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Supporting Information

Alkali doping strategies for flexible and light-weight CZTSe solar cells.

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Part 1:

Figure S1. Three dimensional AFM images of SS 430 (a) with R_a of 43 nm, and SS 430/Cr/Mo_A (b) with R_a of 40 nm.

EXPERIMENT 1

Table S1. Summary of optoelectronic parameters of CZTSe solar cells based on NaF and KF PAS alkali doping strategies based on Mo_1 substrate configuration. Different alkali fluoride layers thickness was studied.

Doping estrategy	Layer thickness (nm)	J _{SC} (mA/cm ²)	V _{OC} (mV)	FF (%)	η (%)	R _s (ohm cm ²)	R _{sh} (ohm cm ²)
	0	23.1	250	26.4	2.1	3.4	24.9
NaF PAS	10	22.9	217	35.5	1.8	2.4	17.6
	20	24	217	38.9	2.0	2.7	26.5
	0	23.6	231	39.9	2.2	2.7	28.8
KEDAG	5	23.9	276	44.2	2.8	1.9	43.1
KF PA5	10	22.2	257	34.8	2.0	4.6	25.3
	15	25.7	309	43.4	3.4	2.5	52.0
Mixed PAS (NaF+KF)	0	23.1	250	26.4	2.1	3.4	24.9
	20+10	19.2	188	36.2	1.3	2.6	19.6

Table S2. Summary of optoelectronic parameters of CZTSe solar cells based on different substrates configurations using Mo/MoNa layers. Na doped Mo layers with 5 at% Na content (MoNa5) were investigated. Different MoNa thickness layers obtained with several sputtering deposition conditions were tested.

Doping Layer estrategy thickness		Sputtering conditions		J _{SC} (mA/cm ²)	V _{OC} (mV)	FF (%)	η (%)	R _s (ohm cm ²)	R _{sh} (ohm cm ²)
	(nm)	Power (W/cm ²)	Pressure (Pa)						
MoNa5	300	2.5	0.6	26.3	322	50.6	4.3	1.5	97.0
	400	2.5	0.6	24.8	228	41.7	2.4	2.4	38.1
	500*	2.5	0.6	21.5	225	41.5	2.0	2.5	36.1
	200+200	2.5	0.6	24.9	239	44	2.6	2.1	43.6
	400*	2.5	0.4	14.3	119	29.9	0.5	0.9	10.1
	400	2.5	0.2	21.0	222	39.7	1.8	3.0	31.0

Note that (*) in Table S2 refers to the presence of Na on the Mo/MoNa substrates surface before the metallic stack deposition. In consequence, alteration of the results and low reproducibility should be expected for the solar cells based on these substrates. As explained in the main document, Na diffusion from the MoNa layer towards the Mo_B or Mo_A cap layers can easily happen upon exposure to the atmosphere, providing Mo_B thickness is too short and/or MoNa layer thickness is too large.

Table S3. Summary of optoelectronic parameters of CZTSe solar cells based on NaF and KF PDT alkali doping strategies using Mo_1 substrate configuration. Low pressure (1.5 mbar) and high pressure (1 bar) PDT processes at 400 °C in Se atmosphere were analyzed. Different alkali fluoride layers thickness was studied.

Doping estrategy	Alkali type	Layer thickness (nm)	J _{SC} (mA/cm ²)	V _{oc} (mV)	FF (%)	η (%)	R _s (ohm cm ²)	R _{sh} (ohm cm ²)
	NaF	0	24.3	233	37.1	2.1	2.8	21.3
		10	21.3	245	34.5	1.8	4.6	23.8
PDT low		20	23.1	266	40.5	2.5	3.6	41
pressure	KF	10	24.0	245	40.9	2.4	2.9	36.2
	Mixed	10+10	22.1	231	35.9	1.8	4	25.6
	(NaF+KF)	20+10	24.4	282	40.5	2.8	3.6	4.0
	NaF	0	23.7	274	40.2	2.6	3.8	41.3
		10	21.9	270	43.4	2.6	2.8	51.8
PDT high pressure		20	22.3	279	41.1	2.6	3.7	45.9
	KF	10	21.8	257	43.5	2.4	2.4	47.0
		20	20.3	211	36.2	1.6	3.5	23.5



Figure S2. SEM top images of CZTSe absorbers grown on flexible SS 430 substrates with different Na content from PAS method: a) Reference cell (no Na), b) 05 nm NaF, c) 10 nm NaF and d) 20 nm NaF.



Figure S3. SEM top images of CZTSe absorbers grown on flexible SS 430 substrates with different K content from PAS method: a) Reference cell (no K), b) 05 nm KF, c) 10 nm KF and d) 15 nm KF.



Figure S4. SEM top images of CZTSe absorbers grown on flexible SS 430 substrates with and without different MoNa layers. a) Reference cell (no Na), b) 400 nm MoNa 0.2 Pa, c) 400 nm MoNa 0.6 Pa d) 300 nm MoNa 0.6 Pa.



Figure S5. XRD patterns of bare SS 430 ferritic substrate, SS430/Cr/Mo $_1$ and SS430/Cr/Mo/MoNa configurations.

Table S4. FWHM of 112 peak, lattice parameters and unit cell volume of CZTSe with different doping cases: reference cell (non doped), SLG underneath, KF and NaF-PAS deposition and MoNa doping.

Doping case	FWHM (°)	a (Å)	c (Å)	V (Å ³)
Ref cell	0.068	5.694	11.347	367.9
KF-PAS	0.071	5.690	11.336	367.0
NaF-PAS	0.064	5.691	11.338	367.2
MoNa	0.078	5.694	11.342	367.7
SLG	0.050	5.694	11.349	368.0



Figure S6. Raman spectra (532.5 nm) of non doped (Reference cell) and Na and K doped (SLG underneath, 20 nm NaF PAS, MoNa and 15 nm KF PAS) CZTSe absorbers from Experiment 1. The Raman shift and FWHM of the main A mode for the different absorbers are shown as inset.

Raman spectroscopy using a 532.5 nm excitation source was performed in the same set of samples analized by SEM, XRD and TOF-SIMS in the main document. The crystalline quality is slightly higher for the reference cell and for the MoNa cases as revealed by the FWHM and Raman shift of the main A mode values. In the case of NaF PAS doped sample, the crystalline quality is the lowest, correlating with the highest value of FWHM and the lowest frequency of the main A mode. The results slightly differ from the ones obtained by XRD (see Table S4), but Raman spectroscopy is a surface sensitive and microscopic technique compared with macroscopic structural information such as the one provided by XRD.



Figure S7. XRD patterns of non doped (ref cell), NaF-PAS and MoNa doped CZTSe absorbers. XRD reference pattern in navy blue of CuCrSnSe₄ phase is added at the bottom.

It seems clear that presence of a CuCrSnSe₄ phase in the non doped CZTSe absorber when compared with the MoNa doped one can be confirmed, since the most intense diffraction peaks for this phase can be easily identified in Figure S5. Additionally, a CrCuO₂ phase could be present in the non doped CZTSe sample, this is indicated by the blue arrow at a Bragg angle of 36.38 °. The question mark at $2\theta = 39.3^{\circ}$, indicates the presence of an unidentified peak which has only been detected in the sample named as ref. cell. In the case of the NaF-PAS doped sample, only a small contribution of the CuCrSnSe₄ phase can be confirmed due to the weak XRD signal for its most intense diffraction peaks.



Figure S8. Average and maximum cell efficiency for flexible CZTSe solar cells produced in Experiment 1 with different doping methods: Ref. case (non-doped), SLG underneath, KF and NaF-PAS deposition and MoNa doping.

EXPERIMENT 2

Table S5. Summary of optoelectronic parameters of flexible CZTSe solar cells based on different Cr barriers (thickness and sputtering conditions) along with a 800 nm Mo_A back contact (see Figure 1, Experiment 2 of the main document).

Cr Sputtering conditions thickness		J _{SC} (mA/cm ²)	V _{OC} (mV)	FF (%)	η (%)	R _s (ohm cm ²)	R _{sh} (ohm cm ²)	
(nm)	Power (W/cm ²)	Pressure (Pa)						
200	2.5	0.45	23.7	231	39.9	2.2	2.7	29
500	2.5	0.45	28.1	285	45.2	3.6	2.2	47
200	3.75	0.15	21.8	164	32.7	1.2	1.8	11
500	3.75	0.15	24.2	209	37.0	1.9	2.3	18

It can be concluded that using lower kinetic energy conditions for the sputtering process of Cr layers is much better for solar cell performance. It is clear that lower pressure and higher power density led to a higher degree of impurities diffusion since an important reduction of the photocurrent can be noticed [1, 2]. The sample with 200 nm Cr went from 23.7 mA/cm² to 21.8 mA/cm², whereas the one relying in 500 nm Cr barrier went from 28.1 mA/cm² to 24.2 mA/cm².

Table S6: Summary of optoelectronic parameters of flexible CZTSe solar cells based on different Cr barriers (thickness) and different Mo configurations (monolayer, bi-layer and trilayer) (See figure 1, Experiment 2 of main document).

Cr thickness	Mo con	Mo configuration		V _{OC} (mV)	FF (%)	η (%)	R _s (ohm cm ²)	R _{sh} (ohm cm ²)
(nm)	Thickness (nm)	Mo type						
200	800	Mo _A	23.7	231	39.9	2.2	2.7	29
500	800	Mo _A	28.1	285	45.2	3.6	2.2	47
200	150+500	Mo _A +Mo _B	25.2	273	46.7	3.2	1.5	51
500	250+500+30	Mo _A +Mo _B +Mo _A	27.4	292	51.7	4.1	0.5	70
1000	250+500+30	Mo _A +Mo _B +Mo _A	26.9	286	33.8	2.6	2.1	16

Table S7: Summary of optoelectronic parameters of flexible CZTSe solar cells based on different Cr barriers (thickness) and different Mo/MoNa layouts (See figure1, experiment 2 of main document). MoNa10 was 200 nm thick and sputtered at 2.5 W/cm² and 0.6 Pa. Note that thinner layers than 500 nm for Mo_B were tried but Na diffusion was observed shortly after the sputtering process on the back contact surface as explained in the main document.

Cr thickness (nm)	Mo/Mol	J _{SC} (mA/cm ²)	V _{OC} (mV)	FF (%)	η (%)	R _s (ohm cm ²)	R _{sh} (ohm cm ²)	
500	250+200+500+30	Mo _A +MoNa+Mo _B +Mo _A	24.1	281	45.6	3.1	2.1	58
500	250+200+500	Mo _A +MoNa+Mo _B	23.4	257	42.4	2.5	2.2	37
1000	250+200+500+30	Mo _A +MoNa+Mo _B +Mo _A	16.4	150	32	0.8	2.1	16

Table S8: Summary of optoelectronic parameters of CZTSe solar cells based on different substrates configurations using Mo/MoNa layers. Na doped Mo layers with 10 at% Na content (MoNa10) were investigated. MoNa layers with different thickness and produced with several sputtering deposition conditions were tested. A 500 nm Cr barrier was chosen to minimize impurities diffusion from the SS substrate. Note that MoNa layers thicker than 200 nm led to Na diffusion on the surface of the samples shortly after their deposit.

Doping Layer estrategy thickness		Sputtering conditions		J _{SC} (mA/cm ²)	V _{OC} (mV)	FF (%)	η (%)	R _{ss} (ohm cm ²)	R _{sh} (ohm cm ²)
	(nm)	Power (W/cm ²)	Pressure (Pa)						
	100	2.5	0.2	26.7	285	43.4	3.3	1.7	36.2
	100	2.5	0.4	25.9	319	51.1	4.2	1.2	104
MoNa10	100	2.5	0.6	26.7	326	50.3	4.4	1.6	84.6
	100	2.5	0.8	22.9	230	36.0	1.9	2.7	20.3
	200	2.5	0.6	24.1	281	45.6	3.1	2.1	16.1

In order to estimate the impact of a higher hole carrier concentration derived from C-V measurements on V_{OC} increase as a consequence of alkali doping, the following equation can be used:

$$\Delta V_{OC} = \frac{k_B T}{q} ln \left(\frac{N_a}{N_{a0}} \right)$$
(S1)

With k_B being the Boltzmann constant, q the elemental charge, T the temperature and Na the net doping profile (minimum from the doping profiles plots) for the alkali doped case, i.e. KF or Mona + Ge, and Na0 the net doping profile for the non-doped sample (ref. cell).

Additional References

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[2] R. Wuerz, A. Eicke, F. Kessler, F. Pianezzi, Influence of iron on the performance of CIGS thinfilm solar cells, Solar Energy Materials and Solar Cells, 130 (2014) 107-117.