Hybrid organic–inorganic spin-on-glass CuCl films for optoelectronic applications

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Abstract

Cuprous halides are among the most studied inorganic materials for excitonic related linear/non-linear optical processes due to their large excitonic binding energies (~ 190 and 108 meV for CuCl and CuBr, respectively). In recent years, we have studied CuCl thin films deposited by vacuum evaporation and sputtering techniques on a variety of substrates. We now report on the extension of this research to the deposition of CuCl nanocrystals on flexible substrates via a spin-on technology. In this study, we present the synthesis, deposition and characterization of CuCl nanocrystals embedded in organic polysilsesquioxane (PSSQ) films on a variety of substrates via the spin coating method. 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 and de-ionized (DI) water with a PSSQ based solution as the host matrix material. The deposited films were heated at 120°C for durations between 1 and 24 h *in vacuo*. The room temperature UV–Vis absorption spectra for all hybrid films, except the as-deposited film, showed both $Z_{1,2}$ and Z_3 excitonic absorption features. Room temperature photoluminescence measurements of all heated films reveal very intense Z_3 excitonic emission at 3.221 eV. Room temperature x-ray diffraction (XRD) of the as-deposited films gave no evidence of the crystallization of CuCl. However, after heating the films, XRD confirmed the preferential growth of CuCl nanocrystals whose average size is $\approx 25\text{--}45$ nm in the $\langle 111 \rangle$ orientation. The CuCl hybrid films showed bright electroluminescent emission at 384 nm when subjected to an ac voltage of about 100 V peak to peak.

1. Introduction

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 [1]. A solid-state phase transition occurs with increased temperature from the zincblende structure (γ -phase) to the wurtzite (β -phase) structure. γ -phase CuCl transforms to β -phase CuCl at 407°C before melting at $\sim 430^\circ\text{C}$ [2]. Its absorption coefficient is of the order of 10^5 cm^{-1} at the peak of the exciton absorption band and the excitons are considered to arise from the allowed optical transition at the centre of the Brillouin zone at $k = 0$ [3]. Two exciton absorption bands

separated by spin-orbit splitting appear in the near ultraviolet region; one band is a doublet and the other is a singlet and are called, respectively, $Z_{1,2}$ and Z_3 [4]. CuCl has large exciton binding energies of the order of 190 meV, which is considerably higher than those of semiconducting III-nitrides and ZnO [5]. The lattice mismatch of CuCl is $<0.4\%$ with respect to silicon substrates [6]. CuCl has been extensively used in the manufacture of electrooptic modulators and optical fibres [7], adsorbent and air purifying agents [8], catalysts [9], solid-state batteries [10] and as a candidate material for blue-UV light-emitting devices [11]. Potential applications include high-density optical storage, laser printing, projection displays, spectro-fluorometry, photo-catalytic reactions, counterfeit

detection, chemical detection, traffic signals, medicine (e.g. the use of UV radiation in treating cancer and cerebral apoplexy) [5]. 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], exposure of a Cu single crystal to Cl_2 gas in an ultra-high vacuum chamber [14], reaction of copper chloride and glycerol [15], solvothermal methods [16] and γ -irradiation [17]. All of these methods require complex equipment and/or high reaction temperatures to synthesize CuCl powders. Currently organic–inorganic hybrid materials have been extensively studied [18–20]. In this paper, CuCl nanocrystals were embedded in polysilsesquioxane (PSSQ) and deposited on a variety of substrates via a simple low temperature spin coating technique to develop prototype devices for a flexible UV/white-light emitter. Spin coating is a suitable technique for the preparation of periodic films on almost all flat materials. The main advantages of spin coating are it requires a relatively short manufacturing time; it is cost effective and it allows for relatively large surface coverage [21, 22].

2. Experiment

CuCl hybrid films were deposited on several substrates including silicon, glass and indium tin oxide (ITO) coated glass, by the spin coating method using a Laurell WS-400A-6PP/LITE spin coater in a clean room environment to avoid contamination. A typical solution was prepared using 0.60 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ powder (Laboratory reagent grade, Fisher Scientific Company) as the copper and chlorine sources and 0.40 g of alpha-D-Glucose powder (99.5% Sigma-Aldrich Inc., Germany), a polyol containing an aldehyde group as the reducing agent with 3 ml of de-ionized (DI) water. The powders were dissolved completely in the DI water after vigorous stirring of the solution. 2.1 g of a PSSQ based solution known as Emulsitone glass forming solution (Emulsitone Company, New Jersey, USA) was added to the CuCl_2 glucose aqueous solution. The solution was stirred for 5 min and finally filtered by using 0.2 μm filter (cellulose acetate filter syringe). Approximately 0.75 ml of the solution was dropped at the centre of the substrate ($2 \times 2 \text{ cm}^2$) and spun. The film was spin coated by gradually increasing the speed from 0 to 5000 rpm over a period of 1 min. The coating was performed at room temperature. The films were subsequently heated at 120 °C for durations between 1 and 24 h *in vacuo*. The structural properties of the hybrid films were measured by using a Bruker D8 Advance X-ray Diffractometer with CuK_α 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 from 5° to 60°. 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 from 300 to 420 nm with a resolution of 4 nm. The photoluminescence (PL) measurements were carried out from room temperature to 15 K by employing a UV Ar⁺ Innova laser

Figure 1. X-ray θ – 2θ diffraction spectra of CuCl hybrid films grown on glass substrates.

with a second harmonic generation BBO crystal producing a 355 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. For the electroluminescent device (ELD) the CuCl hybrid film was deposited on ITO coated glass substrate by the spin coating method. A non-transparent gold contact top electrode was deposited using an Edwards Auto 306A vacuum deposition system at a base pressure of $\sim 1 \times 10^{-6}$ mbar. The electroluminescence (EL) measurements of the test devices were evaluated using a SOFIE spectrophotometer with a photomultiplier tube (spectral range 200–900 nm). The ELD was driven by an ac sinusoidal waveform with a frequency of 60 Hz and a peak-to-peak voltage of 70–130 V.

3. Result and discussion

3.1. Synthesis and structural properties

In CuCl hybrid films, alpha-D-glucose ($\text{C}_6\text{H}_{12}\text{O}_6$), a polyol containing an aldehyde group, was selected as the reducing agent, and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was used as the copper and chlorine source, respectively [5]. The formation of CuCl nanocrystal in the organic material is believed to be via a typical complexation–reduction–precipitation mechanism in the presence of heat that can be described by equations (1) to (4) and summarized in (5) [5]:

Figure 1 shows the room temperature θ – 2θ XRD spectra taken for a selection of films deposited on glass substrates. In these spectra, the non-heated film shows very sharp peaks at $2\theta \approx 16.16^\circ$ and 22.1° which correspond to copper chloride hydrate ($\text{Cu}_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$) [23] and there was no diffraction peak that indicated the formation of CuCl nanocrystals. The films

Figure 2. Average CuCl crystallite size versus annealing time.

heated for 1 and 12 h show two peaks at $2\theta \approx 16.16^\circ$ and $2\theta \approx 28.5^\circ$, which are copper chloride hydrate and (1 1 1) oriented copper chloride (CuCl), respectively. The copper chloride hydrate diffraction peaks disappear entirely for anneal times > 12 h. The film annealed for 18 h shows three different peaks at $2\theta \approx 28.51^\circ$, 47.44° and 56.27° , which correspond to (1 1 1), (2 2 0) and (3 1 1) crystal plane orientations of cubic phase γ -CuCl. This is in excellent agreement with data from our previous evaporated and sputtered CuCl films [6, 24, 27]. The film annealed for 24 h shows only the (1 1 1) and (2 2 0) γ -CuCl peaks albeit with reduced intensity when compared with the 18 h annealed film. It is well known that the size of the full width at half maximum (FWHM) is an indication of the crystal quality [25]. The FWHM of the CuCl (1 1 1) peak was measured and the average crystallite size was estimated using the Scherrer formula [26]. The Scherrer model uses the FWHM to evaluate the average crystal size, which is derived from the overall microcrystalline quality of the probed region. While the statistical distribution of crystallite sizes cannot be determined, the average crystallite size, as inferred by the Scherrer model, is never the less, a useful metric for material quality evaluation. Further studies will include transmission electron microscopy (TEM) to examine this issue in greater detail. The average crystal size of the CuCl hybrid films deposited on glass substrates was 27.9 nm, 29.8 nm, 35.7 nm and 44.7 nm for the 1 h, 12 h, 18 h and 24 h annealed films, respectively. From the XRD measurements, it is clear that the film annealed for 18 h gave the optimum CuCl characteristics, and on further annealing appears to lead to a reduction in the CuCl (1 1 1) peak. The reduction in this peak is linked to an excessive thermal budget, which may result in the reaction of the CuCl crystals with the organic matrix. Confirmation of this reduction in quality is observed in the UV-Vis and PL data, which show that, anneal times > 18 h produce sub-optimal films. The average crystallite size of CuCl increases with the increased annealing times as shown in figure 2.

3.2. Optical properties

Figure 3 shows the room temperature UV-Vis absorption spectra of the CuCl hybrid films deposited on glass substrates.

Figure 3. UV-Vis absorption spectra of CuCl hybrid films grown on glass substrates.

In these spectra the as-deposited films showed no absorption; however all heated films reveal both high and low energy excitonic bands historically called the $Z_{1,2}$ and Z_3 excitons, respectively. It is known that the band structure of CuCl is in reverse order to what is typically observed in semiconductors [27]. The top of the valance band is the split-off hole (Γ_7), roughly 60 meV away from the degenerate heavy-hole and light-hole (Γ_8) bands. The $Z_{1,2}$ and Z_3 excitons originate from the coupling of the lowest conduction-band state Γ_6 to both the uppermost valance band holes Γ_8 ($Z_{1,2}$) and Γ_7 (Z_3), respectively [28]. At room temperature all heated films show the free exciton Z_3 absorption peak at ≈ 379 nm (~ 3.27 eV) and the free exciton $Z_{1,2}$ peak at ≈ 371 nm (~ 3.34 eV), which is in excellent agreement with our previous vacuum evaporated and sputtered films [27, 29, 30]. The absorption intensity increases with the increased annealing times up to 18 h and then reduces slightly. Figure 4 shows the low temperature PL spectra of spin coated CuCl hybrid film, annealed for 18 h, deposited on glass substrates. There are four peaks evident in the spectra measured from 15 to 60 K. The peak centred at 386 nm ($E \approx 3.21$ eV) is the Z_3 free exciton peak. On the higher wavelength side of the free exciton, the peak that occurs at 388 nm ($E \approx 3.19$ eV) is attributed to emission from an exciton bound to an impurity or defect, which has been called the I_1 impurity bound exciton. This impurity or defect has previously been identified as a neutral acceptor, possibly a Cu vacancy [31]. The peak at 390 nm ($E \approx 3.17$ eV) is identified as a free biexciton M [31]. The low intensity peak at 394 nm ($E \approx 3.14$ eV) conventionally labelled N_1 is evident, and likely originates from a biexciton bound to an impurity or defect. Similar to the I_1 bound exciton, the most probable candidate for this impurity or defect is a neutral acceptor [31]. The intensities of the impurity bound exciton I_1 and the impurity bound biexciton N_1 peaks decrease more rapidly in comparison with the free exciton Z_3 as the temperature increases. In the temperature range from 60 K to room temperature, the spectra were dominated by the Z_3 free exciton peak. The dominance and the stability of the Z_3 exciton peak are due to the large binding energy of the order

Figure 4. Temperature dependent PL spectra of CuCl hybrid film annealed at 120 °C for 18 h.

Figure 5. Room temperature PL spectrum of CuCl hybrid film annealed at 120 °C for 18 h.

190 meV. The room temperature Z_3 PL emission at 385 nm ($E \sim 3.22$ eV) is depicted in figure 5.

3.3. Electroluminescence

A cross-sectional view of the ELD test structure is shown in figure 6. Gold (≈ 200 nm thick) contact pads were deposited on the CuCl hybrid layer by the vacuum evaporation technique. In this metal–semiconductor–metal structure, light emission most likely occurs through hot-electron impact excitation of electron–hole pairs. The Au top electrode was non-transparent and EL emission was observed principally through the transparent ITO coated glass. Figure 7 shows the average EL spectrum obtained from five CuCl hybrid ELDs. In the spectrum a peak attributed to the Z_3 free exciton emission at 384 nm ($E \approx 3.22$ eV) is observed when the device was biased with a 100 V ac, 60 Hz supply. EL was observed for ac peak-to-peak voltages in the range 70–130 V. The EL of the hybrid films is in excellent agreement with the values reported for vacuum evaporated CuCl films on silicon [30].

Figure 6. Schematic diagram of the CuCl hybrid ELD.

Figure 7. Average room temperature EL spectrum of five CuCl hybrid EL devices annealed at 120 °C for 18 h.

4. Conclusions

CuCl hybrid films have been successfully deposited on a variety of substrates by the spin coating method based on the hydrothermal reaction of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, alpha-D-glucose and DI water using a glass forming liquid as the host matrix. The deposited films were heated at 120 °C for different times which resulted in the formation of CuCl nanocrystals via a complexation–reduction–precipitation mechanism. A strong room temperature Z_3 free exciton emission at ~ 384 nm was observed for both the PL and EL spectra and was at its most intense for films annealed at 120 °C for 18 h.

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