A new binary phase in the tin monoselenide system: chemical epitaxy of orthorhombic γ-SnSe thin films

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Supporting information

1. Effect of substrate surface treatments

SnSe thin films were deposited onto GaAs(100) substrates treated by several different surface treatments. The XRD results (carried out with an offset of $2°$ during the measurements as described in the experimental section) and corresponding HRSEM images are presented in Fig. S1. The XRD pattern of SnSe deposited onto untreated GaAs substrate (Fig. S1a) points out a film with 3 main reflections, (011),(210),(112), of the new phase of γ- SnSe.[1,2]

Following pre-treatment of the GaAs substrate with sodium hydroxide (NaOH) prior to SnSe deposition, the resulting XRD pattern shows slightly higher peak intensity (Fig. S1c). As in Fig. S1b, HRSEM showed topography with scattered particles, and no continuous layer is obtained (Fig. S1d). Further surface treatment was carried out in aqueous solution of lead nitrate $Pb(NO_3)_2$. XRD demonstrates a small peak corresponding to the (210) reflection from the γ-phase, while the intensity of the (102) reflection of the γ-SnSe phase was almost completely absent (Fig. S1e).

At the same time, a slight increase was obtained in the intensity of the peak corresponding to the γ- SnSe (011) reflection. HRSEM exhibits discontinuous films (Fig. S1f), yet with a large number of considerably smaller grains in comparison to those observed in Figs. S1b,d. Finally, GaAs substrates were treated with a solution containing both NaOH and $Pb(NO_3)_2$. XRD (Fig. S1g) shows the same reflections as mentioned above (Figs. S1a,c,e), yet with considerably higher intensity. The topography HRSEM image indicates a continuous and uniform layer (Fig. S1h), with different grain shapes compared to the plate-like grains typical to the α-SnSe-(orthorhombic phase) and the cube or tetrahedron shaped grains typical for π-SnSe (cubic phase). All XRD peaks have been assigned to the γ- phase of SnSe. ***We conclude that in order to achieve a continuous film, the GaAs surface must be pre-treated with a solution containing both lead cations and NaOH.*** Previous studies reported that Pb^{2+} ions were found to be bound to oxygen on the GaAs substrate surface, most probably in the form of PbO or $Pb(OH)_2$.[3,4] Consequently, this substrate surface pre-treatment was carried out for all samples described hereafter in this work.

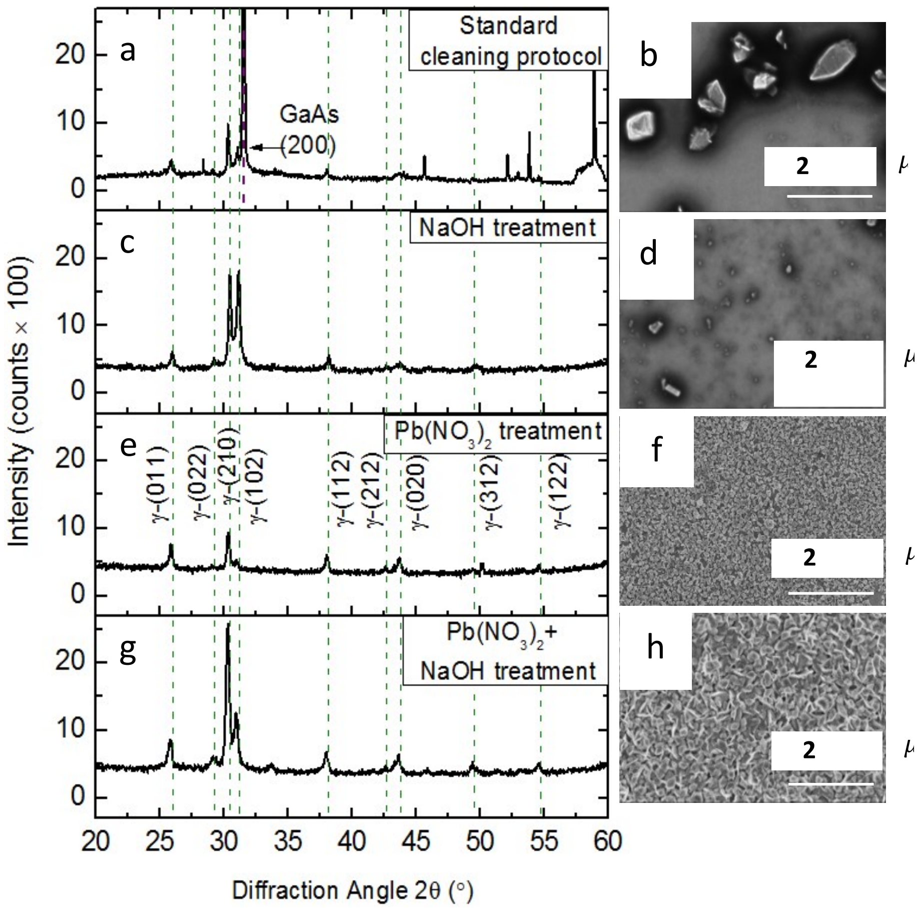

Figure S1: X-ray diffractograms and corresponding HRSEM images of SnSe thin films deposited onto (a,b) GaAs(100) standard cleaning protocol (c,d) GaAs(100) treated with NaOH solution (e,f) GaAs(100) treated with $Pb(NO_3)_2$ solution (g,h) GaAs(100) treated with $Pb(NO_3)_2$+NaOH solution. The latter surface treatment was shown to provide γ- SnSe thin films of highest quality.

2. EDS analyses carried out in the analytical TEM

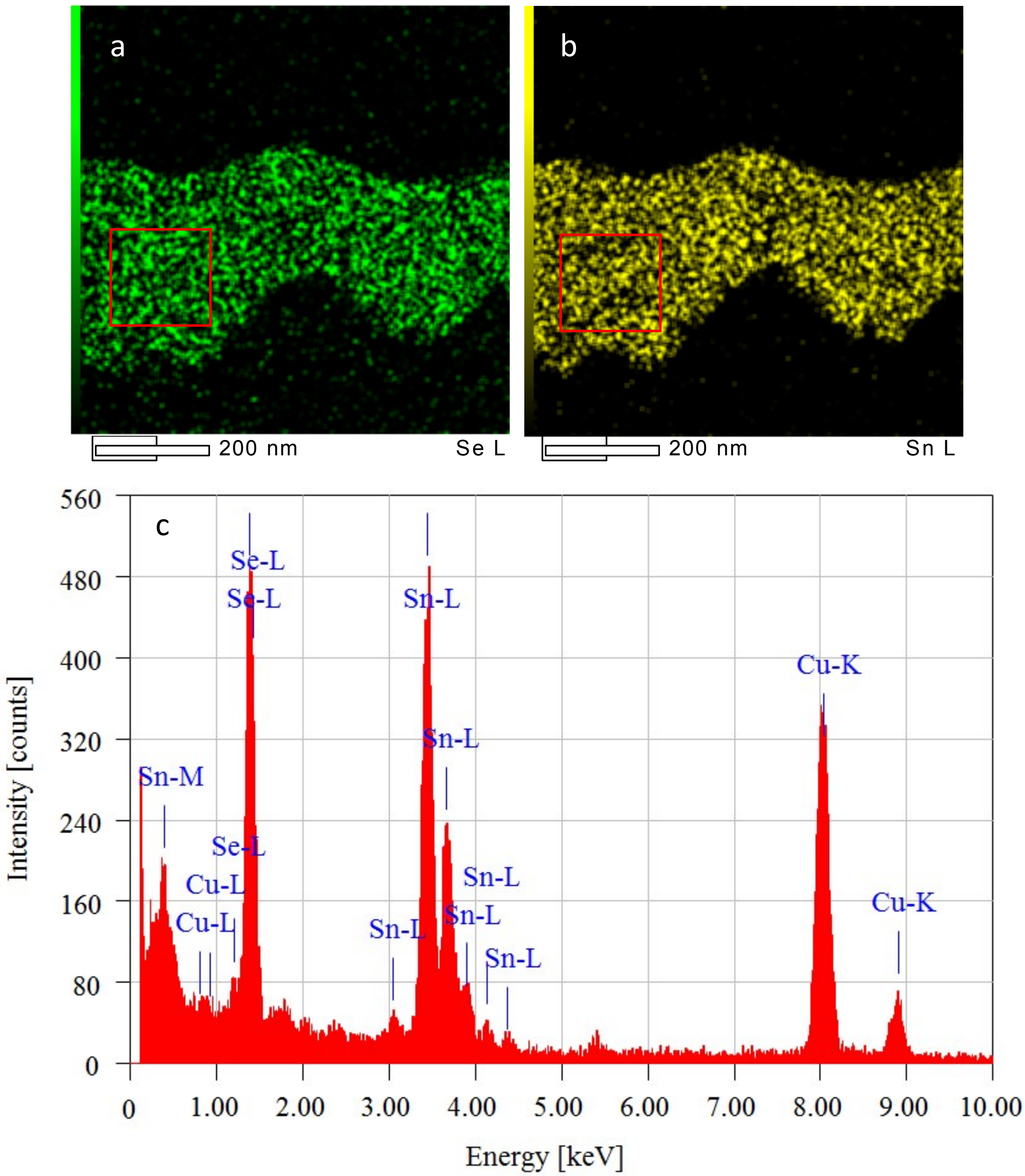

Figure S2: EDS mapping carried out in the TEM for (a) Se L (b) Sn L. (c) EDS spectrum taken in the TEM. Red square in a,b depicts the region from which the EDS spectrum was taken. Quantitative analysis shows an atomic percent ratio of 52(Se):48(Sn).

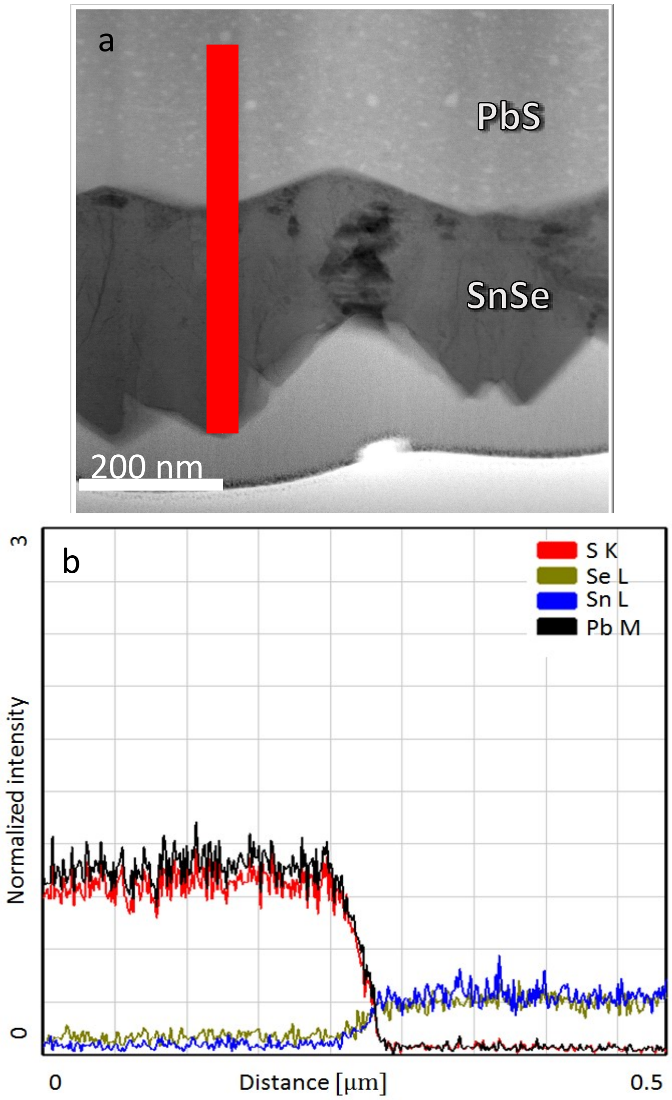

Figure S3: (a) Bright field cross-section TEM image. Line scan in b was taken from top to bottom of red rectangle. (b) EDS line profile of SnSe on PbS taken in the analytical TEM.

References:

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