



	Experiment title: Local structure of metal substitutes in In_2S_3 thin films for intermediate-band solar cells	Experiment number: MA-3671
Beamline: BM08	Date of experiment: from: 11/04/18 to: 14/04/18	Date of report: 18/07/2018
Shifts: 9	Local contact(s): Dr. Giovanni O. Lepore, Dr. Alessandro Puri	<i>Received at ESRF:</i>
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Report:

It is the aim of this project to study the local structure surrounding the metal substitutes in In_2S_3 alloyed with V, Ti, or Nb in order to develop and understand intermediate band materials for application in thin film solar cells. The question of whether the metal atoms are incorporated on octahedral or tetrahedral lattice sites in the defect spinel-type structure of In_2S_3 is particularly important in this regard.

Polycrystalline In_2S_3 thin films with a thickness of approximately 1 μm and substituted with V, Ti, or Nb were prepared by co-evaporation on either glass or silicon substrates [1]. The growth temperature was varied from 300 to 500 $^\circ\text{C}$. The chemical composition was determined by energy dispersive X-ray analysis revealing concentrations of the metal substitutes between 0.1 and 5 at%. Crystal structure and morphology of the films are analysed by X-ray diffraction, Raman spectroscopy, and scanning electron microscopy [1].

EXAFS spectra had to be recorded in fluorescence mode due to the low concentration of the metal substitutes. Unfortunately, the technologically relevant glass substrate contains small amounts of Ti, thus rendering the as-grown films on glass unsuitable for fluorescence measurements. Therefore, a set of thin films were grown on silicon substrates. Additionally, thin films grown on glass substrates were scraped off with a cleaved piece of silicon wafer and mixed with high purity graphite powder. Subsequently, the mixture was ball-milled and then pressed into pellets of 8 mm diameter. TiO_2 and V_2O_5 reference samples were prepared from commercially purchased nanopowders in a similar fashion.

Measurements were first attempted at the Ti K-edge (4.966 keV). However, due to the low beam intensity in this energy range and the low concentration of Ti in the samples, the

fluorescence signal was too weak to record any reasonable spectra. At the V K-edge (5.465 keV), the beam intensity is already significantly higher. The detectable intensity of the resulting V fluorescence was further increased by replacing the Be window sealing the sample chamber towards the detector with a more transmitting Kapton foil. Putting the chamber under vacuum was not possible in this configuration, however, due to the large size of the Kapton window. Therefore, cooling of the samples was not feasible and the spectra were recorded in He atmosphere at room temperature instead. Two different V_2O_5 reference samples, a pure In_2S_3 sample and five different $In_2S_3:V$ samples were then successfully measured in this configuration. The $In_2S_3:V$ samples differed with respect to both V concentration and growth temperature as summarized in Table I. All samples measured were graphite diluted powder pellets, which allowed the simultaneous measurement of a V reference foil in order to precisely align the energy scales of all spectra.

No	T (°C)	V (at%)
1	300	~ 5
2	400	~ 5
3	500	5.3
4	500	3.3
5	500	1.9

Table I: Growth temperature and V concentration for five $In_2S_3:V$ samples measured at the V K-edge.

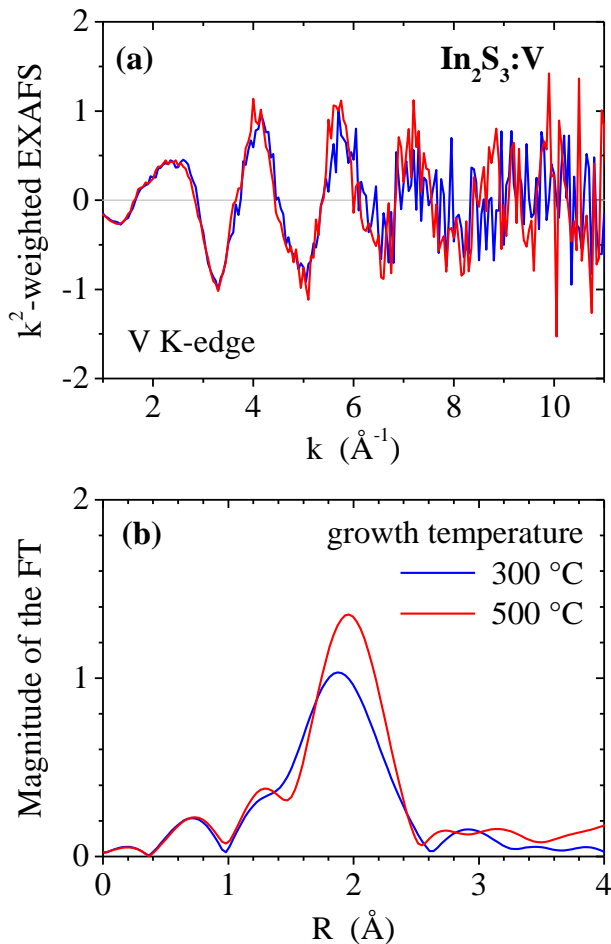


Figure 1: (a) k^2 -weighted EXAFS spectra and (b) magnitude of the Fourier transformation (FT) measured at the V K-edge of $In_2S_3:V$ with ~ 5 at% V grown at either 300 or 500 °C.

Figure 1 (a) shows the k^2 -weighted EXAFS spectra for $In_2S_3:V$ with ~ 5 at% V grown at either 300 or 500 °C. For each plotted spectrum, three or four measured spectra were merged. Reasonable data quality is observed up to a photoelectron wave number of $k \sim 9 \text{\AA}^{-1}$. The corresponding Fourier transformations are plotted in Figure 1 (b). A clear difference in both peak position and peak height is observed, indicating differences in bond length, coordination number and disorder. Similar spectra were obtained for the other three $In_2S_3:V$ samples.

A detailed analysis of all spectra is currently under way using the IFEFFIT software package [2] and the computer code FEFF9 [3]. Changes in the edge position measured for the different spectra could hint at changes in the average valence state of the V atoms. Moreover, structural parameters determined from an analysis of the EXAFS region, including bond length and coordination number, will reveal whether the V atoms are preferably incorporated on octahedral or tetrahedral lattice sites. The latter is crucial for the development of intermediate band materials and will help to understand their formation as a function of growth conditions.

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