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Temperature dependent photoluminescence of nanocrystalline γ -CuCl hybrid films

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ABSTRACT

Organic–inorganic hybrid films combine the basic properties of organic and inorganic materials and offer special advantages that enhance optical, thermal and mechanical properties. We have studied the temperature dependent photoluminescence (PL) of nanocrystalline γ -CuCl hybrid films from 15 K to room temperature in order to investigate the electronic transitions of the hybrid films. The I_1 impurity bound exciton peak is the most intense emission peak at 15 K but the peak intensity decreases rapidly with increasing temperature due to the low binding energy of this exciton bound to an impurity center and above 80 K all three excitonic and biexcitonic peaks, except the Z_3 free exciton emission peak disappeared. The biexciton emission peak intensity follows a quadratic dependency on power in the excitation power range $< 10 \text{ kWcm}^{-2}$. The integrated Z_3 excitonic PL intensity is almost independent of the temperature below 80 K, while above 100 K the PL emission intensity decreases rapidly. Thermal quenching of the Z_3 free exciton PL emission in hybrid films has been observed. The full width at half maximum (FWHM) of the free exciton peak was investigated as a function of temperature and was explained by a theoretical model which considers the scattering of excitons with acoustic phonons and longitudinal optical phonons. The FWHM of the Z_3 free exciton emission peak increases with increasing temperature, and a value of $\sim 76 \text{ meV}$ was deduced for the FWHM at room temperature, which is comparatively better than ZnO (106 meV) and GaN (100 meV) nanostructures. The Z_3 free exciton energy of the hybrid films exhibits a blue shift of 3 meV at 15 K compared to the bulk CuCl samples which may be due to a dead layer effect near the CuCl nanocrystal surface. The exciton energy also presents a blue shift of $\sim 41 \text{ meV}$ with increasing temperature from 15 K to room temperature. The results obtained for the γ -CuCl hybrid films are comparable to those of vacuum evaporated and sputtered CuCl films reported in the literature.

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1. Introduction

CuCl luminescence has been investigated extensively for many years, owing to its interesting structural, optical and electrical properties [1–6]. It is an ionic I-VII compound wide direct band gap semiconductor material with the zinc blende structure. It has attracted renewed interest due to several characteristics such as possessing free exciton binding energies of approximately 190 meV, which are much larger than for III-nitride, III-V and II-VI semiconductors [1]. Due to this large excitonic binding energy CuCl hybrid films have intense Z_3 free exciton PL emission in the UV spectral region at room temperature. Its biexciton binding energy is about 32 meV [7] and biexciton lasing action from CuCl quantum dots embedded in a NaCl matrix has also been reported [8]. At low temperature CuCl exhibits a strongly negative linear expansion coefficient and elastic shear constants that decrease with

increasing hydrostatic pressure which are related to an anharmonic lattice potential [3]. In general, the photoluminescence emission intensity of a semiconductor and ionic crystal decreases monotonically with increasing temperature. This phenomenon is called “thermal quenching” of photoluminescence [9]. In other words the “thermal quenching” phenomenon can be defined as the increase of the non-radiative recombination probability of electrons and holes with increasing temperature. The thermal quenching phenomenon and its theoretical analysis have been extensively studied to describe the temperature dependent photoluminescence intensity of various materials [10–14].

Organic–inorganic hybrid materials are receiving growing attention for building and testing electronic and optoelectronic devices [15–17]. Temperature dependent PL spectroscopic measurements provide a useful insight into the electronic transitions of materials. Thus, in this paper, we present the results of the temperature dependent photoluminescence of γ -CuCl nanocrystalline hybrid films deposited via spin coating techniques in order to determine the thermal quenching behavior and its electronic transitions.

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2. Experimental details

The γ -CuCl nanocrystalline hybrid films with typical layer thicknesses of ~ 200 nm were deposited on glass or flexible substrates by the spin coating method using a Laurell WS-400A-6PP/LITE spin coater in a class 100 clean room to avoid contamination. The coating was performed at room temperature. The nanocrystals were synthesized by a complexation–reduction–precipitation mechanism reaction of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, alpha D-glucose and de-ionized water with an organic polysilsesquioxane (PSSQ) based solution as the host matrix material. The films were subsequently heated at 120°C for 18 hours *in vacuo*. After heating the films, X-ray diffraction (XRD) confirmed the preferential growth of CuCl nanocrystals whose average size is ≈ 35 nm in the $\langle 111 \rangle$ orientation. The details of the solution processes, synthesis and film deposition were described previously [2]. The luminescence properties were studied using temperature dependent photoluminescence spectroscopy in the range between 15 K to room temperature, by employing a UV Ar⁺ Innova laser with a second harmonic generation barium borate crystal producing a 355 nm photo-excitation. The PL spectra were collected on a Jobin Yvon-Horiba Triax 190 spectrometer with a spectral resolution of 0.3 nm, coupled with a liquid nitrogen-cooled CCD detector. The samples were kept under vacuum during the PL measurement, to prevent the oxidation of CuCl nanocrystal hybrid films.

3. Results and discussion

3.1. Excitonic transitions in γ -CuCl hybrid film

The photoluminescence spectra acquired at different temperatures in the range between 15 and 300 K are shown in Fig. 1. Figs. 2 and 3 show the contributions of different recombination centers connected with emission peaks at 15 K and 300 K, respectively. The CuCl photoluminescence peaks were fitted with Lorentzian line shapes to find the FWHM. There are four peaks evident in the spectra measured from 15 to 60 K. At 15 K, the peak centered at 3.213 eV (≈ 385.9 nm) is the Z_3 free exciton peak (Figs. 1 and 2) whereas the room temperature Z_3 free exciton PL emission is at 3.254 eV (≈ 381 nm) which is shown in Fig. 3. The exciton emission energy increases from 3.213 eV at 15 K to 3.254 eV at room temperature. Moving to longer wavelengths of the emission spectra of Figs. 1 and 2, one can observe a peak occurring at 3.191 eV (≈ 388.6 nm). This peak is attributed to emission from an exciton bound to an impurity, which has been called the I_1 impurity bound exciton and the impurity or defect involved in this process has been previously identified as a neutral acceptor, possibly a Cu vacancy [2,18]. The peak at 3.170 eV (≈ 391.2 nm) is identified as a free biexciton M [19]. The low intensity peak at 3.141 eV (≈ 394.7 nm) conventionally labeled

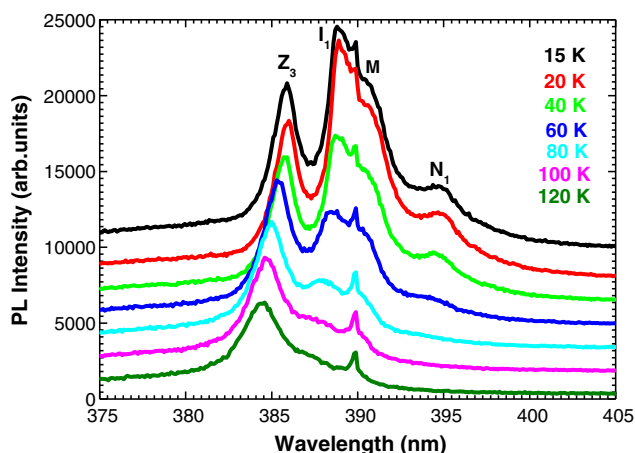


Fig. 1. Photoluminescence spectra of CuCl hybrid film at different temperatures.

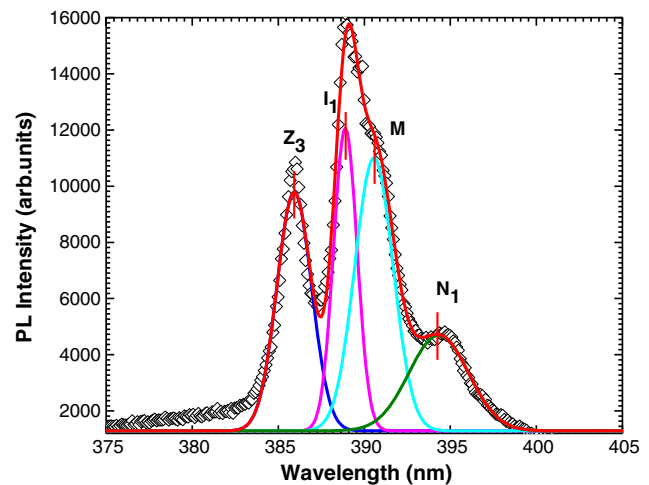


Fig. 2. Fitted photoluminescence spectra of CuCl hybrid films with fit (solid curve) based on Lorentzian line shapes at 15 K.

N_1 is evident, and likely originates from a biexciton bound to an impurity. Similar to the I_1 bound exciton, the most probable candidate for this impurity is a neutral acceptor [1]. The intensities of the impurity bound exciton (I_1) and the impurity bound biexciton (N_1) peaks decrease more rapidly in comparison with the free exciton (Z_3) peak as the temperature increases. In the temperature range from 60 K to room temperature, the spectra were dominated by the Z_3 free exciton peak. The dominance and the stability of the Z_3 exciton peak are due to the large binding energy of the order 190 meV. The bound exciton and biexciton both disappear simultaneously at 100 K. Fig. 4 shows the variation of excitonic (Z_3) and biexcitonic (M) and bound biexciton (i.e. N_1) emission intensities with excitation power analyzed on a double logarithmic scale for the CuCl hybrid film at 15 K. Excitation power dependent PL measurements can be used to confirm the excitonic or biexcitonic nature of the emission. For low power excitation conditions, the excitonic and bound biexcitonic PL emission displays a linear dependence on excitation power, whereas free biexcitonic PL emission typically displays a quadratic dependence on excitation power [20,21]. The biexciton emission intensities for the CuCl hybrid film clearly show an approximately quadratic dependency on excitation power for lower excitation power densities of $< 10 \text{ kWcm}^{-2}$. The free exciton and bound biexcitons show an approximately linear dependence on power, similar to results reported by other researchers for CuCl nanocrystals embedded in NaCl matrices and InGaAs/GaAs quantum

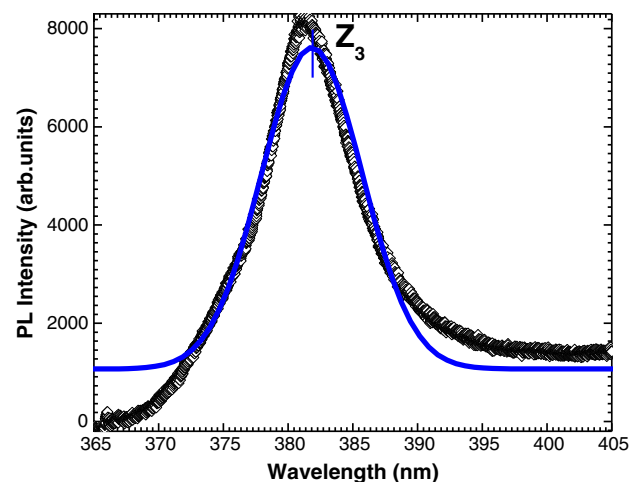


Fig. 3. Photoluminescence spectra of CuCl hybrid films with fit (solid curve) based on Lorentzian line shapes at 300 K.

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