Available online at www.sciencedirect.com
ScienceDirect
Materials Letters 62 (2008) 33 – 36
materials letters
www.elsevier.com/locate/matlet

# Extremely-high-intensity photoluminescence from CuBr films fabricated by film–substrate chemical reaction of CuCl films on KBr-crystal substrate

S. Kondo *, Y. Hata, T. Saito

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

Received 12 January 2007; accepted 19 April 2007
Available online 24 April 2007

## Abstract

High quality CuBr film is fabricated by film–substrate chemical reaction of CuCl on KBr, where CuCl is vacuum-deposited film of the order of ~ 100 nm thickness and KBr is fleshly-cleaved single crystal. The resulting CuBr films show ~ $10^3$ times higher efficiency of free-exciton photoluminescence (PL) than conventional CuBr films. The efficiency exceeds that of conventional CuCl films even by a factor of ~ $10^2$, despite the general recognition that the free-exciton PL from CuBr is much weaker than that from CuCl. The present result encourages us to challenge to rethink the exciton PL in CuBr as well as in CuCl, because the compounds are the model materials for basic and application studies of linear/nonlinear exciton-related PL properties of solids.

*Keywords:* Luminescence; Thin film; Semiconductor; CuBr; CuCl

## 1. Introduction

CuX (X = Cl, Br), typical wide-band-gap semiconductors, are well-known model materials for basic and application studies of linear/nonlinear exciton-related photoluminescence (PL) properties of solids. In the past two decades many workers have attempted to grow CuX films on various substrates to achieve high-intensity exciton PL. For example, high quality CuCl films are successfully grown on (100)NaCl [1], $CaF_2$ [2], (001)MgO [3], (0001)$Al_2O_3$ [4], (110)$TiO_2$ [5] and (100) and (111)Si [6]. Although the films exhibit enhanced exciton PL, however, its intensity still seems very weak as compared with those from improved metal halide films such as $CsPbX_3$ (X = Cl, Br) films [7] for which we have recently observed exciton-related stimulated emission at room temperature [8]. In fact, room temperature-stimulated emission has not yet been reported for CuX (X = Cl, Br), despite the very large binding energies of the CuX excitons (190 meV [9] for CuCl and 108 eV [9] for CuBr) as compared to those of $CsPbX_3$ (60–67 meV [10,11] for $CsPbCl_3$ and 34 meV [10] for $CsPbBr_3$).

The substrates mentioned above are chosen by taking into account not only film–substrate lattice compatibility but also stability of the films against chemical interaction with the substrates. On the contrary, we have attempted to use chemically interacting crystal substrates. For this purpose we first investigated the trend of chemical interaction of CuX with various metal halides using a technique similar to those previously applied to various metal halides [12]. It was disclosed that both CuCl and CuBr have a strong tendency to interact with KX (X = Cl, Br) yielding $K_2CuX_3$. Therefore, we studied PL of CuX films grown on KCl and KBr crystals (which we abbreviate as, for example, CuCl/KBr films). In a just preceding work [13] we found that very thin CuBr/KBr films (thickness, ~ 10 nm) showed $10^2$ or $10^3$ times higher efficiency of free-exciton PL than conventional CuBr films. In the present work we achieved thicker films by a different method, *i.e.*, by means of film–substrate chemical reaction of CuCl films deposited onto KBr-crystal substrates (while in [13] CuBr was directly deposited onto KBr). The resulting CuBr/KBr films showed ~ $10^3$ times higher efficiency of free- and/or bound-exciton PL than conventional CuBr films.

## 2. Experimental

CuX films were vacuum-deposited onto freshly cleaved (100)KCl and (100)KBr substrates ("interacting" substrates), and, for comparison, onto silica-glass and (0001)$Al_2O_3$ substrates ("non-interacting" substrates) by the method employed in previous works [14]. PL from the films were measured *in situ*

---

* Corresponding author.
*E-mail address:* d930963@icpc00.icpc.fukui-u.ac.jp (S. Kondo).

0167-577X/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2007.04.065

in a 45° back-scattering geometry, with the exciting light (from a 500 W Xe-lamp, passing through a monochromator) being incident on the films at right angle, under the exciting-light conditions of ~70 μW/cm$^2$, 3.395 eV and 1.1 nm for the intensity, photon-energy and spectral width, respectively. All the luminescence spectra were corrected for spectral sensitivity of the measuring system.

For all the substrates, “best” films were achieved by depositing the films onto room temperature substrates at a rate of ~10 nm/min. In the case of the non-interacting substrates, for which almost no difference in the PL spectra between the two substrates was observed, post-annealing of the films did not improve exciton PL property, resulting in a slight redshift (probably due to relaxation of exciton confinement effect) of the free-exciton PL and the enhancement of the excitation-light strays, or, Rayleigh scattering in a wide sense. In the case of the interacting substrates, it gave rise to film–substrate chemical reaction depending on the annealing temperature. We note that, once the films (with no cap layer) were exposed to ambient atmosphere, considerable degradation in the characteristics of PL (intensity, its position dependence and excitation-light strays) occurred depending on the exposure time — in the case of the non-interacting substrates, such degradation always occurred when the films were annealed *in situ* above ~110 °C.

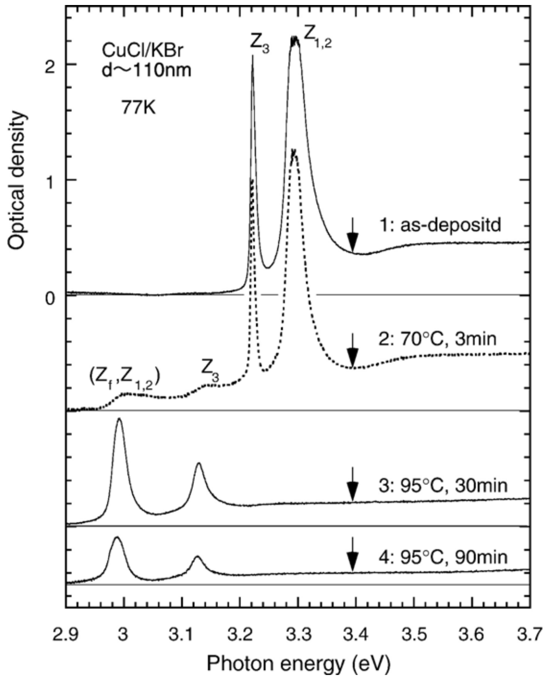

Fig. 2. Absorption spectra at various steps of thermally-induced film–substrate chemical reaction of a CuCl/KBr film. The downward arrows indicate the energy location of the exciting light for the PL spectra shown in Figs. 3 and 4.

## 3. Result and discussion

We first show typical PL spectra of CuBr/Al$_2$O$_3$ (Fig. 1a) and CuCl/Al$_2$O$_3$ (Fig. 1b) films (“conventional” films) grown under “best” conditions, together with the absorption spectra. Almost the same results were obtained for films deposited onto silica-glass substrates. In both films almost the same PL spectrum was observed throughout the scanned area of 6×6 mm$^2$ (resolution, 0.6×1.2 mm$^2$). The ordinates are given on a scale of normalized PL intensity at the left and on a scale of normalized PL efficiency at the right. The former scale is defined as the PL intensity (the emitted-photon number per unit photon-energy width divided by the irradiated-photon number of the exciting light) of the films divided by the maximum of the PL intensity of the CuBr/Al$_2$O$_3$ film, and the latter is defined as the PL efficiency (the emitted-photon number per unit photon-energy width divided by the absorbed-photon number of the exciting light) divided by the maximum of the PL efficiency of the CuBr/Al$_2$O$_3$ film. At 77 K, the PL spectra are composed of a weak Z$_f$ free-exciton band and a broad band (DA band) of donor–acceptor pair recombinations [9] for the CuBr/Al$_2$O$_3$ film (Fig. 1a), and a strong free-exciton band (Z$_3$ band) for the CuCl/Al$_2$O$_3$ film (Fig. 1b). The efficiency of the free-exciton PL from the CuBr/Al$_2$O$_3$ film is much lower (by a factor of ~15) than that from the CuCl/Al$_2$O$_3$ film, similar to hitherto reported results [9]. For both films, however, PL was observed even at room temperature (295 K), unlike the case of the earlier works [9], where PL disappeared at temperatures above 130 K for CuBr/silica-glass and 150 K for CuCl/silica-glass, despite a much stronger excitation light (light source of 2 kW Xe-lamp and spectral width of 20 nm, as compared with our 0.5 kW Xe-lamp and 1.1 nm, respectively) — room temperature PL has recently been reported for CuCl/Si films [6], but with an extremely-high-intensity excitation light of the order of 10 W/cm$^2$ from a laser (as compared with our excitation intensity of ~70 μW/cm$^2$).

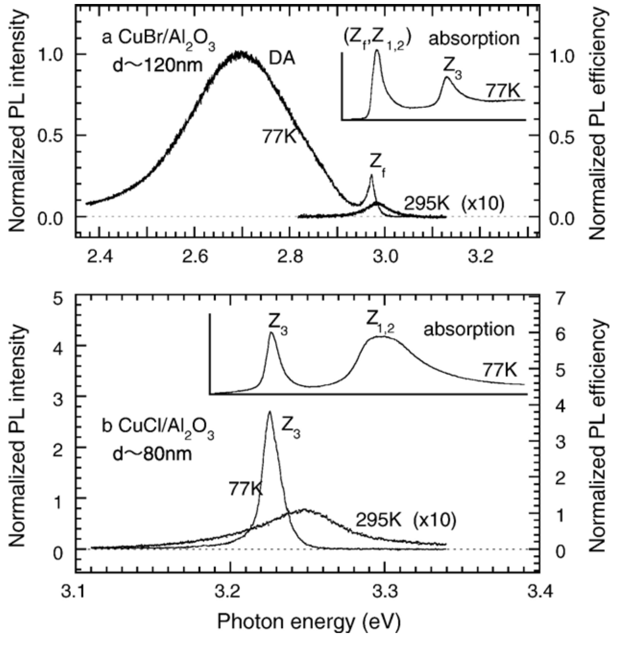

Fig. 1. PL spectra typical of the films grown on non-interacting substrates (Al$_2$O$_3$) are shown together with the absorption spectra.

Fig. 2 shows absorption spectra of a CuCl/KBr film measured *in situ* at 77 K for the as-deposited film (curve 1), and for the film annealed at 70 °C for 3 min (curve 2), 95 °C for 30 min (curve 3) and 95 °C for 90 min (curve 4). The annealing gave rise to solid-state chemical reaction between the film and the substrate yielding CuBr, as clearly seen from the occurrence of the (Z$_f$,Z$_{1,2}$) and Z$_3$ free-exciton absorption bands of CuBr.

Fig. 3 shows the PL spectra at 77 K of the same films. As seen in the inset (where curves 1 and 2 are plotted on a magnified scale) curves 1 and 2 almost coincide with each other in the photon-energy region of CuCl excion (reflecting almost the same CuCl-Z$_3$-absorption