

# Impact on structural, optical and electrical properties of CuCl by incorporation of Zn for n-type doping

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## Abstract

$\gamma$ -CuCl is a wide-band gap ( $E_g = 3.395$  eV at 4 K), direct band gap, semiconductor material with a cubic zincblende lattice structure. A very large exciton binding energy (190 meV), assures efficient exciton-based emission at room temperature. Its lattice constant,  $a_{\text{CuCl}} = 0.541$  nm means that the lattice mismatch to Si ( $a_{\text{Si}} = 0.543$  nm) is  $<0.5\%$ .

$\gamma$ -CuCl on Si—the growth of a wide-band gap, direct band gap, optoelectronics material on silicon substrate is a novel material system, with compatibility to current Si-based electronic/optoelectronics technologies. Both n-type and p-type CuCl will be required for development of homojunction light-emitting diodes (LEDs). The authors report on the impact of incorporation of Zn for n-type doping of CuCl by co-evaporation of CuCl and ZnCl<sub>2</sub>.

Polycrystalline Zn-doped  $\gamma$ -CuCl thin films are grown on Si (1 1 1), Si (1 0 0), and glass substrates by physical vapour deposition. X-ray diffraction (XRD) studies confirm that this n-doped CuCl has a cubic zincblende structure with a preferred (1 1 1) orientation. Several excitonic bands are evident in low-temperature photoluminescence (PL) measurements such as the Z<sub>3</sub> free exciton at  $\sim 388$  nm; I<sub>1</sub>-bound exciton at  $\sim 392$  nm and M free biexciton at  $\sim 393$  nm. Cathodoluminescence (CL) and PL reveal a strong room temperature Z<sub>3</sub> excitonic emission at  $\sim 385$  nm. Electrical measurements indicate n-type conductivity with resistivity  $\sim 34 \Omega\text{cm}$ .

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## 1. Introduction

The need for blue and UV solid-state emitters and detectors has propelled the investigation of several wide-band gap semiconducting materials. Much of the research has focussed on variants of the III-Nitride, III-V and II-VI

compounds. The III-Nitrides are generally grown epitaxially in thin single crystal layers on lattice-mismatched substrates, typically  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (sapphire) or SiC, leading to the generation of misfit dislocations, (densities as high as  $10^{10}\text{cm}^{-2}$ ) which are deleterious to the performance of light-emitting devices produced thereupon [1]. The wide band gap of ZnO (3.3 eV at room temperature [2]) and its binding energy of 60 meV for the free exciton have prompted much investigation of this material. However, it has proven difficult to produce high-conductivity p-type ZnO [3].

The cuprous halides, e.g. CuCl, CuBr and CuI, are ionic I-VII compounds with the zincblende ( $T_d$ ,  $F\bar{4}3m$ ) structure

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at room temperature. With increasing temperature, a solid-state phase transition occurs from the zincblende structure ( $\gamma$ -phase) to the wurtzite ( $\beta$ -phase) structure.  $\gamma$ -CuCl transforms to the  $\beta$ -phase at 407 °C before melting at  $\sim$ 430 °C [4].

Excitonic properties of copper halides have attracted much attention, as the exciton-binding energies (190 meV for CuCl and 108 meV for CuBr) are much larger than those for III-Nitride, III–V and II–VI semiconductors [5]. Over the past decade or so, research on the cuprous halides has focussed on three main areas: (1) Spectroscopic and theoretical studies of band structures and excitonic-based luminescence in CuCl, CuBr and copper halide-mixed crystals [5–7], (2) fundamental photoluminescence (PL) and spectroscopic studies of CuCl quantum dots embedded in NaCl crystals [8,9] and glass matrices [10,11], (3) surface studies of the growth mechanisms involved in the hetero-epitaxy of CuCl single crystals on a number of substrates such as MgO (001) and CaF<sub>2</sub> (111) [12], reconstructed (0001) haematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) [13] and both Si and GaAs [14]. We have previously demonstrated a simple electroluminescent device (ELD) structure based on the deposition of CuCl on Si [15]. Electroluminescence measurements confirm UV light emission at wavelengths of  $\sim$ 380 and  $\sim$ 387 nm due to excitonic behaviour. A further emission occurs in the band gap region at  $\sim$ 360 nm. The most efficient solid-state emitters are p–n junctions; therefore investigations of the possibility of doping CuCl are of great interest. It has been reported that CuCl is p-type in its natural state due to the presence of Cu vacancies resulting from excess halogen [16]. Knauth et al. [17] have performed Hall effect measurements demonstrating p-type semiconductivity of CuBr, which was further enhanced by incorporation of O<sub>2</sub> and a similar mechanism can be expected for CuCl.

To the best of our knowledge there are no reports on the n-type doping of copper halides. In this paper we present preliminary results in the n-type doping of CuCl by co-evaporation with ZnCl<sub>2</sub>. Group II elements, substituting on the Cu site, should act as electron donors. Zn was chosen as a dopant for vacuum-deposited CuCl as co-evaporation of CuCl and ZnCl<sub>2</sub> is possible due to the similar vapour pressures (459 and 356 °C at 10 Pa for CuCl and ZnCl<sub>2</sub>, respectively [18]). Also, importantly, the ionic radii of the Cu (I) and Zn (II) ions in tetrahedral coordination are equivalent with a value of 74 pm [19].

## 2. Experimental

The CuCl, doped with ZnCl<sub>2</sub>, thin film samples with typical layer thicknesses of  $\sim$ 500 nm were grown on Si (111), Si (100) and glass substrates at room temperature using a vacuum deposition method. The evaporator was an Edwards E306A thermal resistance evaporator with a base pressure of  $\sim$ 1  $\times$  10<sup>−6</sup> mbar. Prior to deposition the silicon and glass substrates were degreased in organic solvents and the native oxide was removed from the silicon substrates by

dipping in a hydrofluoric acid solution. The substrates were then rinsed in deionised water and blown dry with a nitrogen gun. Commercially supplied CuCl powder of 99.999% purity (Alfa Aesar), was mixed thoroughly with ZnCl<sub>2</sub> powder of 98% purity (Merck) in proportions of 0–4 mole% ZnCl<sub>2</sub> as weighed on a micro-balance to an accuracy of 0.001 g. The CuCl/ZnCl<sub>2</sub> powder mixture was heated in a quartz crucible and the evaporation rate, which was controlled by monitoring the frequency of a crystal oscillator, was approximately 0.5 nm s<sup>−1</sup>.

X-ray diffraction (XRD) measurements using Bragg–Brentano, glancing angle and rocking curve geometries to investigate the crystallinity of the thin films are performed using a D8 Advance X-ray Diffractometer from Bruker Advanced X-ray Solutions. The X-rays are monochromatic with a wavelength of  $\sim$ 1.54 Å characteristic of a Cu target. The resolution of the diffraction patterns is 0.001° and were analysed using a software package named Eva, provided by the manufacturer.

UV/VIS absorbance and transmittance spectra were recorded on a Perkin Elmer Lambda 40 UV/VIS spectrometer at room temperature in the range of 200–900 nm with a resolution of 1 nm.

A UV Ar ion Innova laser with a second harmonic generation BBO crystal producing a 244 nm line was used to excite PL, which was captured with a TRIAX 190 Jobin Yvon-Horiba spectrometer (resolution 0.3 nm) with liquid nitrogen-cooled CCD detector. The maximum excitation power was  $\sim$ 10 W cm<sup>−2</sup>. Temperature-dependent measurements were performed from room temperature to 10 K.

Room temperature cathodoluminescence (CL) studies were performed using a LEO Stereoscan 440 scanning electron microscope with a typical electron beam energy of 5 keV and probe current of 15 nA. The luminescence was collected by a parabolic mirror, with high collection efficiency ( $\sim$ 80%), placed 1 mm above the sample. The signal collected was transferred onto a Gatan MonoCL instrument equipped with a 1200 lines mm<sup>−1</sup> grating. The spectral resolution was approximately 1 nm.

Resistivity measurements were performed using a conventional four-point probe instrument from Veeco. Carrier concentration and Hall mobility were measured using a van der Pauw method.

## 3. Results and Discussion

### 3.1. Structural properties

Immediately following deposition of CuCl on substrates of glass, Si (111) and Si (100), respectively, XRD measurements were performed to monitor the crystallinity of the deposited CuCl thin films doped with ZnCl<sub>2</sub>. These XRD scans were then compared to the diffraction pattern of undoped CuCl thin films. Indexing of the interplanar spacings using the Bragg equation for the cubic unit cell,  $h^2 + k^2 + l^2 = (4a^2/\lambda^2)\sin^2\theta$ , (where  $h, k, l$  are the Miller indices,  $a$  is the lattice constant,  $\lambda$  the incident radiation

wavelength and  $\theta$  the Bragg angle) confirmed that, consistent with the undoped material, the Zn-doped CuCl film was in the cubic zincblende form as expected at room temperature.

Glass is an amorphous substrate and therefore should have no influence on the crystal orientation of a thin film grown upon it. Fig. 1, curve (a) shows a typical XRD pattern taken in the Bragg–Brentano geometry of undoped CuCl deposited on a glass substrate. In this case the intensity is multiplied by a factor of 10, and an offset applied so it can be clearly represented on the same scale as that of the more intense  $\theta$ – $2\theta$  diffraction pattern of a CuCl film doped with a nominal 1 mole% ZnCl<sub>2</sub>, shown in Fig. 1 curve (b). The measurements were performed under identical conditions. The evaporated CuCl film on glass is polycrystalline with a preferred  $\langle 111 \rangle$  growth direction. A strong peak identified as a CuCl (220) reflection is also clearly evident. The CuCl (111) and (220) peaks occur at  $2\theta = 28.521^\circ$  and  $2\theta = 47.44^\circ$  respectively, corresponding to a lattice constant of 5.416 Å. When compared to curve (b), there is a noticeable improvement in the crystallinity of the CuCl thin film by addition of 1 mole% ZnCl<sub>2</sub> to the evaporation crucible. This trend continued for higher doping levels. The diffraction pattern of the Zn-doped CuCl film is dominated by an intense (111) CuCl peak at  $2\theta = 28.537^\circ$ , no other peaks are readily identifiable in this geometry although there was some evidence of CuCl (220) and (311) reflections when a glancing angle of  $2^\circ$  was used to probe the surface layers of the thin film. The upward shift in the (111)  $2\theta$  peak position indicates a decrease in the lattice constant for the doped samples. A minimum lattice constant of 5.411 Å was found for a CuCl sample doped with a nominal 4 mole% ZnCl<sub>2</sub>. A small spread in the average values of the lattice constant was found over the doping range investigated. The electronegativity of Cl is 3.0, while those of Cu and Zn are 1.9 and 1.6, respectively.

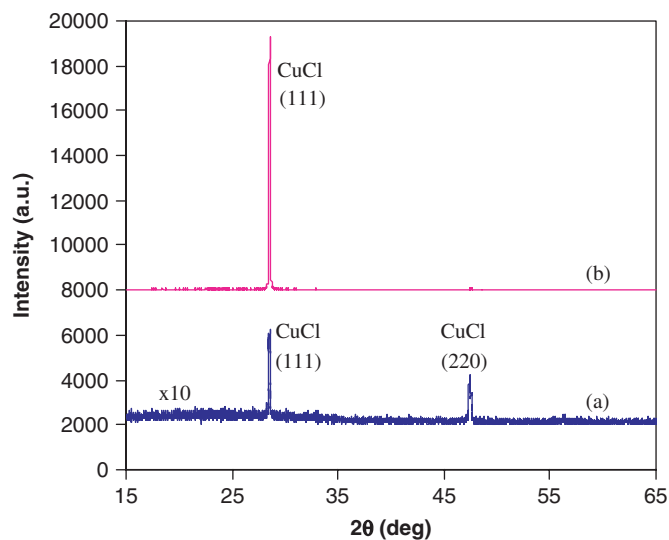


Fig. 1. X-ray  $\theta$ – $2\theta$  diffraction pattern of (a) undoped CuCl on glass ( $\times 10$ ) and (b) CuCl doped with a nominal 1 mole% ZnCl<sub>2</sub>.

An increased electronegativity difference could result in a tighter bonding structure causing a slight decrease in the lattice constant. This is consistent with substitution of some Cu sites by Zn.

Due to the small difference in the lattice constants of  $\gamma$ -CuCl and Si, the Bragg peaks occur at very similar  $2\theta$  values in the XRD spectra. CuCl thin films grown on Si (100) substrates are polycrystalline in nature with no clear epitaxial alignment with the substrate. No significant difference was seen in the structural properties of the CuCl films doped with Zn and the undoped samples on a Si (100) substrate. The only peak seen in the Bragg–Brentano geometry for undoped CuCl grown on a Si (111) substrate is an intense (111) reflection at  $2\theta \approx 28.50^\circ$ . Rocking curves are therefore used to investigate the alignment of the (111) CuCl grains with the underlying Si (111) substrate. Fig. 2, curve (a) shows a rocking curve of a CuCl thin film on Si (111) substrate (solid line) superimposed on a rocking curve of a Si (111) wafer (broken line). A distinct broadening at the base of the rocking curve is seen in the case of the CuCl thin film. This suggests that the CuCl film consists of polycrystalline grains of (111) orientation, which are not in perfect alignment with the Si substrate. In the case of Zn-doped CuCl samples a separation of the CuCl (111) and Si (111) reflections is seen in the rocking curve. This is particularly pronounced in the case of samples doped with a nominal 3–4 mole% ZnCl<sub>2</sub>. A rocking curve of a CuCl film doped with a nominal 3 mole% ZnCl<sub>2</sub> grown on Si (111) is shown in Fig. 2, curve (b). A distinct peak due to the CuCl epitaxial layer occurs at  $14.19^\circ$ , while a second peak from the Si (111) substrate is seen at  $11.6^\circ$ . This separation is not only due to the small lattice mismatch between the Si and CuCl, but mainly caused by a tilt angle between the substrate layer and the epitaxial layer resulting from the misorientation of the Si substrate by  $\sim 2^\circ$  in the  $\langle 110 \rangle$  direction [20]. The measured full-width at half-maximum (FWHM) of  $0.09^\circ$  for the CuCl (111) rocking curve peak compared to  $0.03^\circ$  for the Si (111) peak is indicative of the reasonable crystalline quality of the material.

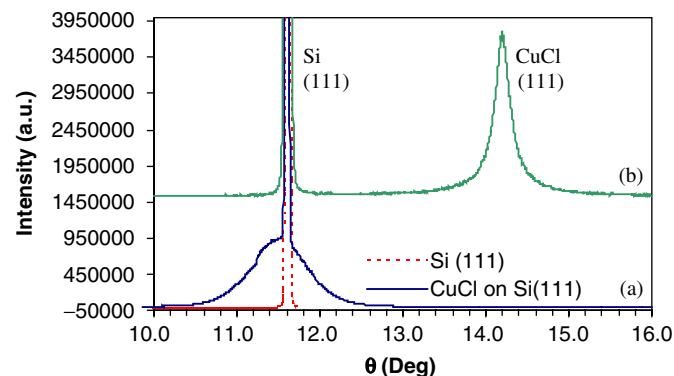


Fig. 2. Rocking curve of Si (111) is compared to (a) rocking curve of CuCl on Si (111) and (b) rocking curve of CuCl doped with a nominal 3 mole% ZnCl<sub>2</sub> on Si (111).

### 3.2. Optical properties

In Fig. 3, the room temperature UV-VIS absorption spectrum of a CuCl thin film doped with a nominal 2 mole% ZnCl<sub>2</sub> on a glass substrate is shown both immediately after deposition (solid line) and one day later (broken line). The main peak results from the contribution of both high- and low-energy excitonic bands, historically called the Z<sub>1,2</sub> and Z<sub>3</sub>, excitons, respectively. The Z<sub>1,2</sub> and Z<sub>3</sub> excitons originate from the coupling of the lowest conduction band state  $\Gamma_6$  to both the uppermost valence band holes  $\Gamma_8(Z_{1,2})$  and  $\Gamma_7(Z_3)$ , respectively [5,21]. The peak at 372 nm (3.34 eV) for the Z<sub>1,2</sub> exciton and a slight shoulder at 379 nm (3.28 eV) corresponding to the Z<sub>3</sub> exciton, agree within the resolution of the instrument with the energy values of the undoped CuCl thin films previously reported by us [22] and are in close agreement with values reported by other authors for room temperature CuCl absorption measurements [21,23]. However, after just one day, the excitonic emission has been completely quenched. This is explained by the fact that CuCl is sensitive to moist air. Under the influence of light and moisture, hydrated oxyhalides of Cu<sup>++</sup> are formed [24]. This reaction can be easily recognised by a colour change in CuCl associated with the presence of the greenish colour Cu<sup>++</sup> ions and appears to be accelerated by the incorporation of Zn into the CuCl crystal. A protective layer is needed to prevent this process as it causes the optical degradation of the films. This layer consists of a spin-coated (or dip-coated) liquid glass layer, which is transparent at the wavelengths of interest. Fourier transform infra-red (FTIR) and XRD analysis has shown this to be an effective means of sealing the undoped CuCl system for many months. We have previously shown that the excitonic emission of the UV/VIS spectrum of an undoped CuCl sample is maintained at the same intensity for at least 3 weeks by capping with liquid glass [15]. Testing the effectiveness of this system to seal the Zn-doped CuCl thin films is currently underway.

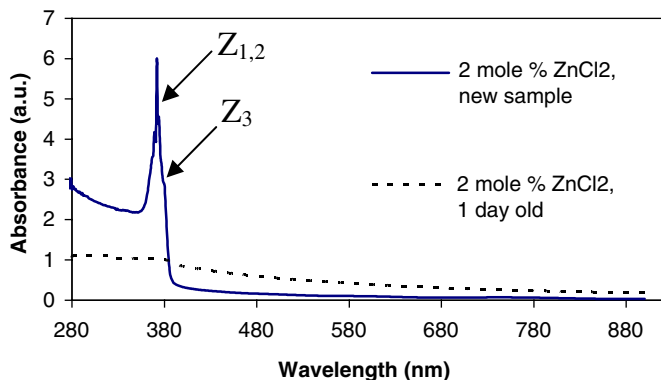


Fig. 3. UV-VIS absorption spectrum of CuCl doped with a nominal 2 mole% ZnCl<sub>2</sub> on glass, measurement taken immediately after deposition (solid line) and 1 day later (broken line).

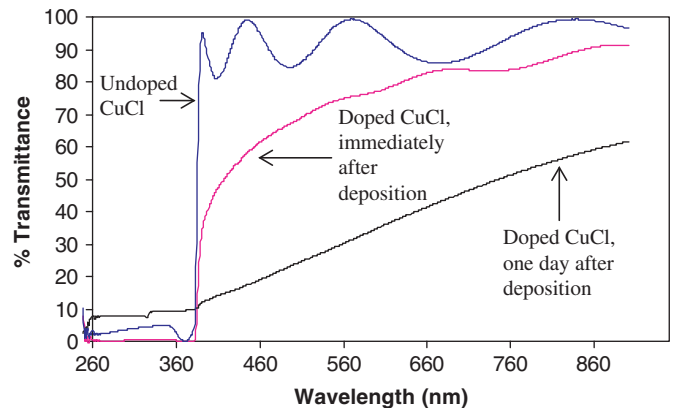


Fig. 4. Transmission spectrum of undoped CuCl on glass, compared to that of CuCl doped with a nominal 2 mole% ZnCl<sub>2</sub> on glass, measurement taken immediately after deposition, and one day after deposition as indicated on the figure.

In Fig. 4 the transmittance spectrum of the same sample, again measured immediately and 1 day after deposition, is compared to the transmittance spectrum of an undoped CuCl thin film.

The slight reduction in the transmission for the freshly prepared Zn-doped sample is not unexpected as it has been previously reported that addition of ZnCl<sub>2</sub> to the flux, in experiments on the growth of CuCl single crystals from the melt, resulted in crystals that were slightly opaque in appearance [4]. By comparing Figs. 3 and 4 we see that the quenching of the excitonic emission 1 day after deposition is accompanied by a decrease in the transmittance of the Zn-doped films. At higher doping levels (nominally 3–4 mole% ZnCl<sub>2</sub>) the transmittance of the films (measured within 30 min after removing from the vacuum chamber) was less than 60% at all wavelengths investigated and below 20% at wavelengths shorter than 450 nm. This is very similar to the transmittance spectrum shown for the sample doped with a nominal 2 mole% ZnCl<sub>2</sub> one day after deposition indicating that some degradation occurs immediately for the higher doping levels investigated.

The optical properties of the Zn-doped samples grown on silicon substrates were investigated using PL and CL. The doped films have strong luminescent properties. A PL spectrum measured at 10 K for a CuCl film doped with a nominal 3 mole% ZnCl<sub>2</sub> on Si (100) is shown in Fig. 5. Similar to the undoped samples, four peaks are evident in the spectrum. The small peak which occurs at  $\sim 3.204$  eV ( $\lambda \sim 387.9$  nm) is the Z<sub>3</sub> free exciton peak. Due to the large binding energy of the free exciton ( $\sim 190$  meV), this peak was also clearly evident in room temperature PL measurements at an energy  $E = 3.228$  eV ( $\lambda \sim 385.1$  nm). On the low-energy side of the free exciton, a peak occurs at  $\sim 3.183$  eV ( $\lambda \sim 390.6$  nm). This is attributed to an emission from an exciton bound to an impurity [5,25], which has been called the I<sub>1</sub>-bound exciton. The impurity has previously been identified as a neutral acceptor, possibly a Cu vacancy [26]. A third peak, which appears at

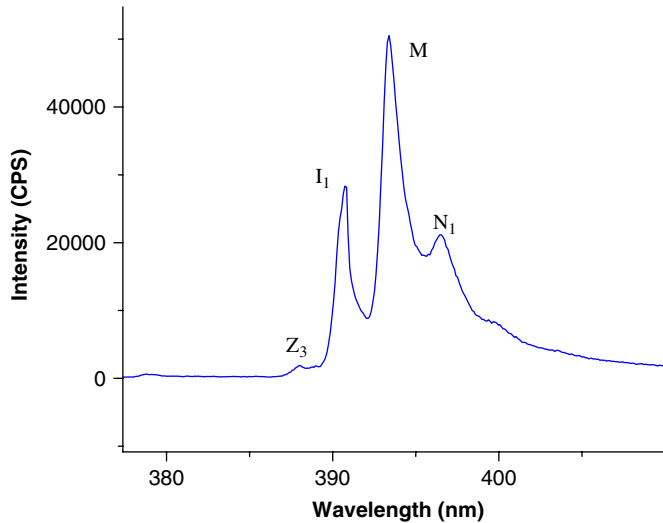


Fig. 5. PL spectrum of CuCl doped with a nominal 3 mole% ZnCl<sub>2</sub> on Si (100) at 10 K.

3.161 eV ( $\lambda \sim 393.3$  nm) is identified as a free biexciton M. The free biexciton results from exciton–exciton collisions resulting in the formation of an excitonic molecule (so called biexciton) [5]. At 3.135 eV ( $\lambda \sim 396.5$  nm) a fourth peak labelled N<sub>1</sub> is evident, and likely originates from a biexciton bound to an impurity. Similar to the I<sub>1</sub> bound exciton, the most probable candidate for the impurity is considered to be a neutral acceptor [5]. The main differences between this PL spectrum and that of the undoped material at 10 K is a slight shift in the peak position towards lower energies and an increase in the intensity of the free and bound biexcitons relative to the free and bound excitons. The low-intensity signal of the Z<sub>3</sub> free exciton at 10 K is to be expected due to the high level of biexcitons being formed. The continued detection of the excitons and biexcitons suggested to be bound to a neutral acceptor indicates that Cu vacancies may remain after the addition of ZnCl<sub>2</sub>. This is not unexpected as excess chlorine could be incorporated into the CuCl crystal structure resulting in a Cu deficiency.

Fig. 6 shows a room temperature CL spectrum of a CuCl thin film doped with a nominal 4 mole% ZnCl<sub>2</sub>. Importantly, even at this relatively high Zn-doping level, the light emission resulting from the electron beam excitation is not quenched. The main features include a strong emission at  $\lambda \sim 384.7$  nm (3.23 eV) assigned to the Z<sub>3</sub> free exciton emission in agreement with the PL spectra, and a broad blue–green emission band centred at  $\sim 510$  nm (2.43 eV). This broad band also occurred in nominally undoped samples with starting CuCl powders of both 97% and 99.999% purity [27] but its exact origin has yet to be determined.

### 3.3. Electrical properties

To determine the conductivity type of the thin films the rectification technique is used whereby the sign of the

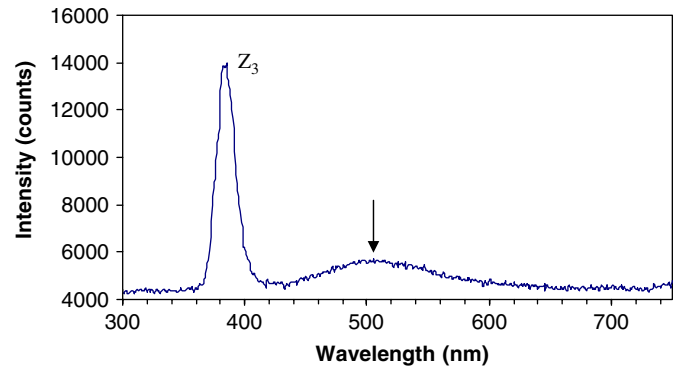


Fig. 6. CL spectrum of CuCl doped with a nominal 4 mole% ZnCl<sub>2</sub> on Si (100) at room temperature.

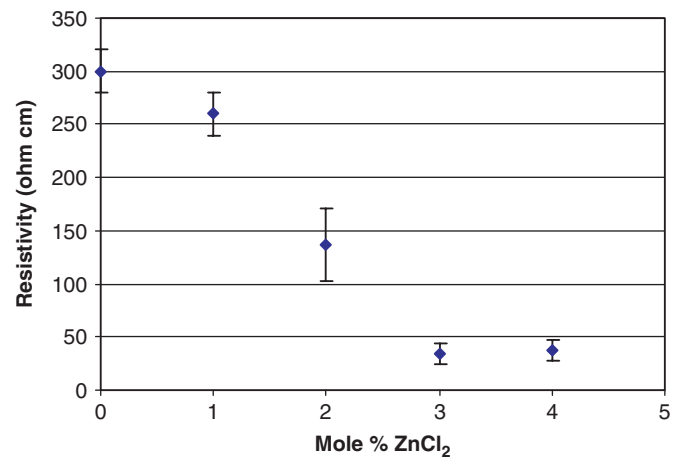


Fig. 7. Resistivity of CuCl thin film as a function of mole% ZnCl<sub>2</sub>.

conductivity is determined by the polarity of a rectified AC signal at a point contact to the semiconductor [28]. In the case of our nominally undoped samples the measured voltage drop is very small and fluctuates from negative to positive, indicating a highly resistive or compensated material. However, measurements on CuCl samples doped by the co-evaporation of ZnCl<sub>2</sub> have indicated without exception that the material is n-type. The resistivity of the samples is investigated using a standard four-point probe and is plotted as a function of mole% ZnCl<sub>2</sub> in Fig. 7. A clear decrease in the resistivity of the CuCl thin film is detected, with values decreasing linearly from an average value of 300  $\Omega$ cm for undoped material to 34  $\Omega$ cm for a sample doped with a nominal 3 mole% ZnCl<sub>2</sub>. Increasing the doping level to a nominal 4 mole% ZnCl<sub>2</sub> resulted in a similar resistivity value again suggesting that a saturation level has been reached.

Preliminary Hall effect measurements indicate that on average the material is n-type with an electron carrier concentration  $n \sim 1.1 \times 10^{16} \text{ cm}^{-3}$  and Hall mobility  $\mu \sim 4.9 \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1}$  for a CuCl sample doped with a nominal 1 mole% ZnCl<sub>2</sub>. However, further research is ongoing on

the fabrication of good ohmic contacts to ensure more reliable Hall measurements.

#### 4. Conclusion

We have grown n-type CuCl thin films with a strong (111) crystalline orientation by co-evaporation of CuCl and ZnCl<sub>2</sub> powders. Both excitonic and biexcitonic emissions are detected by low-temperature PL measurements. A strong room temperature Z<sub>3</sub> free exciton emission occurs at ~385 nm for both PL and CL for doping levels up to a nominal 4 mole% ZnCl<sub>2</sub> co-evaporation. A minimum resistivity of 34 Ωcm was recorded, which represents a reduction in resistivity by a factor of 10 compared to the undoped samples.

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