the Z_3 free exciton. In CuCl thin films grown by MBE,[4] the effective temperature in a low-excitation regime almost agrees with the present results.

Next, we discuss the properties of the excitation spectra of the free-exciton luminescence and bound-exciton one, which reflect the relaxation processes of the excitons. Figures 4 and 5 show the absorption and excitation spectra in the 12-nm thin films of CuCl and CuBr, respectively, where the excitation spectra (b) and (c) are detected at the free-exciton (Z_3 in CuCl and Z_f in CuBr) and I_1 bound-exciton luminescence bands, respectively. The free-exciton excitation spectra of Figs. 4(b) and 5(b) clearly exhibit oscillatory structures with the periods of 26±2 meV in CuCl and 21±2 meV in CuBr corresponding to the LO-phonon energies.[2] These oscillatory structures reflect the hot-exciton properties in the relaxation processes of the free excitons. On the other hand, the excitation spectra detected at the I_1 bound-exciton luminescence shown in Figs. 4(c) and 5(c) have no oscillatory structure, and the spectrum profiles resemble the absorption spectra. The above spectral profiles are the common characteristics of cuprous-halide crystals.[2,12] Although LO-phonon structures of absorption spectra were reported in CuCl thin films,[16,17] they appear at photon energies higher than 3.4 eV, which is out of the spectral-energy range in the present work. Such a

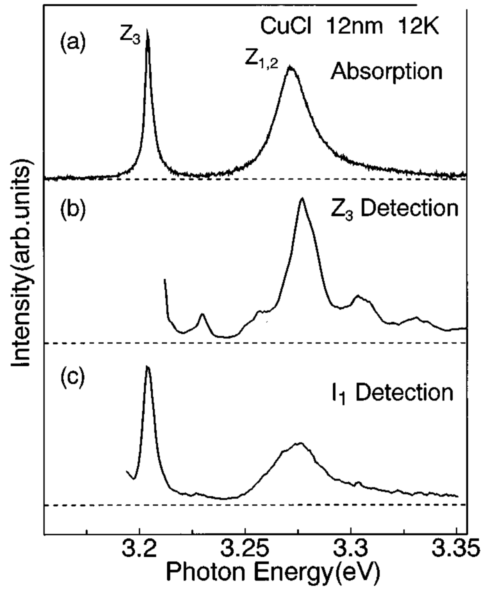

FIG. 4. Absorption (a) and excitation spectra (b) and (c) in the 12-nm thin film of CuCl, where the excitation spectra (b) and (c) are detected at the Z_3 free-exciton and I_1 bound-exciton luminescence bands, respectively. The dashed lines indicate the baselines of the spectra.

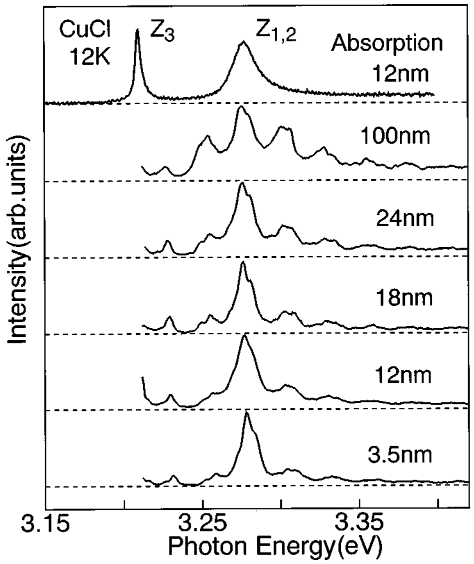

FIG. 6. Excitation spectra detected at the Z_3 free-exciton luminescence band in the CuCl thin films with the various layer thicknesses, where the absorption spectrum of the 12-nm thin film is depicted at the top. The dashed lines indicate the baselines of the spectra.

LO-phonon structure originates from the interaction between the $n=2$ free-exciton and the LO phonon in the exciton-creation process, not from the hot-exciton properties.[1] From the viewpoint of the hot-exciton relaxation, we expect that the excitation spectrum of the bound-exciton luminescence has an oscillatory structure whose phase is opposite to that of the free-exciton luminescence. The disappearance of the oscillatory structure of the bound-exciton luminescence excitation spectrum may be due to the fact that the amount of excitons resonantly scattered by the LO phonon is very small relative to the total amount of photogenerated excitons. This results in the undetectable reduction of the intensity of the excitation spectrum of the bound-exciton luminescence.

From the profiles of the excitation spectra of the free-exciton luminescence in all of the samples, we discuss the layer-thickness dependence of the relaxation processes leading to the free-exciton luminescence. Figures 6 and 7 show the excitation spectra detected at the Z_3 and Z_f free-exciton luminescence bands of the CuCl and CuBr thin films with

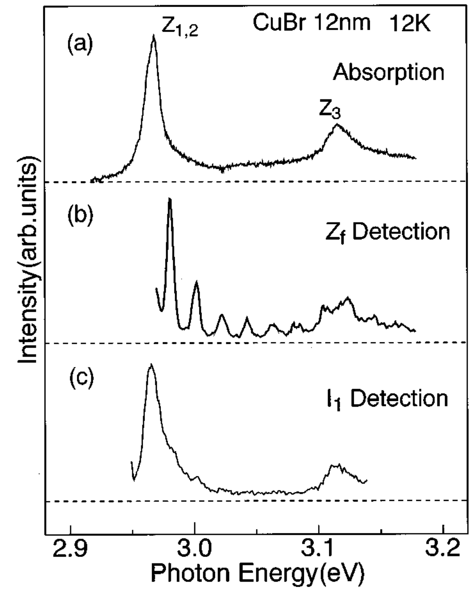

FIG. 5. Absorption (a) and excitation spectra (b) and (c) in the 12-nm thin film of CuBr, where the excitation spectra (b) and (c) are detected at the Z_f free-exciton and I_1 bound-exciton luminescence bands, respectively. The dashed lines indicate the baselines of the spectra.

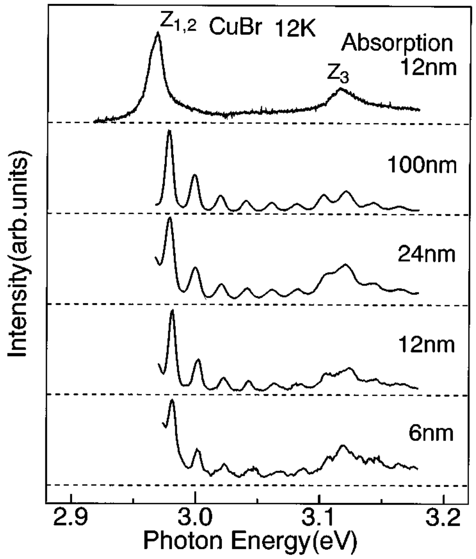

FIG. 7. Excitation spectra detected at the Z_f free-exciton luminescence band in the CuBr thin films with the various layer thicknesses, where the absorption spectrum of the 12-nm thin film is depicted at the top. The dashed lines indicate the baselines of the spectra.

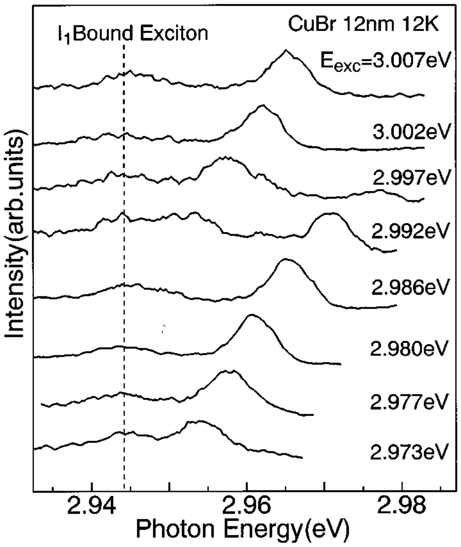

FIG. 8. Free-exciton luminescence spectra excited at various energies between the $Z_{1,2}$ and Z_3 free-exciton energies in the 12-nm CuBr thin film.

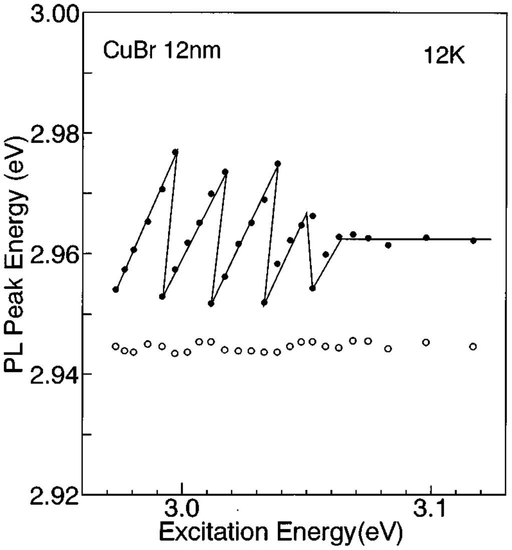

FIG. 9. Excitation-energy dependence of the free-exciton and I_1 bound-exciton luminescence energies in the 12-nm CuBr thin film, where the solid line is a guide for the eyes.

the various layer thicknesses, respectively, where the absorption spectrum of the 12-nm thin film is depicted at the top. From Figs. 6 and 7, it is obvious that the profiles of the excitation spectra do not remarkably change with the decrease of the film thickness. This suggests that the relaxation processes of the free excitons hardly depend on the film thickness. On the other hand, the luminescence properties of the thin films drastically change with the layer thickness, as shown in Figs. 2 and 3. Therefore we consider that the increase of the relative intensity of the free-exciton luminescence to the bound-exciton one is due to the enhancement of the conversion efficiency from the exciton polaritons to photons around the polariton bottleneck region.

Finally, we discuss the excitation-energy dependence of the free-exciton luminescence in the CuBr thin films. Figure 8 shows the luminescence spectra excited at various energies between the $Z_{1,2}$ and Z_3 free-exciton ones in the 12-nm CuBr thin film. It is noted that the excitation energy for the luminescence spectra shown in Fig. 3 is the peak energy of the Z_3 absorption band, ~3.12 eV. It is obvious from Fig. 8 that the energy of the I_1 bound-exciton band is constant, while the energy of the luminescence band above the I_1 band exhibits a remarkable dependence on the excitation energy. In addition, we notice the appearance of two luminescence bands with the energy difference of ~20 meV, which corresponds to the LO-phonon energy, above the I_1 bound-exciton band at the excitation energy of 2.997 eV. Since such an excitation-energy dependence of the luminescence energy is never expected in impurity-related luminescence because of the localization nature, it reflects the properties of the free-exciton luminescence. Here, we cannot assign the origin of the luminescence either to the Z_f exciton branch or to the $Z_{1,2}$ ones, so we simply call it the free exciton, hereafter.

Figure 9 shows the excitation-energy dependence of the energies of the free-exciton and I_1 bound-exciton luminescence bands in the 12-nm CuBr thin film, where the solid line is a guide for the eyes, and the highest excitation energy corresponds to the Z_3 free-exciton energy used for the excitation of the luminescence spectra shown in Fig. 3. The energy of the free-exciton luminescence has the oscillatory dependence on the excitation energy with the period and amplitude of the LO-phonon energy. In the excitation-energy range where there is no oscillation, the free-exciton luminescence energy agrees with the Z_f one. Similar properties of the excitation-energy dependence are observed in all of the CuBr thin films. On the other hand, the free-exciton luminescence energies in the CuCl thin films exhibit no excitation-energy dependence.

The oscillation of the free-exciton luminescence energy indicates intense nonequilibrium at the final stage in the relaxation process of the free excitons; namely, the contribution of acoustic phonons to the radiative process around the polariton bottleneck region is fully negligible. Gross *et al.*[18] reported similar excitation-energy dependence of free-exciton luminescence energy in a CdS bulk crystal with poor quality. They concluded that the reason for the excitation-energy dependence was very short lifetimes of free excitons resulting from the high probability of the nonradiative transitions. In the present case, as discussed above from the film-thickness dependence of the luminescence intensities, the lifetimes of the free excitons are expected to be very short because of a radiative decay mechanism, such as wall collisions. The appearance of the oscillation of the free-exciton luminescence energy indicates that the nonequilibrium of the free excitons in the CuBr thin films is much more remarkable than that in the CuCl ones.

In Fig. 9, the oscillation of the free-exciton luminescence energy disappears at ~3.06 eV, which is about 100 meV higher than the $Z_{1,2}$ free-exciton energy. The energy difference of ~100 meV almost agrees with the binding energy of the $Z_{1,2}$ free exciton, 108 meV.[2] This suggests that the oscillation originates from the relaxation process in the $Z_{1,2}$ exciton branches and that the final stage leading to the radiative decay has no contribution of acoustic phonons. In the excitation-energy region of the continuum transitions above ~3.06 eV, where there is no oscillation of free-exciton luminescence energy, electrons and holes are generated at first, then excitons are formed. It seems that the difference of the initial condition of the exciton formation results in the difference of the relaxation processes in the exciton excitation and in the carrier excitation. Although the mechanism of the oscillation of the free-exciton luminescence energy is now an open question, the complicated polariton dispersions around the bottleneck region of the CuBr crystal[14] may be one of the reasons for it.

IV. CONCLUSIONS

We have investigated the luminescence properties of CuCl and CuBr thin films with layer thickness of 3.5–100 nm from the viewpoint of hot excitons. The thin films were grown on (0001) Al_2O_3 substrates using a vacuum deposition method in high vacuum. We confirmed the growth of the crystalline thin films preferentially oriented along the $\langle 111 \rangle$ crystal axis by measuring the x-ray diffraction patterns. The relative intensity of the free-exciton luminescence to the bound-exciton one in the CuCl and CuBr thin films remarkably increases with the decrease of the thickness. This indicates the enhancement of the radiative efficiency of the free exciton with the decrease of the film thickness owing to a radiative decay channel peculiar to thin films, such as wall collisions. The decay mechanism leads to the nonequilibrium of free excitons. The excitation spectra of the free-exciton luminescence clearly exhibit oscillatory structures with the period of the LO-phonon energy in all of the thin films. The features of the excitation spectra change little with the layer thickness; therefore this indicates that the relaxation processes of the hot excitons hardly depend on the layer thickness. We conclude that the increase of the radiative efficiency in the thin films results from the enhancement of the conversion efficiency from the exciton polaritons to photons around the polariton bottleneck regions. Furthermore, it has been found that the energy of the free-exciton luminescence in the CuBr thin films has an oscillatory dependence on the excitation energy with the period and amplitude of the LO-phonon energy, while that in the CuCl thin films is constant. The oscillation of the free-exciton luminescence energy disappears in the excitation-energy range of the continuum transition. Such an excitation-energy dependence suggests the remarkable nonequilibrium of the free excitons of the CuBr thin films around the polariton bottleneck region.

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