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Review Paper:

A short review of recent advances in copper oxide nanostructured thin films

Ho Soonmin[1*] and Emmanuel Ajenifuja[2]
1. Centre for Green Chemistry and Applied Chemistry, INTI International University, Putra Nilai, 71800, Negeri Sembilan, MALAYSIA
2. Department of Chemical, Metallurgical and Material Engineering, Tshwane University of Technology, Pretoria 0183, SOUTH AFRICA
*soonmin.ho@newinti.edu.my

Abstract

In recent years, there has been appreciable interest in the experimental studies of metal oxide thin films, owing to their excellent optical and electrical properties. Generally, there are two major groups of copper oxide, namely cupric oxide (CuO) and cuprous oxide (Cu_2O) based on the X-ray diffraction data. Researchers have observed that these films are of chemical stability, non-toxicity and undergo low cost production process. Therefore, copper oxide films are often employed in solar cells, cathode in lithium primary cell, gas sensor, electro chromic devices, super capacitor, field effect transistor and electronic device fabrication.

In this work, characteristic of obtained copper oxide films was investigated by using various tools as reported by many scientists. Experimental results showed p-type semiconducting material with band gap from 1.46 to 2.6 eV.

Keywords: Thin films, solar cell, copper sulphide, semiconductor, optoelectronic application.

Introduction

A layer of material prepared on a suitable substrate with thickness ranging from fractions of a nanometer to hundreds of micrometers[1-3] is usually regarded as a thin film. The material and preparation technique of thin films depend on the targeted application[4-6]. Among others, thin films can be synthesized in different forms such as pure metal, alloys, oxides and nitrides. Thin film can be transparent or opaque which strongly depended on film thickness. Thin film preparation is an important process in many applications. Familiar examples of household items made from thin film deposition process are compact discs, mirrors and reflective window-panes. Recent advances in thin film deposition techniques[7-9] have brought about a lot of technological breakthroughs in different areas such as optoelectronics, magnetic recording media, semiconductor devices, light emitting diode, optical coatings, solar cells and tribology.

Thin-film deposition is the process of preparing a thin film or layer on a surface[10-12]. The surface herein referred to could be a blank substrate, any previously deposited layer on a rigid or flexible support. Due to their dimensions, most thin films cannot stand alone, but on suitable substrates. The choice of substrate[13-15] depends on the deposition technique and proposed application of the thin film. Different substrates are used such as soda lime glass, fluorine doped tin oxide, quartz glass, indium tin oxide, silicon wafer, stainless steel and microscope glass slide.

Deposition techniques fall into two broad categories[16-19] based on whether the process is primarily chemical or physical[20]. Chemical deposition mostly involved a fluid precursor which undergoes a chemical change at a solid surface (substrate), leaving a conformal solid layer. Meanwhile, physical deposition uses thermodynamic, electromechanical, or mechanical means to produce a rather directional thin film of solid. For example, in optoelectronics materials synthesis, both physical and chemical processes are mostly used including ion beam deposition, pulse laser deposition, sputtering[21-23], molecular beam epitaxy, atomic layer deposition, spray pyrolysis[24-27] and Langmuir-Blodgett method.

In this work, the synthesis of copper oxide thin films by using various deposition techniques was studied. The obtained experimental findings were highlighted based on the literature review.

Review of Literature

Optoelectronic is the field of technology concerned with electronic device application to the sourcing, detection and control of light. It encompasses the design, manufacture and study of electronic hardware devices that, as a result, converts electricity into photon signals or vice versa for various purposes. Presently, there is an abundance of optoelectronic devices that are used in many applications. These devices include light-emitting diodes, laser diodes, photodetectors, solar cells, optical amplifiers and modulators. With these components, it is possible to generate, modulate, detect and switch photons in an analogous way to electrons in an electrical circuit.

Transparent conducting oxides (TCO) are well known and have been widely used for a long time in optoelectronics industries as well as in research fields. TCOs are used extensively in solar cells, flat panel displays, low-emissivity windows, cathode-ray tubes, electrochromic materials, oven windows, touch-sensitive control panels, defrosting windows in refrigerators and airplanes, invisible security circuits, gas sensors, biosensors, organic light emitting diodes, polymer light emitting diodes, antistatic coatings and cold heat mirrors. In optoelectronics, quantum mechanical effect of light is used on materials in electronic devices such as semiconductors. These effects are photovoltaic, photoconductivity, stimulated emission and radiative recombination.

Copper oxide thin film is an inorganic compound material (as a semiconductor of interest); it has been studied for more than three decades because of the abundance of the constituent elements and its unique properties leading to diverse applications. It is a black solid in bulk form, the Cu-O system forms two well-known oxides: cupric oxide (CuO) and cuprous oxide (Cu_2O) which are red or slightly yellow. Both CuO and Cu_2O films are generally believed to be *p*-type semiconductors having band gap energies in the visible and near infrared regions[28]. Copper oxide has been widely studied for various potential applications such as in lithium ion electrodes[29], sensors[30], high critical temperature superconductors, field emission emitter[31], photocatalyst, resistive switching[32] and also be employed as a solar absorber in solar cell application.

Raksa and co-workers[33] employed CuO as a barrier layer in dye sensitized solar cells as well as improving the grain size of spin-coated ZnO-CuO composite. CuO film has been touted as an efficient selective solar absorber because of its high solar absorbency and a low thermal emittance[34]. Studies have shown that Cu_2O film could be very promising candidate for solar cell applications as well[35,36]. Several deposition techniques have been applied to produce copper oxide films[37-40]. On the other hand, these films have been widely used in lithium batteries due to appropriate band gap value and high optical absorption coefficient.

The behavior of copper oxide thin films such as n-type or p-type mainly depended on the preparation technique, starting raw materials as described by many researchers[41-43]. Studies have shown that the simple deposition techniques such as dip, chemical bath and spray pyrolysis can be used to synthesize CuO films in a simple manner (by using metallic chlorides ($CuCl_2.2H_2O$) as a starting material). Also, copper oxide films have been prepared using a methanolic solution of cupric chloride ($CuCl_2.2H_2O$) in order to study the effects of precursor solvents on the properties of the CuO thin films. The precursor solutions were prepared with ethanol and deionized water at 0.1 M concentrations by dissolving 2.56 g of the salt ($CuCl_2$) in 250 ml of distilled water.

Stoichiometric and microstructural properties of thin films are very important parameter to be considered especially for optoelectronic application. This is because it has direct effect on their interaction with photon (both emission and absorption). Results from structural analyses of copper oxide thin films have presented a favorable disposition for their functionality. Johan and co-workers[28] reported that there was a phase change in cuprite (Cu_2O) thin film to tenorite (CuO) after annealing up to 400 ºC. Meanwhile, the copper oxide thin films annealed at 300°C coexist in two phases (CuO and Cu_2O). For the sample annealed at 400°C, the XRD pattern shows two broad peaks near $2\theta^o = 35.5$ and 38.7° which correspond to the reflections from (-111) and (200) planes respectively (attributed to CuO structure which correspond to a complete evolution of the thin film from Cu_2O to CuO).

Furthermore, morphology investigation revealed that dense spherical and granular structures with no visible defects could be observed. Hence, it is appropriate to regard the crystallites that appeared in images as fragmented grain agglomerations formed with rise in annealing temperature[44]. Notwithstanding, single phase Cu_2O thin films with cuprite structure can be easily obtained by using chemical deposition method.

Optical spectroscopy is the general method for characterizing directly and indirectly the optoelectronic properties of coatings and thin films. Properties such as reflectance, absorbance and transmittance are obtained directly in the region of the electromagnetic spectra. The analysis of transparent conductive coatings needs broader electromagnetic spectra (wavelength range). For example, a typical optoelectronic device, solar control coating or film allows transmission of light in the visible wavelength range but reflects the heat from the near infrared wavelength region to reduce the cooling costs.

Szczyrbowski and co-workers[45] reported that the electrical conductivity of a coating is directly related with its emissivity. Therefore, the amount of heat transfer can be determined by measuring the electrical conductivity of the coating and its spectral reflection in the far infra-red range.

Transparent conducting oxide, CuO thin films were prepared by sol-gel using spin coating method[46]. They found that the optical band gap increased with decrease in the spin coating speeds. This is attributed to shifts in the absorption edge of the CuO films (crystallite size evolutions). However, these results do not agree readily with results reported by Halin and co-workers[47] which indicated an increase in the particle of film microstructure with spinning speed. The discrepancy could be due to other factors such as precursor molarity. It was shown that the decrease in films grain size with increasing spinning rates will contribute to the reduction in optical transparency through scattering phenomenon.

Meanwhile, the study on the variation of optical absorbance with annealing temperature showed that as-deposited CuO film has low absorbance in the visible region, which is the characteristic of CuO. But, after annealing, the absorbance was shifted towards higher wavelengths, which may be due to the molecular water removal after annealing. Correspondingly, the band gap value[44] is found to decrease from 1.64 to 1.46 eV with increasing annealing temperature from 300 to 700 ºC. The lowering of the bandgap value indicates an improvement of the quality of the film because of annealing out of the structural defects and decrease in grain boundary density.

Table 1
Copper oxide thin films have been prepared using various deposition techniques.

References	Characteristics of films
Sreeju et al[48]	• CuO was synthesized using precipitation technique. • TG-DTA: Desorption of physically adsorbed water from 50-220 °C • TG-DTA: Removal of chemisorbed water (220 to 330 °C) • TG-DTA: Thermal decomposition of $Cu(OH)_2$ to CuO from 330 to 554 °C • TG-DTA: complete decomposition at 554 °C • TEM: Elongated spherical nanoparticles with average diameter (36.6 nm) • Magnetic studies: displayed antiferromagnetism • PL studies: Wavelength of 403 nm could be detected in the annealed films (at 600 °C for 120 minutes)
Sahu et al[49]	• Thermal evaporation technique was used to prepare CuO films • FESEM: Significant changes in the average size of films with change in annealing temperature from 400 (51 nm) to 600 °C (293 nm). • FESEM: RMS surface roughness was observed to be 1.8 (as-deposited film), 29.7 (annealed film at 400 °C) and 5.2 nm (600 °C). • Photocatalytic studies: The best photo catalyst could be seen in the annealed film (at 400 °C) and degraded methylene blue (2 hours) and malachite green (160 minutes) easily.
Saucedo et al[50]	• CuO film was prepared using dip coating technique • The thickness of as-deposited film to be about 49-270 nm when the number of coats varied 5 to 14. • Cu_2O film was obtained under rapid thermal annealing treatment in vacuum, 10 minutes, at 450 °C. These films have low resistivity and better crystalline if compared to as-deposited films. • Cu_2O/Cd_2SnO_4 diodes were fabricated and the electrical parameters such as turn-on voltage (V_{to}=1.1 V), ideality factor (n=4.8), saturation current density (J_0=3.2X10^{-5}A/cm^2) were investigated.
Martinez et al[51]	• Average thickness of CuO films prepared using dip-coating method from copper (II) acetate (as precursor) was 240 nm [53]. • The transformation of CuO to Cu_2O film was strongly depended on the rapid thermal annealing process. • The XTD patterns revealed that different structures for the films treated at less than 375 °C (CuO & Cu_2O), 375, 400 °C (Cu_2O) and more than 425 °C (Cu_2O and Cu). • Cu_2O films could be used in solar cell application due to band gap (2.36 eV), optical transmission (75 % for wavelength more than 520 nm), p-type semiconductor, resistivity of 99 Ω.cm, mobility of 0.52cm^{2}V^{-1}s^{-1}.
Chtouki et al[52]	• CuO films were prepared via sol gel method using different precursors such as copper acetate and 2-methoxy-ethanol [54]. • XRD: The obtained CuO films are polycrystalline with the several peaks such as at 31.8°, 35°, 38° and 53°. • SEM: Larger grain size could be observed as the number of deposited layers was increased from five (100 and 200 nm) to seven (200 and 300 nm). • Optical studies: Decrease in the band gap from 1.67 to 1.56 eV, with increasing the number of deposited layers (from five to seven).
Tian et al[53]	• XRD: Composition of CuO and Cu_2O strongly depended on the atmosphere such as oxygen and argon. • SEM: Better crystallinity and bigger particle size could be observed with the increase of Ar/O_2 conditions. • XPS: Peaks at 943 and 962 eV represented Cu^{2+}. While 529 eV contributed to O 1s peak.

	• The films prepared under Ar/O$_2$ ratio 30:7 exhibited the best semiconductor properties, biggest impedance value, excellent photo electro chemical performance
Moumen et al[54]	• CuO films were produced by using spray pyrolysis technique. • These films could be applied in solar cell due to low transmittance (from 30 % dropped to 5 % with temperature increasing from 300 to 375 °C), high absorbance, small bang gap value (1.53 eV). • Acetone sensor was designed and investigated. The good sensing properties were highlighted including determined response (33 %), response and recovery times (160 and 360 seconds).
Xu et al[55]	• CuO films were synthesized using sol gel method. • SEM: the grain size was increased from 4.1 to 39.2 nm when the number of coated layer was increased. • XRD: All samples showed pure monoclinic phase and two peaks [(002) and (111)] were detected. • Optical studies: The band gap reduced (from 2.51 to 1.56 eV) and the absorbance value increased as the film thickness increases
Attieh et al[56]	• The influence of deposition time on the properties of CuO on glass substrate using RF magnetron sputtering was investigated. • Film thickness (minimum 160 nm) exhibited excellent photocatalytic activity. These films are very stable and could be applied for the degradation of methylene blue from wastewater. • XRD: Deposition times of 600, 1200 and 1800 seconds provided crystal size of 6.67, 8.87 and 9.09 nm. • Optical studies: the reducing in band gap (2.2 to 1.73 eV) with increasing film thickness (160 to 490 nm)
Hoa et al[57]	• The effect of concentration of copper ion on the properties of films was studied by using spin coating method. • XRD: All the films show polycrystalline and two significant peaks [(002) and (111) plane]. • XRD: Average particle size was found to be increased from 28.4, 40.4 and 48.6 nm, as the concentration of copper ion was increased. • Optical studies: The films prepared using lower concentration of copper ion (0.15 M) produced higher band gap energy (2.15 eV), if compared to 0.25 M (2.1 eV). • These films could be used in solar cell due to minimum resistivity (0.085 Ω.cm), absorption length (99 nm) and absorption figure of merit (12.79 $Ω^{-1}$.cm^{-1}.).
Reza et al[58]	• CuO films were synthesized using sputtering method. • SEM, XRD: Better crystallinity and morphology structure could be achieved for the films prepared under higher sputtering power and temperature. • The best experimental conditions for photocatalytic degradation of organic pollutant was using 300 W and 300 °C.
Sangwaranatee et al[59]	• The influence of the oxygen flow rate on CuO films produced by reactive magnetron sputtering was investigated. • The reduce in the deposition rate from 10.9 to 6 nm/s when oxygen rate was increased (5 to 20 sccm). • The obtained films could be applied in solar cell because of transmission value (about 37 % in the visible region) • FESEM: The films prepared at lower oxygen rate indicated small grain and smooth surface if compared to higher oxygen rate.
Othmane et al[60]	• SILAR method was used to prepare CuO films. • XRD: The bigger crystallite size (10-24 nm), smaller dislocation densities (10 to 1.74 x 10^{-3}nm^{-2}) and strain (3.43 to 1.42 x10^{-3}), indicating the films are better crystallization as the number of deposition cycle was increased from 30 to 50 cycles. • EDX: The presence of copper (25.7 to 41.5 %) and oxygen (74.2 to 58.5 %) in all samples.

Yahya et al[61]	• Magnetron sputtering was applied to prepare CuO films • Raman spectroscopy: The presence of different structures depended on oxygen flow rates such as 8 (Cu_4O_3), 9 (Cu_2O, $Cu4O_3$), 10 (Cu_2O, $Cu4O_3$), 15 (Cu_4O_3), 17 sccm (CuO). • PCE: The films prepared using oxygen flow rate of 8 sccm (0.04 %) have the highest power conversion efficiency if compared to 9 (0.012 %), 11 (0.002 %) and 13 sccm (0.009 %).
Yahya et al[62]	• Microwave activated reactive sputtering method was used to prepare Cu_2O, CuO and Cu_4O_3 films. • SEM: The thickness was confirmed for the films prepared under different oxygen flow rates such as 10 (454 nm), 14 (458 nm) and 17 sccm (479 nm). • XRD: CuO is the dominant under oxygen flow rates of 17 sccm or greater. However, the present of Cu_2O and Cu4O3 could be detected at oxygen flow rate (11 to 16 sccm)
Jeung et al[63]	• p-type Cu_2O thin films were prepared using sputtering method onto glass substrate. • XRD: As-deposited films exhibited prominent peak at (111) plane. XRD peak intensity was reduced with increasing oxygen partial pressure. • The annealed films (550 °C) have the highest Hall mobility value (61 cm^2/Vs).
Nafarizal et al[64]	• CuO and Cu_2O films were formed due to the high and low density of oxygen in the plasma. • The thickness and deposition rate were reduced rapidly as the oxygen flow ratio was more than 7 %. • Transition from cuprous oxide to cupric oxide can be represented by $Cu_2O + \mathit{1/2}O_2$ to produce 2CuO.
Sangwaranatee et al[65]	• Glass slide and silicon wafer were applied as substrate during the preparation of CuO film using dc reactive magnetron sputtering. • XRD: All the films prepared under various operating pressures showed monoclinic with two major peaks (with (111) and (002) plane). • Optical studies: Absorbance value reduced with increasing operating pressure • The luminous transmittance was observed about 20-50 % in the visible region for all samples.
Cong et al[66]	• TEM: Images of the annealed films indicated porous film (diameter 50-150 nm), polycrystalline structure, lattice spacing (0.316-0.343 nm). • Gas sensing: Response of 3.3 to 500 ppm ethanol gas was observed (at 250 °C) with rapid response and recovery time (52 & 42 seconds). • The sensor response increases (1.3 to 3.3) with increasing ethanol gas concentration from 10 to 500 ppm.
Jamal et al[67]	• Spray pyrolysis was used to synthesize copper oxide films onto silicon (111) substrate. • XRD: The obtained films are polycrystalline, with monoclinic phase (a=4.68Å, b=3.417Å, c=5.122Å, β=99.78°) • Optical studies: transmittance increased in visible and infrared region. • Gas sensing: Results showed that CuO films indicated a fast response of 15 seconds and recovery time (21 seconds) with sensitivity of 16% at temperature of 150 °C if compared to 30 °C (25 % - sensitivity) and 100 °C (16 % - sensitivity). • Higher sensitivity value makes this sensor to detect the lower gas molecule concentration on the surface.
Avila et al[68]	• Dip coating method was used to prepare Cu_2O and CuO films. • XRD: The principal phase such as CuO (230 °C) and Cu_2O film (260 °C and above) at different temperatures. • FTIR: Peaks at 3660-2690 cm^{-1} represented OH, NH, CH_2 vibration; 1561 cm^{-1} attributed to COO^- asymmetric stretching and CN stretching; 1402 cm^{-1} contributed to symmetric C=O stretching.

Table 1 shows the characteristics of copper oxide thin films reported by many researchers. The experimental results supported that these films could be used in solar cell, gas sensor and optoelectronic device.

Conclusion

In this report, we presented the preparation of CuO and Cu_2O films by using various deposition methods. The obtained films could be used in gas sensor, solar cell and optoelectronic devices as reported by different researchers. Better crystallinity and morphology surface could be observed in annealed films if compared to as-deposited films. The p-type semiconducting materials with band gap values ranged between 1.46 to 2.6 eV have been described.

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