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Effect of chlorine doping on electrodeposited cuprous oxide thin films on Ti substrates

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Highly photoactive Cl-doped Cu_2O films were electrodeposited potentiostatically on Ti substrates. Optimum deposition potential was determined by Linear-Sweep Voltammetry measurements. The influence of chlorine doping on grain size, crystallite shape and orientation was examined using scanning electron microscopy and X-ray diffraction. X-ray photoelectron spectroscopy confirmed the presence of Cl due to doping. Mott–Schottky electrochemical impedance analysis showed the p-type conductivity for undoped Cu_2O films and n-type conductivity for Cl-doped Cu_2O films. Analysis also showed that the carrier concentration of Cu_2O thin films varied with Cl concentration of the deposition bath. Spectral responses of the resulting films were investigated in a photo-electrochemical cell to optimize the $CuCl_2$ concentration of the deposition bath to obtain highly photoactive films. Photocurrent measurements further confirmed that the conductivity of these Cl-doped Cu_2O films was n-type while undoped films showed p-type conductivity at a bath pH 9.3. The resistivity of Cu_2O films decreased with the Cl concentration and the resistivity obtained for the Cl-doped Cu_2O films with the highest photoactivity was about 10^2 Ωcm at 30 °C. The low resistance and high photoactivity of Cl-doped cuprous oxide thin films make them more suitable for solar cell and other applications.

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1 Introduction The need for sustainable energy technologies has invigorated research in many photovoltaic systems with increasing emphasis placed on balancing cost and performance. As a semiconducting material, cuprous oxide (Cu_2O) shows many important characteristics useful for photovoltaic, water photoelectrolysis, and sensor applications [1–3]. In photovoltaics, the observed conversion efficiencies of Cu_2O based solar cells have remained far below the theoretically predicted value, regardless of the method of growth of Cu_2O and the mode of fabrication of the cells. To date, the highest photovoltaic conversion efficiency (5.38%) has been achieved through a Ga_2O_3/Cu_2O hetero-junction solar cell [4]. Many factors such as the bulk non-radiative recombination, recombination through interface defect states, the high series resistance, the difficulty of preparing high-quality n-type Cu_2O films, lack of a suitable n-type hetero-junction partner and difficulties encountered in the doping of Cu_2O thin films have prevented the resulting solar cells reaching higher efficiencies. Therefore, a systematic investigation into the above is essential for improving the efficiency of Cu_2O based solar cells and other devices.

Use of electrodeposition to fabricate Cu_2O thin films is a well established preparation method. It has been reported that chlorine doping is an effective process to reduce the resistivity of Cu_2O thin films. In order to reduce the resistivity, chlorine doping has been used for Cu_2O thin films grown on ITO/Au substrates [5], reduced graphene oxide (rGO) electrodes [6], Au/Si substrates [7] and Cu substrate [8] previously. The purpose of this letter is to discuss the fabrication of low resistive highly photoactive n-type cuprous oxide thin films by chlorine doping using electrodeposition process. The paper presents a method of obtaining thicker, chlorine doped Cu_2O films of uniform

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coverage by electrodeposition on Ti substrates. It was observed that due to doping, the resistivity of the films decreased by four orders of magnitude while maximizing the photoresponse (in a PEC).

2 Experimental Electrodeposition of Cu_2O thin films was potentiostaticly performed using potentiostat (HD HOKUTO DENKO HAB-151) on Ti substrates and accomplished in a three-electrode electrochemical cell containing an aqueous solution of a mixture of lactic acid (3 M), cupric sulphate (0.45 M) and sodium hydroxide (NaOH). All the chemicals used were reagent grade without further treatment. The counter electrode was a platinum plate and, a saturated calomel electrode (SCE) was used as the reference electrode. Prior to the film deposition, substrates were cleaned with detergent, diluted HNO_3, in an acetone bath and finally, with distilled water. pH of the electrolyte was adjusted to 9.3 by adding a 4 M sodium hydroxide solution to the bath that was maintained at 60 °C. Optimization of the above pH value and the deposition temperature of the electrolytic bath was achieved by measuring the photo-activity of the deposited films. As the Cl precursor, $CuCl_2$ was used and its concentration was varied in the range of 0.005 M to 0.1 M in the solution to control the Cl-doping in Cu_2O thin films. Throughout the deposition of the films, the pH and the temperature were monitored and they remained unchanged. Growth parameters used to prepare Cu_2O films were obtained through Linear-sweep Voltammetry measurements. Working electrodes used for voltammetric curves had a contact area of $\sim$ 4 mm^2 with the electrolyte. X-ray diffraction measurements were made using a SHIMADZU (XD-D1) X-ray diffractrometer. In order to make the photoresponse measurements, all Cu_2O thin films were investigated in a three electrode photoelectrochemical cell containing a 0.1 M sodium acetate solution. Detailed experimental procedure has been discussed elsewhere [9]. The electrochemical impedance measurements were carried out at dark in the 0.1 M sodium acetate solution (pH 8.35) using potentiostat (HD HOKUTO DENKO HAB-151), lock-in amplifier (STANFORD-SR 830) and a home made oscillator. A sinusoidal modulation of 10 mV was applied at a frequency of 10 kHz. Before capacitance measurements, the native CuO layer on the surface of the electrode was removed by dipping for 5 s in a 1 M acetic acid solution. The surface Morphology of the films and devices was determined by a scanning electron microscope (Philips XL40). In order to measure the resistivity of Cl-doped Cu_2O films, current–voltage (I–V) measurements were performed using a Keithley-2100 multimeter. For I–V measurements, contacts were made through silver dots placed on the film surface and the Ti substrate. The resistivity of the Cl-doped Cu_2O films was calculated from the slope of the I–V measurements made at 30 °C. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Multi Lab 3000 VG Thermo Scientific surface analysis system using Mg K_α (1253.6 eV) under ultrahigh vacuum conditions at pressures in the 10^{-9} Torr range.

3 Results and discussion Figure 1 shows linear-sweep voltammetry measurements for different Cl concentrations of the bath. It shows a well defined minimum that varies with the Cl concentration in the bath. Obtained potential minima against the Saturated Calomel Electrode (SCE) were at –410 mV, –350 mV, –290 mV, –275 mV, –260 mV, and –225 mV for the undoped Cu_2O film and films deposited with $CuCl_2$ concentrations of 0 M, 0.005 M, 0.01 M, 0.05 M, 0.08 M, and for 0.1 M, respectively. Films were fabricated by setting the deposition potentials at the above values that correspond to the maximum deposition current for the formation of thin films with Cu_2O stoicheometry. In contrast, others [5–7] have reported the formation of Cu_2O thin films at different deposition potentials. This difference is attributed to different deposition parameters and substrates that have been used. In order to obtain Cu_2O thin films of similar thicknesses, different deposition times were used. Film thicknesses were calculated by Faraday's law [10] assuming that only single phase Cu_2O was deposited and the density of Cu_2O films was equal to the bulk density which was 8920 kg/m^3. Calculated thickness of the films deposited at –275 mV versus SCE for 45 min was found to be $\sim$2 μm indicating that the electrodeposition parameters can be controlled to obtain thicker Cu_2O thin films in contrast to smaller thicknesses limited upto about 700 nm obtained by Han et al [5] using different deposition parameters and substrates. Figure 2 shows the XRD spectra of undoped and Cl-doped Cu_2O thin films. XRD peaks are consistent with single phase Cu_2O films. However, the undoped Cu_2O film shows a preferred orientation to yield a strong (220) peak which reduces its intensity to become even with other peaks for the 0.005 M Cl-doped Cu_2O film.

Further increase in the Cl concentration indicates a change in orientation to produce a stronger (200) peak for 0.05 M Cl-doped film. The intensity of the (200) peak reduces for 0.08 M and 0.1 M Cl-doped thin films but remains stronger compared to other XRD peaks in the
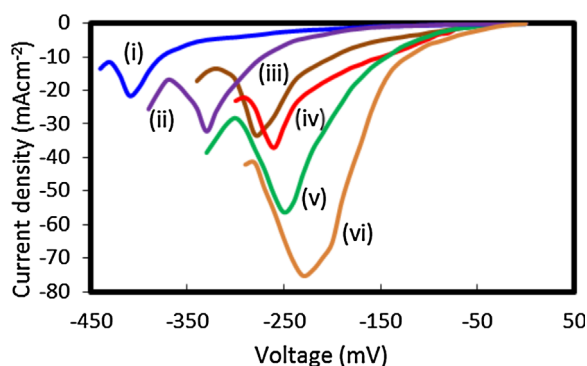

Figure 1 Linear-sweep voltammetry measurements on a Ti substrate for aqueous solutions (pH 9.3) of lactic acid (3 M), cupric sulphate (0.45 M), and NaOH in the presence of (i) 0 M, (ii) 0.005 M, (iii) 0.01 M, (iv) 0.05 M, (v) 0.08 M, and (vi) 0.1 M $CuCl_2$ concentration.
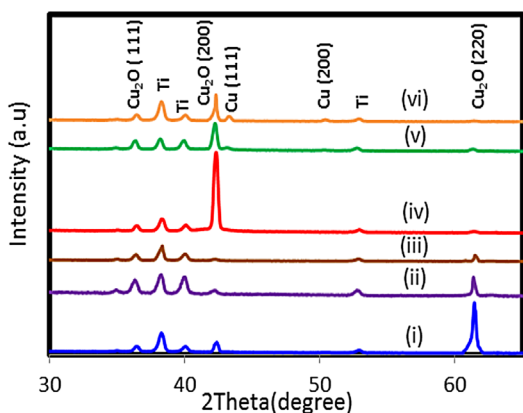
Figure 2 XRD spectra of Cu_2O thin films deposited on Ti substrates for aqueous solutions (pH 9.3) of lactic acid (3 M), cupric sulphate (0.45 M) and NaOH in the presence of (i) 0 M, (ii) 0.005 M, (iii) 0.01 M, (iv) 0.05 M, (v) 0.08 M, and (vi) 0.1 M $CuCl_2$ concentration.

spectra. XRD spectra in (Fig. 2) also show the evolution of peaks due to formation of Cu in the film when the $CuCl_2$ concentration is increased above 0.05 M. The reduction of (200) peaks and the evolution of Cu peaks in the film causes the photoactivity to reduce indicating that best results in the context of photoactivity can be achieved for 0.05 M Cl-doped Cu_2O thin film as shown in (Fig. 4). It can be noted from the higher intensities of Cu_2O peaks compared to those of Ti substrate peaks in the XRD pattern of 0.05 M Cl-doped Cu_2O film that the film contains a thick coverage of polycrystalline Cu_2O making a significant contribution to improved photoactivity. The acceptor/donor concentration (N) can be quantified by the Mott–Schottky equation [11]:

$$\frac{1}{C^2} = \left(\frac{2}{e\varepsilon\varepsilon_0 N}\right)\left[V - V_{fb} - \frac{k_B T}{e}\right], \tag{1}$$

where C represents the capacitance of the space charge

region, ϵ_0 is the vacuum permittivity, ϵ (6.6) [12] is the dielectric constant of Cu_2O, e is the electron charge, V is the electrode applied potential, k_B is the Boltzmann constant, T is the absolute temperature, and N is the acceptor/donor concentration. The temperature term is generally small and can be neglected. The Mott–Schottky plots collected from Cu_2O prepared at different bath Cl concentrations are presented in (Fig. 3a). According to the Mott–Schottky equation (1), a linear relationship of C^{-2} vs. V can be observed. The slopes determined from the analysis of Mott–Schottky plots were used to estimate the acceptor/donor concentration using equation (1). A positive slope indicates an n-type conductivity, while a negative slope points to a p-type behaviour. Mott–Schottky plot for samples deposited at undoped bath showed a negative slope, indicating that the resulting cuprous oxide films were p-type. The samples deposited using Cl added bath gave rise to Mott–Schottky plots having positive slopes, indicating that the resulting films were n-type. Figure 3b shows the electrical resistivity and carrier concentration of Cu_2O films as a function of $CuCl_2$ concentration in the electrolytic bath. The resistivity of undoped Cu_2O films was of the order of $\sim 10^6 \Omega$cm. As shown in (Fig. 3b), the doping caused the resistivity of the films to decrease drastically initially, and then gradually with the increasing concentration of $CuCl_2$ in the solution, that is, by adjusting the Cl concentration in the solution, the resistivity of the Cu_2O film could be controlled. By analysis of the Mott–Schottky curves, it was found that the carrier concentration of cuprous oxide films varied with the Cl concentration of the deposition bath. Figure 3b shows the calculated carrier concentrations of Cu_2O films deposited at different Cl concentrations. As can be seen, with the increasing Cl concentration the carrier concentration increases from 6.1×10^{16} cm^{-3} (undoped films) to 7.62×10^{19} cm^{-3} (at 0.05 M Cl-doped films). Carrier concentration then decreases slightly with increasing $CuCl_2$ concentration due to the formation of Cu, which has been confirmed by the XRD spectra. Simultaneously, the
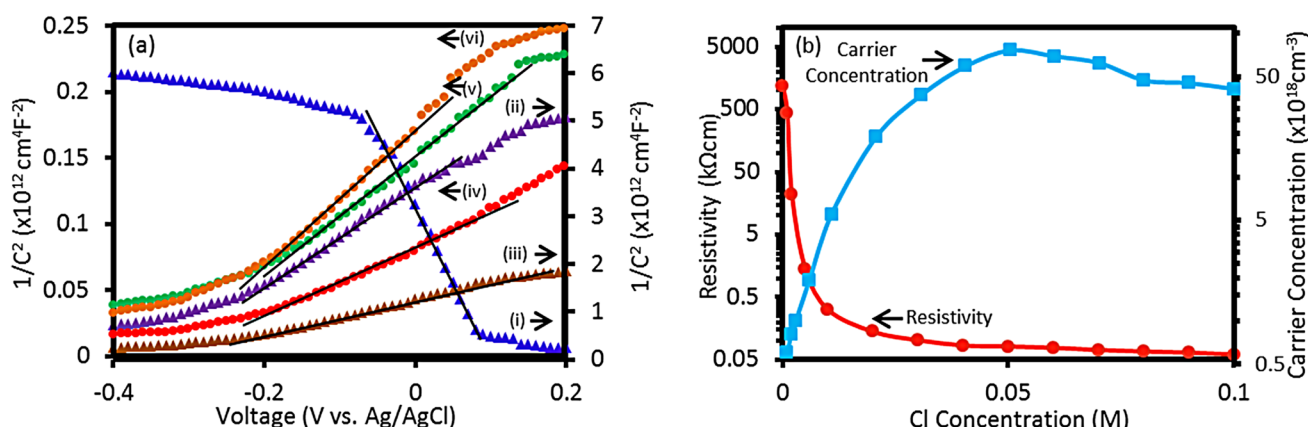

Figure 3 (a) Mott–Schottky plots under dark in a 0.1M NaAc solution at 10 kHz of (i) 0 M, (ii) 0.005 M, (iii) 0.01 M, (iv) 0.05 M, (v) 0.08 M, and (vi) 0.1 M $CuCl_2$ concentrations in the electrolyte. (b) Resistivity and carrier concentration of the Cu_2O films prepared at different $CuCl_2$ concentrations in the solution (direction of the arrow indicates the vertical scale appropriate for each plot.).
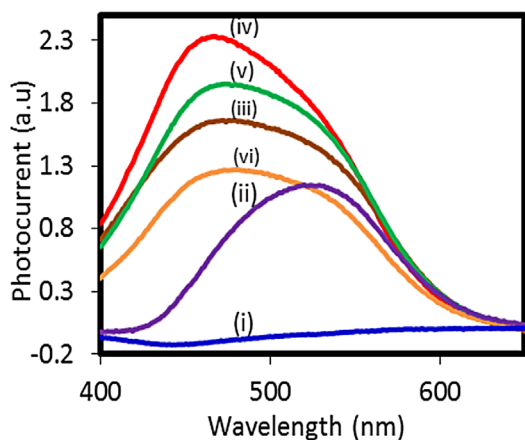
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Figure 4 Spectral response of Cu_2O films in a PEC as a function of (i) 0 M, (ii) 0.005 M, (iii) 0.01 M, (iv) 0.05 M, (v) 0.08 M, and (vi) 0.1 M $CuCl_2$ concentration in the solution.

formation of Cu causes the resistivity to decrease further and the lowest resistivity obtained in this study was 61 Ωcm for 0.1 M Cl-doped Cu_2O film. The spectral response measurements shown in (Fig. 4) show a variation consistent with the carrier concentration, showing the maximum photoactivity at highest carrier concentration in the films. The reduction in resistivity with chlorine doping in this study was achieved with different deposition parameters, compared to those reported earlier by Han and Tao on Cu_2O films deposited on Au substrates [5]. It is an indication that the nature of the substrate also has an effect on the deposition parameters. It can be interpreted that the doping by Cl takes place by replacing the divalent oxygen atoms by the monovalent Cl thus contributing an additional donor electron to the film causing the film resistivity to decrease and the conductivity type to change as shown by the photoreponse measuremnts discussed below. During the measurements, the applied potential was maintained at 0 V versus SCE. Figure 4 shows the spectral response characteristics of the undoped and concentration dependent chlorine doped Cu_2O thin film samples. The negative photoresponse corresponding to the undoped sample further confirms the p-type conductivity of the undoped Cu_2O film sample. However, it can be clearly seen that there is a positive photoresponse for the chlorine doped Cu_2O film samples indicating a reversal of conductivity of the films to n-type. The increasing $CuCl_2$ concentration of the solution increases the positive response resulting in the maximum positive photoresponse at a $CuCl_2$ concentration of 0.05 M. Further increase in the concentration leads to a decreasing but positive photoresponse agreeing with XRD results that show the formation of Cu impurities contributing to the reduction of photoactivity. The formation of Cu impurities in the Cu_2O film at Cl concentrations above 0.05 M can be understood in terms of the reaction kinetics in the deposition bath. At large Cl concentrations, the deposition currents appear to increase causing the rate of deposition to increase. At large deposition rates, the H^+ concentration under the electrode surface microenvironment

increases rendering the generating Cu_2O to reduce further into Cu as explained by the reactions (2) and (3):

$$2Cu^{2+} + H_2O + 2e^- \rightarrow Cu_2O + 2H^+, \qquad (2)$$

$$Cu^{2+} + 2e^- \rightarrow Cu. \qquad (3)$$
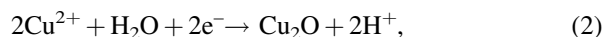
The presence of copper in the film thus degrades the photoactivity of Cu_2O films. The maximum photoresponse measured of 0.05 M Cl-doped Cu_2O film showed an increase in the photoactivity by approximately 20 times compared to that of the undoped Cu_2O film sample. It is believed that the surface morphology and doping concentration of the deposited Cl-doped Cu_2O films on the Ti substrate are the main factors that influence increased photoactivity and thus the light harvesting efficiency. These results are in good agreement with the recent results published by Q. Bai et al [13] where they show, using the first-principles calculations, the existence of Cl on oxygen sites as substitutionals giving rise to an n-type conductivity behavior. Figure 5 shows SEM pictures obtained for a Cl-doped and undoped Cu_2O thin films which show films with good uniform polycrystalline coverage. The gradual reduction of polycrystalline grain size from micro range to nano range with increased Cl concentration from 0.005 M to 0.1 M is noticeable. For undoped Cu_2O samples with the (220) orientation (Fig. 5i), the grains show a triangular prismic shape with grain size of $\sim$ 1 μm. For 0.05 M Cl-doped samples with the (100) orientation (Fig. 5iv), the grain shape changes from triangular prisms to 4-sided pyramids with a 4-fold symmetry. Also the grains have a relatively uniform distribution with an average size of $\sim$ 0.1 μm. Thus the chlorine doping plays a dual role i.e. increasing the photoactivity and decreasing the average grain size of the polycrystalline films even though the presence of Cl is not seen in the XRD data. The morphological changes observed though SEM data in this study are in good agreement with those observed by Wang et al. [14] on electrodeposited Cu_2O thin films. In order to investigate the incorporation of chlorine into the film and the chemical states of the ions present, Energy-Dispersive X-ray Spectroscopy (EDS) and X-ray Photoelectron Spectroscopy (XPS) measurements were made. EDS spectrum in (Fig. 6a) shows the elemental composition of Cl-doped Cu_2O films without showing the presence of Cl in the films due to its low concentration, that is, the Cl concentration is below the detection limit of the EDS technique. The presence of Cl in the films was confirmed by XPS measurements. In the XPS measurements, all binding energies have been corrected for sample charging effect with reference to the C1s line at 284.6 eV. Figures 6b, c, and d show the XPS measurements made on undoped and Cl-doped Cu_2O thin films. Figure 6b shows the Cl 2p spectra obtained for undoped and Cl-doped Cu_2O samples. The presence of Cl 2p peak at the binding energy at 198 eV, is an indication of the presence of 0.8 at.% Cl in the 0.05 M Cl-doped Cu_2O film. The position of this Cl 2p peak was found to be consistent with the values reported in literature [15]. The XPS spectra in (Fig. 6d) show that the
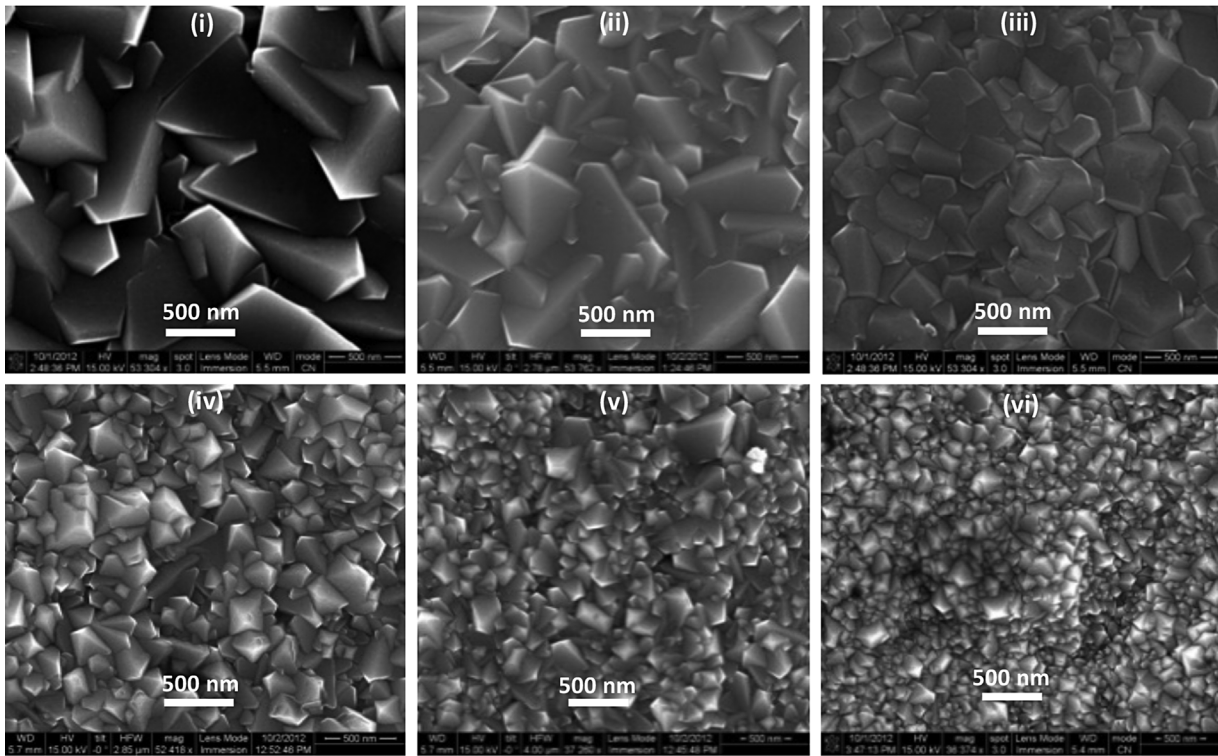
Figure 5 SEM pictures of Cu_2O thin films deposited on a Ti substrate for aqueous solutions (pH 9.3) of lactic acid (3 M), cupric sulphate (0.45 M) and NaOH in the presence of (i) 0 M, (ii) 0.005 M, (iii) 0.01 M, (iv) 0.05 M, (v) 0.08 M, and (vi) 0.1 M $CuCl_2$ concentration.
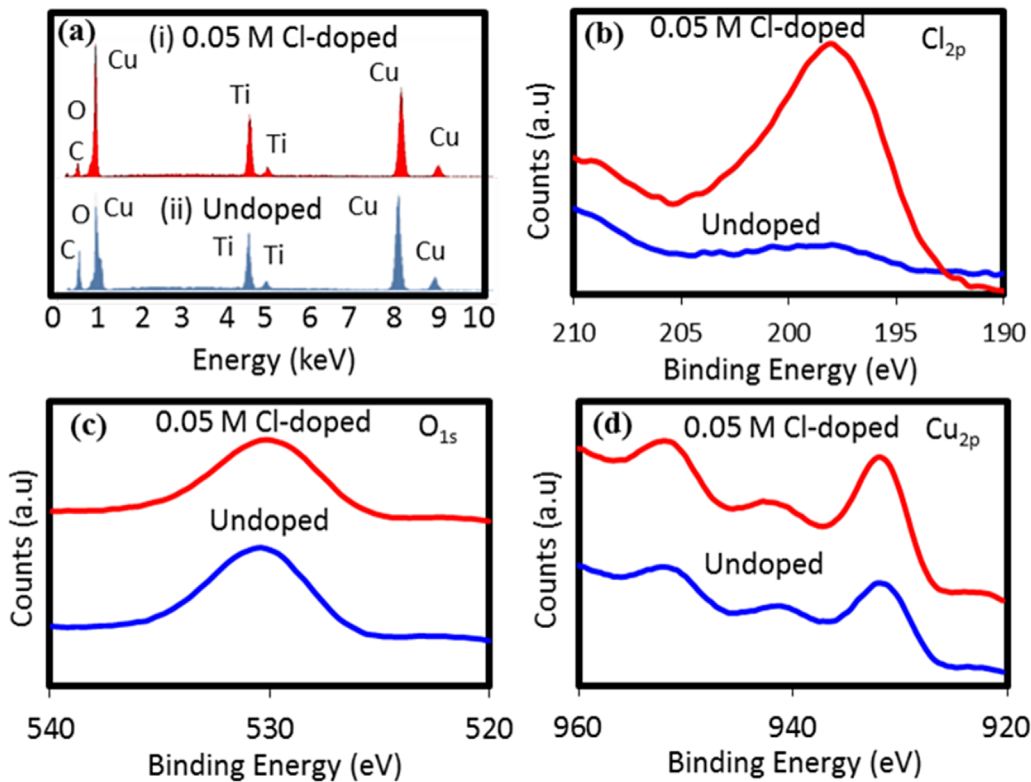

Figure 6 (a) EDS picture and XPS spectra of (b) Cl_{2p}, (c) O_{1s} and (d) Cu_{2p} region core-level peak of 0.05 M Cl-doped and undoped Cu_2O thin film.

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binding energies of the Cu $2p_{1/2}$ and Cu $2p_{3/2}$ are 952.5 and 932.6 eV, respectively, which are consistent with those observed at 952.5 and 932.18 eV [16] for Cu (I) oxidation state. Weak shake-up peaks of Cu (II) were also observed at 962.7 and 942.7 eV respectively indicating the slight oxidation of some Cu (I) ions possibly present on the surface and its vicinity to CuO form. The compositional analysis made using XPS spctra revealed that the Cu/O atomic ratio was about 1.86 for undoped Cu_2O samples and 2.46 for 0.05 M Cl-doped Cu_2O samples. The deviation from normal 2:1 stocheometry of Cu_2O in the undoped and 0.05 M Cl-doped Cu_2O films can be interpreted in terms of Cu and oxygen vacancies available in the samples. Low Cu/O atomic ratio in the undoped Cu_2O thin films is consistent with copper vacancies thus giving rise to p-type conductivity whereas, the high Cu/O ratio in the Cl-doped thin films indicates the existence of oxygen vacancies giving rise to n-type conductivity [17].

4 Conclusions $CuCl_2$ concentration in the deposition bath of lactic acid (3 M) and cupric sulphate (0.45 M) can be optimized to obtain Cl-doped Cu_2O thin films with low resistivity and high photoactivity. As revealed by Linear-Sweep Voltammetry measurements, XRD, SEM, XPS, Mott-Schottky plots, resistivity, carrier concentration, and photoresponse, the optimum concentration of $CuCl_2$ 0.05 M and deposition potential of -275 mV versus SCE resulted in films having an n-type conductivity with a resistivity of $\sim$100 Ωcm and at 30 °C the peak photoactivity increased by a factor of $\sim$20.

References

[1] R. N. Briskman, Sol. Energy Mater. Sol. Cells **27**, 361 (1992).
[2] M. Hara, T. Konda, M. Komoda, S. Ikeda, K. Shinohara, A. Tanaka, J. N. Kondo, and K. Domen, Chem. Commun. **3**, 357 (1998).
[3] H. Zhang, Q. Zhu, Y. Zhang, Y. Wang, L. Zhao, and B. Yu, Adv. Funct. Mater. **17**, 2766 (2007).
[4] T. Minami, Y. Nishi, and T. Miyata, Appl. Phys. Express **6**, 044101 (2013).
[5] X. Han, K. Han, and M. Tao, Electrochem. Solid-State Lett. **12**, H89–H91 (2009).
[6] S. Wu, Z. Yin, Q. He, G. Lu, X. Zhou, and H. Zhang, J. Mater. Chem. **21**, 3467 (2011).
[7] S. Pelegrini, C. I. L. de Araujo, R. C. da Silva, A. D. C. Viegas, and A. A. Pasa, ECS Trans. **31**, 143 (2010).
[8] J.-W. Ci, W.-C. Tu, W.-Y. Uen, S.-M. Lan, J.-X. Zeng, T.-N. Yang, C.-C. Shen, and J.-C. Jhao, J. Electrochem. Soc. **161**, D321–D326 (2014).
[9] W. Siripala, L. D. R. D. Perera, K. T. L. De Silva, J. K. D. S. Jayanetti, and I. M. Dharmadasa, Sol. Energy Mater. Sol. Cells **44**, 251 (1996).
[10] A. Paracchino, J. C. Brauer, J. E. Moser, E. Thimsen, and M. Graetzel, J. Phys. Chem. C **116**, 7341 (2012).
[11] N. Mott, R. Proc. Soc. Lond. A **171**, 27–38 (1939).
[12] E. C. Heltemes, Phys. Rev. **141**, 803 (1966).
[13] Q. Bai, W. Wang, Q. Zhang, and M. Tao, J. Appl. Phys. **111**, 023709 (2012).
[14] L. C. Wang, N. R. de Tacconi, C. R. Chenthamarakshan, K. Rajeshwar, and M. Tao, Thin Solid Films **515**, 3090 (2007).
[15] Y. C. Zhang and J. Y. Tang, Mater. Lett. **61**, 3708 (2007).
[16] M. C. Biesinger, L. W. M. Lau, A. R. Gerson, and R. St. C. Smart, Appl. Surf. Sci. **257**, 887 (2010).
[17] P. Grez, F. Herrera, G. Riveros, A. Ramirez, R. Henriquez, E. Dalchiele, and R. Schrebler, Phys. Status Solidi A **209**, 2470 (2012).