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Optical characterization of Copper Oxide thin films prepared by reactive dc magnetron sputtering for solar cell applications

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Abstract: Cu2O thin films have been deposited using reactive dc magnetron sputtering technique using an Edward Auto 306 Magnetron Sputtering System. Transmittance and reflectance data in the range 300 nm-2500 nm were obtained using UV-VIS NIR Spectrophotometer Solid State 3700 DUV for all the thin films samples that were prepared. Transmittance values of above 70% were observed. The optical measurements were simulated using SCOUT 98 software to determine optical constants and optical bad gap of the thin. The optical properties in these films were varied by varying oxygen flow rate at constant powerof 200 W. Optical studies show a direct allowed transition and a shift in the optical absorption edge as the oxygen flow rate varies at constant argon flow rate and other deposition parameters. These results show that single phase Cu2O thin films can be synthesized at a relatively low substrate temperature using the reactive dc magnetron sputtering technique. Band gap values of 1.62 eV –2.54 eV is observed. The surface sheet resistivities at room temperature of 298 K were found to vary with the deposition parameters and film thickness. Urbach energy varied between 0.6 ×10-4 to 1.92 ×104.

Keywords: Cuprous Oxide; thin films; Optical properties; dc magnetron sputtering technique; solar cell applications

1. Introduction

Copper Oxide is an attractive material for photovoltaic applications. It is naturally a p- type semiconductor due to negatively charged Copper vacancies with a direct band gap of approximately 2 eV (2) which is sufficiently close to the optimal band gap under AM1.5 radiation spectrum. It is abundant on earth, non toxic, and exhibits fairly high minority carrier diffusion lengths, high absorption coefficient in the visible region, and large exciton binding energy (11). The theoretical photoelectric conversion efficiency is 20%. However, there have been relatively few attempts to fabricate photovoltaic cells with Cuprous Oxide. The optimization of Cu2O solar cells is slowed down by the lack of clear understanding of its electronic and thermodynamic properties, and by the difficulties in the doping process. Early attempts focused on metal Cu2O Schottky solar cells because Cu2O is natively p-type and is hard to be doped n-type. However, it is believed that there will not be a significant improvement with this structure beyond the highest practical photoelectric conversion efficiency currently reported at 1.76% (9). When Cu2O is placed in contact with a metal to form a Schottky barrier, most metals reduce Cu2O to form a Copper rich region at the interface, which dictates the barrier -height magnitude (5). This is why the barrier heights range between 0.7 and 0.9 eV, regardless of the choice of metal. These oxidation phenomenon's coupled with inter diffusion of Copper results in low efficiencies in the order of 1%, necessitating design of heterojunction.

Copper Oxide is a semiconductor which shows varying optical behaviour because of stoichiometric deviations arising from its methods of preparation and parameters (14). It has been reported that many of the methods of growing Copper Oxide result in a combined growth of Copper (I) Oxide (Cu2O) and Copper (II) Oxide (CuO) (14). A range of direct optical band gap energies has also been reported for Cu2O and CuO (3) semiconductor films in the literature, depending on the method of fabrication and stoichiometry. Sputter deposition of Copper Oxide films on glass are reported to have high transparency, with a slightly yellowish appearance, and absorbs usually at wavelengths below 600 nm, whilst CuO absorbs strongly throughout the visible spectrum and is black in appearance. The current applications areas of Copper Oxide thin films include solar cells and electro-chromic devices (17). Copper Oxide films have been reported to have band gap energy values which make them suitable for application as absorbers for solar energy conversion (Ogwu et al., 2005).

Copper Oxide semiconductors have been studied for several reasons such as: the natural abundance of starting material Copper (Cu); the ease of production by Copper oxidation; their non-toxic nature and the reasonably good electrical and optical properties exhibited by Cu2O. Cupric Oxide (CuO) is a p-type semiconductor having a band gap of 1.21–2.1 eV and monoclinic crystal structure (3). Cuprous oxide (Cu2O) is also a p-type semiconductor having a band gap of approximately 2.2 - 2.9 eV and a cubic crystal structure (3). Its high optical absorption coefficient in the visible range and reasonably good electrical properties constitute important advantages and render Cu2O as the most interesting phase of copper oxides (3). Several methods such as: thermal oxidation (13); electrodeposition (15); chemical conversio, chemical brightening (14); spraying (3); chemical vapor deposition (20); plasma evaporation (3); reactive sputtering (4); and molecular beam epitaxy (8) have been used to prepare Copper Oxide thin films. In most of these studies, a mixture of phases of Cu, CuO and Cu2O is generally obtained and this is one of the nagging problems for non-utilizing Cu2O as a semiconductor. Pure Cu2O films can be obtained by oxidation of Copper layers within a range of temperatures followed by annealing for a small period of time. Cu2O is one of the oldest semiconducting materials which are useful in solar cell applications.

Balamuruga and Mehta, (3) studied nanocrystalline Cu2O thin films. The films were synthesized using an activated reactive evaporation technique. Structural and optical characterizations of these films were carried out using, glancing angle X-ray diffractometer; Fourier transform infrared spectrometer; transmission electron microscope; and UV-VIS-NIR spectrophotometer. The nanocrystalline size in these films was varied by changing the deposition parameters. Furthermore, optical spectroscopy studies on nanocrystalline Cu2O showed a direct allowed transition and a shift in the optical absorption edge from the bulk value with nanocrystalline size and stoichiometry of these films. These results show that a single phase nanocrystalline Cu2O thin films can be synthesized at a relatively low substrate temperature using the activated reactive evaporation technique. These studies indicate that nanocrystallinity results in the stability of cubic Cu2O phase in these films.

Papadimitropoulos (16) studied Copper Oxide films which were grown by oxidation of vacuum evaporated Copper layers on silicon substrates. Oxidations were performed at atmospheric pressure, in a nitrogen–oxygen mixture 10% in oxygen and at temperatures varying between 185 °C and 450 °C, the optical properties of films were studied with spectroscopic ellipsometry measurements within the energy range 1 to 3.5 eV. These measurements were analysed using the Tauc–Lorentz (TL) model (16) to simulate the dispersion of the complex refractive index of disordered films. It was shown that the TL model describes satisfactorily the refractive index dispersion of these Copper Oxide films. The band gap, as defined by the TL model, was found equal to 2.3 eV for Cu2O and between 1.05 eV and 1.2 eV for CuO. It was shown that the gap of the Cu2O films was free of localized states, which was not the case for the gap of CuO.

Ogwu et al., (14) sputtered Copper Oxide films on glass substrates by reactive radio frequency (rf) magnetron sputtering, using a solid Copper target and an Argon–Oxygen gas atmosphere. Optical transmission in the prepared films was measured by spectrophotometer in the 400–850 nm wavelength regions. A maximum transmission of between 40% and 80% for Copper Oxide films prepared at a low rf power of 200 W was observed, for the Oxygen flow rates investigated. The optical band gap values of the films ranged between 2.05 and 2.4 eV. Hailing Zhu (6), prepared Cu2O thin films on quartz substrate by reactive direct current magnetron sputtering. The influences of Oxygen partial pressure and gas flow rate on the structures and properties of deposited films were investigated. The as-deposited Cu2O films were found to have a very high optical absorption in the visible spectra under 600 nm and were endowed with photocatalytic reactivity under the visible light.

In dc reactive magnetron sputtering, the physical properties of the deposited films critically depend on the sputtering parameters such as oxygen partial pressure, sputtering pressure, substrate temperature, sputtering power and distance from the target to the substrate. Post deposition annealing or deposition at higher substrate temperature has been found to result in these films having predominant Cu2O phase (18). In this paper, we reported the results of depositing nano- structured Cu2O thin films by dc reactive magnetron sputtering process under the effect of oxygen flow rate on the optical properties of these Cu2O thin films was also investigated.

2. Experimental techniques

2.1 Preparations of thin films

The glass substrates were cleaned in dilute chromic acid to remove metallic particles and organic stains or surface contaminants and thereafter rinsed thoroughly with distilled water and ethanol to remove any acidic residues and allowed to dry completely. The substrates were then introduced into the vacuum chamber. Thin films of Copper Oxide were deposited on microscope glass substrates (25 mm × 25 mm × 1 mm). The distance between the source and substrate was 15 cm. The starting materials were a solid copper target (99.99 % purity) and two gases namely, Oxygen (reactive gas) and Argon (sputtering gas). The deposition chamber was evacuated to a base pressure of 5 x 10-6 mbar. Argon gas was then introduced into the sputter chamber at fixed flow rate of 20 Sccm and the target was pre-sputtered in pure argon atmosphere for 15 min to remove oxide layers and other contaminants on the surface of the target.

After pre-sputtering and turning-off of dc power, Oxygen gas was admitted to reach the required sputtering pressure and the dc power supply was turned on again to start the thin-film deposition. The flow of Oxygen into the deposition chamber was monitored using mass flow controllers and gas regulators interfaced to a computer. The pressure during deposition was maintained at 5.5 x 10-3 mbar. Sputtering was done for 15 minutes. Pure Argon (99.99% purity) was used as the sputter gas and pure Oxygen (99.999% purity) as the reactive gas. Copper Oxide thin films were prepared under different Oxygen flow rates (2.5 …25 Sccm) and the other deposition parameters such as power (200W), substrate temperature (325 K) and sputtering pressure were held constant.

The sputtering conditions maintained during the growth of Copper Oxide thin films were set after some preliminary experimental studies. Quartz crystal monitor mounted in the sputtering unit was used to measure the film thickness. This process was repeated for all samples in this research study
The investigated deposition parameters are indicated in table 2.1.

Table 2.1: Deposition conditions of the prepared copper oxide films

Argon flow rate	20 Sccm
Oxygen flow rates	2.5,5,7.5….25 Sccm
Power	200 W
Target copper	Copper 99.9 %
Substrate	Microscope slide
Deposition time	15 min
Substrate temperature	325 K
Base pressure	5 x 10^{-5} mbar
Oxygen partial pressure	4.0 x 10^{-3} mbar
Sputtering pressure	5.5 x 10^{-3} mbar

2.2 Thin film thickness measurements

Thin film thickness was estimated using Tencor alpha step surface profilometry (resolution of 5 Ǻ) equipment with a diamond stylus of radius 12.5 µm. During measurement, the stylus was moved across the film surface while keeping the sample and the sample stage stationary. The step created during the deposition process enabled the film's thickness to be read directly as the step height. SCOUT 98 software was also used to simulate the film thickness. This was used to validate the measurements obtained by Tencor alpha step surface profilometry equipment with comparisons to thickness with Quartz crystal monitor.

2.3 Optical measurements

Optical measurements (reflectance and transmittance) in the spectral range from 300 nm - 2500 nm were carried out using UV/VIS/NIR 3700 double beam Shimadzu spectrophotometer. Photons of selected wavelengths and beam intensity Io (photons/cm2-s) were directed at the film of thickness (t) and their relative transmissions observed. Wavelengths of photon are selected by the spectrophotometer. Photons with energies greater than band gap (Eg) are absorbed while those with energies less than Eg are transmitted. The spectrophotometer had two radiation sources; a deuterium lamp for UV range and a halogen lamp for visible (VIS) and near infrared (NIR) range. The radiation source changed automatically to access the wavelength range during measurements. During transmission measurements, samples were placed in front of the integration sphere and behind it during reflection measurements.

SCOUT 98 software was used to simulate transmittance data to get the optical constants like absorption coefficient among others. Drude, OJL, Tauch Lourntz, Extended Drude and Harmonic Oscillator models were used to simulate the data. These models are inbuilt in the SCOUT 98 software (19).

The models simulate refractive index, dielectric function, absorption coefficient real and imaginary parts and energy loss parameters.

2.4 Sheet resistivity measurements

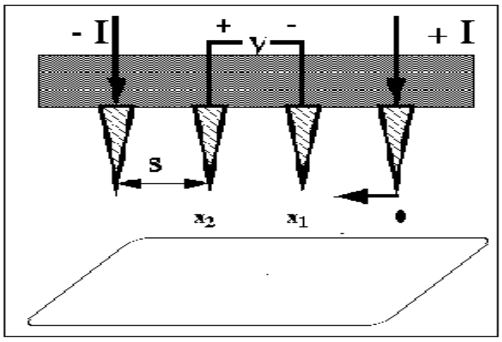

Figure 2.1: Schematic diagram of a four point probe used to measure surface sheet Resistance (1)

The four point probe technique (figure 2.1) was used to measure the sheet resistivity of the Cuprous Oxide and Aluminum doped ZnO semiconductor thin film samples. With a symmetrical square geometry adopted, the four leads from the probe head were connected to Keithley Source Meter via relay switching circuit as per the Van der Pauw set-up for Voltage and Current measurements (1).

2 Result and Discussion.

3.1 Optical characterization of CuxOy thin films

The optical transmittance of Copper Oxide films prepared at 200 W, dc power and 5, 7.5… 22.5 Sccm Oxygen flow rate is shown in figure 3.1. The optical transmittances of the films show a strong dependence on the flow rate during deposition; the optical transmittance decreased with an increase in Oxygen flow rate during deposition. This behaviour was observed for all the films deposited. Figure 3.1 summarizes the inter-relationship between the Oxygen flow rate and the optical transmission. There is observable shift in absorption edge (figure 3.1).

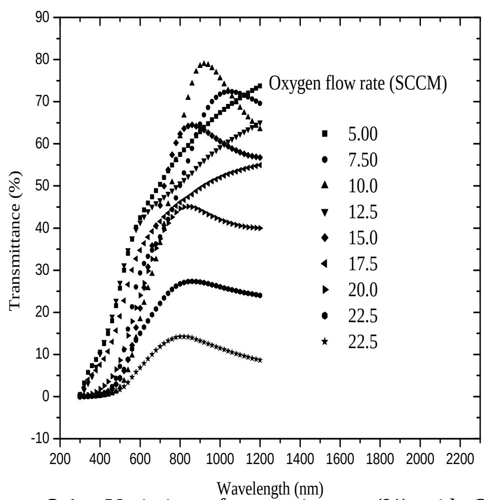

Figure 3.1: Variation of transmittance (%) with Oxygen flow rate

The reflectance spectrum for Copper Oxide films figure 3.2 shows low reflectance values in the visible spectrum. This when compared to the above transmittance indicates that it has a high absorption coefficient making it a good absorber material for solar cell applications. This agrees very well with Ogwu (15) who observed low values of reflectance (%) bellow 45 % for Copper Oxide thin films.

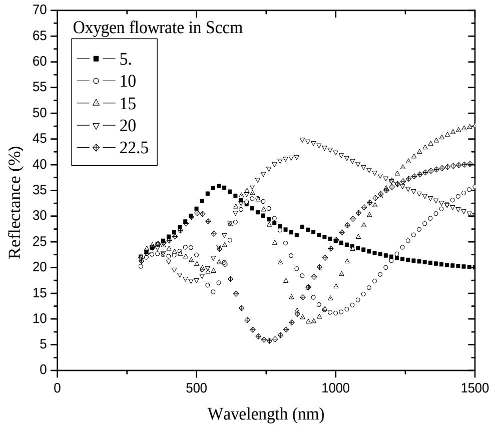

Figure 3.2: Spectral graphs showing variations of reflectance (%) with Oxygen flow rate in Sccm.

3.2 Simulated and experimental graphs for Copper Oxide transmittance data

The experimental and simulated data for transmittance data were plotted against wavelength for the different gas flow rates. Figure 3.3 (a., d) are samples of the fitted data using SCOUT 98 software**.**

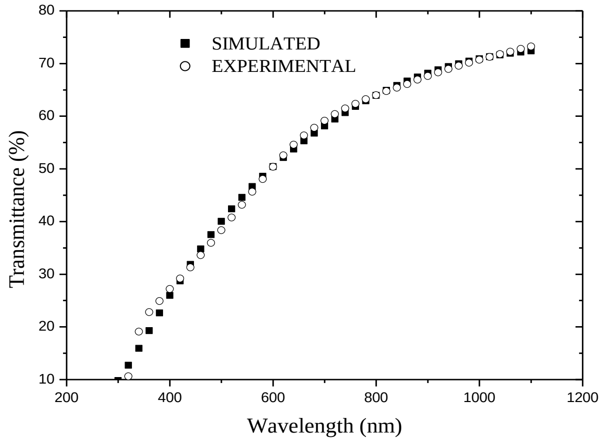

Figure 3.3 (a): Oxygen flow rate of 5 Sccm

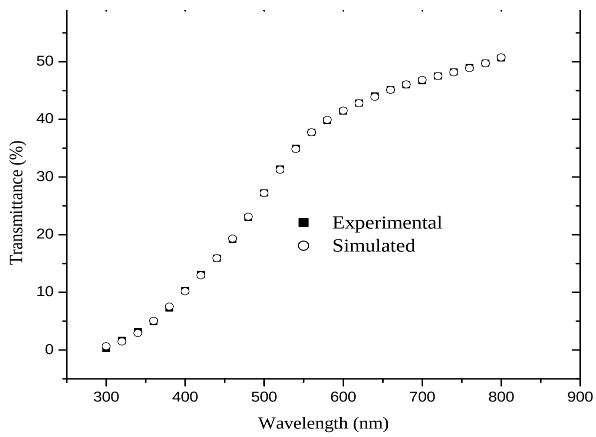

Figure 3.3 (b): Oxygen flow rate of 7.5 Sccm

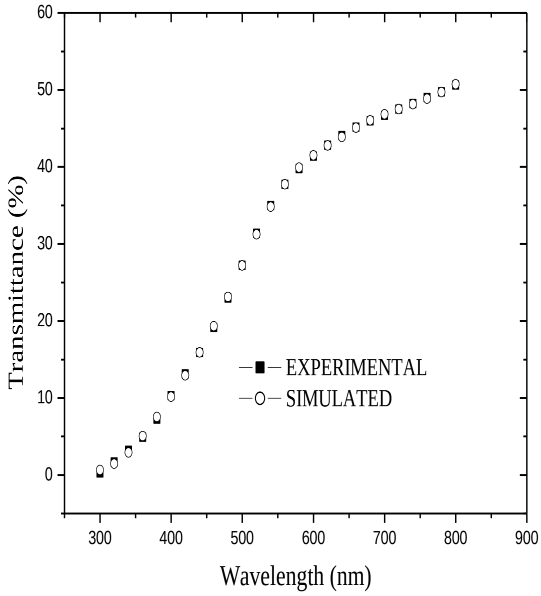

Figure 3.3 (c): Oxygen flow rate of 7.5 Sccm

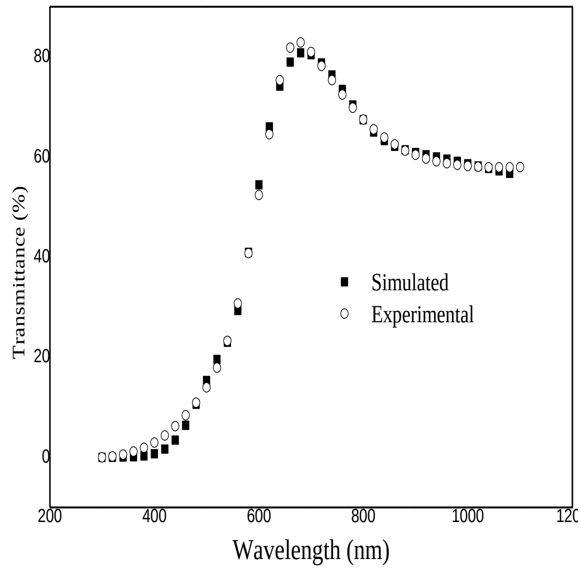

Figure 3.3 (d): Oxygen flow rate of 15 Sccm

Figure 3.3(a-d): Simulated and experimental graphs of sampled thin films of Copper Oxide at various Oxygen flow rates (Sccm).

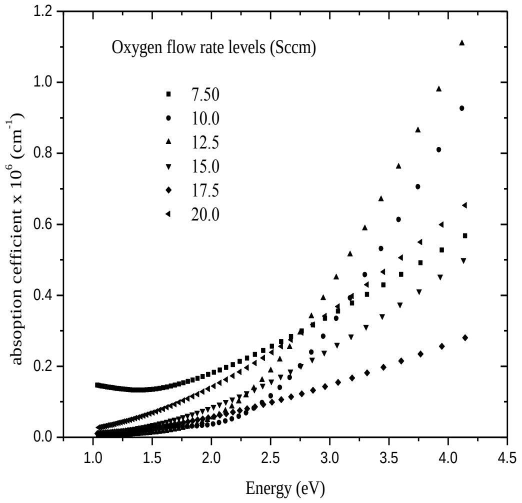

Figure 3.4: Variation of α (cm^{-1}) versus energy (eV) for different oxygen gas flow rates

3.3 Optical band gap and Urbach energy for Copper Oxide thin films

From figure 3.4 it was observed that the variation of α (cm-1) versus energy (eV) which is near straight line indicates the presence of direct optical transition. The absorption edge tail width is long showing levels of defects called Urbach energy. The Copper Oxide formed had relatively low transmittance with low values of optical band gap.

Table 3.1: Optical band gap for Copper Oxide at different oxygen flow rate

Gas flow rate (Sccm)	Optical band gap eV ±0.02	Urbach energy eV ±0.02 $\times 10^{-4}$
5	2.09	1.82
7.5	2.02	0.63
10	1.62	0.61
12.5	1.82	1.07
15	2.11	1.13
17.5	2.32	1.23
20.	2.43	1.43
22.5	2.54	1.92

The optical band gap of the thin film as simulated by SCOUT 98 software shows a decrease in band gap as the Oxygen flow rate increased up to at 10 Sccm (table 3.1 and figure 3.5) then increases again. This can be attributed to recombination and variation in Oxygen doping levels. This also corresponds to the variation of Urbach energy with flow rate as indicated in figure 3.6 and table 3.2 .

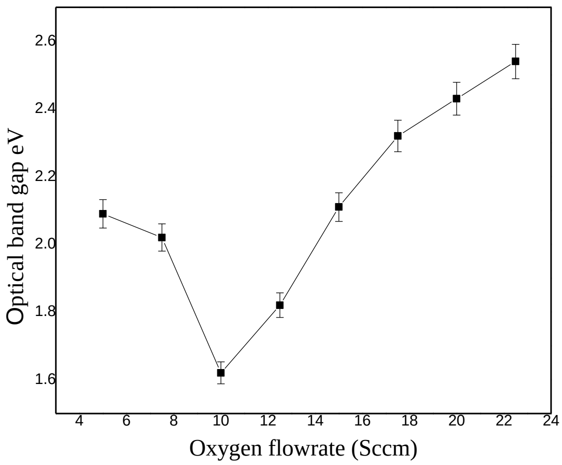

Figure 3.5: Variation of optical band gap with various levels of Oxygen flow rate (Sccm)

The values of the band gaps were 1.62 eV and 2.54 eV. This band gap depends on the kinetics of formation of the oxides. The kinetics of the formation of oxides of Copper during thin film deposition is dependent on following factors:

1- The nucleation rates of Cu, Cu2O and CuO during the

2- The sticking coefficient / sticking probability of the particles

3- Re-evaporation and migration by the impinging copper and

4- The different growth rates of the nucleated specie

All of the above factors depend on the power and gas pressure in the deposition chamber during the sputtering process. At 10 Sccm the band gap is 1.62 eV. At this band gap the Copper Oxide thin film makes a good absorber material for solar cell application.

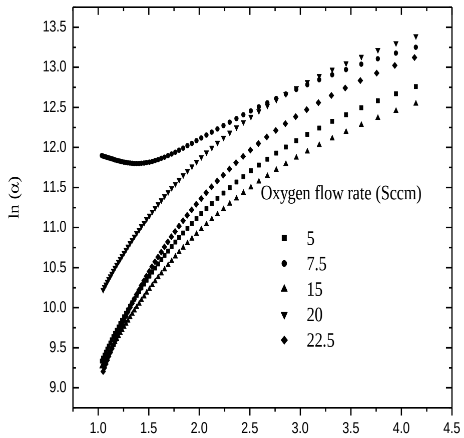

Figure 3.6: Spectral graph for determination of Urbach energy for Copper oxide films

According to Kawaguchi and Muthe (7,10) the effective sticking probability is important in deducing the type of oxide formed i.e. Cu2O or CuO. This depends on the Oxygen to Copper flux ratio, but not on the individual flux values during deposition. It is also observed that the kinetics of CuO formation is much slower than that of Cu2O. They further proposed that CuO formation is based on the reaction

$$Cu_2O + O \longrightarrow 2CuO$$

Since the extent of dissociation of the starting oxygen molecules during deposition into atomic Oxygen and Oxygen ions depends on the applied power during deposition, the ratios of Oxygen ions to Copper atoms and atomic Oxygen to Copper atoms, which determine the phase stability regime for Cu2O and CuO formation (10) depended on the power applied during deposition.

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