	Experiment title:	Experiment number: MA5300
Beamline:	**Date of experiment**: from: 15/04/2022 to: 19/04/2022	**Date of report**:
Shifts: 12	**Local contact(s)**: Valentina Bonino	*Received at ESRF:*

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Report:

Overview

Earth-abundant semiconducting materials are a potential solution for large-scale deployment of solar cells at a lower cost [1]. Among them, zinc phosphide (Zn_3P_2), thanks to its direct bandgap (1.53 eV), high absorption coefficient and long minority-carrier diffusion length (>5 μm), Zn_3P_2 is a promising solar absorber [2]. We investigate four morphology types of high-quality Zn_3P_2 nanowires (NWs) fabricated using molecular beam epitaxy (MBE). This technique is increasingly adopted in the fabrication of single-crystal nanostructures with enhanced functionality and excellent optical properties.

In this context, a better understanding on the interplay between the growth parameters and the chemical composition and structure in the nanometer scale is required to improve further the performance of this material. For this purpose, a multimodal approach that combines spatially resolved X-ray fluorescence (XRF) and X-ray absorption near-edge spectroscopy (XANES) with nanometer resolution was performed. In the initial proposal, the optical emission was also included in the study, but because no XEOL signal was visible, and more space for phase structure analysis was given.

Method

ID16B beamline was used because of the high flux density and the nanometric resolution achivable (beamsize 76 x 77 (V x H) nm^2, monochromatic energy E = 9.6 keV – Zn K edge-, and photon flux $\phi = 1.22 \times 10^{10}$ ph s^{-1}). The 7/8 + 1 bunch mode was the filling mode of the storage ring. 2D XRF maps were first acquired and, in selected NWs, single point XAS measurements were taken along their length and their edges. Four samples having varing stoichiometry and geometry were obtained with different gas relative pressures V/II and temperatures T by the MBE growth. namely: A) V/II = 1 T= 250 °C, B) V/II = 1.45 T= 250 °C, C) V/II = 1.6 T= 250 °C, and D) V/II = 1 T= 200 °C. NWs were grown on InP substrate by using In nanoparticles as catalist[3]. For the characterization, NWs were dispersed on Si_3N_4 membranes. The four morphologies are shown in Figure 1(a-d) together with their expected composition as a funciton of the V/II flux ratio employed (Figure 1e)[3]. Two thin films with a Zn/P ratio of 60%/40% and 55%/45%, were used as references for XANES.

Results and discussion

All samples showed similar XANES with a modulation of the post-edge structure characterized by two different peaks. This feature was in agreement with the XANES from the standard samples, which had quite similar spectra, Figure 2a (see arrows).

From a preliminary analisis of the results, a difference on the ratio intensity of these two peak was found as a function of the sample (Figure 2b):

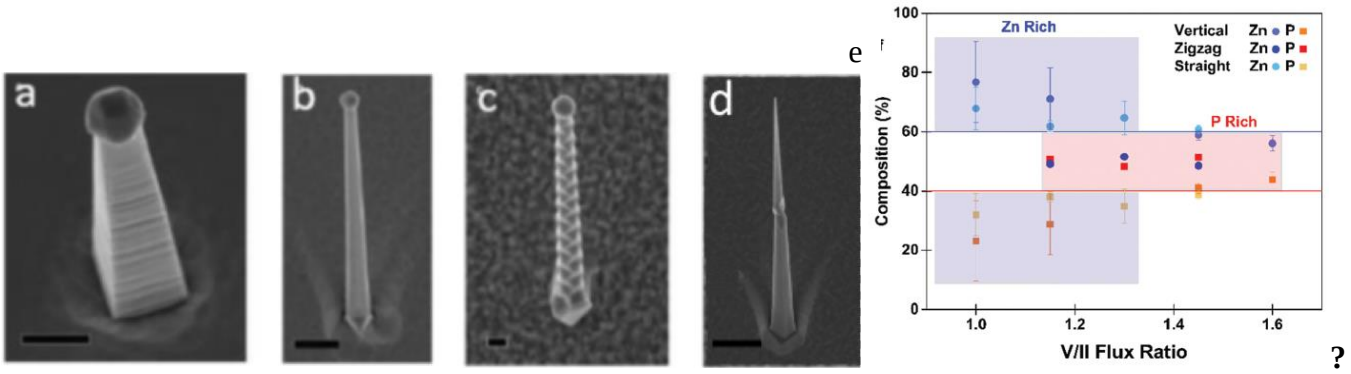

Figure 1. (a-d) STEM images of the four morphologies of Zn_3P_2 NWs synthesized by MBE: (a) vertical, (b) straight tilted, (c) zig-zag, and (d) sharp. Scale bars 500 nm. (e) Composition % vs. V/II flux ratio adopted in the growth for different morphologies [3].

- Vertical NWs from sample B and C, displayed similar XANES with the first peak dominating compared to the second one. Therefore, despite the variation in the V/II flux ratio, the Zn environment seems to be the same. This suggest that the both samples share the same phase composition, which is probably related to the NWs with their chemical composition close to the stechiometric one (Zn/P = 60/40, Figure 1b).
- The spectra from samples B, and C are the most similar to the one collected from the standards. This evidence is in agreement with the fact that their phase composition is determined by the stoichiometric ratio (close to Zn_3P_2).
- Straight tilted NWs from sample A showed the two peaks at the same intensity.
- Sharp NWs from sample D presented a second peak more prominent compared to the first one. Considering that both sample A and D were produced with V/II = 1, and that both samples showed a higher second peak compared to samples B and C, the difference in structure is probably associated to a stoichiometric composition poorer in Zn (closer to ZnP_2) and with a different phase composition compared to sample B and C.

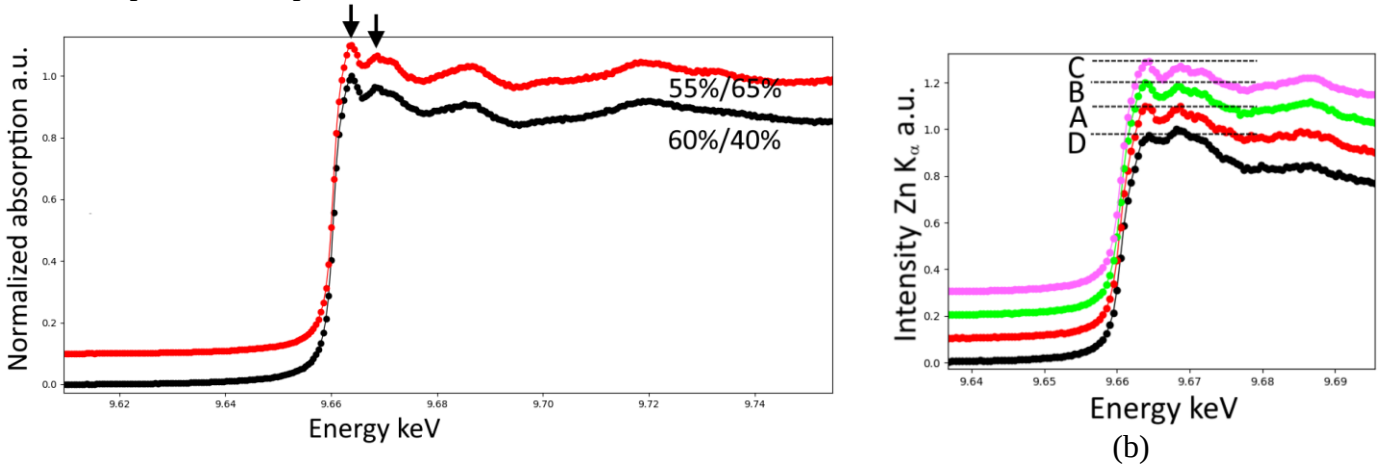

Figure 2: (a) XANES spectra from the standards (Zn/P ratio of 60%/40% and 55%/45%) and (b) sample A,B,C,D. Black arrow in Figure 2(a) indicates the characteristic two peak feature that varies in the samples.

Conclusions

In conclusion, different Zn enviroments have been observed which testify the presence of difference phases which are probably mainly associated to the V/II flux ratio and consiquently to their stoichiometric ratio. In order to get more information on the corresponding Zn/P ratio, XRF fluorescence maps have to be analyzed. Moreover, the acquisition of other XANES references, measured or simulated, will also help disentangling the phase composition that seems to be a combination of the two stoichiometric phases Zn_3P_2 and ZnP_2.

References

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