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COPPER (I) OXIDE THIN FILM PREPARED BY SPRAY COATING METHOD

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In this work, the copper oxide was manufactured by a simple and scalable spray coating technique from copper acetate solution in air. The investigation included the optimal concentration of copper acetate monohydrate and glucose finding and the determination of beneficial deposition temperature. What is more, to obtain single phase Cu2O the thermal post treatment at 300°C in an inert atmosphere of nitrogen was implemented. Due to that the resistivity of the layer was reduced from 23.2 Ω*cm to 21 Ω*cm. Also, the transformation of CuO in as deposited layer to Cu_2O after additional treatment was confirmed by XRD analysis. The grain size calculated by Scherrer equation increased from 6.17 nm to 10.42 nm. The charge carrier concentration and mobility for pure Cu_2O were 2.99e+16 1/cm3 and 3.44 cm2/(V*s) respectively. It should be highlighted that this measurement was not possible for a deposited layer. In addition, the first attempt to use copper oxide in perovskite solar cells as hole transporting material (HTM) was made. Due to the gentle nature of perovskite, the thermal Cu_2O was deposited on top of it with thicknesses of 4.5 nm, 9 nm, and 18 nm. The results revealed that the use of Cu_2O improves the electrical parameters of perovskite solar cells compared to the reference sample without HTM. However, obtained IV parameters are much lower than that for devices with Spiro-OMeTAD.

METHOD DEVELOPMENT

STEP 1 Cu(CH3COO)2·H2O and REDUCING AGENT OPTIMALIZATION

Table 1 Band gap energy (E_g), work function (ϕ) and resistivity (ρ) of the copper oxide coating produced from precursors of various concentrations.

Concentration of $Cu(CH_3COO)_2 \cdot H_2O$ [mM]	Eg [eV]	ϕ [eV]	ρ [Ω·cm]
0.35	2.4	4.97	-
0.7	2.45	5.08	40,1
1.05	2.45	5.00	41
1.4	2.55	4.97	37,3

No significant differences in band gap energies as well as in work function values.

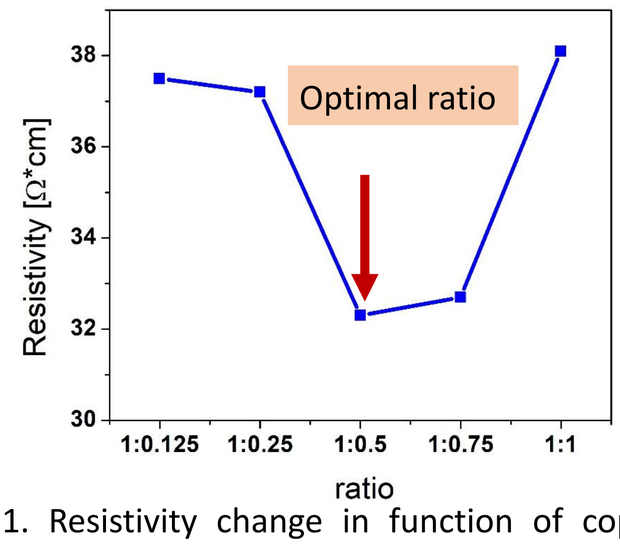

Figure 1. Resistivity change in function of copper acetate to glucose ratio.

STEP 2 DEPOSITION TEMPERATURE

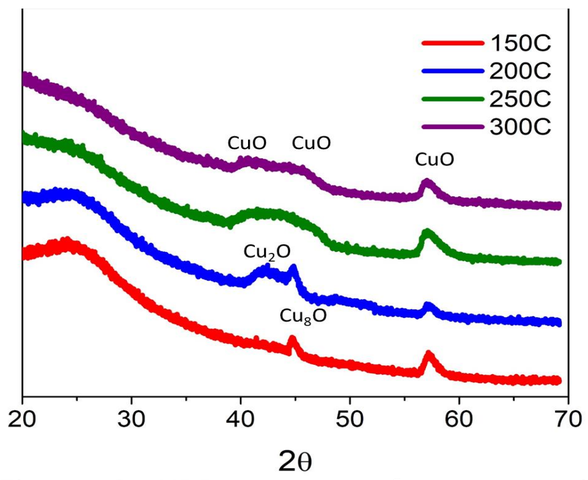

Figure 2. XRD spectra of copper oxide layer manufactured at different temperatures

Table 2. Calculated parameters of copper oxide manufactured at different temperature.

Temperature [°C]	ρ [Ω*cm]	Eg [eV]	ϕ [eV]
150	-	2,5	-
200	30	2,5	5,16
250	40.9	2,5	5,08
300	37.4	2	5,12

Different layer composition depending on the temperature. At 150°C the coating is a mixture of a CuO (57°) and not stable Cu8O (44.5°). With temperature increasing the Cu8O peak disappears. Cu2O (131) peak at 42° shows up at 200°C, it is broadened at 250°C and finally at 300°C only three CuO peaks are visible 41.5°, 45° and 57°.

STEP 3 HIGH TEMPERATURE POST TREATMENT

Additional high temperature post treatment at 300°C in an inert atmosphere of nitrogen.

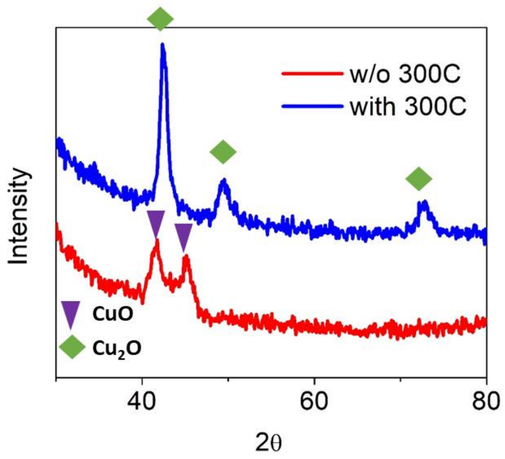

Figure 3. XRD diffraction of manufactured copper oxide layers.

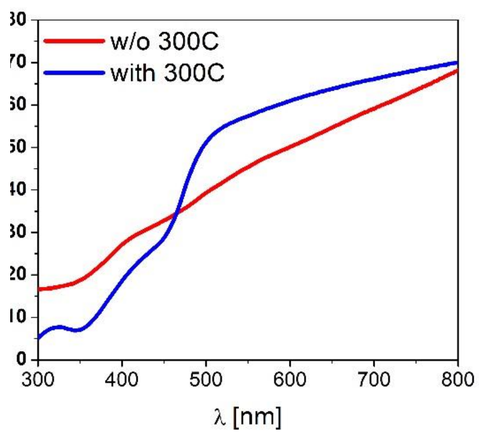

Figure 4. Transmission plot of copper oxide thin films with and without heating in nitrogen at 300°C.

Additional high temperature layer treatment at 300°C in a protective atmosphere of nitrogen allows for the reduction of Cu(II) to Cu(I), the layer resistivity slightly decreased from 23.2 Ω*cm to 21 Ω*cm and the grain size calculated by the Scherrer equation increased from 6.17 to 10.42 nm.

SOLAR CELL MANUFACTURING

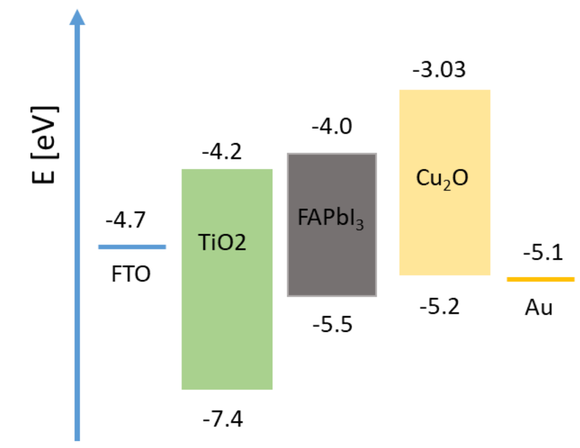

Figure 5. Band diagram of manufactured perovskite solar cell

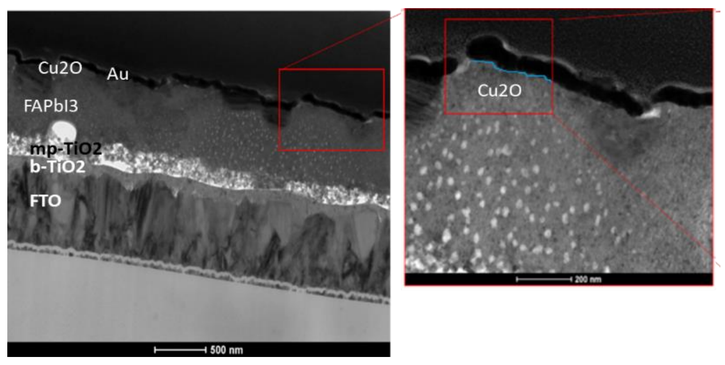

Figure. 6 TEM cross-section of a perovskite cell with thin Cu_2O layer

Table 3. I-V parameters of perovskite solar cells with copper oxide as HTL

	Jsc [mA/cm²]	Voc [mV]	FF [-]	η [%]
Ref.	13.4	315	0.31	1.30
Spiro	25.58	966.99	0.654	16.18
4.5 nm Cu_2O	17.83	654.01	0.508	5.91
9 nm Cu_2O	17.8	805	0.38	5.4
18 nm Cu_2O	12.7	612	0.43	3.38

The results indicated that reference perovskite solar cell with no HTM has worse IV parameters than those with Cu_2O HTM. It was found that for the thinner copper oxide the better electrical parameters are observed.

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"Doping of metal oxides with particular emphasis on copper oxide, by spray coating method to reduce its resistivity for use in a thin-film heterojunction and perovskite solar cells"