

# The use of wide-bandgap CuCl on silicon for ultra-violet photonics

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## ABSTRACT

$\gamma$ -CuCl is a wide-bandgap ( $E_g = 3.395\text{eV}$ ), direct bandgap, semiconductor material with a cubic zincblende lattice structure. Its lattice constant,  $a_{\text{CuCl}} = 0.541\text{ nm}$ , means that the lattice mismatch to Si ( $a_{\text{Si}} = 0.543\text{ nm}$ ) is  $<0.5\%$ .  $\gamma$ -CuCl on Si - the growth of a wide-bandgap, direct bandgap, optoelectronics material on silicon substrates is a novel material system, with compatibility to current Si based electronic/optoelectronics technologies. The authors report on early investigations consisting of the growth of polycrystalline, CuCl thin films on Si (100), Si (111), and quartz substrates by physical vapour deposition. X-ray diffraction (XRD) studies indicate that CuCl grows preferentially in the  $\langle 111 \rangle$  direction. Photoluminescence (PL) and Cathodoluminescence (CL) reveal a strong room temperature  $Z_3$  excitonic emission at  $\sim 387\text{nm}$ . A demonstration electroluminescent device (ELD) structure based on the deposition of CuCl on Si was developed. Preliminary electroluminescence measurements confirm UV light emission at wavelengths of  $\sim 380\text{nm}$  and  $\sim 387\text{nm}$ , due to excitonic behaviour. A further emission occurs in the bandgap region at  $\sim 360\text{nm}$ .

**Keywords:** Copper Chloride; Wide-bandgap semiconductor; ultra-violet; silicon; Electroluminescence; Cathodoluminescence; Photoluminescence; Exciton

## 1. INTRODUCTION

To date the materials of choice for blue and ultra-violet light emitting and solid-state laser diodes consist of a number of variants of the III-Nitrides. These are generally grown epitaxially in thin single crystal layers on lattice-mismatched substrates, typically  $\alpha\text{-Al}_2\text{O}_3$  (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. In recent years much research has been focussed on improving the quality of epitaxial growth of GaN and its related alloys on  $\text{Al}_2\text{O}_3$  and SiC substrates. The introduction of epitaxial lateral overgrowth (ELOG) techniques<sup>1,2</sup> has facilitated the production of III-Nitride films with threading dislocation densities of  $10^4\text{-}10^5\text{ cm}^{-2}$  - a reduction by 3-4 orders of magnitude with respect to conventional metalorganic chemical vapour deposition techniques<sup>3,4</sup> but still very high compared to mature technologies such as Si or GaAs. A major reason for this high threading dislocation density is a fundamental lattice mismatch between the film and substrate. For example, in the case of GaN epitaxy on (0001)  $\alpha\text{-Al}_2\text{O}_3$ , the lattice misfit is as high as 13.9%<sup>5</sup>.

The cuprous halides, e.g. CuCl, CuBr and CuI, are ionic I-VII compounds with the zincblende ( $T_d, F\bar{4}3m$ ) structure at room temperature. With increasing temperature, a solid-state phase transition occurs from the zincblende structure ( $\gamma$ -phase) to the wurtzite ( $\beta$ -phase) structure. A second solid-state transformation to a high temperature cubic phase ( $\alpha$ -phase) also occurs for CuBr and CuI but not for CuCl<sup>6</sup>.  $\gamma$ -CuCl transforms to the  $\beta$ -phase at 407°C before melting at  $\sim 430^\circ\text{C}$ <sup>7</sup>.

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-V and II-VI semiconductors<sup>8</sup>. 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<sup>8-10</sup>, (2) Fundamental photoluminescence and spectroscopic studies of CuCl quantum dots embedded in NaCl crystals<sup>11,12</sup> and glass matrices<sup>13,14</sup>, (3) Surface studies of the growth mechanisms involved in the heteroepitaxy of CuCl single crystals on a number of substrates such as MgO (001) and CaF<sub>2</sub> (111)<sup>15</sup> and reconstructed (0001) haematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>)<sup>16</sup>. One group of researchers has examined the surface growth mechanisms in the heteroepitaxy of single crystalline films of CuCl on both Si and GaAs substrates by molecular beam epitaxy<sup>17</sup>. This study however, focussed on the fundamental physics of the island growth process and the nature of the interfacial bonding.

In this paper we present preliminary results in the investigation of a new blue-UV light emitting material system,  $\gamma$ -CuCl on Si. The small lattice mismatch ( $<0.5\%$ ) between Si and CuCl suggests that the growth of high quality, low dislocation density epitaxial CuCl thin films on Si substrates should be possible. This offers potential for a *paradigm shift* in wide-bandgap semiconductor growth: “blue” optoelectronics on Si wafers.

## 2. EXPERIMENTAL

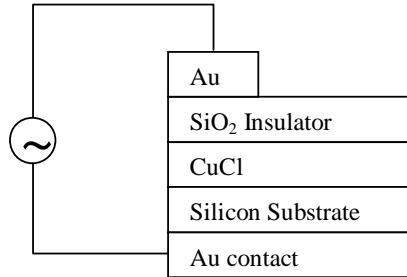
The CuCl thin film samples with typical layer thicknesses of  $\sim 500$  nm were grown on Si (100), Si (111) and glass substrates at room temperature using a vacuum deposition method at a base pressure of  $\sim 1 \times 10^{-5}$  mbar. Prior to deposition the silicon substrates were degreased in organic solvents and the native oxide was removed by dipping in a hydrofluoric acid solution. The substrates were then rinsed in deionised water and blow-dried with a nitrogen gun. Commercially supplied CuCl powders of 97% (Merck) and 99.999% (Alfa Aesar) purity, respectively, were heated in a quartz crucible and the evaporation rate, which was controlled by monitoring the frequency of a crystal oscillator, was approximately  $0.5 \text{ nms}^{-1}$ .

X-ray diffraction (XRD) measurements using Bragg-Brentano 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  $\sim 1.54\text{\AA}$  characteristic of a Cu target. The resolution of the diffraction patterns is  $0.01^\circ$ .

A UV Ar ion Innova laser with a second harmonic generation crystal producing a 244nm line was used to excite photoluminescence (PL), which was captured with a TRIAX 190 spectrometer. The excitation power was  $\sim 100\text{W/cm}^2$ . Temperature dependent measurements were performed from room temperature to 10K.

Room temperature cathodoluminescence (CL) studies were performed using a LEO Stereoscan 440 scanning electron microscope with an electron beam of 5-10keV and probe current of 15nA. 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 grating. The spectral resolution was approximately 1 nm.

The electroluminescence (EL) characteristics were investigated using a single-insulating-layer thin film electroluminescent (TFEL) device structure consisting of a CuCl active layer grown on a silicon substrate and a SiO<sub>2</sub> insulating layer. A schematic diagram of the TFEL test device structure is shown in Fig.1



**Fig. 1** Diagram of the electroluminescent device structure.

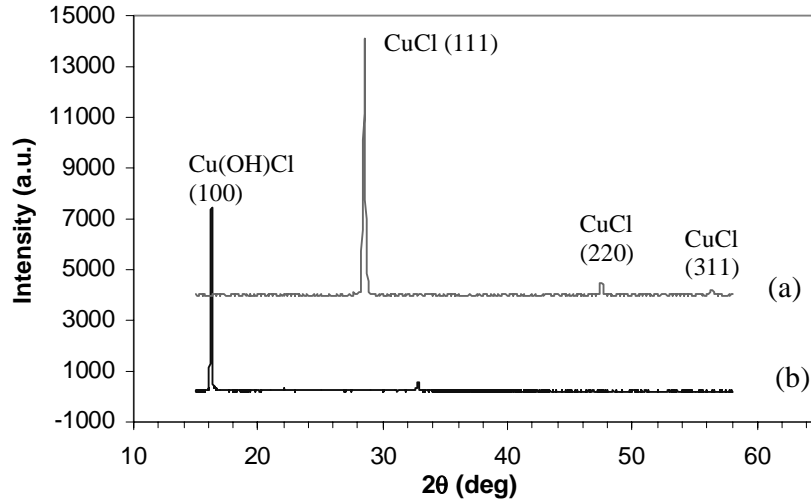
An Au contact ~100nm thick was deposited on the unpolished side of the Si substrate using an Edwards Scancoat sputtering system. This was annealed at 300°C, for 5 minutes to ensure a good ohmic contact. The CuCl thin film ~500nm was deposited on the polished Si surface as described above. The SiO<sub>2</sub> insulating layer ~300nm thick was deposited from a liquid glass solution using a dip coating method. Finally a top gold electrode was sputter deposited as before. The EL measurements of the test devices were evaluated using a SOFIE spectrophotometer with a photomultiplier tube (spectral range of 200-900 nm). The ELD device was driven by an a.c. sinusoidal waveform with a frequency of 1kHz and a peak-to-peak voltage of 100V.

### 3. RESULTS AND DISCUSSION

Immediately following deposition of CuCl on substrates of glass, Si (100) and Si (111), respectively, XRD measurements were performed to monitor the crystallinity of the deposited CuCl thin films. These XRD scans were then compared to powder diffraction software files provided by the manufacturer and to the trace of the starting CuCl powder which was compressed into a pellet and measured. Indexing of the interplanar spacings

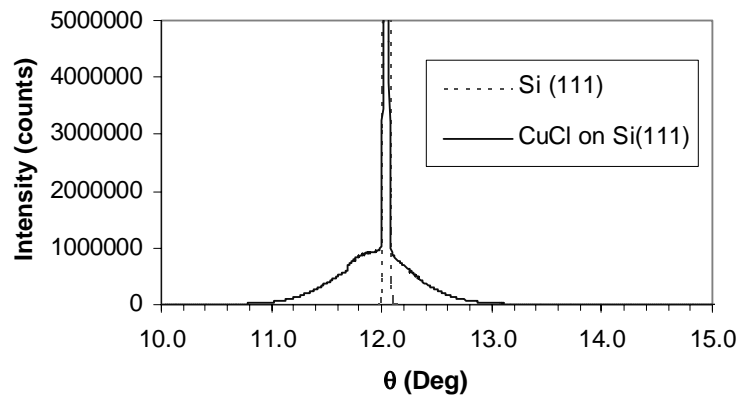
using the Bragg equation for the cubic unit cell,  $h^2 + k^2 + l^2 = \frac{4a^2}{\lambda^2} \sin^2 \theta$ , (where  $h, k, l$  are the Miller indices,

$a$  = lattice constant,  $\lambda$  = incident radiation wavelength and  $\theta$  = Bragg angle) confirmed that the CuCl 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. 2(a) shows a typical XRD pattern taken in the Bragg- Brentano geometry of CuCl deposited on a glass substrate. The evaporated CuCl film on glass is strongly oriented in the <111> direction, confirming that this is the preferred growth direction of the CuCl. Small CuCl (220) and (311) reflections are also evident at  $2\theta \approx 47.50^\circ$  and  $2\theta \approx 56.35^\circ$  respectively.



**Fig. 2** X-ray  $\theta$ - $2\theta$  diffraction pattern of CuCl on glass (a) Immediately after deposition (b) 2 weeks after deposition

One challenge associated with the use of CuCl is that it is sensitive to moist air. Under the influence of light and moisture, hydrated oxyhalides of  $\text{Cu}^{++}$  are formed<sup>6</sup>. This reaction can be easily recognised by a colour change in CuCl associated with the presence of the greenish colour  $\text{Cu}^{++}$  ions. Two weeks after deposition the CuCl sample was examined again in the x-ray diffractometer. The resulting XRD spectrum is shown in fig. 2(b). It can be clearly seen that a complete recrystallisation of the CuCl thin film has taken place. The spectrum is dominated by an intense peak at  $2\theta \approx 16.28^\circ$ , which is attributed to the (100) reflection of Cu(OH)Cl formed by the reaction of CuCl with moist air. This is consistent with reports by other authors<sup>18</sup>. Suitable storage conditions are therefore necessary to prolong the lifetime of uncapped CuCl samples and a protective layer is needed to prevent this reaction. This layer consists of a spin-coated (or dip coated) liquid glass layer, which Fourier Transform Infra-Red (FTIR) and XRD analysis has shown to be an effective means of sealing the CuCl system for many months.

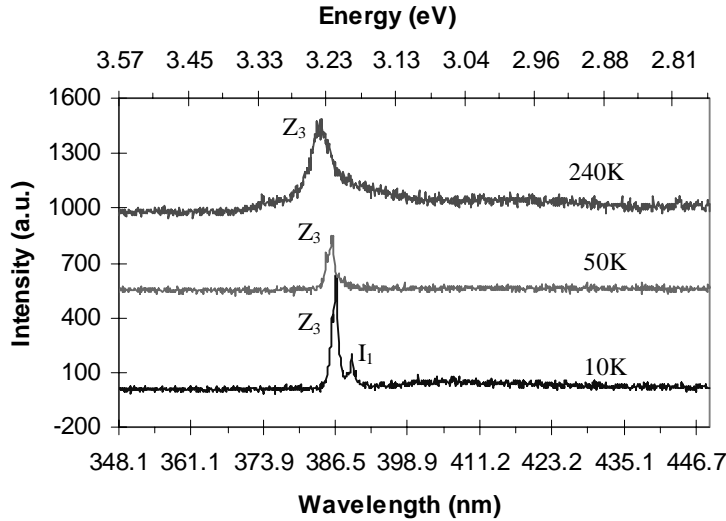


**Fig. 3** Rocking curve of CuCl on Si (111) compared to rocking curve of Si (111)

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. The only peak seen in the Bragg-Brentano geometry for 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. 3 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 (dashed 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.

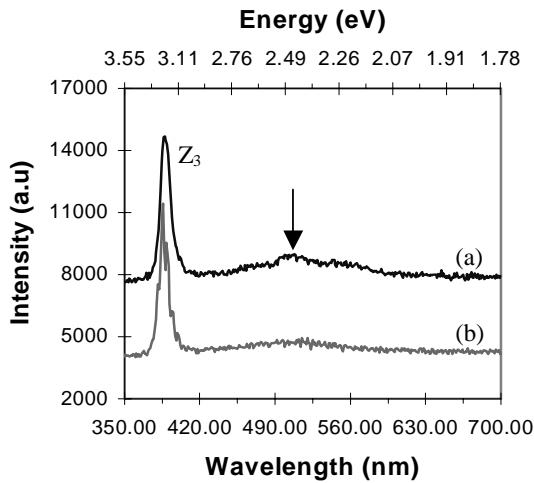
PL spectra for a CuCl on Si (100) sample, grown from CuCl powder of 97% purity, measured at 10K, 50K and 240K respectively are shown in fig. 4. Two peaks are evident in the spectrum taken at 10K. The main peak which occurs at  $\sim 3.208\text{eV}$  is the  $Z_3$  free exciton peak. On the low energy side of the free exciton peak a second peak occurs at  $\sim 3.184\text{eV}$ . This is attributed to an emission from an exciton bound to an impurity<sup>8,19</sup>, which has been called the  $I_1$  bound exciton. The impurity has previously been identified as a neutral acceptor, possibly a Cu vacancy<sup>20</sup>. At 50K only the  $Z_3$  exciton peak is visible and has shifted slightly to an energy  $\sim 3.221\text{eV}$ . The disappearance of the  $I_1$  bound exciton at 50K is considered to be due to the thermal dissociation of the bound state as the binding energy of the bound exciton has been reported to be  $\sim 22\text{meV}$ <sup>8</sup>. At 240K we see a broad  $Z_3$  exciton peak centred at  $\sim 3.238\text{eV}$ . The observed shift in position of the  $Z_3$  exciton with increasing temperature agrees quite well with the values reported by other authors<sup>21</sup>.



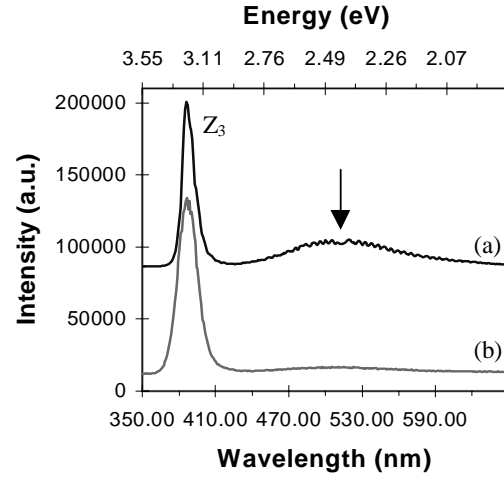
**Fig. 4** Photoluminescence spectra of CuCl 97% on p-Si (100) at 10K, 50K and 240K

The main feature of the room temperature CL spectrum (fig. 5) is a strong emission at  $\sim 387\text{nm}$  ( $3.21\text{eV}$ ). A broad blue-green emission band centred at  $\sim 520\text{nm}$  can also be identified. Comparing spectra labeled (a) and (b) it is noted that these features were common to samples with starting CuCl powders of both 97% and 99.999% purity, respectively, suggesting that they are intrinsic features. The emission at  $3.21\text{eV}$  is assigned to the  $Z_3$  exciton emission. Room temperature excitonic emission is possible due to the large binding energy of the free exciton ( $\sim 190\text{meV}$ ) in CuCl. CL was also investigated as a function of CuCl thickness. Fig. 6 shows an example of CL spectra for a  $1000\text{nm}$  (a) and a  $100\text{nm}$  (b) CuCl film on Si (100) prepared from CuCl powder of 97% purity. It is clearly seen that the intensity ratio of the  $Z_3$  excitonic emission to the broad defect band emission ( $\text{Int. } Z_3/\text{Int. broad band}$ ) decreases dramatically with film thickness from  $\sim 8.0$  for the  $100\text{nm}$  film to

~4.8 for the 1000nm film. This suggests that this blue-green emission originates in the bulk of the CuCl crystal, not at the CuCl/Si interface.

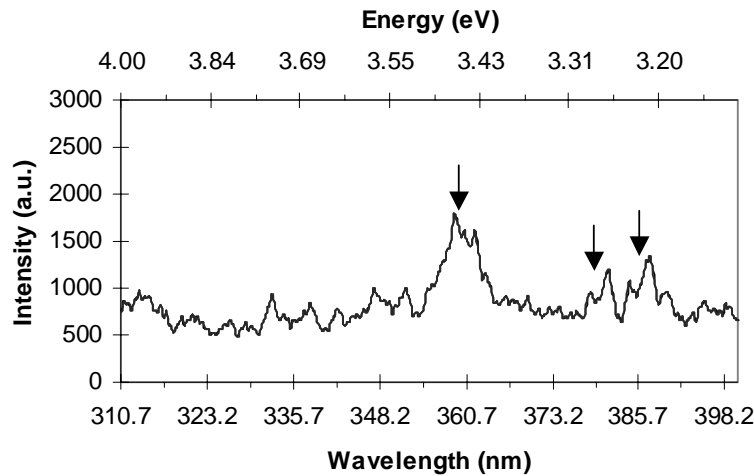


**Fig. 5** CL spectra of CuCl on Si (100) (a) CuCl powder purity = 97% (b) CuCl powder purity = 99.999%



**Fig. 6** CL spectra of CuCl on Si (100) (a) Thickness ~1000nm (b) Thickness ~100nm

The results of the EL measurement are shown in fig. 7. As the Au electrode was non-transparent, emission was observed only from the edges of the electrode; hence the intensity of the spectrum is rather low.



**Fig. 7** Electroluminescence spectrum of CuCl on Si (100) at room temperature

The main feature of the spectrum is a broad band centred on 360nm (3.45eV) due to emission from the direct band-to-band transition. Two further peaks can be identified at ~380nm (3.27eV) and ~387nm (3.21eV). The peak at ~387nm agrees with the  $Z_3$  excitonic emission also seen in room temperature CL measurements as already discussed. Taking into account the broad nature of these peaks, the energy separation of 60meV is

consistent with that of the  $Z_{1,2}$  and  $Z_3$  excitons observed in room-temperature UV-Vis absorption measurements<sup>22</sup>. These 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<sup>8,23</sup>. Therefore the emission at ~380nm could be tentatively assigned to a  $Z_{1,2}$  excitonic emission.

#### 4. CONCLUSION

We have grown polycrystalline  $\gamma$ -CuCl on Si (111) and Si (100) substrates. CuCl grows preferentially in the <111> direction. Low temperature PL studies show at least two excitonic peaks – the free and bound excitons. CL measurements reveal a strong room temperature  $Z_3$  excitonic emission at  $\approx$ 387nm. We have demonstrated a simple electroluminescent device structure based on the growth of CuCl on silicon with light emission occurring across the direct band-gap and from excitonic emission. This indicates that potential exists for this material system in applications for UV light emitting devices.

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#### REFERENCES

1. Nakamura, S., Senoh, M., Nagahama, S., Iwasa, N., Yamada, T., Matsushita, T., Kiyoku, H., Sugimoto, Y., Kozaki, T., Umemoto, H., Sano, M. & Chocho, K. "InGaN/GaN/AlGaIn-based laser diodes with modulation-doped strained-layer superlattices grown on an epitaxially laterally overgrown GaN substrate." *Appl. Phys. Lett.* **72**, 211-213 (1998).
2. Zheleva, T.S., Nam, O.-H., Bremser, M.D. & Davis, R.F. "Dislocation density reduction via lateral epitaxy in selectively grown GaN structures." *Appl. Phys. Lett.* **71**, 2472-2474 (1997).
3. Marchand, H., Wu, X.H., Ibbetson, J.P., Fini, P.T., Kozodoy, P., Keller, S., Speck, J.S., DenBaars, S.P., & Mishra, U.K. "Microstructure of GaN laterally overgrown by metalorganic chemical vapor deposition." *Appl. Phys. Lett.* **73**, 747-749 (1998).
4. Mukai, T., Takekawa, K. & Nakamura, S. "InGaIn-based blue light-emitting diodes grown on epitaxially laterally overgrown GaN substrates." *Jpn. J. Appl. Phys. Part 2*, **37**, L839-L841 (1998).
5. Ambacher, O. "Growth and applications of group III-nitrides." *J. Phys. D: Appl. Phys.* **31**, 2653-2710 (1998).
6. Schwab, C. & Goltzené, A. "Cuprous halides." *Prog. Crystal Growth Charact.* **5**, 233-275 (1982).
7. Soga, M., Imaizumi, R., Kondo, Y. & Okabe, T. "A method of growing CuCl single crystals with flux." *J. Electrochem. Soc.: Solid State Science*, **114** 388-390 (1967).
8. Nakayama, M., Ichida, H. & Nishimura, H. "Bound-biexciton photoluminescence in CuCl thin films grown by vacuum deposition". *J. Phys. Condens. Matter*, **11**, 7653-7662 (1999).
9. Wyncke, B. & Bréhat, F. "Far-infrared reflectivity spectroscopy of cuprous chloride, cuprous bromide and their mixed crystals." *J. Phys. Condens. Matter*, **12**, 3461-3484 (2000).
10. Heireche, H., Bouhafs, B., Aourag, H., Ferhat, M. & Certier, M. "Electronic and optical properties of copper halides mixed crystal  $\text{CuCl}_{1-x}\text{Br}_x$ ." *J. Phys. Chem. Solids*, **59**, 997-1007 (1998).
11. Masumoto, Y. & Ogasawara, S. "Photostimulated luminescence of quantum dots." *J. Lumin.* **87-89**, 360-362 (2000).
12. Ikezawa, M. & Masumoto, Y. "Observation of homogeneous broadening of confined excitons in CuCl quantum dots." *J. Lumin.* **87-89**, 482-484 (2000).

13. Kurisu, H., Nagoya, K., Nakayama, N., Yamamoto, S. & Matsuura, M. "Exciton and biexciton properties of CuCl microcrystals in an SiO<sub>2</sub> matrix prepared by sputtering method." *J. Lumin.* **87-89**, 390-392 (2000).
14. Sasai, J., Tanaka, K. & Hiraio, K. "Preparation and second-order nonlinear optical properties of CuCl nanocrystal-doped glass films." *Scripta mater.* **44**, 1225-1228 (2001).
15. Yanase, A. & Segawa, Y. "Nucleation and morphology evolution in the epitaxial growth of CuCl on MgO(001) and CaF<sub>2</sub>(111)." *Surf. Sci.* **357-358**, 885-890 (1996).
16. Guo, Q., Gui, L. & Wu, N. "CuCl growth on the reconstructed surface of (0001) haematite." *Appl. Surf. Sci.*, **99**, 229-235 (1996).
17. Nishida, N., Saiki, K. & Koma, A. "Heteroepitaxy of CuCl on GaAs and Si substrates." *Surf. Sci.*, **324**, 149-158 (1995).
18. Lin, C.T., Schönherr, E., Schmeding, A., Ruf, T., Göbel A. & Cardona, M. "Growth of CuCl single crystals composed of pure isotopes." *J. Cryst. Growth*, **167**, 612-615 (1996).
19. Shuh, D.K. & Williams, R. S., "Line-shape and lifetime studies of exciton luminescence from confined CuCl thin films." *Phys. Rev. B* **44**, 5827-5833 (1991).
20. Certier, M., Wecker, C. & Nikitine, S. "Zeeman effect of free and bound excitons in CuCl." *J. Phys. Chem. Solids* **30**, 2135-2142 (1969).
21. Kaifu, Y. & Komatsu, T. "Exciton line-width and exciton-phonon interaction in CuCl." *Phys. stat. sol. (b)* **48**, K125 (1971)
22. O'Reilly, L., Natarajan, G., McNally, P.J., Cameron, D., Lucas, O.F., Martinez-Rosas, M., Bradley, L. & Reader, A. "Growth and characterisation of wide-bandgap, I-VII optoelectronic materials on silicon." *J. Mater. Sci.: Mater. Electron.*, accepted for publication (2005).
23. Goldmann, A. "Band structure and optical properties of tetrahedrally coordinated Cu-and Ag-halides." *Phys. stat. sol. (b)* **81**, 9-47 (1977).