Supporting Information

Thioether functionalised Gallium and Indium Alkoxides in Materials Synthesis

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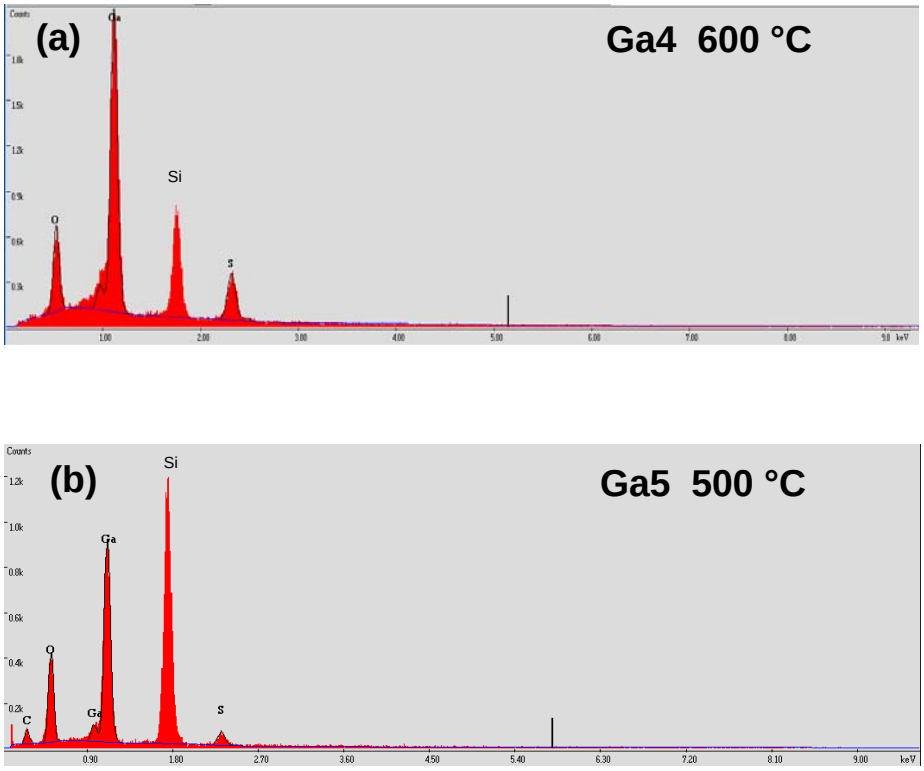

Figure S1: EDX spectra of films obtained by LPCVD grown at (a) 600 °C using **Ga4** and (b) 500 °C using **Ga5**. The carbon contamination of the film derived from the gallium alkoxide derivative of the tertiary alcohol is clearly visible in the EDX spectrum (b).

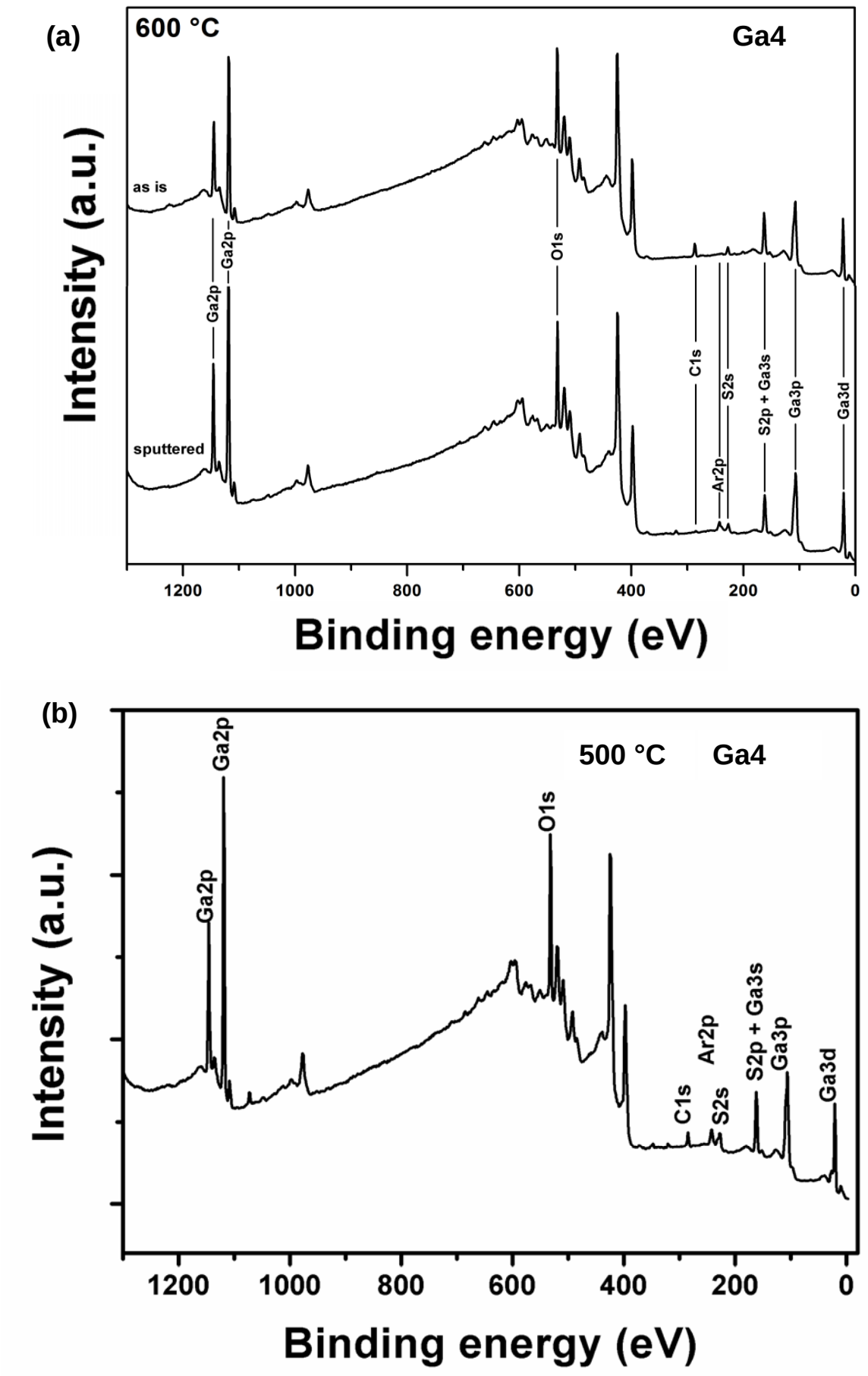

Figure S2: XPS survey of films obtained by LPCVD using **Ga4** grown at (a) 600 °C before and after sputtering and (b) 500 °C after sputtering. Spectra measured with Al Kα radiation at room temperature.

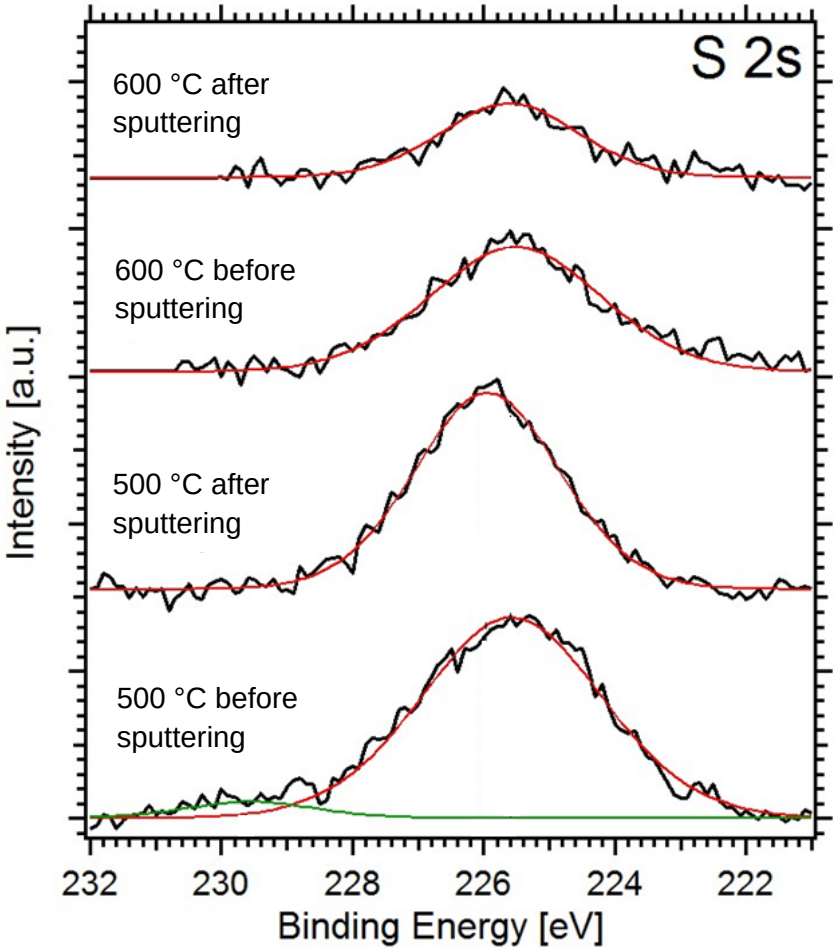

Figure S3: XPS spectra of the S2s peak of CVD deposits using **Ga5** at 500°C and 600 °C recorded with an Al Kα lab source.

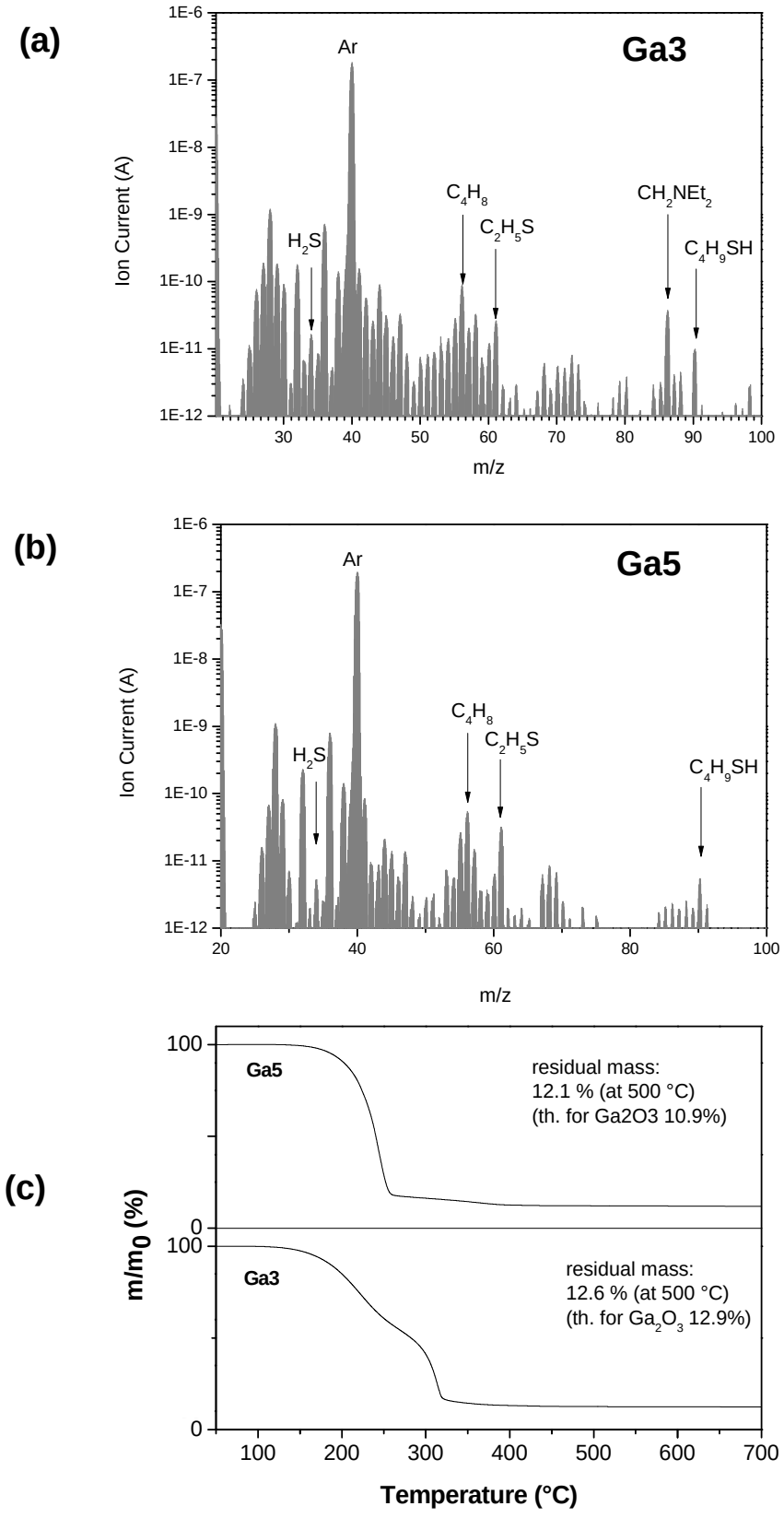

Figure S4: (a) Mass spectra of the decomposition products using (a) **Ga3** with the major fragments associated to the amino and thioether functionality as well as a significant fraction of hydrogen sulphide and (b) **Ga5** as the only Ga alkoxide with symmetric thioether alcoholate ligands suitable for LPCVD. (c) shows the TG analysis with a two-step decomposition for **Ga3** (observed for Ga1-Ga4) and the unusual single step decomposition for **Ga5**.

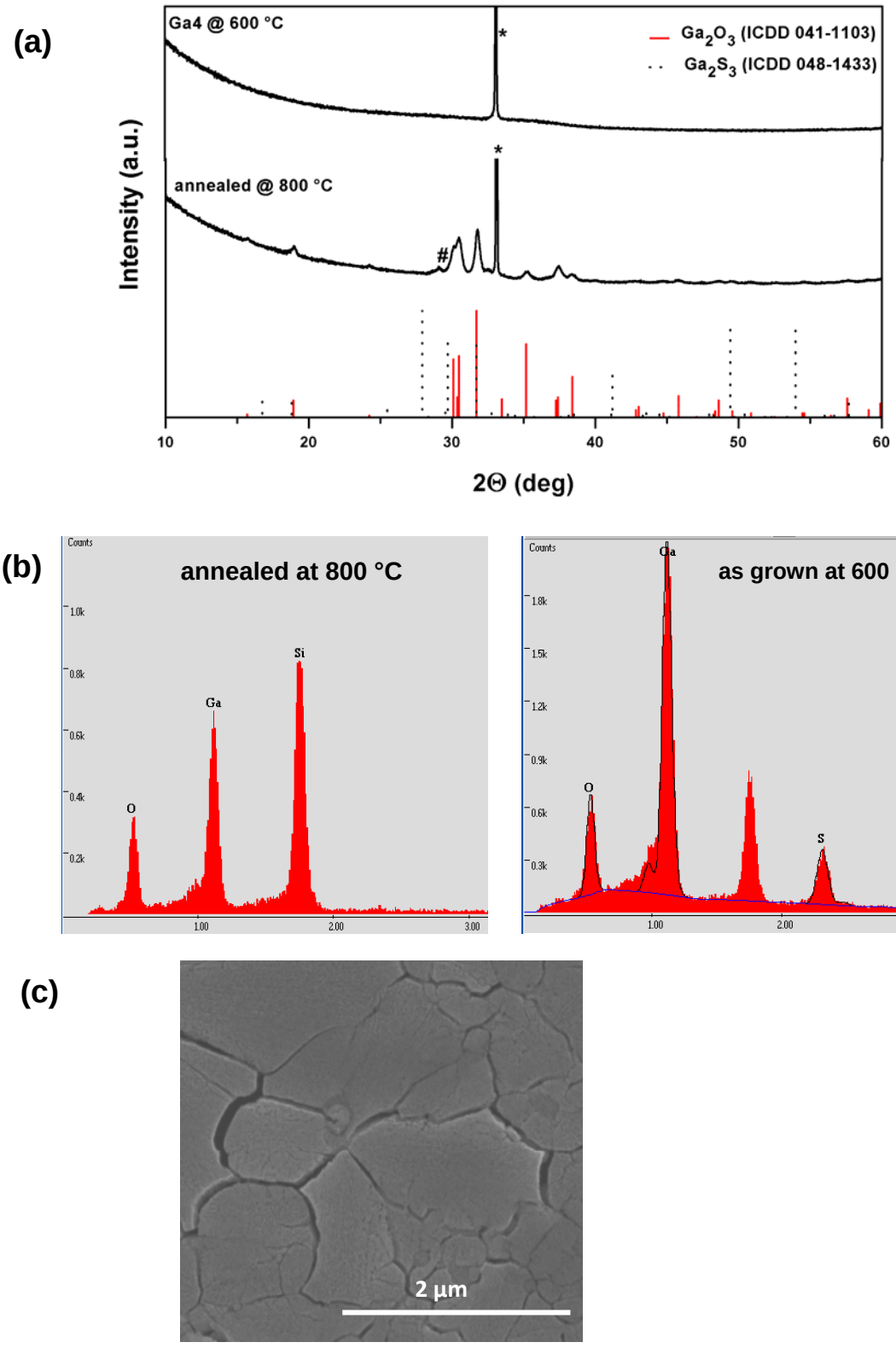

Figure S5: (a) Thin film of $Ga_2O_{3-x}S_x$ prepared using **Ga4** at 600°C and annealing at 800 °C for 2h under vacuum. The film crystallises and shows the monoclinic Gallium oxide phase. * denotes the signal of the substrate and # a secondary phase, which could not be assigned to a common oxide or sulphide phase. (b) EDX spectra of the annealed sample, without any signal of sulphur in the coating, and the as grown sample. (c) The coating cracks during the thermal processing and appears to be partially porous in the SEM image.

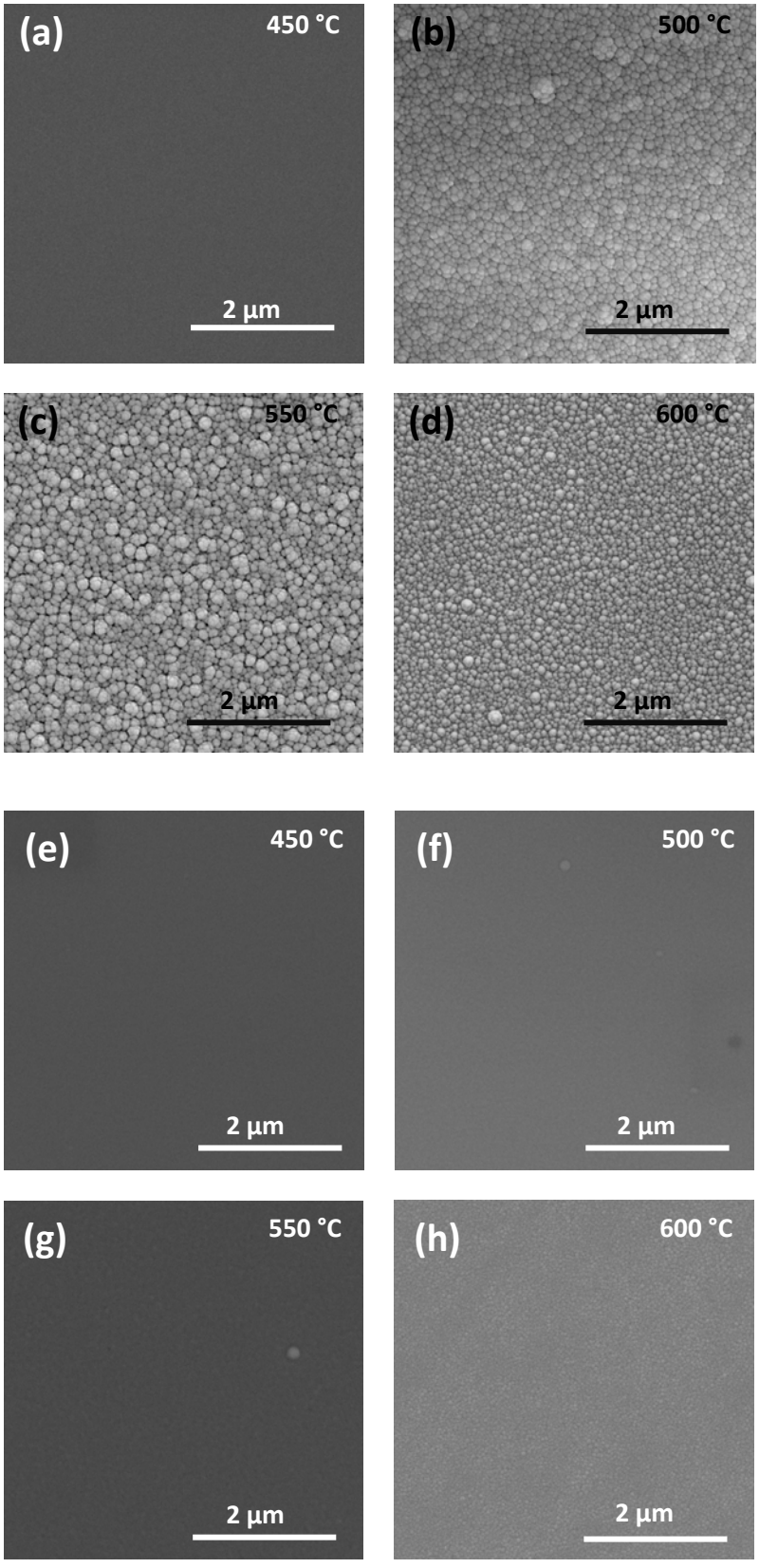

Figure S6: SEM images of LPCVD deposits using **Ga3** (a-d) and **Ga4** (e-h) as precursors at 450 °C – 600 °C substrate temperature.

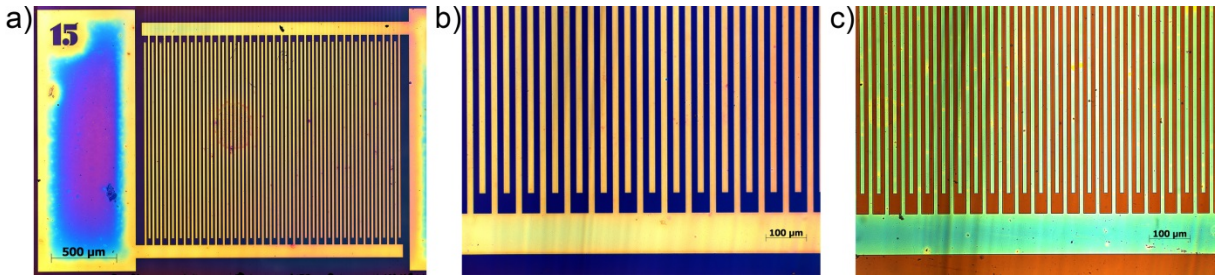

Figure S7: Micrographs of samples used for impedance measurements with interdigitating Pt finger electrodes beneath a Ga_2O_3 thin film. On one type of sample the electrode width and spacing are 15 µm each – (a) and (b); on the second type of samples electrode width and spacing are 10 µm each (c).

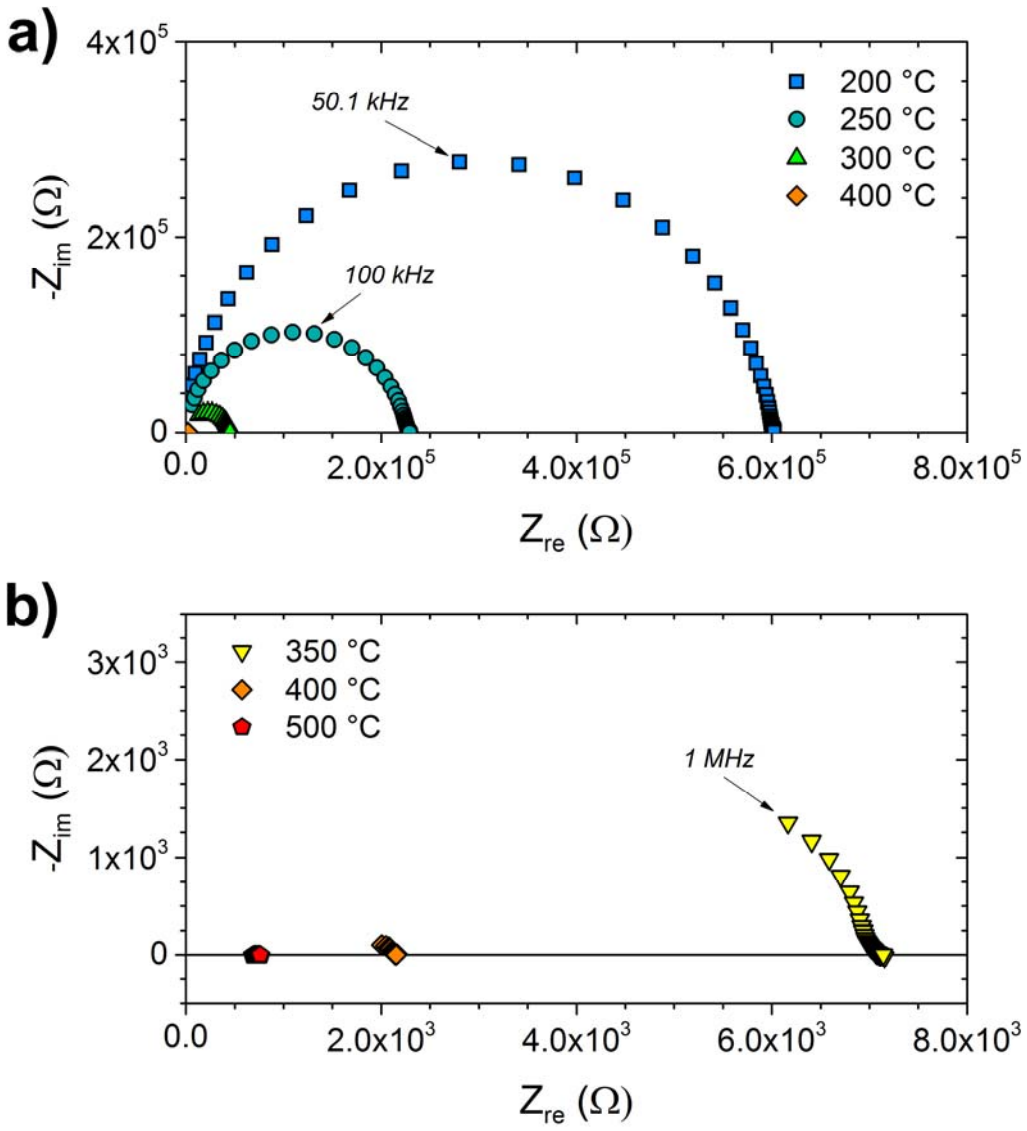

Figure S8: Impedance spectra (Nyquist plot) measured on amorphous Ga_2O_3 at various temperatures – a) 200 – 400 °C, b) 350 – 500 °C. The thin Ga_2O_3 films were deposited using $[Ga(O^tBu)_3]_2$ at 600 °C.

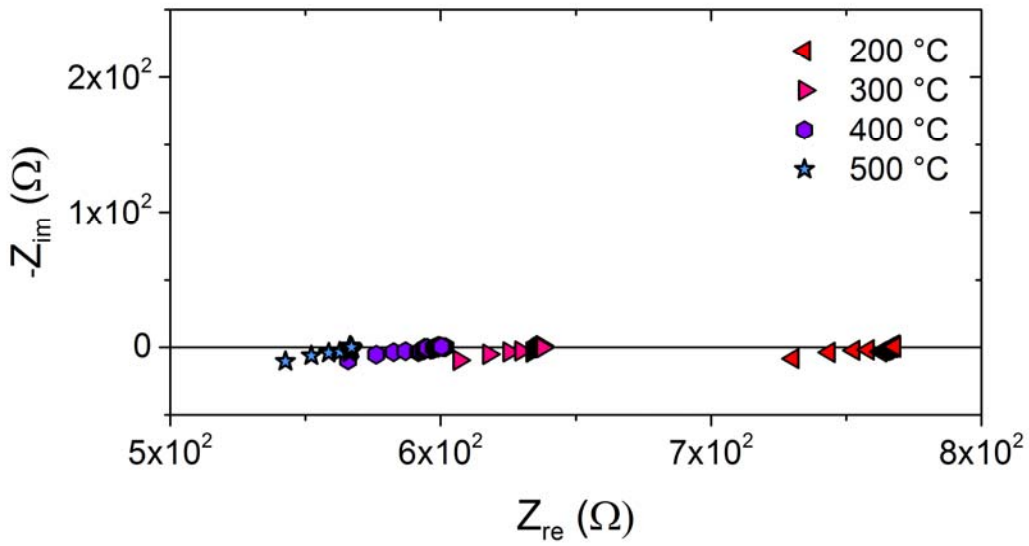

Figure S9: Impedance spectra (Nyquist plot) measured on amorphous $Ga_2O_{3-x}S_x$ (x=0.37) at 200 – 500 °C. The thin Ga_2O_3 films were deposited using **Ga4** at 600 °C.

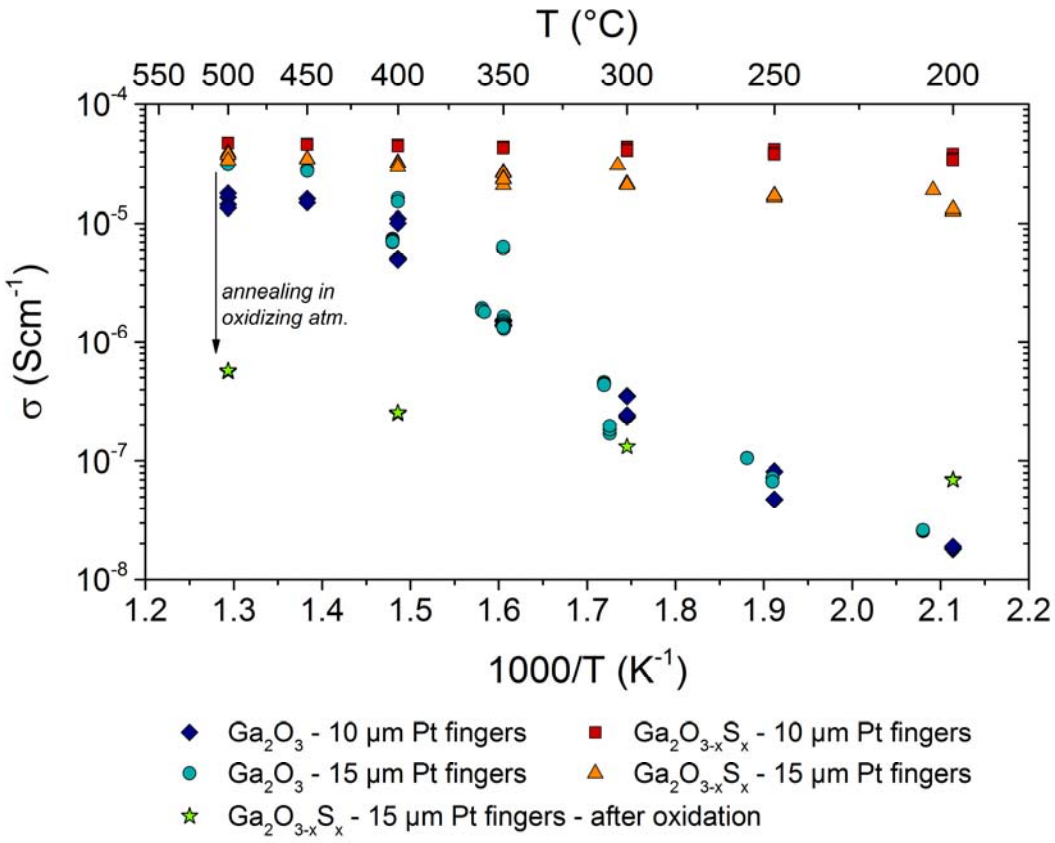

Figure S10: Arrhenius diagram of the conductivities of amorphous Ga_2O_3 (diamonds and circles) and $Ga_2O_{3-x}S_x$ (squares and triangles) thin films. The values shown by the stars were measured on a sulfur containing sample after annealing in oxygen containing atmosphere.

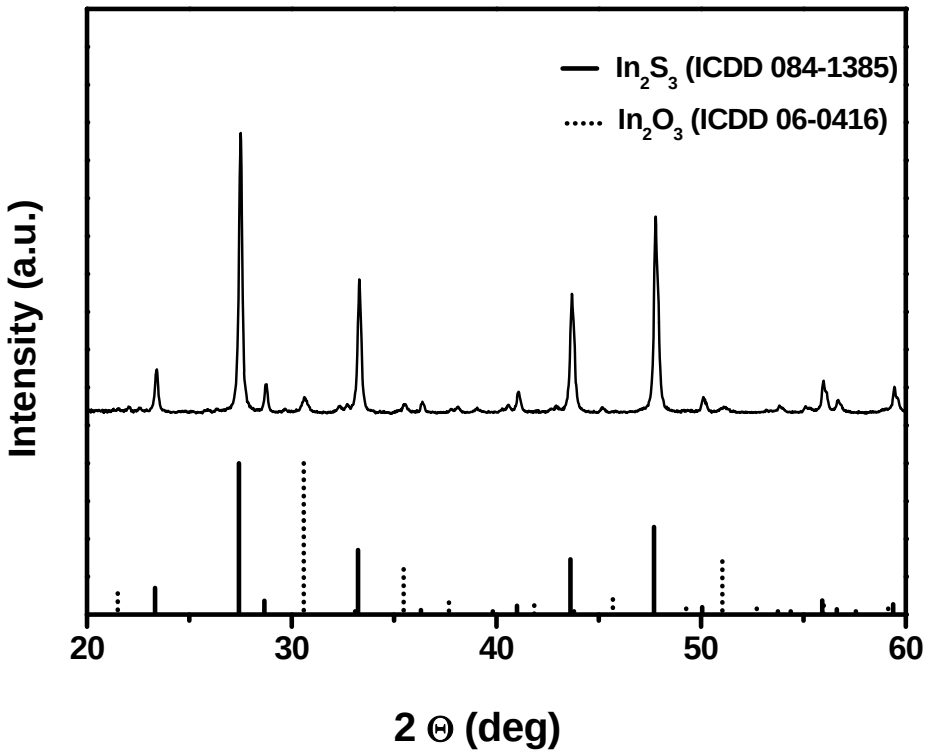

Figure S11: XRD pattern of hydrogen sulphide treated In_2O_3 showing >90% conversion to In_2S_3. The treatment was carried out at 500 °C for 60 min.

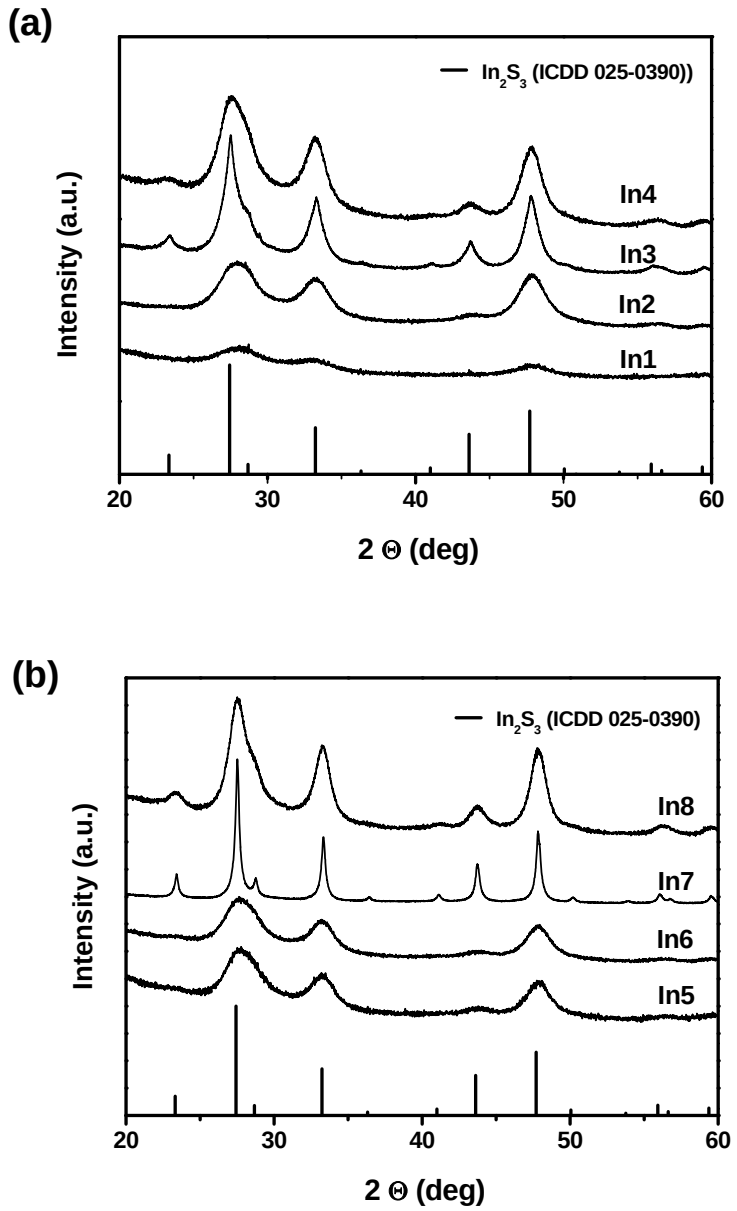

Figure S12: XRD pattern of $In_2O_{3-x}S_x$ powders obtained by thermal decomposition in squalane using indium alkoxides (a) **In1-In4** with secondary alkanols and (b) **In5-In8** with tertiary alkanols.

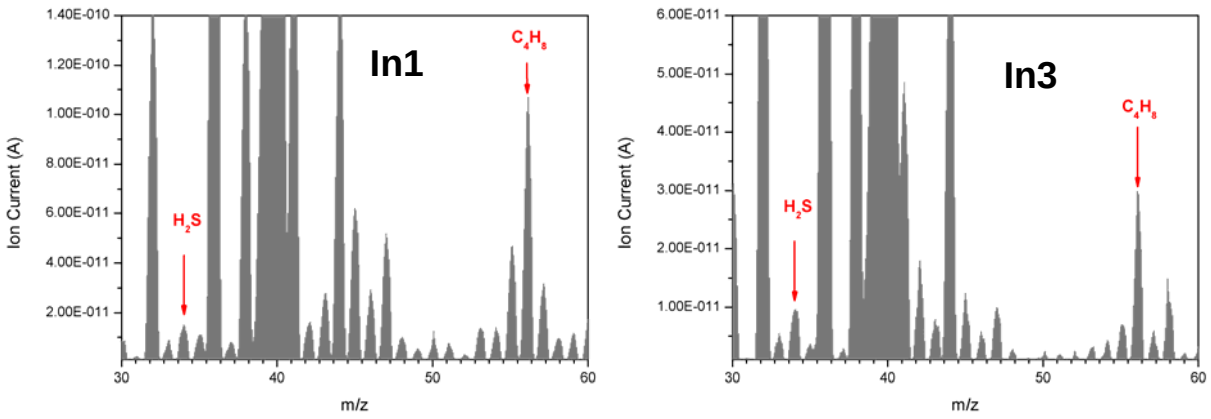

Figure S13: Section of the mass spectra of the decomposition products using **In1** and **In3** A higher amount of hydrogen sulphide is obtained, when compared to the butene signal (**In1**: 1/10; **In3**:1/3), which can be only formed by C-S bond scission.

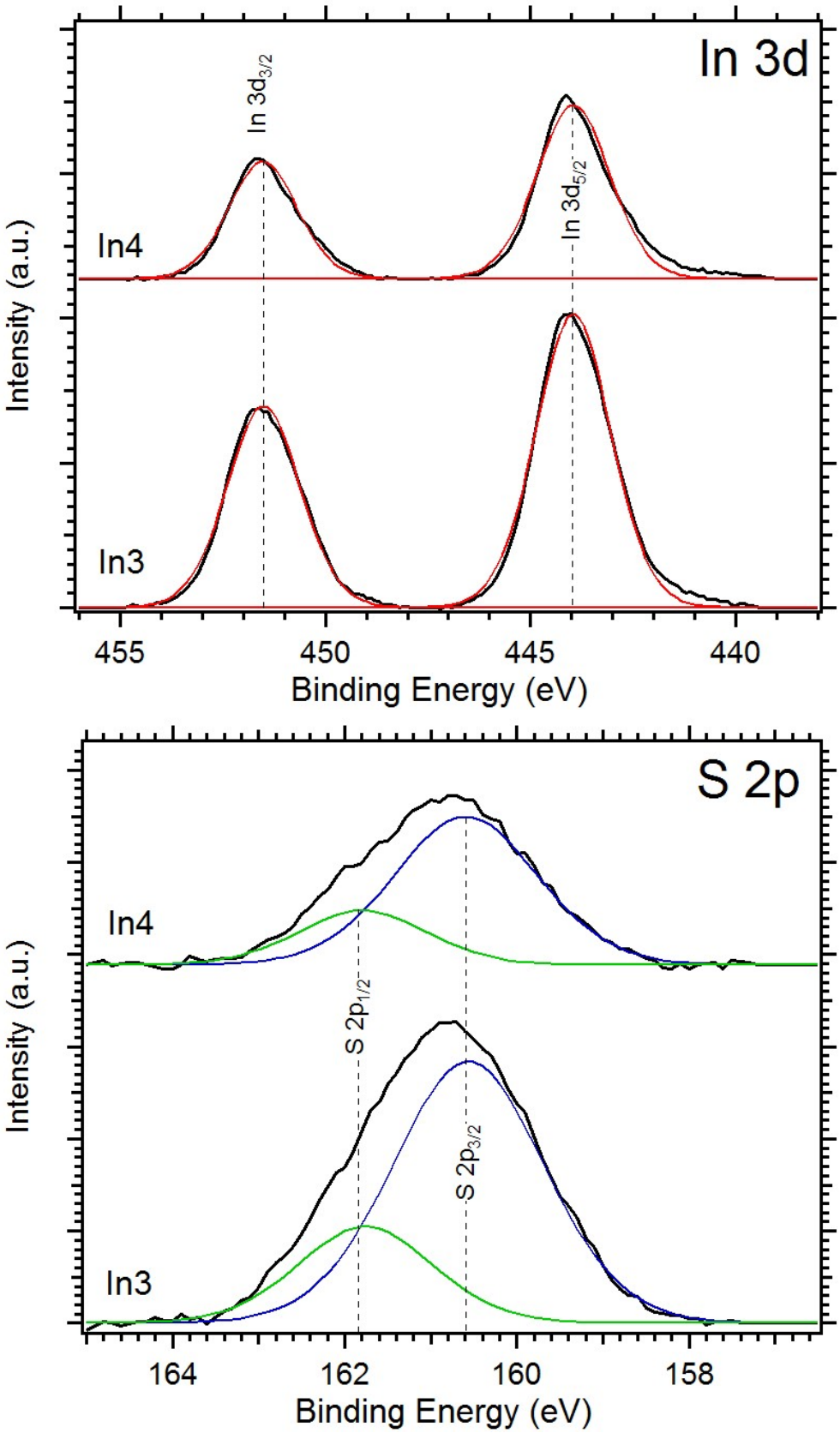

Figure S14: XPS spectra of the In3d peak and the S2p peak (with the common splitting) of particles synthesised using **In3** and **In4** recorded with an Al Kα lab source

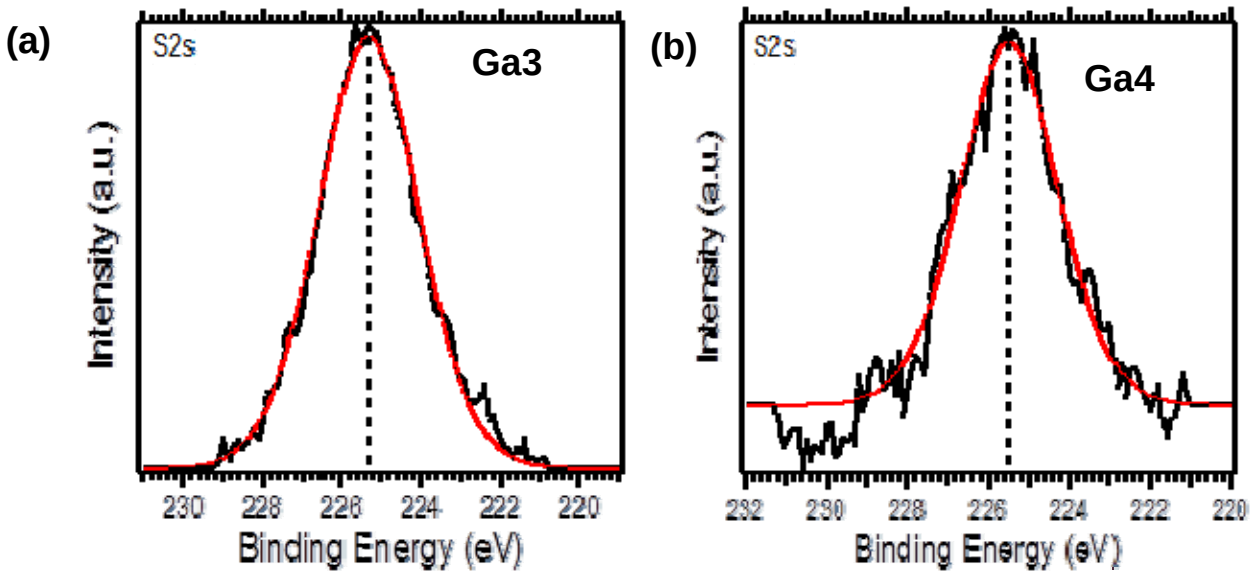

Figure S15: XPS spectrum of the S2s peak of $Ga_2O_{3-x}S_x$ powder decomposed in squalane using (a) **Ga3** and (b) **Ga4** recorded with an Al Kα lab source.

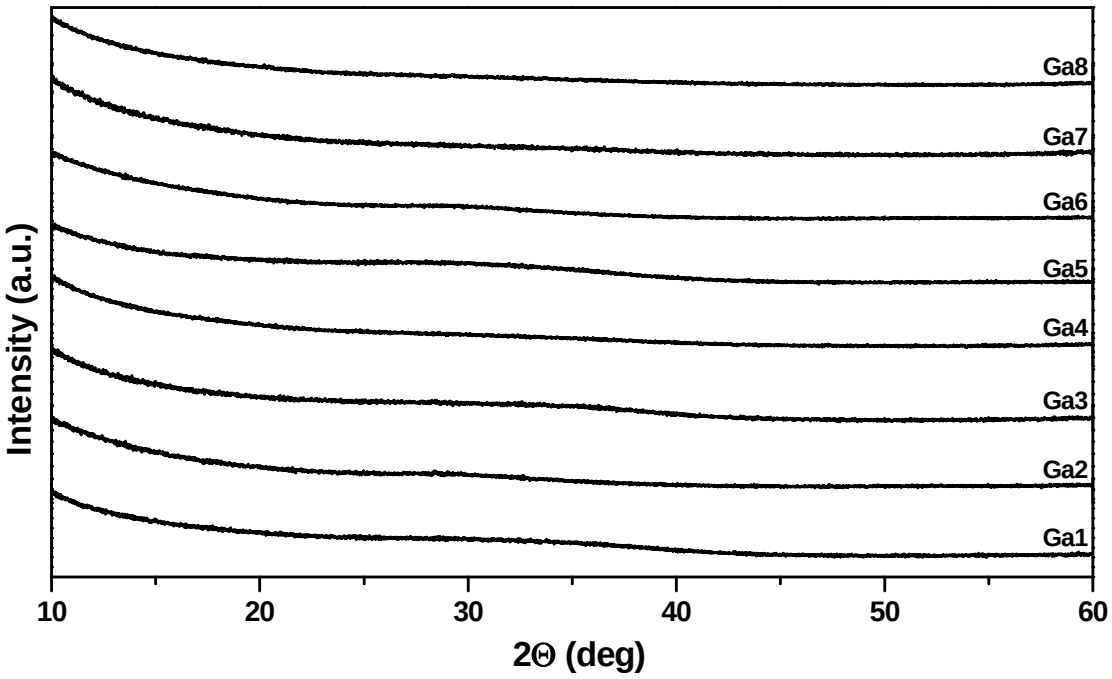

Figure S16: XRD pattern of $Ga_2O_{3-x}S_x$ powders obtained by thermal decomposition in squalane using gallium alkoxides **Ga1-Ga8**.