electronic materials

MDPI

Supporting Materials

Copper-Content Dependent Structural and Electrical Properties of CZTS Films formed by "Green" Colloidal Nanocrystals

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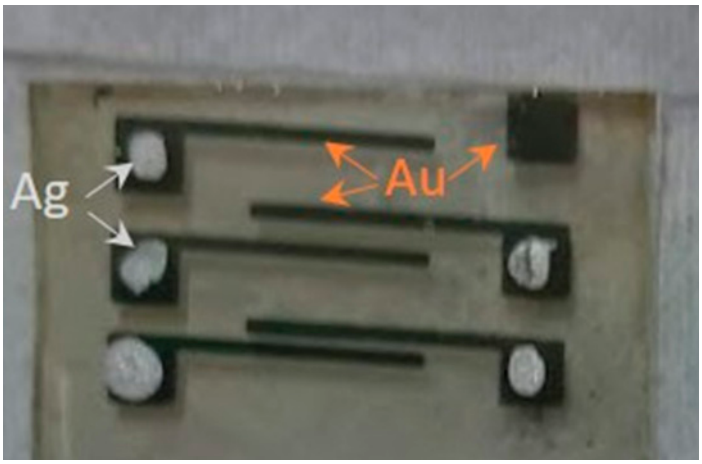

Figure S1. A representative photograph of the sample used for electrical measurements of the CZTS NC films in this work. NC film is deposited on a glass substrate by spin-coating, gold contacts deposited on the NC film by thermal evaporation, silver paste on top of the gold contact pads, and thermal paste on the bottom of the substrate.

Table S1. Elemental compositions (in atomic %) derived from XPS on the CZTS NC samples with different nominal Cu content for the initial and annealed films. The sulfide sulfur (S^{2-}) associated with the NC structure and thioglycolate associated with the NC surface (S^{1-}) are taken into account, which is the most suitable approach for representing the composition of TGA stabilized CZTS colloidal NCs according to our previous work [1].

	$Cu_{0.25}$ 120 °C	$Cu_{0.25}$ 220 °C	Cu_2 120 °C	Cu_2 220 °C	Cu_4 120 °C	Cu_4 220 °C	Ideal Cu_2ZnSnS_4
Cu	9	6	22	16	34	16	25
Zn	39	30	25	21	21	46	12.5
Sn	5	6	7	10	2	4	12.5
(S^{2-} + S^{1-})	47	59	46	53	43	35	50

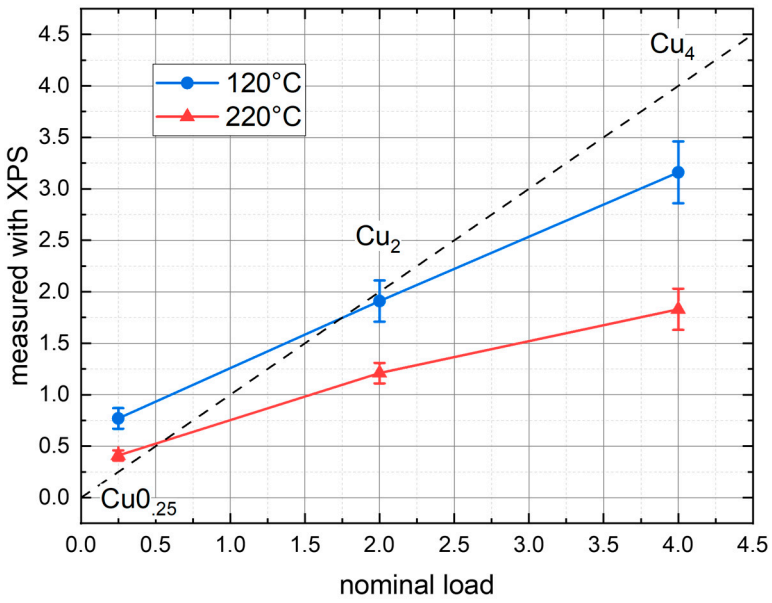

Figure S2. XPS-derived copper contents in CZTS films, normalized for sulfur content (S_4) for comparison with the stoichiometric kesterite Cu_2ZnSnS_4. The data correspond to the films heated at 120 °C (initial) and 220 °C (annealed). The dashed line is an eye guide for the ideal case of matching the measured amount of copper with its nominal load.

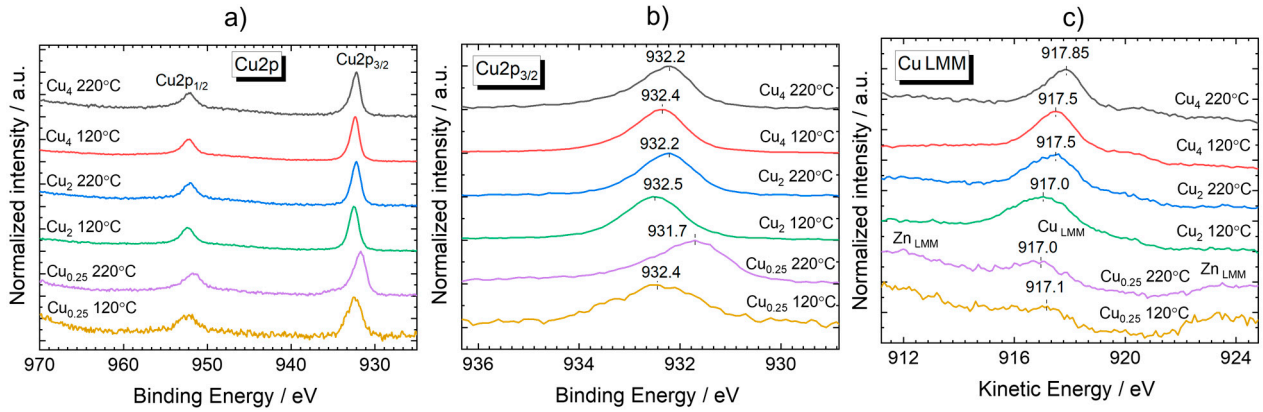

Figure S3. Extended Cu2p (a), narrow $Cu2p_{3/2}$ (b), and Cu_{LMM} Auger (c) high-resolution XPS spectra of pristine and annealed CZTS NC films synthesized with different nominal copper contents.

Table S2. Vibrational modes of carboxylic groups detected in the middle-infrared spectra of Cu_4, Cu_2, and $Cu_{0.25}$ initial (*i.e.* heated at 120 °C) and annealed at 220 °C samples.

Sample	ν(COO) sym. /cm^{-1}	ν(COO) asym. /cm^{-1}	Δ/cm^{-1}	Most Probable Assignment [2,3]
Cu_4 120 °C	1395	1570	175	Zn- or Cu- **chelate** bonding
Cu_2 120 °C	1380	1565	185	
	1385	1645 (shoulder)	260	Sn-bonding
$Cu_{0.25}$ 120 °C	1390	1590	200	Zn- or Cu- **bridging** bonding
Cu_4 220 °C	1390	1590	200	Zn- or Cu- **bridging** bonding
Cu_2 220 °C	1380	1590	210	
$Cu_{0.25}$ 220 °C	1390	1590	200	

References

1. Stroyuk, O.; Raevskaya, A.; Selyshchev, O.; Dzhagan, V.; Gaponik, N.; Zahn, D.R.T.; Eychmüller, A. "Green" Aqueous Synthesis and Optical Characterization of Colloidal Cu_2ZnSnS_4 Nanocrystal Inks. *Sci. Rep.* **2018,** *8*, 13677.

2. Nakamoto, K. Infrared and Raman Spectra of Inorganic and Coordination Compounds: Part A: Theory and Applications in Inorganic Chemistry. John Wiley & Sons Inc.: Hoboken, NJ, USA, 2009.
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