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## Bandgap Tuning of High Mobility Magnetron Sputtered Copper (I) Oxide Thin Films for Perovskite Solar Cell Applications

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### ABSTRACT

We report on the successful growth optimization of an inorganic p-type copper oxide (Cu<sub>2</sub>O) thin films for various energy applications. First, Cu<sub>2</sub>O thin films of a typical thickness of 100 nm are deposited on fluorine-doped tin oxide (FTO) coated glass substrates by DC-reactive magnetron sputtering, followed by their in-depth characterization with different techniques, including scanning electron and atomic force microscopies, UV-Vis, X-ray diffraction and photoelectron spectroscopies, to probe their structural, optical, and morphological properties. Surface topology analysis revealed homogeneous, compact, and uniform sputtered deposited films. The as deposited films layers have shown a preferential crystal orientation of (111) and a stoichiometry of CuO, at the surface, which is believed to be mainly due to the oxidization effect of the non-capsulated surface, while a short-duration argon etching (~ 5 s) has revealed the growth of Cu<sub>2</sub>O films stoichiometry. Finally, during the reactive plasma deposition, films were grown under nitrogen gas flow to improve their hole-mobility, followed by a systematic annealing at various temperatures ranging from 100 to 250 °C to improve their crystalline structure. Hall effect measurement confirmed that the Cu<sub>2</sub>O thin film are p-type, with extremely high electronic properties, including an electrical conductivity of  $2.6 \times 10^2$  S/cm, a hole mobility of about 30 cm<sup>2</sup>/Vs and a charge carrier density around  $5 \times 10^{19}$  cm<sup>-3</sup>, making them a serious candidate for a hole transport layer in perovskite solar cells.

### 1. Introduction

Cuprous oxide (Cu<sub>2</sub>O) is a well-established p-type material and its conductivity is directly correlated with the oxygen rich or poor layers due to the variation in growth processes [1]. Such growth processes usually result in copper (I) oxide Cu<sub>2</sub>O and copper (II) oxide CuO (i.e. cupric oxide) [2,3] films mainly due to the oxidization process of copper films. The optical properties vary for both Cu<sub>2</sub>O and CuO as reported previously [4-7] mainly due to the growth process resulting in rich or poor oxygen bonding. It has been reported that Cu<sub>2</sub>O confirms an optical bandgap between 2.10 and 2.60 eV [4,5], whereas for CuO, it is between 1.3 and 2.1 eV [6,7]. Such optical properties open the path to use such layers as a buffer for energy conversion devices. In general, copper oxide films show high transparency with light absorbing capability at wavelengths below 600 nm, whereas metal rich oxide films absorbs strongly in the visible spectrum range [2].

As reported by Richardson [8], such oxide films can be used for architectural and aerospace applications because of the capability to tune the optical properties. In addition, their high light transmission along with their lower electrical resistivity makes these films suitable as light window layer for optoelectronic devices, where their carrier transportation helps to generate electricity using energy conversion devices. However, it has been found that cuprous oxide can result in higher electrical resistivity due to growth conditions and/or post-oxidization effect [1,9].

Previously, Hossain et al. numerically confirmed Cu<sub>2</sub>O as an alternative hole transport material (HTM) with a power conversion efficiency of 24% [10]. Later, some experimental studies also confirmed the usage of this material to replace the expensive Spiro-OMETAD layer [11-16] as a HTM. Due to the perfectly aligned valance band, carrier injection becomes ideal from the absorber layer. Many attempts have been conducted to fabricate Schottky junction, hetero-junction, and homo-junction devices using Cu<sub>2</sub>O

as a light harvesting layer [17]. However, the limitation arises mainly from the high bandgap (>2 eV) which results in poor light absorption capability in longer range with a very low short circuit current ( $J_{sc}$ ) [17].

Various techniques have been used to fabricate Cu<sub>2</sub>O thin films, including magnetron sputtering [18], copper oxidation [19], and atomic layer deposition (ALD) [20]. Unintentionally doped Cu<sub>2</sub>O films are naturally p-type due to the native defects identified as negatively charged copper vacancies ( $V_{Cu}^-$ ) rather than interstitial oxygen ( $O_i^-$ ). Also, nitrogen doping has been used to prepare samples containing high density of holes of about  $10^{18}$  cm<sup>-3</sup> [21,22].

The aim of our work is to optimize the DC-reactive magnetron sputtering growth of Cu<sub>2</sub>O films at different temperatures by probing their structural, morphological, and electrical properties. The main focus was put on the evolution of preferred crystalline orientation as a function of the process temperatures.

### 2. Experimental Methods

All chemicals were purchased from Sigma Aldrich™ and used as received. Fluorine doped tin oxide (FTO) coated commercial borosilicate glass substrates with dimensions of 3 cm × 3 cm × 1.5 mm were used in the present work. The pre-coated FTO with a 100 nm thick layer has led to a very low sheet resistance of about ~10 Ω/square. Prior to the deposition, the substrates were systematically cleaned up inside an ultrasonic bath for 5 min using acetone, isopropanol, and deionized water. Samples were then dried with nitrogen blow and used immediately for deposition. Cu<sub>2</sub>O films were deposited by DC magnetron sputtering (Torr International's MagSput™ series CRC 600) with a power density of 1.5 W/cm<sup>2</sup>, using Cu target (99.999% purity), at various temperatures ranging from 100 °C to 250 °C, under oxygen and nitrogen flow, with a background pressure of about 10 mTorr. The chamber base pressure was about 10<sup>-5</sup> Torr as pumped down by the turbo molecular pump. Cu<sub>2</sub>O films of a typical thickness of 100 nm were thus grown, and their structural and morphological characterizations show that the deposited film quality is

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rather homogeneous over the entire sample surface with an optimized optical and structural property. The deposition time was kept at 30 min, the relative oxygen to total flow ratio ( $r(O_2) = O_2/Ar$  flows) at 11.5% (namely 15 sccm of  $O_2$  vs. 120 sccm of Ar and 10 sccm of  $N_2$ ), while the temperature deposition (TD) was varied from 100 to 250 °C in step of 50 °C (i.e. four TDs, namely 100, 150, 200 and 250 °C). Perovskite layer was formed on the top of the by thermal evaporation technique from the source powder of  $PbI_2$  (Sigma-Aldrich) and  $CH_3NH_3I$  (Dyesol) by changing the ratio. The estimated thickness was checked using the crystal monitor of the system by changing the density and z-factor. It varied between 300 to 500 nm based on the ration of source powders.

### 3. Results and Discussion

#### 3.1 XRD Analysis

The structural analysis of the sputtered thin films was performed by X-ray diffractometer (XRD, Rigaku XRD™) at diffraction angles  $2\theta$ , ranging from 10° to 80°. Fig. 1 shows the XRD pattern obtained for four as-deposited films, at temperatures of 100 °C, 150 °C, 200 °C and 250 °C (no annealing treatment was performed on these films after the deposition. XRD signal is shown after smoothing the signal with OriginLab™ software). The analysis shows a clear preferential growth tendency of the films along the (111) direction of  $Cu_2O$  phase. For the samples grown at higher temperature, the (111) peak becomes more intense and starting from 200 °C. The (211) phase orientation takes place (peak located at 42 degree). The (211) peak becomes then more intense with respect to the deposition temperature. These crystalline changes could be attributed to the coalescence induced grain growth during the temperature process where unlike the larger nuclei, the smaller ones can easily rotate in order to minimize the interfacial energy. Indeed, with increasing temperature, the atoms gain sufficient energy to be structurally reoriented within the crystal lattice leading thereby to a more stable structure with enhanced crystalline quality.

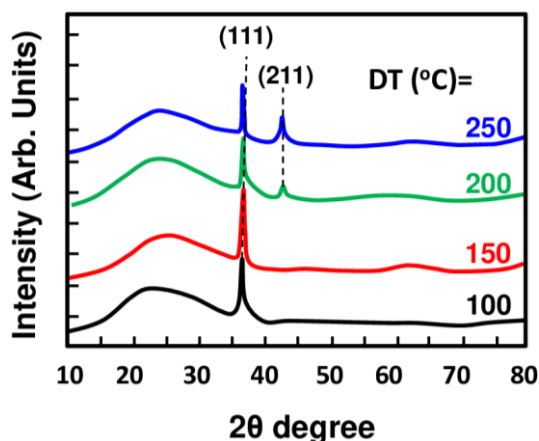


Fig. 1 Representative X-ray diffraction patterns of the  $Cu_2O$  films grown at 100, 150, 200 and 250 °C without any post annealing process

The average crystallite size for each different orientation was estimated by the well-known Debye-Scherrer equation and summarized the crystalline sizes in Table 1. All the calculated values are found in the range of 45–50 nm.

Table 1 Crystallite size calculations

$2\theta$	Measured FWHM	$\theta$	FWHM (rad)	Crystallite Size (nm)
36	0.34	16.60	0.003393	45.48
42	0.34	21.60	0.003254	48.90

#### 3.2 XPS Analysis

Surface analysis by X-ray photoelectron spectroscopy is performed on series of metal oxides using Escalab 250Xi (Thermo Fisher Scientific). The spectra analysis and fitting was conducted using Avantage software. The source is monochromatic Al K alpha and its energy is 1486.68 eV. The pass energy is 20 eV for all narrow scans and 100 eV for survey scans. Number of scans for each spectrum is 10 for high resolution spectra and 1 for survey spectra. The survey spectra showed a good quality metal oxide with some reduced presence of elements and carbon species contamination. Regarding the oxygen chemical states analysis, the carbon spectra fitting has been used to identify the amount of oxygen related to carbon species which can be deducted from the total oxygen to conclude the oxide related oxygen. The amounts of oxide related oxygen using Biesenger et al. [23] <https://doi.org/10.30799/jtfr.026.21050101>

method as well as all elemental atomic percentages have been measured. The  $Cu_2O$  films grown at the lowest employed temperature, namely 100 °C, show the presence of  $CuO$  phase (note that all the other parameters were kept the same, including  $O_2$ , Ar and  $N_2$  flow, deposition-time and power-density). XPS analysis reveals the presence of adsorbed oxygen and the presence of  $Cu^{2+}$  atoms at the surface, as indicated by the satellite peak located at 951 eV. However, after Ar etching for about 30 s, the XPS spectra indicate that the films have rather the typical stoichiometric composition of  $Cu_2O$ , as displayed in Fig. 2. The same behavior was then observed for the films grown at 150 °C, 200 °C and 250 °C.

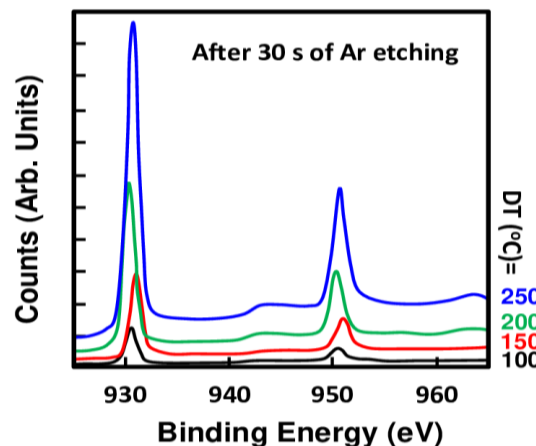


Fig. 2 Typical XPS spectra of  $Cu_2O$  films grown at various temperatures, showing the stoichiometry of  $Cu_2O$  material

#### 3.3 Surface Morphology Analysis by SEM

The representative SEM micrographs of the as-deposited  $Cu_2O$  films are displayed in Fig. 3. First, the films are shown to cover homogeneously the entire surface of the glass substrates. For films grown at 100 °C, small grains sizes of about 60 nm in diameter were the most observed ones, which is in good agreement with the XRD analysis. The grains are then found to be smaller with respect to the deposition temperatures, and are in the range of 50 nm, 40 nm, and 30 nm, for deposition temperatures of 150 °C, 200 °C and 250 °C, respectively.

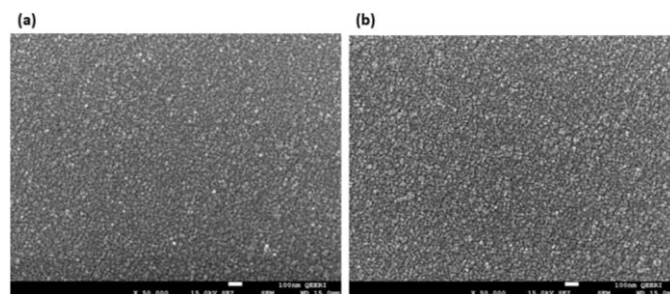


Fig. 3 Typical SEM micrographs of the copper oxide layers prepared on glass substrates, as deposited at (a) 100 °C and (b) 250 °C

#### 3.4 Surface Topology Analysis by AFM

The surface roughness of the as-deposited  $Cu_2O$  films at 250 °C has been investigated by means of atomic force microscopy. Clear change in the surface morphology was systematically observed with respect to the growth temperature, in agreement with SEM analysis. Fig. 4 shows the contact-mode AFM image of the  $Cu_2O$  film as-deposited at 250 °C on glass substrate, showing an average RMS of 30.54 nm.

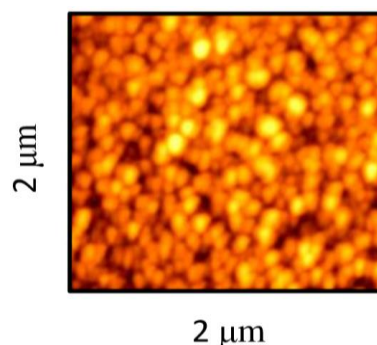


Fig. 4 Contacting mode AFM image of the  $Cu_2O$  layer prepared on glass at 250 °C

### 3.5 Optical Characterization

The optical properties of the as-deposited  $\text{Cu}_2\text{O}$  films were also investigated through the UV-Vis spectroscopy (Jasco V100™), in the range of 380–890 nm wavelengths. The obtained spectra are summarized in Fig. 5(a-d). As known, copper oxide is a direct bandgap semiconductor material [10]. We have found that the band gap is 2.56 eV at 100 °C, and decreased then to 2.50 eV (and is stable at this value) for  $\text{DT} \geq 150$  °C is stable regardless to the temperature).

The  $\text{Cu}_2\text{O}$  band gap was found to vary from 2.56 eV for films deposited at 100 °C to 2.50 eV for those deposited at  $\text{DT} \geq 150$  °C. This bandgap variation is believed to be due to the strong dependence of electronic states on the effective exciton mass, in addition to the bandwidth changes, dielectric confinement, and possible quantum confinement [24].

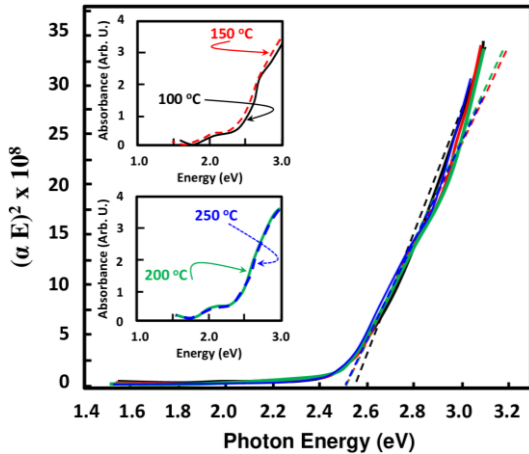


Fig. 5 Bandgap estimation of the various copper oxide films deposited on glass substrates at (a) 100 °C, (b) 150 °C, (c) 200 °C, and (d) 250 °C

Generally, in polycrystalline semiconductor films, the optical absorption can be affected by many parameters, including the stoichiometric deviation such as the metal to oxygen ratio, grain size. Yet, the illustrated graphs displays rather continuous optical spectra, which could in fact happen due to the stability of the measured films during the characterization process (i.e. films degrade slowly) [24–26].

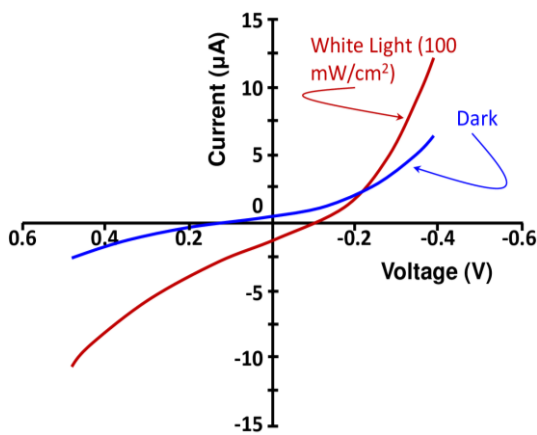


Fig. 6 I-V measurement of  $\text{Cu}_2\text{O}$  based perovskite solar cells

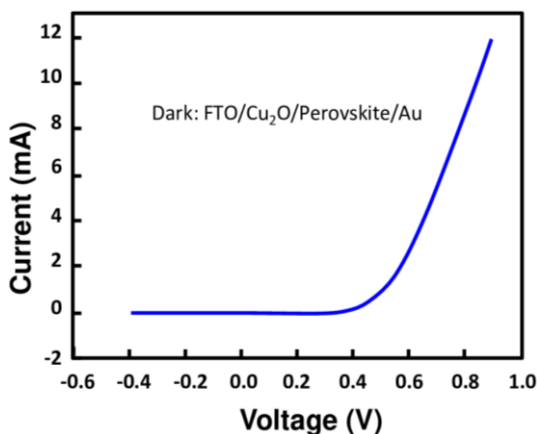


Fig. 7 Dark I-V measurement of  $\text{Cu}_2\text{O}$  based perovskite solar cells  
<https://doi.org/10.30799/jtfr.026.21050101>

### 3.6 Electrical Characterization

Four-point measurements were conducted on the  $\text{Cu}_2\text{O}$  films to measure their electrical surface conductivity, which was about 100 S/cm for films grown at 100 °C. Electrical conductivity was found to be less affected by the deposition-temperature. This average value is estimated somehow lower due most probably to the oxidation of the samples through their exposition to an open air for a long time. However, while a nitrogen doping was carried out during the reactive plasma sputtering of the films, electrical conductivity was improved by 100% and reached 200 S/cm. Table 2 summarizes the electrical properties of the deposited films at various temperatures. The I-V characteristics of the cells were performed by photo electrochemical set. This is the most fundamental characterization tool to measure the conversion efficiency of a cell. The measured structure as shown in Figs. 6 and 7 is for FTO/ $\text{Cu}_2\text{O}$ /CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/Au. All the structures showed a diode-like behavior for dark and under light. For this type of ETM free structure, current generation under illumination can be observed. Although the feasibility of such films for perovskite solar cell is clearly demonstrated in this work, an optimization step is highly needed to obtain higher photo conversion efficiency.

Table 2 Electrical properties of the  $\text{Cu}_2\text{O}$  films as a function of the growth temperature and annealing process

TD (°C)	Electrical conductivity (S/cm)	
	Before annealing in N <sub>2</sub>	After annealing in N <sub>2</sub>
100	104	185
150	106	189
200	109	191
250	115	200

Electrical conductivity and Hall mobility ( $\mu_{\text{HALL}}$ ) of the  $\text{Cu}_2\text{O}$  films deposited at 250 °C after annealing in nitrogen were measured at room temperature with appropriate ohmic contacts. Van der Pauw technique [27,28] was used to minimize the contact effects. The films were found to be p-type and the values of electrical conductivity, mobility of the charge carriers and carrier density measured were 216 S/cm, 28.6 cm<sup>2</sup>/Vs and  $4.72 \times 10^{19}$  cm<sup>-3</sup>, respectively. The carrier concentration values obtained from these measurements agree well with those reported so far [29–36] by DC magnetron sputtering techniques used in this study with minimal controlling deposition parameters is recorded. The enhancement of carrier concentration was due to the presence of copper vacancies in our films. Fig. 8 shows the corresponding PL measurement of different structures. Excitation wavelength at 680 nm was used to irradiate the films with an equal intensity. For PL measurement, FTO glass substrates were used to mimic the real device structure. A strong quenching of the PL intensity has been observed once integrating  $\text{Cu}_2\text{O}$  as a hole transfer material, which is attributed to the better charge transport material quality.

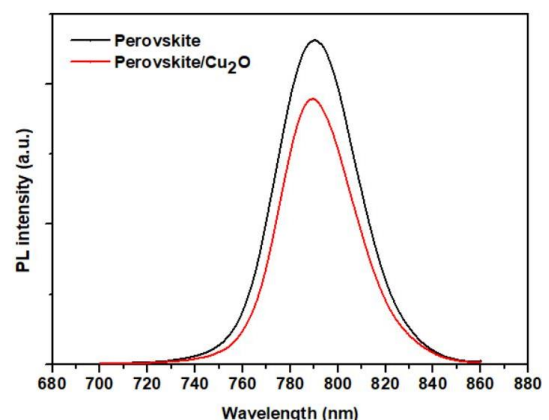


Fig. 8 PL measurement with clear quenching for  $\text{Cu}_2\text{O}$ /perovskite layers

## 4. Conclusion

The synthesis of cuprous oxides ( $\text{Cu}_2\text{O}$ ) thin films by a direct current (DC) reactive magnetron sputtering technique has been demonstrated at various temperatures and their structural properties were systematically investigated, including crystal orientation, grain size and lattice parameters. Only two primary peaks corresponding to (111)<sup>cu</sup> and (200)<sup>cu</sup> orientations indicating polycrystalline nature were found for all the deposited films. The relative peak intensity was found to be higher for increased deposition temperatures indicating thereby a better

crystallinity. SEM analysis demonstrated that the films were compact throughout the entire sample surface, with no observed pinholes. The surface morphology of the films was strongly dependent on the deposition temperatures as a function of the film-thickness and changes from rough surface (grains of about 60 nm in diameter were measured at 100 °C) to much smoother surface observed at higher deposition temperatures. This variation in DT can play a vital role in forming Cu<sub>2</sub>O films, which can be directly implemented as energy application layer (e.g. hole transport material) with no further fine-tuning. Although a photovoltaic effect was clearly observed; showing a short current of  $2.61 \times 10^{-6}$  A and an open circuit voltage of 100 mV, the efficiency is quite small and further optimizations are needed to optimize the whole device. However, the films were found to be p-type, with extremely high electronic properties, such as an electrical conductivity above  $2 \times 10^2$  S/cm, a hole mobility of about 30 cm<sup>2</sup>/Vs and a charge carrier density around  $5 \times 10^{19}$  cm<sup>-3</sup>.

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