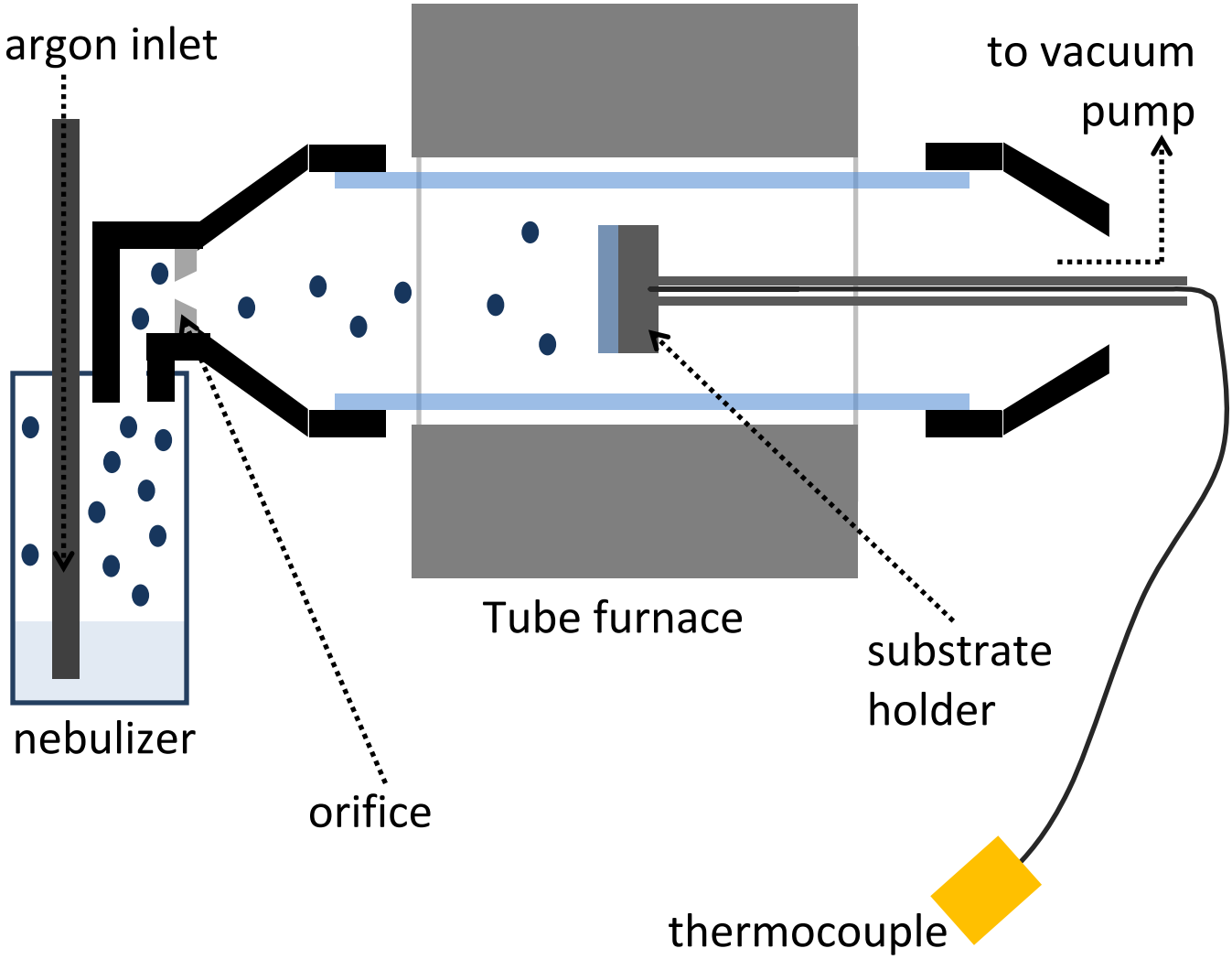
Electronic Supplementary Material (ESI) for ChemComm.

Spray pyrolysis of CZTS nanoplatelets

Supplementary information

Figure S1: schematic of spray pyrolysis apparatus



EDS in the SEM

The chemical microanalysis of the reaction products were performed by energy dispersive X-ray spectroscopy (EDS) in a FEI NNS450-FEG SEM equipped with Oxford Instruments Aztec Synergy system and X-Max 50mm^2 SDD detector with resolution of 127 nm at MnKα. The analyses were performed at accelerating voltages of 5 kV in the SEM in order to reduce contribution from the substrate material. Quantitative analyses were obtained from the CZTS thin films on Mo substrate by scanning square areas of about 10 μm on the side. Quantification procedures follow the PAP model [Jean-Louis Pouchou and Francoise Pichoir "Quantitative analysis of homogeneous or stratified microvolumes applying the model 'PAP'", p. 31 – 104, in Electron probe Quantification. Eds. K.F.J. Heinrich and Dale Newburry, Plenum Press, New York, 1988] incorporated in the Aztec system. Polished flat reference samples of homogeneous chalcopyrite $CuFeS_2$, ZnS, SnO_2 (purchased from Astimex Scientific LtD., Toronto Canada) were used to collect matrix correction factors for Cu L, Zn L, S K, Sn L lines at 5 kV and scanning conditions replicating the sample collection data. Pure Co was used as the beam reference standard as utilized by the Oxford Aztec system [P.J. Statham, Prospects of single standard quantitative analysis with SDD, Microscopy and Microanalysis, 15 (Suppl 2), p. 528-529, 2009]. The concentration values reported in Table 1 are average from multiple analysis locations and the standard deviation is listed next to elemental concentration value.

TEM-EDS

The chemical microanalysis of the reaction products were performed by energy dispersive X-ray spectroscopy (EDS) in a CM300 TEM equipped with EDAX Genesis EDS system and 30 mm^2 Si(Li) detector with resolution of 127 nm at MnKα at 300 kV. The EDS analyses in the TEM were quantified using the thin-film approach with carefully determined k factors from homogeneous CuS, ZnS, SnO_2 and $ZnSiO_4$ pure standards (from Micro-Analysis Consultants LtD., Cambridgeshire UK) using the parameterless method. [Van Cappellen, Microscopy Microanalysis Microstructures 1, 1990, 1.]

Selected TEM analyses are shown in Table 2. The uncertainty in determining the atomic concentrations were estimated by adding the error in determination of the corresponding k-factor in the standards as function the net intensity error and the error for the net intensity measurements for each element in the sample. Sample thickness of the analyzed area was estimated with an average uncertainty of about ±50 nm, which was taken into account in the reported overall uncertainty for the elemental concentrations.

Determination of accurate k factors

Accurate determination of chemical composition in the TEM based on the thin-film approach depends upon utilizing accurate and precise k factor values. Such values can be established from homogeneous standard samples with precisely known composition for which the thickness of the analyzed particles is known or they are sufficiently thin so that no absorption and fluorescence takes place. Practically such conditions are not easily obtainable in general case. To overcome this approach the parameterless method can be utilized to determine precise k factors that represent values not modified by absorption.(Van Cappellen, Microscopy Microanalysis Microstructures 1, 1990, 1.)

For the analysis of the studied reaction products homogeneous CuS, ZnS, SnO_2 and $ZnSiO_4$ pure standards mounted on lacey-carbon coated nickel TEM grids were used. Wedge shaped crystals were selected from each standard sample and about 15 analyses were obtained at 300 kV and probe diameter of 50 nm from regions of decreasing thickness. The plots of the total net intensity of the measured peaks versus the calculated k factors (S and O were used as reference elements) allow a polynomial curve to be fitted and the intercepts allowed the values of the $k_{Cu/S}$, $k_{Zn/S}$, $k_{Sn/O,}$ $k_{Zn/O}$ to be determined. The $k_{Sn/S}$ was estimated using the measured Zn:S, Zn:O, Sn:O ratios. The uncertainty in measuring the peak intensities due to the counting

statistics was determined to be in the range of 1.8 to 2.5%, which directly translates into the precision of the determined k factor values.