

## SUPPORTING INFORMATION

### Uncovering details behind the formation mechanisms of $\text{Cu}_2\text{ZnGeSe}_4$ photovoltaic absorbers

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Figure S1 shows the Auger composition profiles for samples T1 to T6, including the evolution of Cu, Zn, Ge, Se and Mo. These profiles were used to create Figure 6. It must be taken into consideration that the sputtering time is dependent on the material properties such as the density of the film, therefore it may not correspond to the actual thickness of each layer.

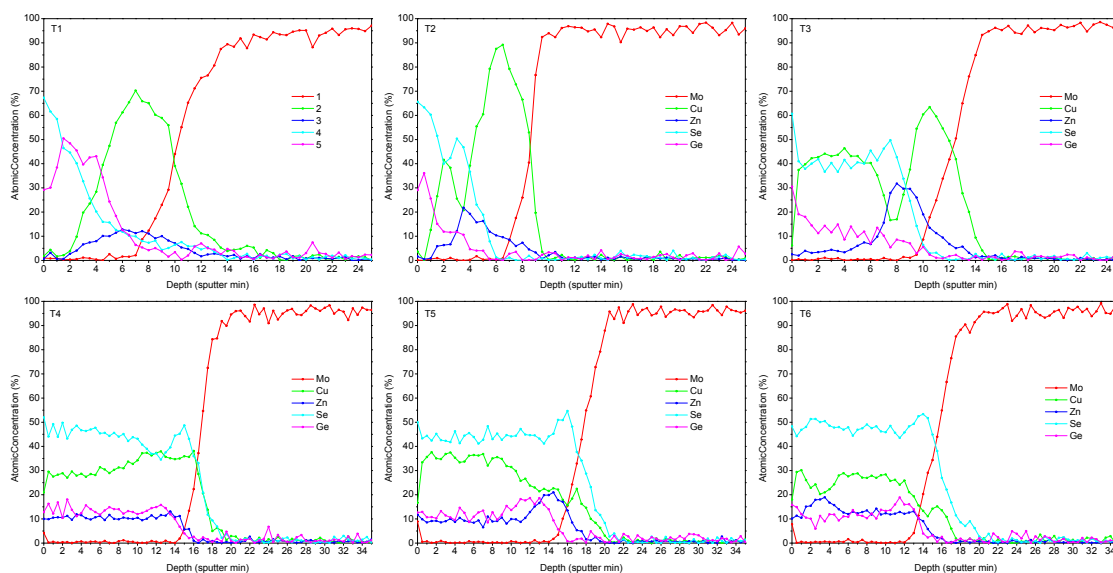


Figure S1. Auger profiles for samples T1 to T6.

In Figure S2 the different Raman spectra obtained with 532 nm and 785 nm excitation wavelengths in samples T1 to T6.

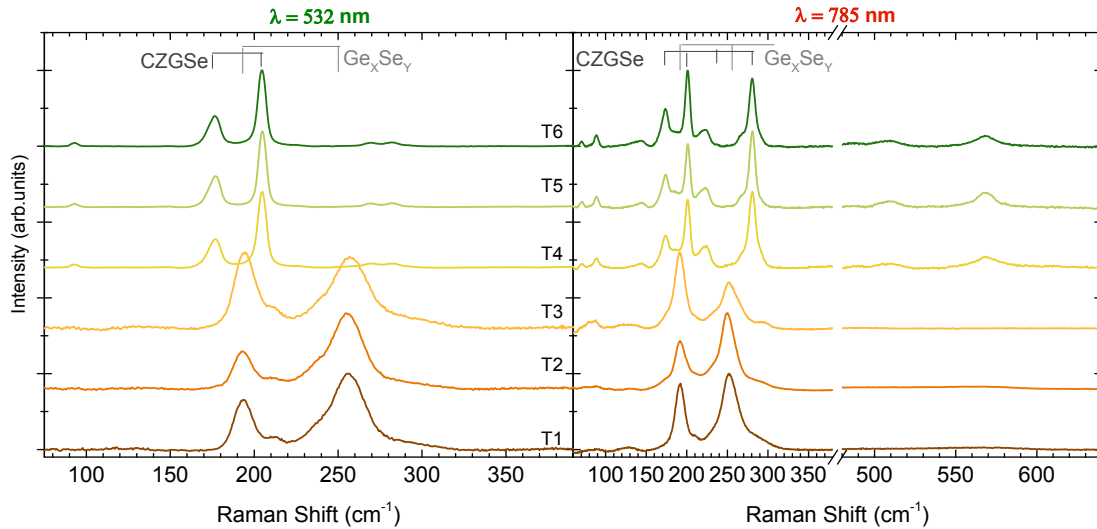


Figure S2. Complete Raman analysis of samples T1 to T6 using 532 nm and 785 nm excitation wavelengths.

Figure S3 and S4 shows the 442 and 785 nm Raman spectra of the three samples at different polishing stages. For all the samples, the two main observed peaks at the surface are around 193 and 250  $\text{cm}^{-1}$  corresponding to  $\text{Ge}_x\text{Se}_{1-x}$  with  $x < 0.1$ .

For sample T1 the only observed changes as the sample is polished are a small widening of the peaks and an increase of the spectrum noise, something explained by the thinning of the samples, and confirming that  $\text{Ge}_x\text{Se}_{1-x}$  with  $x < 0.1$  is the dominant phase, with no evidence of other chalcogenide phases.

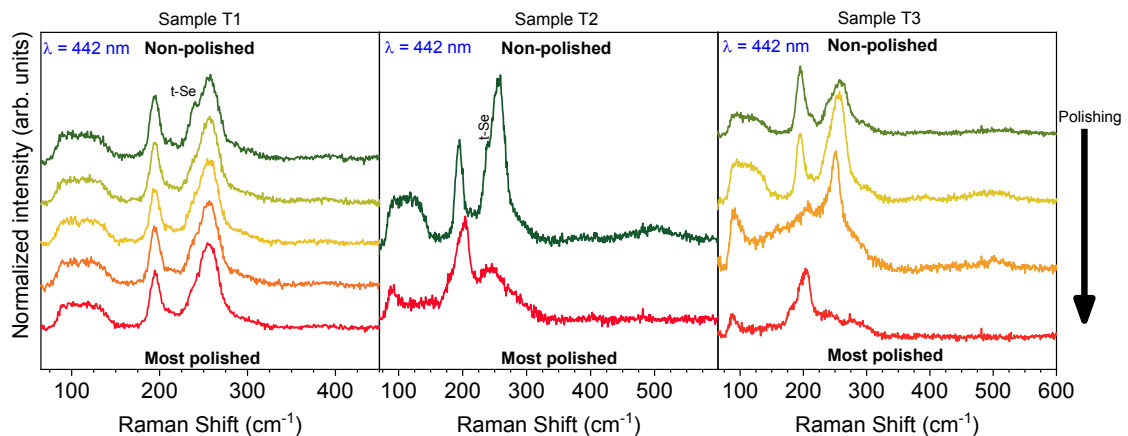


Figure S3. Raman spectra of samples T1, T2, and T3 obtained using 442 nm excitation wavelength. Each spectrum is measured after one polishing cycle with a diamond film.

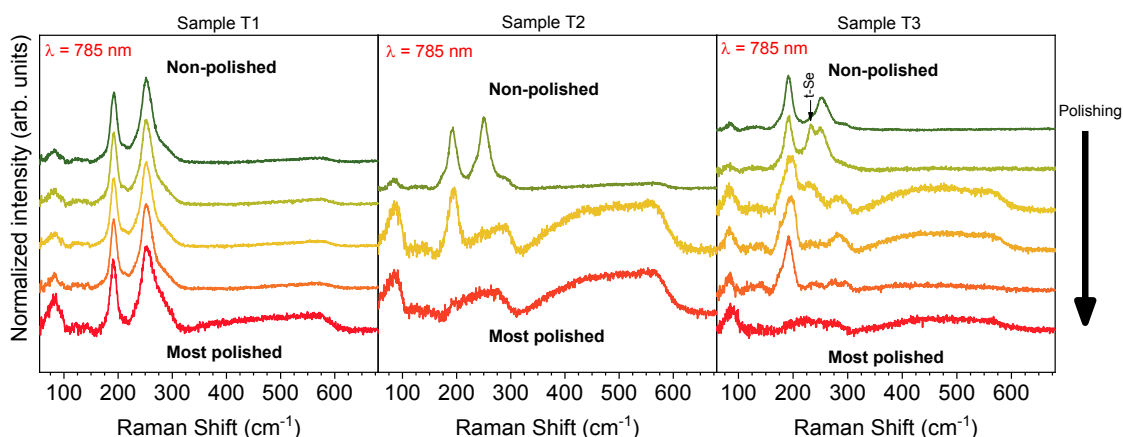


Figure S4. Raman spectra of samples T1, T2, and T3 obtained using 785 nm excitation wavelength. Each spectrum is measured after one polishing cycle with a diamond film.

In the case of sample T2, peak around  $250\text{ cm}^{-1}$  disappears after the first polishing cycle, while peak around  $193\text{ cm}^{-1}$  can still be observed. After a second polishing cycle,  $193\text{ cm}^{-1}$  peak also disappears, while broad peak around  $292\text{ cm}^{-1}$  is still observed in 785 nm spectra. However,  $193\text{ cm}^{-1}$  peak does not disappear in 442 nm spectra, but it is shifted to  $203\text{ cm}^{-1}$ . A similar behavior can be observed for sample T3, since  $250\text{ cm}^{-1}$  peak disappears as the sample is polished and  $193\text{ cm}^{-1}$  peak lasts longer, but it eventually disappears in 785 nm spectra too. In addition, trigonal selenium is detected in all three sample.

It is possible to assign the observed peaks for T2 and T3 polished samples to  $\text{Cu}_2\text{GeSe}_3$  or  $\text{Cu}_2\text{GeSe}_4$  phases,<sup>1,2</sup> strongly supporting the presence of these ternary phases during these stages. It is also possible, especially in the last 442 nm spectra of samples T2 and T3, that the peaks correspond to some intermediate phase between  $\text{Cu}_2\text{GeSe}_3$  and  $\text{Cu}_2\text{ZnGeSe}_4$ .

## References

- 1 G. Marcano et al. *Solid State Communications*, 146, 2008, 65–68
- 2 S.G. Choi et al. *J. Appl. Phys.* 114, 2013, 033531