Evaluation of the Microstructural, Electronic and Optoelectronic Properties of γ–CuCl Thin Films and Their Fabrication on Si Substrates

A Thesis Submitted in Partial Fulfilment of the Requirements for the Degree of Doctor of Philosophy (Electronic Engineering)

By

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Declaration

I hereby certify that this material, which I now submit for assessment on the programme of study leading to the award of Doctor of Philosophy is entirely my own work and has not been taken from the work of others save and to the extent that such work has been cited and acknowledged within the text of my work.

Student Number: _ _ _ _52178803_ _ _ _ _ Signed: _

Date: _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _

Dedication

This thesis is dedicated to almighty God, the most merciful and most compassionate for providing all the resources for this work.

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List of Publications

1. F.O. Lucas, A. Mitra, P.J. McNally, S. Daniels, A.L. Bradley, D.M. Taylor and D.C. Cameron "Evaluation of the Chemical, Electronic and Optoelectronic Properties of γ–CuCl thin films and their Fabrication on Si Substrates" *J. Phys. D: Appl. Phys.* **40** (2007) 3461
2. F.O. Lucas, L. O'Reilly, G. Natarajan, P.J. McNally, S. Daniels, A. Mitra, D. Cameron, K. Durose and Y.Y. Proskuryakov "Morphological, Optical and Electrical Properties of γ–CuCl thin films deposited by Vacuum Evaporation" *J. Mater. Sci.: Mater. Electron.* DOI 10.1007/s10854-007-9309-2 (2007)
3. A. Mitra, F.O. Lucas, L. O'Reilly, P.J. McNally, S. Daniels and Gomathi Najtarajan "Towards the Fabrication of a UV light Source based on CuCl thin Films" *J. Mater. Sic.: Mater. Electron* DOI 10.1007/s10854-007-9178-8 (2007)
4. L. O'Reilly, F.O. Lucas, G. Natarajan, P.J. McNally, S. Daniels, A. Mitra, L. Bradley, Gomathi Natarajan and D.C. Cameron "Characterisation of n-type γ–CuCl on Si for UV Optoelectronic" *J. Mater. Sci.: Mater. Electron* DIO 10.1007/s10854-007-9173-0 (2007)
5. F. O. Lucas, L. O'Reilly, G. Natarajan, P.J. McNally, S. Daniels, A. Mitra, L. Bradley, D. Cameron and D.M. Taylor "Encapsulation of the Heteroepitaxially Grown of Wide Band Gap γ–CuCl on Silicon Substrates" *J. Cryst. Growth*, **287** (2006) 112
6. L. O'Reilly, F.O. Lucas, G. Natarajan, P.J. McNally, S. Daniels, A. Mitra, L. Bradley, D. Cameron and A. Reader "Impact on Structural, Optical and Electrical Properties of CuCl by incorporation of Zn for n-type Doping" *J. Cryst. Growth*, **287** (2006) 139

7. G. Natarajan, L. O'Reilly, F.O. Lucas, P.J. McNally, S. Daniels, A. Mitra, L. Bradley and D. Cameron "Growth of CuCl thin films by Magnetron Sputtering for Ultraviolet Optoelectronic applications" *J. Appl. Phys.* **100** (2006) 033520

8. L. O'Reilly, F.O. Lucas, P. J. McNally, A. Reader, Gomathi Natarajan, S. Daniels, D. C. Cameron, A. Mitra, M. Martinez-Rosas and L. Bradley "Room-Temperature Ultraviolet Luminescence from γ–CuCl on Silicon substrates" *J. Appl. Phys.*, **98** (2005) 113512

9. L. O'Reilly, G. Natarajan, P.J. McNally, D. Cameron, F.O. Lucas, M. Martinez-Rosas, L. Bradley and A. Reader "Growth and characterisation of Wide Bandgap I–VII optoelectronic materials on silicon" *J. Mater. Sci. Electron. Mater.* **16** (7) (2005) 415

Abstract

Cuprous chloride is a direct wide bandgap (E_g = ~ 3.4 eV) semiconductor with a large excitonic binding energy (~ 190 meV). In this study, CuCl has been deposited by the vacuum evaporation method on a variety of substrates (amorphous silica glass, indium tin oxide (ITO) coated on glass and Silicon (100)) substrates, encapsulated and characterized as a potential material for optoelectronic applications. Some of the samples were also oxygen plasma treated for durations of 1, 2 and 3 minutes, respectively.

Room temperature x-ray diffraction (XRD) measurements show that CuCl grows preferentially in a (111) orientation irrespective of the underlying substrate. Microstructural properties of the films gave nearly the same values for untreated CuCl films deposited on glass, ITO and Si substrates (particle size, L = 9.6 nm ± 1 nm). On the other hand, the microstructural properties of the plasma treated films vary as a function of plasma treatment duration.

At 10 K, the photoluminescence (PL) spectrum of the untreated CuCl/Si films using 244 nm excitation reveals four peaks: the Z_3 free exciton occurring at 3.203 ± 0.003 eV, the I_1 impurity bound exciton located at 3.181 ± 0.003 eV, the M free biexciton occurring at 3.160 ± 0.003 eV and N_1 impurity bound to bi-exciton located at 3.135 ± 0.003 eV. However, the 20 K PL spectra of the untreated CuCl films deposited on all three substrates (using a 325 nm excitation) revealed only the Z_3 free exciton, the I_1 impurity bound exciton and the N_1 impurity bound biexciton at 3.204 eV, 3.18 eV and 3.152 eV, respectively, irrespective of the underlying substrate. The room temperature PL spectra of the films were dominated by the Z_3 free exciton. The measured band gap increased as the temperature increases, which is opposite to most conventional semiconductors. This anomalous effect is believed to be related to electron-phonon renormalization or coupling of the electronic structure of CuCl. On the other hand the PL spectra of the O_2 plasma immersed film were all mainly dominated by the free Z_3 free exciton only. In addition, at low temperatures a broad band ascribed to an oxygen related emission process is observed at ~ 3 eV in all the plasma treated samples. The band gap of the O_2 plasma immersed films follow the anomalous temperature dependency in a similar manner to the untreated films; however the plasma treated films were less sensitive to temperature.

Both steady state DC and AC impedance spectroscopy experiments suggested that the untreated CuCl is a mixed ionic-electronic semiconductor material. Room temperature steady state DC measurements using reversible electrodes (Cu) gave an Ohmic response while using irreversible electrodes (Au) gave an exponential I–V behaviour, both in conformance with Wagner's defect chemistry analysis of a mixed ionic-electronic material. An electronic conductivity of the order of 2.3×10^{-7} S/cm was deduced to be in coexistence with Cu^+ ionic conductivity using irreversible electrodes (Au), while a total conductivity of the order of 6.5×10^{-7} S/cm was obtained using reversible electrodes (Cu) at room temperature. The Arrhenius plot of the electrical characteristics of the untreated films reveal two distinct regimes corresponding to electronic conduction below ~ 270 K and a Cu^+ extrinsic ionic conduction mechanism

above that temperature. Due to the fact that at low temperatures, the thermal energy is inadequate for maintaining considerable ionic motion, it follows that the mode of conduction at lower temperatures is ascribed to electronic processes. On the other hand, the Arrhenius plot of the plasma treated films showed a single regime throughout most of the temperature range. This is interpreted to be an electronically dominant conduction mechanism. The large increase in the conductivity of the treated CuCl films (over 100 fold) is ascribed to effect of oxygen introducing an acceptor state in CuCl films. This is due to the fact that oxygen dissolves in cuprous halides on substitutional anionic sites.

Cathodic deposition of Cu metal via electrolytic decomposition was observed when a steady state voltage greater than 5 V was applied to both the untreated and the plasma treated films. This poses a great challenge in utilizing this material to fabricate optoelectronic devices under the influence of steady state source.

The untreated films were successfully encapsulated using organic polysilsesquioxane (PSSQ) and cyclo olefin copolymer (COC) dielectrics. However, both encapsulants failed to prevent the O_2 plasma immersed films from oxidising, and this will also represent a future challenge for this technology.

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