



Reduction of the impact of atmospheric ageing effects on spin coated γ -CuCl nanocrystalline hybrid films



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ABSTRACT

γ -CuCl ($E_g = 3.395$ eV at 4 K) is an ionic I–VII compound semiconductor material with the zincblende structure at room temperature. This is one of the most studied inorganic materials for excitonic related linear/non-linear optical processes due to its large excitonic binding energy. One challenge linked with the use of CuCl is that it is sensitive to moist air i.e. CuCl is not stable in ambient conditions; it forms oxyhalides of Cu^{2+} within a few hours or days of exposure to air. Therefore the use of CuCl for long-term applications is limited. To eliminate this drawback we have investigated the use of spin-coated organic–inorganic CuCl hybrid films. In an organic–inorganic hybrid film, the inorganic material is mixed with organic materials (polymer) to improve its physical, chemical, thermal and electrical properties, process simplicity, and stability. The impacts of atmospheric ageing effects on nanocrystalline CuCl hybrid films were investigated in order to avoid extra capping layer to protect CuCl degradation and extended its use in large scale applications. We show that CuCl-based hybrid films produced in this fashion have useful lifetimes of up to 3 months, which is approximately a two orders of magnitude improvement in the previously published usable lifetimes for optical emission in these materials, opening up the possibility that organic–inorganic CuCl hybrid films can indeed be useful materials for optoelectronic applications.

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1. Introduction

At present, III–N compound semiconductor materials have been the most successful materials for the fabrication of short wavelength optoelectronics and also white light emitting diodes (WLED) [1]. III–N compound semiconductor materials such as GaN, InGaN and AlGaN have a wurtzite lattice structure with typically direct band gap energies from 1.9 to 6.2 eV depending on the composition. The growth of GaN single crystal epilayers is still a difficult task because of the lack of high quality non-polar and low-cost substrates lattice matched to GaN. Therefore, they are grown epitaxially in thin single crystal layers on suitable substrates. Zinc Oxide (ZnO) is another promising wide direct band gap II–VI semiconductor material with the wurtzite structure for efficient room temperature ultra-violet (UV) light emitting devices. The exciton binding energy of ZnO is 60 meV [2], which is comparatively larger than GaN and ZnO is usually deposited naturally as n-type semiconductor material. It is still difficult to produce highly conductive

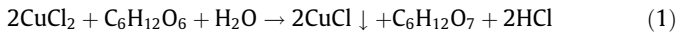
p-type ZnO semiconductor material [3]. Therefore, for the time being, homo-junction based optoelectronics applications of ZnO are limited. CuCl is one of the most studied inorganic materials for excitonic related linear/non-linear optical processes due to its large excitonic binding energies. Excitonic-based luminescence in CuCl crystals has attracted much attention for the past few decades [4–10].

Copper (I) chloride, commonly known as cuprous chloride, is a chemical compound with the formula CuCl. At room temperature and atmospheric pressure, the prevalent phase of CuCl is called γ -CuCl. Intrinsic γ -CuCl ($E_g = 3.395$ eV at 4 K) has a direct, wide band-gap, and is an ionic I–VII compound semiconductor material with a zincblende structure at room temperature [11]. There are many physical and chemical procedures that have been demonstrated in preparing CuCl powders, nanocrystals and thin films, such as the reduction of copper (II) chloride (CuCl_2) with elemental copper in concentrated hydrochloric acid solution [12], ion implantation combined with post-heating at high temperatures [13], the reaction of copper metal with tetrachlorocarbonate [14], carbonation of palladium in a solution containing cupric sulphate-chloride [15], thermal decomposition of organic copper compounds [16], exposure of copper single crystals to chlorine gas in an ultra high vacuum chamber [17], reaction of copper oxide with ammonium

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chloride at 673 K and an ion implantation method combined with post heating at high temperatures [18]. Almost all of these techniques require complicated equipment, high reaction temperatures, utilize toxic reactants and organic solvent, or produce pollutive byproducts. Recently, Zhang et al. demonstrated the hydrothermal reaction of copper (II) chloride (CuCl_2) and alpha-D-glucose ($\text{C}_6\text{H}_{12}\text{O}_6$), a mild renewable, inexpensive and non-toxic reducing agent, in the presence of distilled water and at a temperature of 120 °C to synthesise purified CuCl nanocrystals [19]. It was suggested that the formation of nanocrystalline CuCl powder from this method is by a complexation-reduction-precipitation mechanism, and the equation for the process was summarised as:



One challenge linked with the use of CuCl is that it is sensitive to moist air, i.e. CuCl is not stable in ambient conditions as it forms oxyhalides of Cu(II) within a few hours of exposure to air. In hybrid materials, it is possible to combine organics and inorganics in a nano-composite [20–28]. Previously, CuCl thin films with usable lifetimes (optical and electronic properties) of up to 28 days were fabricated using an extra layer of polysilsesquioxane (PSSQ) and cyclo olefin copolymer (COC) on the top of CuCl active layer [29]. In this study, the CuCl hybrid films were kept in open ambient atmospheric conditions to observe ageing effects. The impact of atmospheric ageing effects on nanocrystalline CuCl hybrid films is important for electroluminescence device fabrication as optimal properties must not deteriorate for typical device working lifetimes i.e. months to years.

2. Experimental

The γ -CuCl nanocrystalline hybrid films were deposited on the aforementioned substrates by the spin coating method using a Laurell WS-400A-6PP/LITE spin coater in a clean room environment to avoid contamination. The coating was performed at room temperature. The nanocrystals were synthesized by a complexation–reduction–precipitation mechanism reaction of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, alpha D-glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) and de-ionized (DI) water with an Organic Polysilsesquioxane (PSSQ) based solution as the host matrix material. The films were subsequently heated at 120 °C for durations 18 h *in vacuo*. The details of the solution processes, synthesis and film deposition were described previously [30]. The structural properties of the hybrid films were measured by using a Bruker D8 Advance X-ray Diffractometer with Cu $K\alpha$ radiation of wavelength $\lambda = 1.54056 \text{ \AA}$. The X-ray diffraction (XRD) measurements were carried out in the locked coupled mode in the 2θ range of 5–60°. Surface morphology and composition of as-deposited and heat treated CuCl hybrid films were investigated using an ‘EVO LS 15’ scanning electron microscope developed by Carl Zeiss. An accelerating voltage of 15–19 keV and probe current of $\sim 800 \text{ pA}$ were set up for this experiment. The FTIR absorption spectra were recorded on a Perkin–Elmer GX FTIR system to obtain 16 cm^{-1} resolution spectra in the range 400–4000 cm^{-1} . Samples were scanned 30 times (absorbance mode), in order to exploit the instrumental noise reduction algorithms. The optical absorption properties of the CuCl films were studied at room temperature using a Perkin Elmer Lambda 40 UV–VIS spectrometer in the range 300–750 nm with a resolution of 1 nm. The Photoluminescence (PL) measurements were carried out by employing a UV Ar+ Innova laser with a second harmonic generation BBO crystal producing a 325 nm photoexcitation. The PL spectra were collected on a Jobin Yvon–Horiba Triax 190 spectrometer with a spectral resolution of 0.3 nm, coupled with a liquid nitrogen-cooled CCD detector. The electroluminescence (EL) measurements of the test devices were

evaluated using a SOFIE spectrophotometer with a photomultiplier tube (spectral range 200–900 nm). Electroluminescent devices (ELDs) fabricated from CuCl were driven by an ac sinusoidal waveform with a frequency of 60 Hz and a peak-to-peak voltage of 70–130 V. Details of the ELD fabrication appear elsewhere [30].

3. Results and discussion

3.1. Structural and morphological

Fig. 1 shows the room temperature θ - 2θ X-ray diffraction spectra of as deposited (ASD) nanocrystalline CuCl hybrid films and for films exposed to atmosphere for periods of 1–6 months, these having been deposited on glass substrates. In these spectra, the ASD films show three different peaks at $2\theta \approx 28.51^\circ$, 47.44° and 56.27° , which correspond to (111), (220) and (311) crystal plane orientations of cubic phase γ -CuCl, respectively [31,32]. The observations are: (i) for samples aged up to four months there is no significant change in peak intensity and FWHM of all peaks, (ii) for the five month aged sample, the (111) peak position shifts slightly from $2\theta \approx 28.5^\circ$ to 28.6° , which may be due to absorbed moisture this result co-inside with the FTIR result. (iii) for the five and six months aged samples, the (311) CuCl peak disappears and a new peak appears at $2\theta \approx 15.95^\circ$, which corresponds to Cu(OH)Cl (100) and this peak intensity is now relatively higher than the CuCl (111) peak [33]. This is most likely due to moisture absorption and FTIR spectroscopy measurements provide corroborative evidence, which will be discussed shortly.

A typical scanning electron microscopy (SEM) image of the CuCl hybrid film deposited on a silicon substrate is shown in Fig. 2. The SEM micrograph shows that a distribution of CuCl crystal clusters of non-uniform size is scattered across the surface. The average grain size is estimated to be $\approx 175 \text{ nm}$. The grain sizes obtained from the SEM analysis are much larger than the particle sizes deduced from the XRD analysis, via the Scherrer method, which yielded an average crystallite dimension of $\approx 36 \text{ nm}$ [30]. Consequently, the grain clusters observed in the SEM analysis can be considered as polycrystalline domains, which themselves consist of clusters of nanocrystals. Similar results were reported for sputtered CuCl and CuCl:Zn thin films using atomic force microscopy (AFM), SEM and XRD analysis [34].

3.2. Fourier transform infrared (FTIR) spectra

Fig. 3 shows FTIR spectra of the same ASD and CuCl hybrid films on Si aged for 1–6 months. The strong absorption peak at

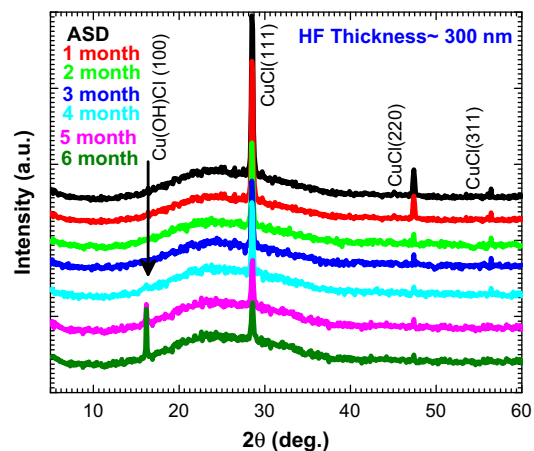


Fig. 1. θ - 2θ XRD spectra of CuCl hybrid films deposited on glass substrates.

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