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Raman scattering quantitative assessment of the anion composition ratio in Zn(O,S) layers for Cd-free chalcogenide based solar cells

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Supplementary information

The detailed conditions of the radio-frequency (rf) sputtering process with indication of used target and O_2/Ar ratio for each sample are presented in Table S1. Rf power was 1 W/cm^2 and substrate temperature was 150^o C.

Table S1: Details of the reactive rf magnetron sputtering process.

No.	Target	O_2/Ar	S/(S+O)
1	ZnS (2)	1.6 %	0.06
2	ZnS (1)	1.7 %	0.08
3	ZnS(1)	1.5 %	0.11
4	ZnS(1)	1.3 %	0.21
5	ZnS(1)	1.1 %	0.28
6	ZnS (2)	0.8 %	0.52
7	ZnS(1)	0.9 %	0.77
8	ZnS(1)	0.8 %	0.83
9	ZnS(1)	0.5 %	0.91

Comments: Target (2) has a higher material density that target (1)

The crystal structure was studied by X-ray diffraction (XRD) in θ/2θ configuration using a Bruker D8 diffractometer with copper K_α radiation. Obtained patterns are presented in Figure S1. As shown in this figure, samples with S/(S+O) ≤ 0.3 show two peaks that have been identified with 100 and 002 hexagonal peaks, while S-rich samples show only one peak that has been assigned to the 111 peak of the cubic structure. This suggests the existence of a phase transition in the samples from the hexagonal to the cubic crystalline structure. In addition, the diffractogram from the sample with S/(S+O) close to 0.5 shows a very broad band with very low intensity, in agreement with the worsening of the crystalline quality that has also been observed by Raman.

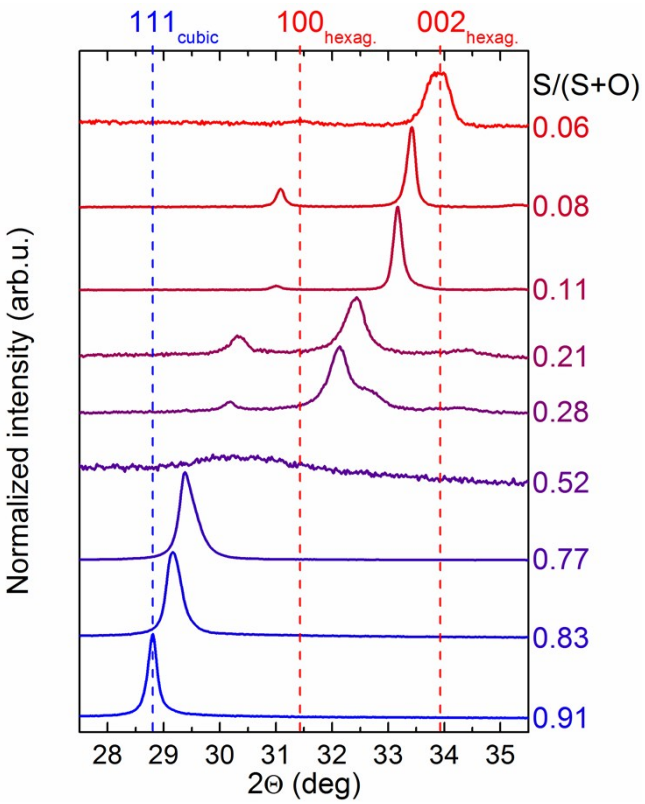

Fig. S1: XRD patterns of sputtered Zn(O,S) films on Mo.

Figure S2 plots the X-ray photoelectron spectroscopy (XPS) spectra measured from a representative sample (corresponding to the sample with S/(S+O) = 0.28). Here each of the spectra corresponds to the data obtained at a different depth, which was changed by sputtering the samples with an Ar^+ beam (4 keV source energy) with a rate of 20 nm/min. Analysis of the intensity of the peaks allowed to obtain the S and O contribution and as result the S/(S+O) content ratio in the samples.

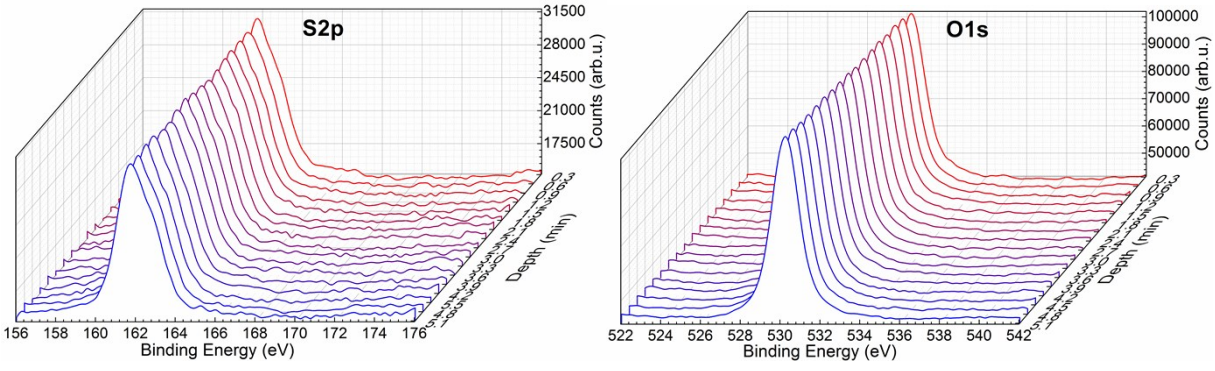

Fig. S2: Depth resolved XPS S2p (left) and O1s (right) spectra of a thin film with S/(S+O) = 0.28.

The Raman scattering spectra of Zn(O,S) solid solutions excited by 532 nm laser line are shown in Fig. S3. As it seen, spectra are similar to those measured with the 325 nm laser line excitation (shown in Figure 2 in the manuscript). Here, it is clearly seen that the signal to noise ratio deteriorates at the extremes of the solid solution, i.e. for S/(S+O) ratio close to 0 and to 1. This is related to the fact that these samples have a higher bandgap and therefore are farer away from the resonant conditions when using the green laser line as excitation light.

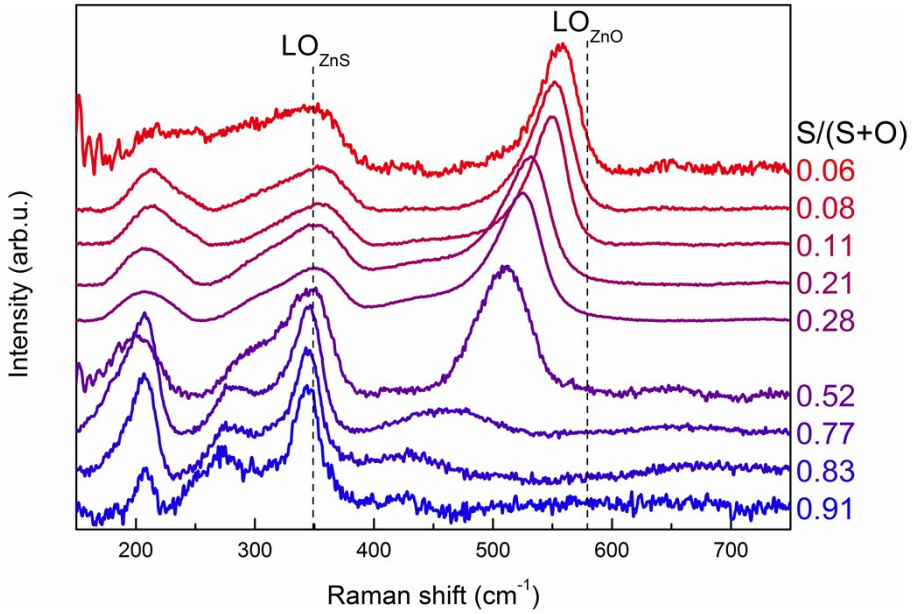

Fig. S3: Raman spectra of Zn(O,S) solid solutions excited by 532 nm laser line, normalized to the intensity of the most intense peak (LO_{ZnO} for samples with S/(S+O) < 0.5, LO_{ZnS} for samples with S/(S+O) > 0.5). Numbers on the right correspond to the average composition measured by XPS at the 100 nm surface region from the different samples.