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UV emission on a Si substrate: Optical and structural properties of γ-CuCl on Si grown using liquid phase epitaxy techniques

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Considerable research is being carried out in the area of wide band gap semiconductor materials for light emission in the 300–400 nm spectral range. Current materials being used for such devices are typically based on II–VI and III-nitride compounds and variants thereof. However, one of the major obstacles to the successful fabrication of III-N devices is lattice mismatch-induced high dislocation densities for epitaxially grown layers on non-native substrates. γ-CuCl is a direct bandgap material and an ionic wide bandgap I–VII semiconductor with a room temperature free exciton binding energy of ~190 meV (compared to ~25 meV and ~60 meV for GaN and ZnO, respectively) and has a band gap of 3.4 eV ($\lambda \sim 366$ nm). The lattice constant of γ-CuCl (0.541 nm) is closely matched to that of Si (0.543 nm). This could, in principle, lead to the development of optoelectronic systems based on CuCl grown on Si. Research towards this end has successfully yielded polycrystalline γ-CuCl on Si(100) and Si(111) using vacuum-based deposition techniques [1]. We report on developments towards achieving single crystal growth of CuCl from solution via Liquid Phase Epitaxy (LPE) based techniques. Work is being carried out using alkali halide flux compounds to depress the liquidus temperature of the CuCl below its solid phase wurtzite-zincblende transition temperature (407 °C [2]) for solution based epitaxy on Si substrates. Initial results show that the resulting KCl flux-driven deposition of CuCl onto the Si substrate has yielded superior photoluminescence (PL) and X-ray excited optical luminescence (XEOL) behavior relative to comparitively observed spectra for GaN or polycrystalline CuCl. This enhancement is believed to be caused by an interaction between the KCl and CuCl material subsequent to the deposition process, perhaps involving a reduction in Cl vacancy distributions in CuCl. This paper presents a detailed discussion of a CuCl LPE growth system as well as the characterization of deposited materials using X-ray diffraction (XRD), room temperature and low temperature PL, and XEOL.

1 Introduction There is a large body of research in the area of wide band-gap semiconductor materials for light emission in the 0.3–0.4 μm spectral range as well as for high temperature electronics. Optoelectronic devices operating beyond the 3 eV range applications in environmental contaminant decomposition [3], UV lasers and sensors [4], novel optical storage media and violet–blue–green LEDs, to name but a few. Particular attention has been paid to the II–VI group materials and III-nitrides which are promising materials for short wavelength optical devices. In addition, ZnO, with a direct band-gap of 3.37 eV and an exciton binding energy of 60 meV, is a candidate material for efficient room temperature ultraviolet LEDs. However, the difficulty of growing reproducible, low-resistivity p-type ZnO has limited its development [5]. GaN (and alloys formed with In and Al) are used for high temperature/power electronic devices as well for short wavelength optoelectronics. Their large direct band gaps, high electron velocities and thermal stability make them ideal for high-frequency control devices as well as for white LEDs. However, the fundamental mismatch between GaN and its substrates results in large densities of dislocations, which degrades device performance.

In working towards the development of single crystal CuCl on Si, we have recently constructed a Liquid Phase Epitaxy (LPE) system based on the sliding boat mechanism [6]. The LPE technique is used widely for the growth of high quality crystalline layers, for which it is ideally suited, owing to its near-equilibrium nature. The technique has been successfully applied to the growth of single crystal III–V growth, notably GaAs and its alloys [7]. A number of issues immediately preclude conventional CuCl LPE growth, however. The zinc-blende to wurtzite phase change at 407 °C is problematic for single crystal growth of this material, as it induces a large strain and consequent dislocation generation within the grown crystal during the phase transition. Secondly, there is a known reaction between CuCl and Si in excess of approximately 250 °C [8]. Fortunately, CuCl readily forms eutectic solutions with a number of flux compounds, allowing for the precipitation of CuCl out of the melt below the phase transition temperature [9]. Our initial work has focused on the KCl–CuCl binary system, which with a sufficiently large amount of KCl flux can also allow for CuCl deposition below the previously mentioned Si reaction temperature.

2 Experimental

Our LPE apparatus utilizes the sliding boat approach, wherein a high-grade machined graphite bin is used to contain the melt constituents during a heating and cooling regime. A quartz push rod, driven by a computer controlled stepper motor, is used to drive these melt bins over a second graphite piece containing the substrate material at a predetermined time during the cooling process. These pieces are supported within a quartz glass tube, which sits into a cylindrical bore, 3-zone tube furnace. A proportional-integral-derviative (PID) controller provides temperature control and the zones are calibrated to ensure a flat temperature profile. The furnace can be rolled back on tracks to allow visual observation of the melt *in situ* during an applied temperature regime. The system supports a high-vacuum capability (10^{-5} mbar) as well as high purity Argon gas flow.

For the melt composition, a mixture of KCl–CuCl was prepared in a 23:77 ratio, by molar weight. From the KCl–CuCl phase diagram presented in [10], this percentage produces a liquidus temperature of approximately 245 °C. Commercially available CuCl beads of 99.99% purity (Sigma-Adlrich) were used, and kept in storage under vacuum until use. CuCl is hygroscopic and measures must be undertaken to ensure that the material does not become contaminated on exposure to ambient atmosphere. CuCl used for growth runs is stored in vacuum, and the exposure time from storage to placement within the LPE system is minimized to a few tens of seconds. Similarly, the KCl used was commercially available 99.99% purity (Sigma-Aldrich) powder. The KCl is also hygroscopic so before use within a melt mixture, the KCl is baked out over a period of 8 hours to sufficiently dehydrate it.

Substrate preparation is also of importance, and a number of organic and inorganic regimes have been utilized for cleaning and etching. In all cases, a HF etch was used, resulting in a hydrogen terminated surface with hydrophobic properties. Si⟨111⟩ substrates were used, as previous work has shown that CuCl exhibits preferential growth along this crystallographic orientation [11]. Once the KCl–CuCl mixture and substrate was loaded into the LPE system, a temperature ramp, dwell stage and controlled cool was applied. The substrate and the KCl–CuCl mixture were exposed to the melt at 245 °C for a period of 40 minutes before removal of excess melt at 210 °C.

The XEOL measurements were performed at HASYLAB am DESY, Hamburg, Germany [12], utilizing the continuous spectrum of synchrotron radiation from the DORIS storage ring bending magnet. The ring operated at a positron energy of 4.45 GeV and at typical currents of 80–170 mA. Spectra are acquired using an Ocean Optics 2000 USB Spectrometer, with a detector range from 200 nm to 1100 nm.

Room temperature PL measurements were carried out using a 325 nm UV He–Cd excitation laser. The PL was measured by a liquid Nitrogen cooled CCD detector in conjunction with a 40× objective lens. For temperature dependant measurements, a standard closed circuit liquid Helium cryostat was used. Excitation was provided by a 244 nm laser, supplied by the frequency doubling of the 488 nm line from an Argon ion laser using a BBO crystal. Diffraction measurements for this work were acquired using a Bruker AXS D8 Advance X-ray diffractometer.

3 Results and discussion

Initial samples grown by the LPE methodology outlined have yielded CuCl films on a ⟨111⟩Si substrate, with thicknesses typically in the range of 5–13 μm. The crystalline quality of the films was examined using XRD in the Bragg–Brentano (θ–2θ) configuration. The samples examined were found to be of a textured polycrystalline nature. Figure 1 shows the resulting θ–2θ scan of the deposited material onto the Si⟨111⟩ substrate. There are notable peaks attributed to CuCl at ~28.5°, ~33° and ~47.5°, representative of the ⟨111⟩, ⟨200⟩ and ⟨220⟩ γ-CuCl reflections respectively. There also exist a number of smaller peaks that are attributable to the orthorhombic compound, K_2CuCl_3 [13]. Since these are very preliminary growth runs, exact control of thickness has yet to be established which is caused by poor wipe off of residual melt material subsequent to the deposition process. From the phase diagram, it is noted that when the KCl–CuCl melt enters its solid state again, the K_2CuCl_3 compound as well as CuCl are formed. A X-ray peak around $2\theta \sim 44.5°$ corresponds to the orthorhombic η-Cu_3Si compound that had previously been observed as the reaction between the CuCl and Si substrate [14] at temperatures above 250 °C, though it is greatly diminished in intensity relative to previous

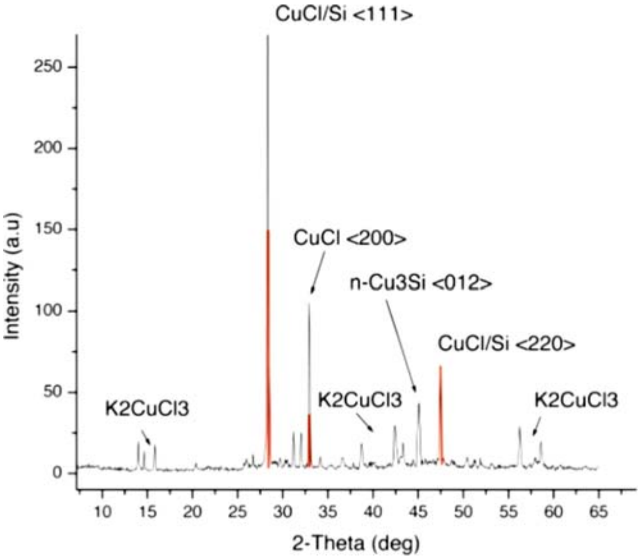

Figure 1 (online colour at: www.pss-a.com) θ–2θ X-ray diffraction scan of a typical CuCl film (5–13 µm thickness) deposited from a 23:77% mixture by molar weight, grown on a Si⟨111⟩ substrate. Red bars represent known CuCl reflections obtained from powder diffraction files.

CuCl vacuum deposited sample measurements. A higher percentage of KCl would most likely eliminate the formation of the η-Cu_3Si compound by further depressing the liquidus temperature below the reaction temperature.

Temperature dependent PL measurements indicate a strong room temperature emission for all grown films. At 12.5 K, the PL measurement of the film reveals four discernable peaks: the M free biexciton at 3.190 meV (~391 nm) as well as the I_1 bound biexciton occurring at 3.135 meV (~389 nm) [15]. The newly observed peaks at $\lambda \sim 370$ nm and $\lambda \sim 376$ nm (labeled X_1 and X_2 in Fig. 2) are unknown in normal CuCl. We believe they are the result of the use of the KCl salt and may be due to the influence of the K_2CuCl_3 compound on the luminescence. Polycrystalline CuCl consists of numerous interstitials and vacancies, which act as non-radiative recombination centres, trapping electrons and holes. The most probable of these are Cu^+ and Cl^- ion vacancies [16]. It is possible that the introduction of KCl can provide sources of hopping Cl^- ions, which could act to fill a number of the anion Cl^- vacancies in a process analagous to that described in [17]. This could lead to an increase in the density of available carriers for excitonic processes. The K_2CuCl_3 may also be involved, however this mechanism is speculative at present and requires further study. This luminescence enhancement effect can also be seen clearly in the XEOL spectra in Fig. 3, where a strong luminescent peak occurs at $\lambda \sim 402$ nm. Data was acquired at room temperature, which results in a red shift of the luminescence compared to PL (carried out at 12.5 K). The XEOL spectrum of a nominally undoped single crystal GaN (on Al_2O_3 substrate) is shown on the inset of the Fig. for comparison. The GaN sample was grown via the epitaxial lateral overgrowth (ELO) technique and has a thickness ranging between 5–7 µm. Previous PL measurements of the GaN sample show a yellow band emission at $\lambda \sim 550$ nm [18]. The well-known Al_2O_3 peak at $\lambda \sim 694$ nm is also clearly visible. This spectrum was taken under identical experimental conditions. It can be clearly seen that the luminescence from the KCl–CuCl film is considerably (2–3 orders of magnitude) brighter than that of the GaN sample. It is also approximately an order of magnitude brighter then previously observed vacuum deposited CuCl samples studied with XEOL [19].

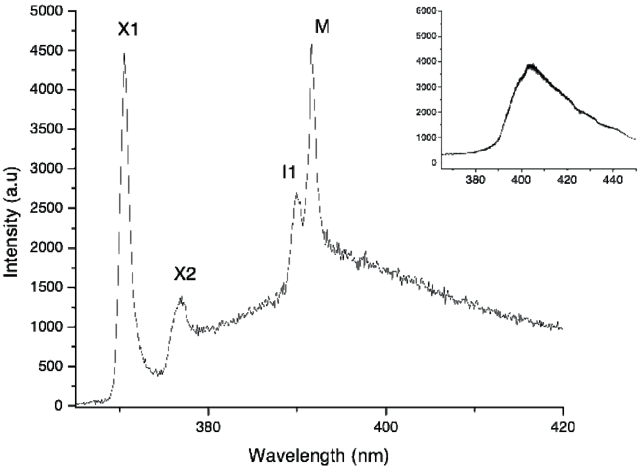

Figure 2 12.5 K photoluminescence spectrum for a typical CuCl film deposited on Si. Inset: Room temperature PL measurement for the same sample. Two previously unobserved peaks, labeled X1 and X2, occur at 370 nm and 376 nm, respectively.

4 Conclusions We report on early investigations on the deposition of γ-CuCl via LPE. To date this has yielded samples of a textured polycrystalline nature. We use a KCl salt to depress the liquidus temperature of the melt below

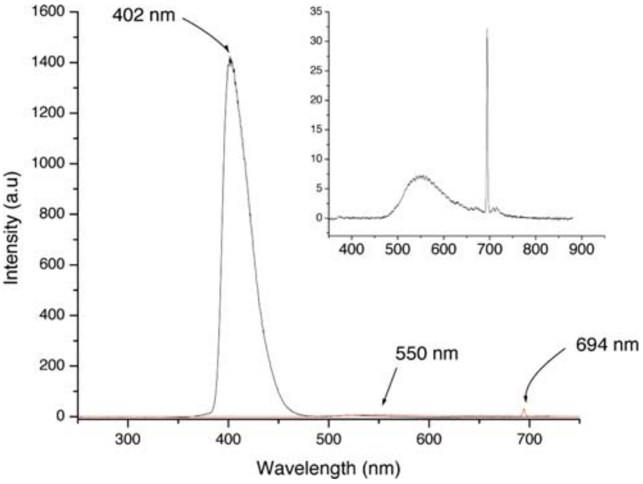

Figure 3 (online colour at: www.pss-a.com) XEOL spectrum of KCl–CuCl deposited on Si substrate. Inset is epitaxially grown GaN on Al_2O_3 substrate on the same intensity scale.

the β-CuCl to γ-CuCl phase transition point as well as below the known CuCl/Si reaction point. This has also resulted in dramatic improvements in luminescence from CuCl grown with this melt composition, as evidenced by XEOL and PL measurements. We speculate this may be due to the filling of Cl^- anion centers in the CuCl crystal by contributions from the KCl or the compound, K_2CuCl_3. Further refinement of the growth technique and parameters should allow for the successful epitaxial deposition of single crystal γ-CuCl material via LPE onto lattice-matched Si substrates.

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