Characterisation of n-type γ-CuCl on Si for UV optoelectronic applications

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The use of co-evaporation of $ZnCl_2$ with CuCl in order to achieve n-type conductivity in CuCl is reported herein. Linear current-voltage (IV) characteristics in the range of ±4V have been measured using Cu-Au electrical contacts. Room temperature Hall effect measurements show some evidence of a mixed conduction mechanism. On average the samples exhibit n-type conductivity with a bulk electron carrier concentration $n \sim 1 \times 10^{16}$ cm^{-3} and Hall mobility $\mu \sim 29$ $cm^2v^{-1}s^{-1}$ for a CuCl sample doped with a nominal 3 mole % $ZnCl_2$. By use of an *in situ* CaF_2 capping layer, transmission > 90% is achieved. At room temperature a strong Z_3 free excitonic

emission occurs at ~385 nm using both photoluminescence and x-ray excited optical luminescence, indicating the high optical quality of the doped material.

1. Introduction

To date, blue-UV light emitting and laser diode research has been dominated by investigations of the group III nitrides such as GaN and InGaN. These are hexagonal materials typically grown on lattice mismatched substrates such as sapphire or SiC. This lattice mismatch is a major factor leading to the generation of misfit dislocations with densities as high as 10^{10} cm^{-2} which can impact on the performance of light emitting devices produced thereupon [1,2]. The introduction of epitaxial lateral overgrowth (ELOG) techniques [3,4] has facilitated the production of III-Nitride films with threading dislocation densities reduced by 3-4 orders of magnitude with respect to conventional metalorganic chemical vapour deposition techniques but it is still very high compared to mature semiconductor technologies. We offer a radically different approach in the field of wide-bandgap light emitting semiconductors - γ-CuCl on Si.

γ-CuCl is a wide-bandgap (E_g = 3.395eV at 4 K), direct bandgap, semiconductor material with a cubic zincblende lattice structure. Its very small lattice mismatch to Si (<0.5%) indicates potential compatibility with current Si based electronics/optoelectronics technologies. We have previously demonstrated the room temperature operation of an ultra-violet electroluminescent device fabricated by the growth of CuCl on Si [5]. Since the excitonic binding energy is of the order of 190 meV, the electron-hole recombination and subsequent light emission at ~ 380 and ~ 387 nm is mediated by excitonic effects. In order to improve the efficiency of the light emission we ultimately aim to fabricate a CuCl p-n

homo-junction light emitting device on a near-lattice matched Si substrate. The electrical and optical characterisation of n-type CuCl is presented in this paper,

2. Experimental Details

The CuCl, doped with $ZnCl_2$, thin film samples with typical layer thicknesses of ~500 nm were grown on Si (111), Si (100) and glass substrates at room temperature using a basic physical vapour deposition method as previously described [6].

Cu-Au metal contacts (approx. 300nm thick) were co-evaporated in a standard Van der Pauw-type configuration. Following the metal deposition the samples were annealed at $150^{o}C$ for 5 minutes in Ar gas. Electrical measurements were carried out using a commercial HL5500PC Hall Effect apparatus from ACCENT. The Hall voltages are obtained in the Van der Pauw configuration at typical current values of 0.1-1.0 µA. Eight different measurements are taken and averaged to determine a single Hall voltage in order to minimise noise effects.

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

Room-temperature photoluminescence (PL) measurements were performed using a Labram HR800 micro-PL system from Jobin-Yvon Horiba with a 325nm He-Cd laser which was focussed to a diameter of ~ 1 µm on the sample surface using a x40 UV objective lens.

X-ray excited optical luminescence (XEOL) was excited using white beam synchrotron x-ray radiation at the F1 beam line using the radiation of the DORIS bending magnet source

at HASYLAB-DESY (Hamburger Synchrotronstrahlungslabor am Deutschen Elektronen-Synchrotron) in Hamburg. Luminescence was captured using an optical fibre and an Ocean Optics model USB2000 spectrometer in the wavelength range of 200 – 875nm.

3. Results and Discussion

The resistivity of the CuCl samples doped by the co-evaporation of $ZnCl_2$ was investigated using a standard four point probe. We have detected an approximately tenfold decrease in resistivity for the samples doped with a nominally 3 mole % $ZnCl_2$ compared to undoped CuCl. Details of the resistivity measurements can be found elsewhere [6]. Ohmic contacts to CuCl doped with a nominal 2-3 mole % Zn in the range of ±4V were achieved using Cu-Au co-evaporated metal contacts. A thermal anneal at 150^oC for 5 minutes in Ar gas improved the uniformity of the contact pairs in the Van der Pauw structure.The average measured current values at 5V ranged from 1-2μA for a CuCl sample doped with a nominal 3 mole % $ZnCl_2$. This is a distinct improvement compared to the undoped CuCl in which the maximum current was ~10nA for metal contacts with a linear IV response.

Van der Pauw resistivity and Hall effect measurements were carried out on samples with doping levels of 1-3mole% $ZnCl_2$. In the case of the sample with nominally 1 mole % doping, Hall measurements were not possible using the HL5500PC Hall Effect apparatus from ACCENT due to contact problems. Results were obtained for CuCl samples doped with nominally 2-3 mole % $ZnCl_2$. N-type conductivity was detected in ~70% of the performed Hall measurements on each sample. This peculiar behaviour of observing both types of conductivity for the same sample may reflect an electrical instability in the Zn-doped CuCl samples. This may result from two competing conductivity mechanisms, namely electron conduction from the substitution of Cu by Zn and hole conduction due to the presence of Cu vacancies which are known to be present in undoped material [7] and may also be introduced due to excess chlorine from co-evaporation with $ZnCl_2$.

D.C. Look *et al*. have reported that the seeming electrical instability for p-ZnO can often be traced to noisy Hall effect measurements [8]. If contact noise is high, as in our case, a noise spike during just one of the eight Van der Pauw measurements can greatly affect the final result. Figure 2 shows the range of measured carrier concentration and mobilities of the n-type samples as a function of nominal mole % $ZnCl_2$.

For these CuCl samples doped with a nominal 2 mole % $ZnCl_2$ the average electron carrier concentration $n \sim 9 \times 10^{14} cm^{-3}$ and Hall mobility $\mu \sim 45 cm^2v^{-1}s^{-1}$. For the sample doped with nominally 3 mole % $ZnCl_2$ the measured average concentration increased by approximately one order of magnitude to $n \sim 1 \times 10^{16} cm^{-3}$ and the average Hall mobility reduced somewhat to $\mu \sim 29$ $cm^2v^{-1}s^{-1}$. It is important to note that the doping efficiency of the CuCl/$ZnCl_2$ co-evaporation method is very low. The maximum net donor concentration measured for 3 mole % $ZnCl_2$ $\sim 10^{16}$ cm^{-3} is much smaller than the theoretical maximum Zn concentration of $7 \times 10^{20} cm^{-3}$. Therefore the activation efficiency could be as small as 0.001% for this doping method.

We have previously reported that doping of CuCl by co-evaporation with $ZnCl_2$ results in the quenching of the excitonic emission one day after deposition measured by UV-VIS spectroscopy and is accompanied by a decrease in the transmittance of the Zn-doped films [6]. For optoelectronic device applications both the electrical conductivity and the optical transmission should be as high as possible [9]. Therefore it is important to ensure that the transmissivity is not compromised by doping. The drop in transmission as the doping level is increased can be overcome by using a suitable capping layer evaporated *in situ* to seal the Zn-doped CuCl from the atmosphere before opening the vacuum chamber. CaF_2 has previously been used as a confining/protective layer in the growth of CuCl quantum well structures [10]. It was chosen for its stability in air and because it is closely lattice matched to both CuCl and Si ($a_{CaF2} = 5.46$ Å) .A transparent 400nm thick CaF_2 capping layer was evaporated over a Zn-doped CuCl film without

breaking the vacuum. The transmission of the CuCl film doped with nominally 3 mole % $ZnCl_2$ and capped by evaporating CaF_2 is greater than 90% in the range of 400-900nm (Fig. 3). This confirms that the low transmission of the uncapped sample is due to a fast reaction with the air resulting in an opaque film surface. The CaF_2 capping layer did not prevent the degradation of the film but delayed it by up to two weeks. The interference fringe pattern in the transmission spectrum indicates that the film surface was highly reflecting and there was not much scattering or absorption loss in the film [9].

Several excitonic bands are evident in low temperature photoluminescence (PL) such as the Z_3 free exciton at ~3.20 eV; the I_1 bound exciton at ~3.18 eV and the M free biexciton at ~3.16 eV [6]. The room temperature PL spectrum (Fig. 4) is dominated by the Z_3 free excitonic emission resulting from the recombination of electrons and holes from the lowest conduction band state Γ_6 and the uppermost valence band state Γ_7 [11]. The energy of the Z_3 emission at 3.230eV with a full width at half maximum (FWHM) of 70meV is slightly red-shifted and broader compared to the values of 3.235eV and 66 meV, respectively, recorded for undoped CuCl on Si. This compares well to the FWHM of 70meV recently reported for room temperature UV emission in GaN grown on Si (111) [12] indicating the high optical quality of the CuCl thin films on Si. Interference fringes with a spacing of 0.4 -0.5eV are evident in the range of 2.1 eV- 2.75 eV. These fringes remained after the excitonic emission had been quenched following degradation of the film.

X-ray excited optical luminescence (XEOL) is a technique whereby x-ray absorption produces core electron excitation [13]. Optical emissions occurring essentially via all possible radiative recombination paths are captured using a spectrometer. The use of a white beam synchrotron source is especially efficient as the x-ray photon flux is great enough to ensure rapid collection of luminescence data (typically in 30s). For the CuCl films, a number of XEOL emissions are generated under x-ray excitation, as shown in Fig. 5. The main peak is the well known near band-

edge Z_3 free exciton emission at an energy of ~3.21 eV. Similar to PL, the peak position is slightly red-shifted compared to the energy of ~3.23 eV measured for undoped CuCl. A broad green emission band centred at ~2.39 eV is consistent with cathodoluminescence (CL) data performed on both undoped [14] and Zn-doped material [6]. Thickness dependent CL spectra have shown that the emission originates in the bulk of the CuCl film [15] and therefore may be related to grain boundaries. Three emissions occurring at energies greater than the CuCl bandgap at approximately 3.49eV, 3.70eV and 3.95eV, respectively are also detected. These are also seen in the spectrum of a silicon substrate shown for comparison in the inset and therefore cannot be attributed to a CuCl optical transition. The origin of these peaks is currently under investigation.

4. Conclusions

Working towards our ultimate goal of developing CuCl p-n homojunction UV light-emitting devices on Si substrates, we have grown n-type CuCl thin films by co-evaporation with $ZnCl_2$. Although the doping efficiency is low, with a maximum carrier concentration ~ 1×10^{16} cm^{-3} achieved by doping with nominally 3 mole % $ZnCl_2$, the concept of n-type doping of CuCl has been realised. Optical properties are not compromised by doping. Room temperature PL and XEOL spectra are dominated by an intense, narrow UV emission at ~ 3.2 eV. This work has illustrated that CuCl on Si is a promising novel material system for future wide-band gap devices compatible with current electronic technology.
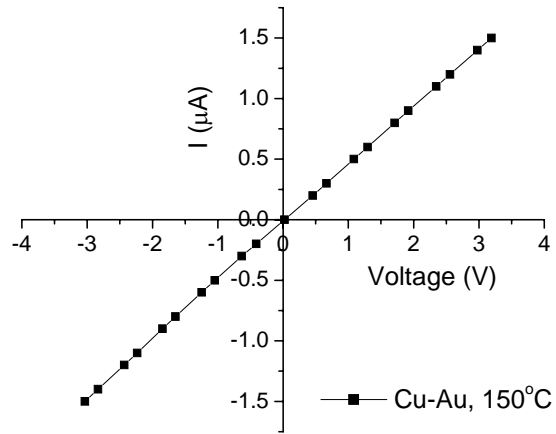
Figures

Fig. 1 Linear IV characteristics of CuCl doped with a nominal 3 mole % ZnCl$_2$ with Cu-Au
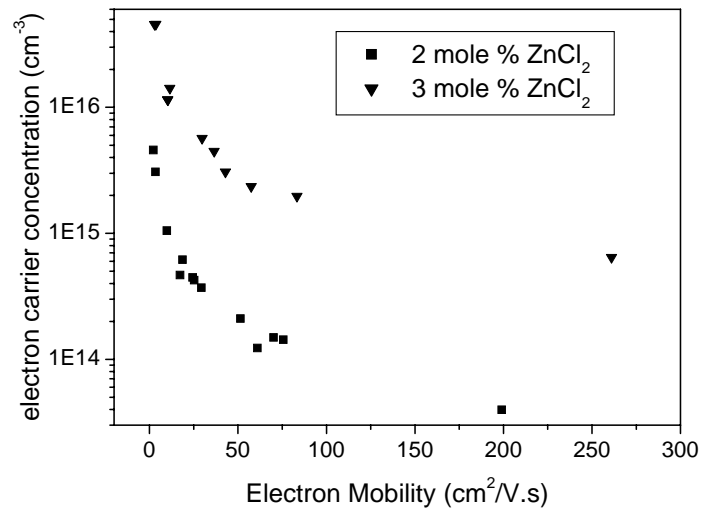
metal contacts

Fig. 2 Electron carrier concentration vs. mobility extracted from room temperature Hall effect

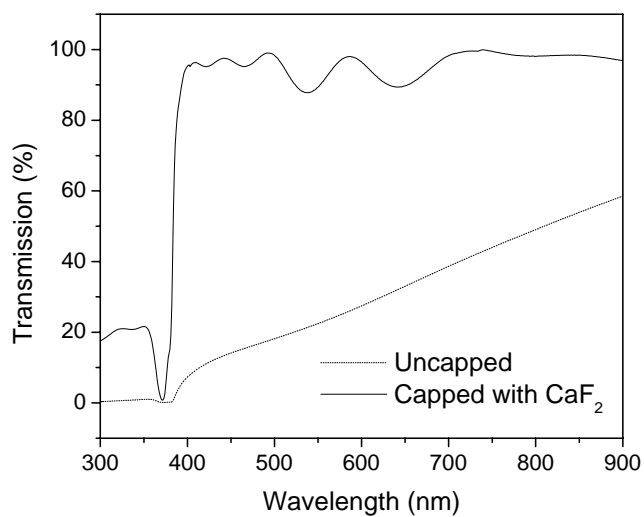measurements of CuCl samples doped with nominally 2 and 3 mole % ZnCl$_2$

Fig. 3 Transmission spectrum of CuCl doped with a nominal 3 mole % $ZnCl_2$, as deposited uncapped and with an *in situ* CaF_2 capping layer
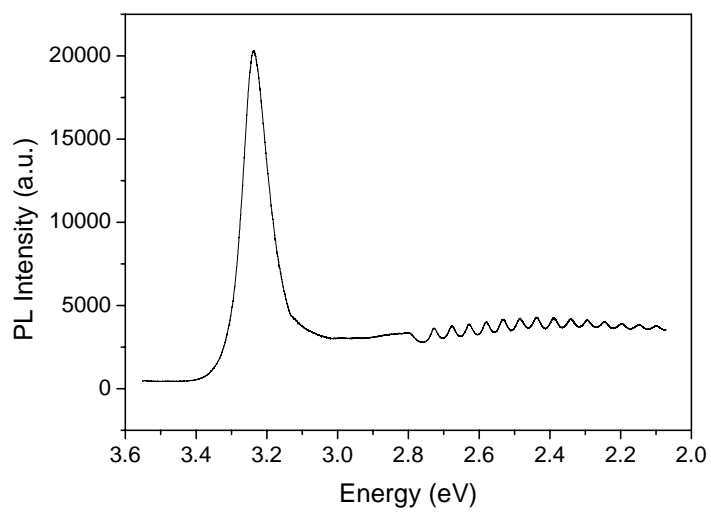

Fig. 4 Room temperature PL spectrum of CuCl doped with a nominal 3 mole % $ZnCl_2$ and capped with
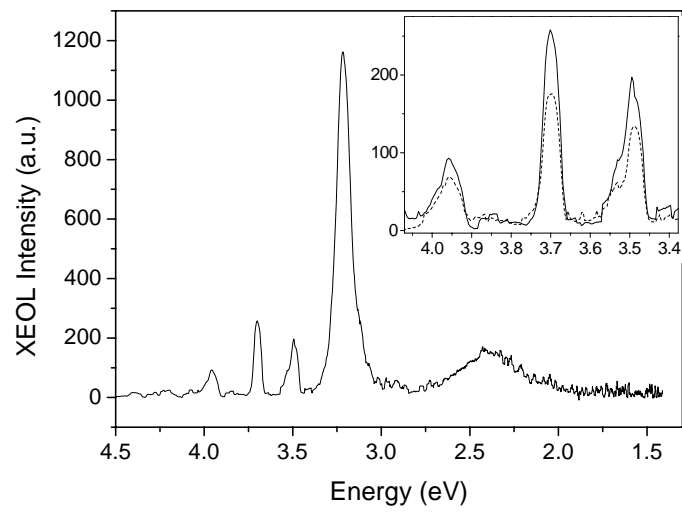
CaF_2

Fig. 5 XEOL of CuCl doped with a nominal 3 mole % $ZnCl_2$ (uncapped)

Inset: XEOL spectrum of Silicon (broken line) compared to that of the CuCl (solid line)

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