Zn Doped Nanocrystalline CuCl Thin Films for Optoelctronic Applications

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ABSTRACT

We report on the use of Zn as an n-type dopant in CuCl thin films for optoelectronic applications, wherein maximum n-type doping of the order of 10^{18} cm^{-3} has been achieved. Zn doped nanocrystalline CuCl thin films are successfully deposited on glass and Si substrates by pulsed dc magnetron sputtering. Structural and morphological properties are investigated using X-ray diffraction (XRD) studies and Scanning Electron Microscopy (SEM), respectively. The conductivity of the CuCl:Zn films is examined using the four point probe technique. An order of magnitude increase in the conductivity of CuCl, by the doping with Zn is reported herein. The doped CuCl films display strong room temperature cathodoluminescence (CL) at $\lambda \sim 385$nm, which is similar to that of the undoped films. Hall Effect measurements show an n-type conductivity of the doped films.

INTRODUCTION

The search for wide band gap semiconductor materials has great importance in the optoelectronics industry due to their interesting applications in the development of solid state emitters [1, 2]. Zincblende γ-CuCl is a direct band gap (~3.39 eV at room temperature) compound semiconductor with much larger excitonic binding energy (~ 190 meV) [3] when compared to the III-N [4] and ZnO [5] semiconductors. This high binding energy of CuCl guarantees excitonic luminescence at room temperature and beyond. Further to this, it has a relatively small lattice mismatch with Si (< 0.4 %), which may improve the reliability of the light emitting devices made out of these based on CuCl/Si structures. All of these advantages of CuCl can be used for the development of an exciton based semiconducting optical emitter by effectively doping the material system.

Numerous reports on the electrical characteristics of CuCl have been published so far. The total electrical conductivity and the electron hole conductivity in copper halides have been reported by Wagner *et al.* many years ago [6]. They reported p-type conductivity for the as deposited copper chloride films due to the presence of copper vacancies caused by the excess halogen. The p-type conductivity in CuBr has been demonstrated by Knauth *et al.* using Hall Effect experiments [7]. The first report of the n- type doping of the CuCl films was performed by the co-evaporation of ZnCl$_2$ and CuCl by O'Reilly *et al.* [8]. They reported a relatively low carrier concentration of the order of 10^{16}/ cm^3 for the doped CuCl films due to the simultaneous inclusion of Zn and Cl in the CuCl film.

Here we present the first report on the pulsed dc magnetron sputtering deposition of the CuCl: Zn films on glass and Si substrate using a CuCl/Zn target. Unlike the co- evaporation of CuCl with $ZnCl_2$, this method can avoid the problem of the inclusion of Cl along with the Zn in to the CuCl film, as was outlined in [8].

EXPERIMENTAL

CuCl:Zn was deposited using pulsed dc magnetron sputtering of a CuCl/Zn target, by varying the wt% Zn in the target from 0-5, on ultrasonically cleaned glass and Si substrates. An ENI RPG-100 pulse generator was used to drive a planar magnetron fitted with the target. Sputtering was carried out in pure argon atmosphere at a pressure of $5.5x10^{-3}$ mbar with a target to substrate distance of 6 cm. The power density at the target and duty cycle of the pulse used were 1.73 W/cm^2 and 40%, respectively. The substrate was kept at floating potential and the thickness of the samples was 350 ± 20 nm.

The sheet resistance and thickness of the film was measured using a four point probe measurement set-up (Veeco), and Nano-R Atomic Force Micrograph (AFM), and thereby resistivity can be calculated. X-Ray diffraction analysis was carried out using Copper Kα radiation of wavelength 1.54 Å from a Bruker D8 advance instrument to determine the crystallinity of the CuCl/Zn films. Morphology of the thin films was investigated using Scanning Electron Microscopy. UV/Vis absorption spectra of the films were explored using a Perkin Elmer Lambda 40 UV/Vis spectrometer in a range of wavelength from 320-420 nm. The room temperature cathodoluminescence studies were carried out using LEO Stereoscan 440 SEM coupled with a Gatan MonoCL instrument. Carrier concentration and Hall mobility were determined by the van der Pauw method.

RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction spectra of the Zn doped CuCl films deposited by sputtering of the CuCl target with wt % of Zn varying from 0-5. All of the XRD spectra gave prominent peaks of CuCl, with a strong orientation along the (111) plane (corresponding to a 2θ value of 28.5°). The XRD spectra also show peaks corresponding to (220) and (311) plane orientations, with 2θ values of 47.6° and 56.3° respectively. All the peak positions are in good agreement with the corresponding ICDD data for polycrystalline CuCl. The XRD spectra indicate that the Zn doping doesn't degrade the structural properties of the CuCl, but improves the crystallinity of the CuCl, by texturing the orientation along the (111) direction. It can be observed from the XRD analysis that the intensity of the (111) peak has the highest value for the 3 wt % Zn doped sample. The average crystalline sizes of the undoped as well as the doped CuCl films, calculated using Scherrer equation was found to vary between ~ 37 and 49 nm.

The conductivities of the CuCl:Zn films are investigated using the sheet resistance values of the films, deduced from the four point probe measurements. The conductivity of the undoped CuCl film is calculated as ~ 4 x 10^{-3} S cm^{-1} and that of the 1, 3 and 5 wt% Zn doped samples are ~ 1 x 10^{-2}, 2 x 10^{-2} and 9 x 10^{-2} Scm^{-1} respectively. Thus far, the conductivity of the CuCl thin film can be increased by an order of magnitude by the doping with Zn.
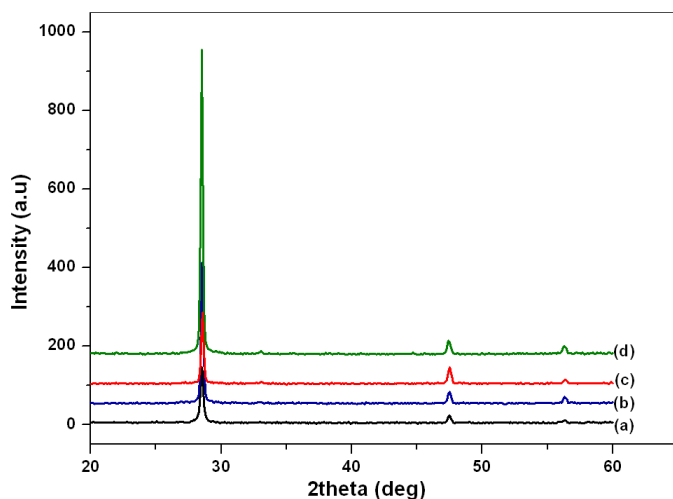
Figure 1. XRD θ–2θ spectra of the undoped (a) CuCl and (b) 1 %, (c) 5 % and (d) 3 % (wt %) Zn doped samples.

Preliminary Hall effect measurements illustrate an n type conductivity of the Zn doped CuCl films, with an average carrier concentration of ∼ 1 x 10^{18} cm^{-3} and a Hall mobility of ∼ 10^{-1} $cm^2V^{-1}s^{-1}$ for the 3 wt % Zn doped films, for example.

It is important to confirm that the n-doping process does not impact negatively on the unique excitonic behaviour of the deposited γ-CuCl films. Thus, Figure 2 shows the room temperature UV-Vis absorption spectra of the CuCl:Zn films deposited on glass substrates, with a varying wt % of Zn in the target.
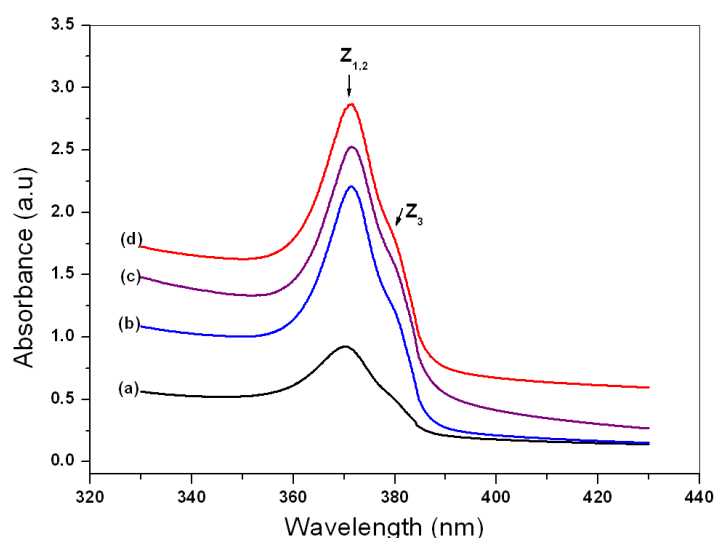
Figure 2. UV-Vis absorption spectra of the (a) 0 %, (b) 1 %, (c) 3 % and (d) 5 % (wt%) Zn doped CuCl thin films.

The absorption peaks are separated from each other for ease of observation. All undoped samples including the doped films confirm the presence of the low energy and the high energy excitonic bands, labelled Z_3 and $Z_{1,2}$, respectively. The peak positions of Z_3 and $Z_{1,2}$ are at ~ 379 nm and ~372 nm respectively, which are in good agreement with the previously reported data for the undoped CuCl [8].

Figure 3 shows the SEM image of a typical 3 wt % Zn doped CuCl film. It illustrates the presence of the triangular grains in the films.
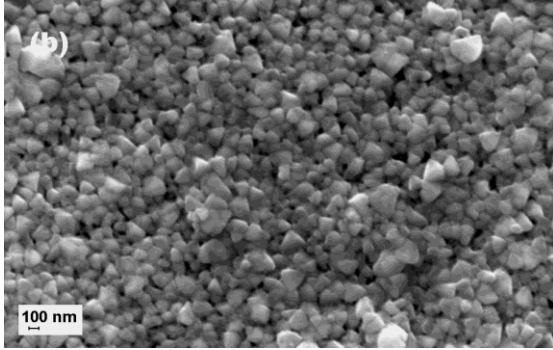
Figure 3. Scanning Electron Micrograph (SEM) image of a typical 3 wt % Zn doped CuCl film.

The grain size obtained from the SEM picture is higher than that inferred using XRD analysis. All the remaining samples (undoped, 1 and 5 % Zn doped) also show the similar trend. The observed grains in the SEM image can be considered as clusters of the nanocrystalites [9].

The room temperature CL measurements on all samples revealed identical excitonic features. A typical room temperature CL spectrum of the 3 wt % Zn doped CuCl film is shown in figure 4. The strong emission at a wavelength of ~ 384.7 nm (~ 3.22 eV) corresponds
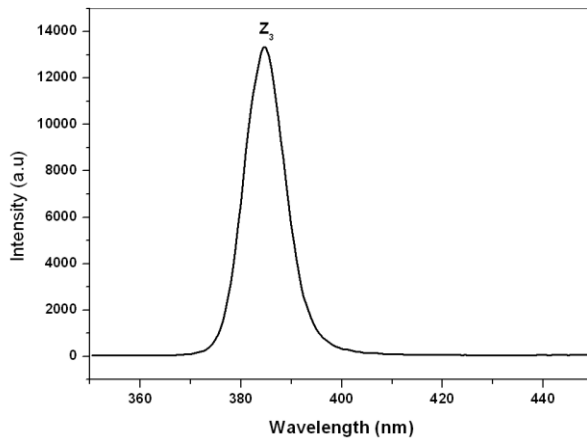
Figure 4. Room temperature cathodoluminescence spectrum of a typical 3 wt % Zn doped CuCl film.

to the well known Z_3 free exciton peak of CuCl, and this is in good agreement with the previous reports. The Z_3 free excitonic emission is due to the coupling of the lowest conduction-band state Γ_6 to the uppermost valance-band hole Γ_7. This indicates that the doping of Zn has no harmful effect on the luminescence properties of the CuCl.

CONCLUSIONS

Zn dopant is used to achieve n-type doping of γ-CuCl thin films, which are deposited by pulsed dc magnetron sputtering of CuCl targets containing a controlled wt% of Zn. The conductivity of CuCl films can be controllably increased by an order of magnitude by the incorporation of Zn in the CuCl film. Hall effect measurements confirm the doping to be n-type, and XRD, UV-Vis absorption and CL measurements confirmed that the controlled incorporation of Zn in CuCl films does not significantly alter the structural, absorption and luminescence properties of CuCl.

ACKNOWLEDGMENTS

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