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Development in the Preparation of Cuprous and Cupric oxide Thin Films in the last Decade : A Review

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Abstract: Metal oxide semiconductors have wide applications in technological areas such as electronics, opto-electronics, bio-chemical sensors, coating systems and catalysis.Thisarticle is a review of the preparation and characterisation of cuprous and cupric oxide thin films. This particularly reports the research work done in the past one decade.

Keywords: Cuprous oxide, Cupric oxide, Characterisation

1. Introduction

The two basic requirements for materials to be used for solar cell windows are high optical absorption in the visible range and low electrical resistivity. Synthesis of inorganic nano structures with reliable low cost and well defined morphology have drawn attention for the structural, optical and electrical characterisation and their applications in various fields. Among different metal oxide materials Cu based materials are of great interest because of their applications. Copper oxide has fascinating properties for alternative photovoltaic devices and photo electrodes in high efficiency photo electrochemical cells. It is a semiconductor and also the best absorbing material for photovoltaic devices. To use Cuprous or Cupric oxide in Photo Electro Chemical Cell it should be prepared as a thin film type electrode. A thin layer of Cuprous and Cupric oxide can absorb sun light radiation. For both cuprous and cupric oxide the band gap value is less than 2.5eV. They have high absorption coefficient and photosensitive properties which are well suitable for solar cells. Further, these Copper oxides have low toxicity and good environment acceptability and their constituents are cheap and plentiful in nature. These properties make Cu-O compound the best absorber layers in photovoltaic devices. Hence, the Copper oxide thin film is advantageous for the photovoltaic applications.

2. A Review on Cuprous and Cupric Oxide Thin Film Preparation

Wang,L., 2006, prepared Cu_2O with copper sulphate and lactic acid. The lactic acid was to stabilize Cu (II) ions at a bath pH higher than 7.0. He observed that the growth rate of the film depended on the deposition time at a constant temperature of 60˚C and a constant pH of 9.0, 10.0 and 12.5. He also observed that if deposition time increased the growth rate would decrease because the effect on conductivity in the cell by indium tin oxide was replaced by a less conductive material i.e. Cu_2O. Also, he prepared both n and p type cuprous oxide thin films.Wijesundera et al., 2006, investigated the potentiostatic electrodeposition of cuprous oxide and copper thin films. Electrodeposition was carried out in an aqueous solution containing sodium acetate and cupric acetate. The results of their investigation show that the single phase polycrystalline Cu_2O can be deposited from 0 to -300 mV vs SCE. Also, the co-deposition of Cu and Cu_2O started at -400 mV vs SCE. At the deposition potential from -700 mV vs SCE a single phase Cu thin films were produced. Single phase polycrystalline Cu_2O thin films with cubic grains of 1–2 μm could be possible at the deposition potential around –200 mV (SCE).Akimoto et al., 2006, prepared Cu_2O on glass substrate by reacting magnetron splitting method. Diwakar et al., 2006, prepared CuO thin film for photo electro chemical splitting of water. He observed that the optical band gap varies from 1.72-1.79eV. The films prepared at low sintering temperature (400-500°C) yield higher photo current and are efficient for photo splitting of water. He also observed that the resistivity increases with thickness and observed that the thicker films are less effective in photo conversion.Mahalingam et al., 2006, developed Cu_2O thin film by cathodic reduction of copper II lactate solution at a potential of -0.555 V Vs SCE, at a bath pH9 and at a bath temperature 70°C.

Longcheng and Meng, 2007, electrochemically deposited Cu_2O by varying solution pH and produced p-n homojunction of Cu_2O.Mattew J. Siegfried et al., 2007, prepared CuO by anodic deposition in acidic media of copper acetate (pH5.5-6.4). The band gap and flat band potential are estimated to be 1.37eV and 0.26V in a 0.1M Na_2HPO_4 solution with pH9.2. Guo et al., 2007, electrodeposited Cu_2O microcrystals. A perfect Cu_2O octahedral and mono disperse colloid spheres were obtained. Wang et al., 2007, cathodically electro deposited cuprous oxide films from 0.4 M copper sulphate bath containing 3 M lactic acid. The bath pH was carefully adjusted from 7.5 to 12.0 by controlled addition of 4 M NaOH. The electrodeposition was done on Sn-doped indium oxide substrates. The influence of electrodeposition bath pH on grain orientation and crystallite shape was examined. Authors found that three orientations, namely, (100), (110), and (111) dominate as the bath pH is increased from ~ 7.5 to ~ 12.Singh et al., 2007, synthesized cuprous oxide nanostructures by anodic oxidation of copper through a simple electrolysis process employing plain water as an electrolyte. No special electrolytes, chemicals, and surfactants were used. Platinum was taken as cathode and copper as anode.

Sumy et al., 2008, deposited Cu_2O on stainless steel substrate at pH12 and obtained triangular pyramidal morphology and when pH>14, crystallites are with octahedral morphology. If pH≥12, a single phase Cu_2O coating oriented in the (111) direction was obtained. Also, he observed that Cu_2O is stable only in the potential range -0.30V to -0.50V and at high pH. Jeyathileke et al., 2008, prepared n-p and p-n homojunction cuprous oxide thin film in aqueous acetate bath. He observed that conductivity type of the film depends on pH and also the cupric ion concentration.

Jayatissa et al., 2009, prepared cuprous oxide (Cu_2O) and cupric oxide (CuO) thin films by thermal oxidation of copper films coated on indium tin oxide (ITO) glass and non-alkaline glass substrates. The formation of Cu_2O and CuO was controlled by varying oxidation conditions such as oxygen partial pressure, heat treatment temperature and oxidation time. The experimental results suggest that the thermal oxidation method can be employed to fabricate device with good quality Cu_2O and CuO films.Hu et al., 2009, electrodeposited Cu_2O thin films on an indium tin oxide (ITO) coated glass by a two-electrode system with acid and alkaline electrolytes under different values of direct current densities. Copper foils were used as the anodes, and the current density between the anode and cathode varied between 1 mA cm^{-2} and 5 mA cm^{-2}. It was obtained that the microstructure of Cu_2O thin films produced in the acid electrolyte changes from a ring shape to a cubic shape with the increase of direct current densities. The micro structure of Cu_2O thin films produced in the alkaline electrolyte has a typical pyramid shape. The electro crystallization mechanisms were considered to be related to the nucleation rate, cluster growth, and crystal growth. Different current densities with the same deposition time were applied to investigate the initial stage of nucleation and cluster growth.Mc Shane et al., 2009, observed obvious photocurrent enhancement of n-type Cu_2O films by controlling the dendritic branching electrochemical deposition growth. Han and Tao, 2009, found that n-type Cu_2O deposited in a solution containing 0.01 M copper acetate and 0.1 M sodium acetate exhibits higher resistivity than p-type Cu_2O deposited at pH13 by two orders of magnitude. Kunhee and Meng, 2009, also produced p-n homojunction Cu_2O solar cell. It has efficiency only of 0.1% due to high resistivity of p and n Cu_2O layers.

Aiping Chen et al., 2010, prepared Cu_2O and CuO on Si substrate by pulsed laser deposition and studied the structural and optical characteristics. Swarup Kumar et al., 2010, fabricated nano sized CuO film and found that the band gap is 3.1 eV and confirmed that the increases in band gap is due to quantum confinement effect resulting from decrease in the dimension of structure and the size. Mahalingam et al., 2010, prepared CuO on ITO by electrodeposition and studied the effect of deposition potential on the physical properties. Wijesundera et al., in 2010, electrodeposited single-phasic Cu_2O on Ti/CuO electrodes in an aqueous solution containing 0.1 M sodium acetate and 0.01 M cupric acetate in the potential range of -250 to -550 mV/SCE. Well-covered photoactive n-type Cu_2O thin films were electrodeposited on the Ti/p-CuO electrode at -550 mV vs SCE in similar electrolytic conditions in which Cu_2O was deposited on the Ti substrate. It was concluded that the thicknesses of the CuO and Cu_2O semiconducting layers and annealing of the CuO/Cu_2O hetero-junction played a major role in enhancing the photoresponse in the PEC water splitting.

Wenyan et al., 2011, electrodeposited Cu_2O and studied its photo electrochemical properties. He studied the variation of deposition potential with crystal growth and observed that when deposition potential is more negative the particle size decreases. Rajani, K. V et al., 2011, reported on the direct formation of Cu_2O by microwave plasma oxidation of pulsed dc magnetron sputtered Cu films. The grain size was found to be from 20 to 30 nm and the resistivity around 66 ohm cm. Also the optical absorption coefficient value is around 10^5/cm for Cu_2O film.Wijesundera, 2011, electrodeposited Cu_2O thin film for fabrication of CuO/Cu_2O heterojunction using an electrodeposition technique for solar cell applications and he observed that resistivity was high and of the order of 10^4 to10^6 ohm-cm. Wilman et al., 2011, fabricated Cu_2O/Al-doped ZnO heterojunction solar cell on FTO coated glass plate. The highest efficiency of 0.6% was obtained with a Cu_2O film deposited at -0.6V vs Ag/AgCl. Also they obtained open circuit voltage of 0.29V, short circuit current density of 7.12% and a fill factor of 0.292. This was attributed to better compactness and purity of the Cu_2O film than those of the Cu_2O films deposited at other potentials. Wilman Septina et al., 2011, developed Cu_2O thin film and found that the grain size decreases as the potential increases and was due to frequencies of nucleation of Cu_2O crystals during deposition that tends to be higher when the applied potential becomes more negative. Mohd Rafie Johan, 2011, found that the band gap of CuO is in between 1.21eV and 1.51eV and Cu_2O, between 2.10 eVand 2.60 eV.A.N.

Ahmad Rahnama et al., 2012, prepared CuO nanoparticles via simple precipitation method at different reaction temperatures. They observed that the crystalline size and crystallisation increased with the increase in the temperature from 10 to 115°C. The band gap of the samples was calculated to be in the range of 1.9 eV to 2.9 eV. Ezenwa, 2012, deposited CuO on glass substrate by chemical bath deposition using copper sulphate and EDTA. He found that the optical band gap was about 1.7eV. Also he obtained the absorption approximately of 0.87 at the wavelength range of 300-320 nm. Jundale, 2012, synthesized CuO by sol-gel using cupric acetate and methanol. They also calculated that the conductivity varies from 10^{-6} to 10^{-5} (ohm cm)$^{-1}$. Sadeghi, 2012, prepared copper oxide thin film by PVD on glass substrate at 90 nm thickness and post annealing at different temperature 200-400°C. The band gap varies from 1.8 eV to 2.56 eV.Paula Grez et al., 2012, electrodeposited n-Cu_2O on fluorine-doped tin oxide pre-deposited glass substrates from aqueous solution of Cu (II) acetate. The potential applied was -0.450V vs SMSE at 70°C. They obtained high crystallinity cubic Cu_2O and a strong preferential growth along the (200) and (220) directions. Hiroki Kidowaki et al., 2012, fabricated CuO/ZnO and ZnO/CuO heterostructures on indium tin oxide by electrodeposition. They used copper sulphate and lactic acid and the pH of the solution was adjusted to 12.5 by NaOH. The solar cell with a CuO/ZnO structure provided power conversion efficiency (η) of 1.1×10^{-4} %, fill factor (FF) of 0.25, short-circuit current density (Jsc) of 1.9 mAcm^{-2} and open-circuit voltage (Voc) of 2.8×10^{-4} V. The optical absorption of CuO is in the range of 400 to 700 nm and the crystal size was found to be 49 nm.Zainelabdin et al., 2012, prepared CuO/ZnO nanocorals p-n heterojunction on ITO substrate at low temperature of 60°C. The contact resistance of Au and ITO to CuO and ZnO were found to be about 3.2×10^{-3} ohm and 1.7×10^{-3} ohm respectively.Wei et al., 2012, fabricated p/n type Cu_2O films by electrochemical deposition using different electrolytes and optimising pH level. The growth rate of n-Cu_2O was tuned from (100) to (111) by decreasing the applied potential and the growth of p-Cu_2O was grown over the layer with the same (111) orientation that facilitated the formation of a homojunction with high quality interface.

Laxmi, J et al., 2013, studied the optical properties of hydrothermally synthesized Cu/Cu_2O/CuO nanocrystals. The average crystallite size of the sample was found to be around 27 nm. The absorption spectra show two broad peaks situated at 354 nm and 466 nm respectively and each absorption peak corresponds to two different phases. The absorption in the visible region of the spectrum gave evidence of the presence of oxygen. The optical band gap was calculated by Tauc's plot. Two different band gaps corresponding to two different phases, Cu_2O and CuO were evaluated for each sample. Cetinkaya et al., 2013, fabricated CuO/p-Si Schottky diodes by CBD and sol-gel methods and studied its characterization. They observed that the film grown by CBD is denser than the film grown by sol-gel method and found that the average size of CuO particle is approximately equal to 15 nm.

Xishun Jiang et al., 2014, electrodeposited Cu_2O nanocrystalline thin film on Ti substrate using sodium acetate and cupric acetate for different potentials (-0.1, -0.3, -0.5,-0.7, and -0.9 V) and studied its optical properties. Electrodeposition was carried out under potentiostatic condition at different applied potentials (-0.1, -0.3, -0.5,-0.7, and -0.9 V) with respect to the reference electrode. The optical band gap value varies from 1.69 eV to 2.03 eV.Chen et al., 2014, deposited Cu_2O thin film by chemical bath deposition and studied the influence of deposition temperature on growth process. They used copper sulphate as the copper precursor. The crystal size varies in the range of 33-51nm and the band gap varies from 2.47 eV to 2.61 eV when the deposition temperature is in the range of 60-90°C. Also the UV-Vis absorption spectra show a blue shift.

3. Conclusion

According to the review on the fabrication of copper oxide thin film, it is observed that different methods and different precursors were used to fabricate Cu_2O. Hence, this article may serve the need of the future researchers who involve in developing copper oxide thin films that can well be used as an absorbing layer in Solar cell.

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