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Stoichiometry control of sputtered CuCl thin films: Influence on ultraviolet emission properties

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We demonstrate that the chemical composition of the sputtered CuCl thin films could be finely controlled by adjusting the bias to the substrate. The films deposited without any intentional bias were Cl rich ($CuCl_{1+x}$), a bias of −22 V yielded stoichiometric CuCl, and a further increase in the negative bias resulted in Cl deficient films ($CuCl_{1-x}$). The crystalline and optical properties were found to be associated with the chemical composition. Cl rich films showed a deep level green emission at around 515 nm in addition to ultraviolet (UV) excitonic emission. The stoichiometric films have higher optical quality, exhibiting a sharp UV emission at around 385 nm at room temperature, compared to nonstoichiometric samples. Visible luminescence related to deep level defects was not observed in the stoichiometric films. Changes in energy of the flux from the target and the subsequent ion bombardment on the substrate surface are correlated with the variations in chemical composition and their impact on the film microstructure and UV emission. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2364665]

Wide band gap semiconductors such as GaN (Ref. 1) and ZnO (Ref. 2) have been widely investigated to realize short wavelength photonic devices. These materials are mostly grown on substrates such as SiC or sapphire.[3] However, a large lattice mismatch in these systems leads to high dislocation densities at the film-substrate interface, which are deleterious to device performance. Copper (I) chloride, a wide band gap semiconductor (E_g=3.4 eV), can be considered as a potential alternate as it has close lattice matching (mismatch <0.4%) with silicon substrates. CuCl also has attractive optical characteristics including a strong UV emission at room temperature and a large exciton binding energy of 190 meV.[4] So far, the investigations on CuCl have been focused on spectroscopy and the epitaxial growth on different substrates.[5] It has been reported that CuCl is hygroscopic in nature. When it is exposed to atmosphere for extended periods, it tends to absorb moisture and the film surface suffers from the formation of oxihalides.[6] Our group has recently demonstrated that a suitable capping layer could solve this problem.[7] We have also explored the possibility of exploiting CuCl for Si based UV optoelectronics.[8,9] Controlling the stoichiometry in the deposited films is essential, as the chemical composition has a significant role in determining the UV emission properties. In the present report, CuCl thin films were deposited by radio frequency (rf) magnetron sputtering and it has been shown that the chemical stoichiometry could be finely tuned by applying a suitable bias to the substrate. The structural, optical, and luminescence characteristics were studied as a function of chemical stoichiometry.

CuCl thin films were deposited using rf magnetron sputtering in an argon atmosphere on Si(111) and glass. The argon gas pressure was maintained at 1.1×10^{-3} mbar and the target to substrate spacing was 6 cm. Details on the deposition conditions can be found elsewhere.[9] The rf power density at the target was 0.5 W/cm^2. Applying a rf bias to the substrate, the substrate potential was varied from the floating potential (−1.6 V) to −62 V. The thickness of the samples was found to be 400±15 nm.

Compositional studies were performed with a LEO Stereoscan 440 scanning electron microscope and Princeton Gamma Tech energy dispersive x-ray (EDX) analyzer. X-ray photoelectron spectroscopy analysis of the samples was carried out in a VG Microtech electron spectrometer using Mg $K\alpha$ ($h\nu$=1253.6 eV) radiation. The crystallinity was examined by x-ray diffraction analysis using a Bruker AXS D8

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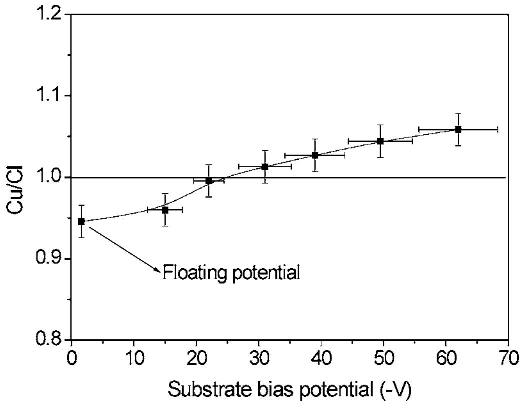

FIG. 1. Variation of Cu/Cl ratio with substrate bias.

Advance instrument with Cu $K\alpha$ radiation with a wavelength of 1.54 Å in Bragg-Brentano geometry. The absorption spectra of the samples were recorded using a Perkin Elmer Lambda 40 UV/visible spectrophotometer. Room temperature cathodoluminescence (CL) studies were performed with a Gatan MonoCL instrument.

Figure 1 shows the variation in the Cu/Cl ratio (obtained from EDX analysis) on increasing the negative substrate bias up to −62 V. The film deposited without any substrate bias is chlorine rich (CuCl_{1+x}) and the chlorine content decreases upon making the bias more negative. Stoichiometric CuCl films were obtained at a bias of −22 V. The films become chlorine deficient (i.e., copper rich, CuCl_{1-x}) with further increases in the negative substrate bias.

In addition to EDX, the samples were also subjected to x-ray photoelectron spectroscopy (XPS) analysis in order to confirm the change in composition with the applied substrate bias. Cu $2p_{3/2}$ core level spectra of the samples deposited at various substrate biases were compared as shown in Fig. 2. It is clearly evident that the spectral peak position shifts towards lower binding energy for the sample deposited at −22 V bias, compared to that deposited at floating potential. A further shift in the same towards lower binding energy is observed when the negative bias is increased to −62 V. In principle, a shift towards lower binding energy indicates a decrease in the positive charge of the atom.[10] In the present case, a shift towards a lower binding energy indicates a decrease in the positive charge on Cu. This reveals that there is a decrease in the chlorine content on varying the bias from floating potential to −62 V. Hence, the shift in the core level spectral emission of Cu $2p_{3/2}$ towards the lower binding energy on increaseing in negative substrate bias confirms the trend seen from EDX analysis.

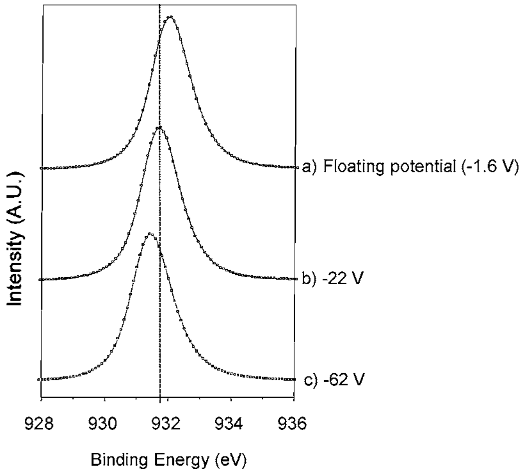

FIG. 2. Cu $2p_{3/2}$ core level XPS spectra of the samples deposited at different substrate bias voltages.

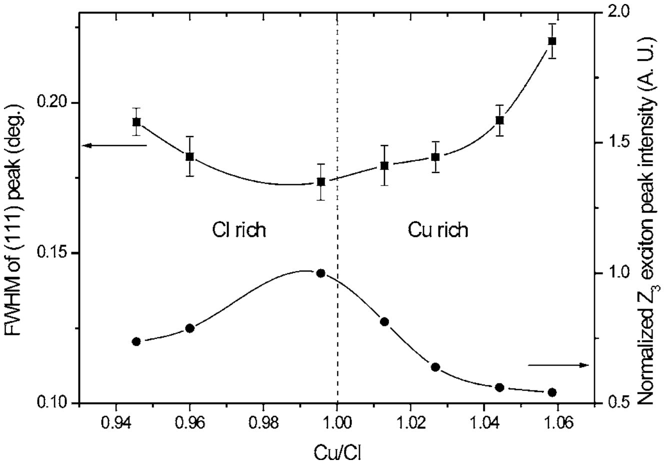

FIG. 3. Variation in the FWHM of XRD (111) peak and Z_3 exciton peak with Cu/Cl ratio.

X-ray diffraction showed that the films were strongly oriented in (111) direction (see XRD pattern in Ref. [9]). Two characteristic exciton peaks, Z_3 and Z_{12}, were observed in the optical absorption spectrum (see absorption spectrum in Ref. [9]). Figure 3 shows the variation of the full width at half maximum (FWHM) of (111) diffraction intensity and the Z_3 optical absorption intensity as a function of Cu/Cl ratio. The FWHM of the x-ray diffraction peak is related to the structural quality of the film and a smaller FWHM indicates higher crystalline quality.[11] The FWHM of the (111) diffraction peak is smaller and Z_3 optical absorption is higher when the Cu/Cl ratio is 1, which indicates that the stoichiometric sample has good crystalline and optical quality. The sample quality is degraded with deviations from stoichiometry. This plot also indicates that there is a correlation between the microstructure and the optical properties.

Figure 4 shows the room temperature cathodoluminescence spectra of Cl rich, stoichiometric, and Cu rich samples. An intense UV emission appears at a wavelength of around 385 nm due to Z_3 excitonic mediated recombination for all the three samples. The optical quality of the films can be assessed based on two important properties: (i) the width of the Z_3 exciton emission and (ii) the existence of deep level green emission. A smaller FWHM of the Z_3 emission and absence of any deep level emission represent higher optical quality.

In the Cl rich samples (deposited at floating potential), a green emission centered at ~515 nm is observed in addition to the exciton emission. In the stoichiometric and Cu rich samples, there is no trace of the above mentioned green emission, and the exciton emission is the only feature observed. Subband gap emission such as that seen in the chlorine rich samples is generally considered to originate from

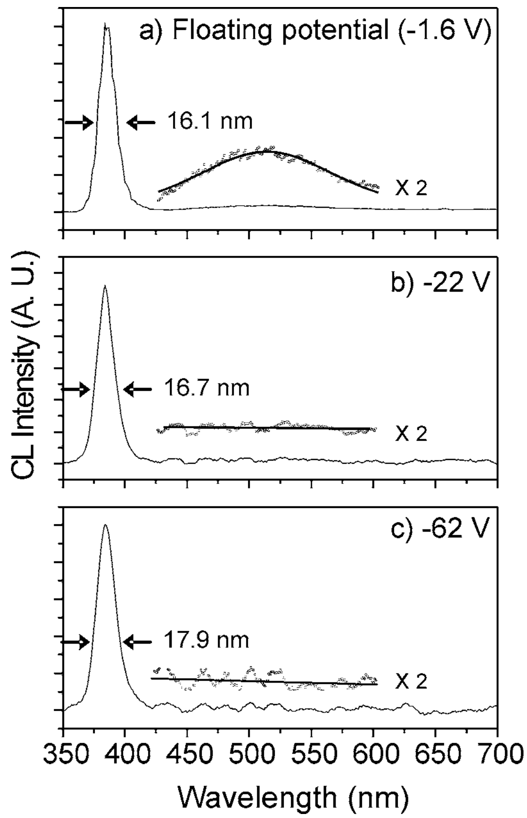

FIG. 4. CL spectra for the samples with different substrate bias voltages.

nonstoichiometry and/or defects. A similar deep level emission originating from nonstoichiometry is reported by several authors[12] for UV emitting ZnO thin films. It is reported to be caused by different intrinsic defects such as an oxygen vacancy (V_O), a zinc vacancy (V_{Zn}), interstitial zinc (I_{Zn}),[13] etc. This green emission is only seen in the Cl rich samples whereas it is not observed in the stoichiometric and Cu rich samples. Hence, it is suggested that copper vacancies or chlorine interstitials could be the origin of the green emission observed in the CL spectra.

The FWHM of the Z_3 emission peak from Cl rich, stoichiometric, and Cu rich samples were 16.1, 16.7, and 17.9 nm, respectively. A noticeable increase in the FWHM for Cu rich samples indicates the degradation of optical quality. Although the Cl rich sample has a smaller FWHM for Z_3 emission, it suffers from the deep level emission from nonstoichiometric defects, whereas the stoichiometric sample has a strong UV emission without any deep level emission, indicating its high optical quality and low defect density.

It is interesting to investigate the variation in composition with the substrate bias, as biasing results in a selective removal of chlorine. When the substrate has only floating bias applied (approximately −1.6 V), the growing film is Cl rich and biasing reduces the Cl content. Applying a negative bias to the substrate induces an intentional ion (argon) bombardment on the growing surface. Increasing the negative bias increases the number and energy of the ions impinging on the film surface. Any displacement or desorption of particles on the film surface depends on the energy transfer in a collision and thereby on the masses of the projectile and surface particles. A large displacement yield is obtained if the mass of the projectile matches the mass of the surface particle.[14] Among the surface particles, Cu and Cl, the mass of Cl is closer to that of the projectile (argon); hence, a larger surface displacement yield is expected for Cl. This could be related to the decrease in Cl content on biasing the substrate. Increasing the bias voltage results in desorption of a higher number of Cl atoms from the film surface. Therefore, the film composition progresses towards the stoichiometry with increasing the negative bias, and the films become Cu rich for a further increase in the negative bias.

In summary, we have demonstrated that the film composition could be finely controlled by adjusting the substrate bias. The chemical stoichiometry has a strong correlation with the crystalline and optical qualities of the films. Cathodoluminescence showed a strong UV exciton emission and a green emission from deep levels for Cl rich samples. This deep level green emission could be eliminated on attaining stoichiometric or copper rich films. Stoichiometric samples were found to have the highest optical quality. As the elemental content can be finely controlled using substrate bias, it may be possible to vary the intrinsic doping levels and so tune the electrical properties of the material.

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