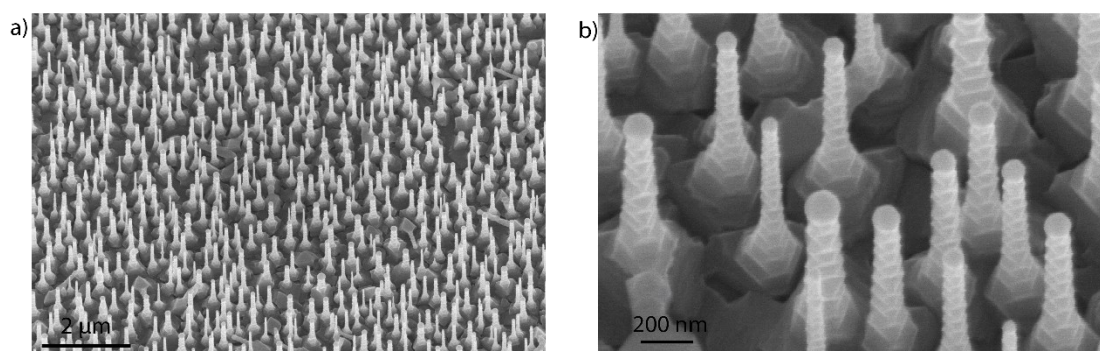


## Final Report - Sustainable Synthesis of Earth-Abundant Inorganic Nanomaterials for Energy Applications

### Summary

The overall scientific goal of the project to epitaxially grow zinc phosphide ( $Zn_3P_2$ ) nanowires while eliminating scarce elements of the process was successfully achieved. Sn-catalysed  $Zn_3P_2$  nanowires were demonstrated to grow epitaxially on Si (111) substrates with high nanowire density. This yields in highly optically absorbing samples, promising for use as photovoltaic absorbers. An unexpected result found through this project is that this type of nanowires grows with a pseudo-pentagonal cross-section. This peculiarity goes against standard crystal symmetry, but we have been able to show that a new mechanism, not related to defects such as penta-twins or quasi-crystals, has resulted in this morphology. The underlying mechanism is related to the symmetry of the epitaxial relationship and the difference in surface energies of the  $Zn_3P_2$ , as explained in more detail later on. The first publications based on these results are currently under preparation, and together with several international collaborations we are working on further characterisation and potential device integration of these samples. The project has therefore helped the researcher develop their research and use it to help build their international scientific network.

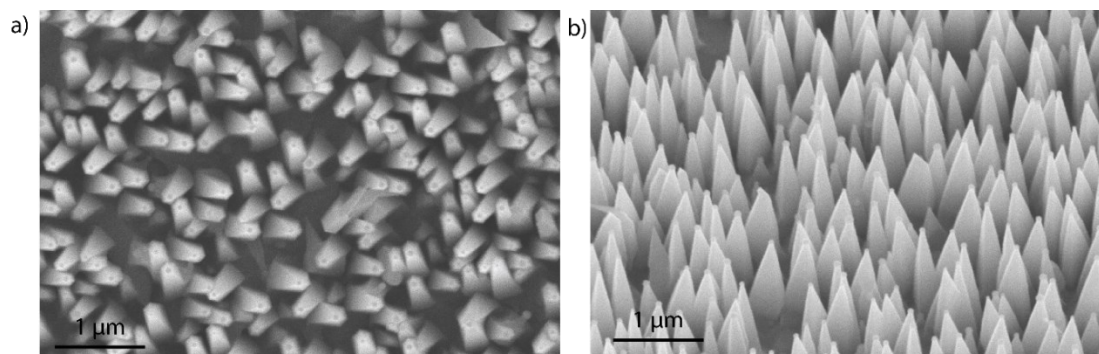
### Scientific work



**Figure 1.** a) Overview SEM image of  $Zn_3P_2$  nanowires grown on InP (111)A substrates taken at a tilt of  $30^\circ$ . b) Higher magnification SEM image of  $Zn_3P_2$  nanowires taken at a tilt of  $30^\circ$ .

The starting results of this project was In-catalysed growth of  $Zn_3P_2$  nanowires on InP substrates, as shown in Figure 1. These nanowires showed that the growth using metalorganic chemical vapour deposition (MOCVD) of  $Zn_3P_2$  nanowires was possible, however, the use of scarce elements (In) goes against the motivation of using the earth abundant  $Zn_3P_2$ . What we did learn from these experiments were a suitable parameter space for the material to grow with the precursors we have (diethyl zinc (DEZn) and phosphine ( $PH_3$ )), which was an excellent starting point for Sn-catalysed growth. The first step was to investigate the formation of Sn nanoparticles on InP and Si surfaces using tetraethyl tin (TESn) as the precursor. We could controllably deposit Sn particles on InP substrates in the 500-550 °C range, while temperatures as high as 600 °C were needed for Si substrates. We found that higher temperatures generally resulted in higher particle density and smaller diameters. However, this trend was not true for all wafer orientations. For example, InP (111)B substrates showed more desirable properties when it came to the deposition of In particles over (111)A, but for Sn it would only form  $\mu m$  sized particles that could not be used for

vapour-liquid-solid (VLS) growth of nanowires. Instead, InP (111)A substrates achieved a more uniform deposition of Sn nanoparticles that could be used as VLS catalysts.

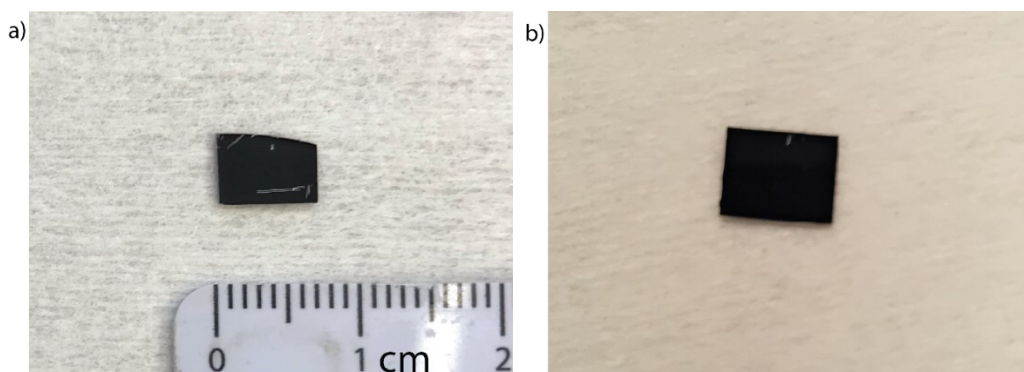


**Figure 2.** SEM images showing (a) the top view and (b) tilted view (30°) of pseudo-pentagonal  $Zn_3P_2$  NWs grown on Si (111) substrates with Sn as a catalyst.

Once nanoparticles could reproducibly be deposited, we continued with the growth. The growth of purely Sn-catalysed  $Zn_3P_2$  nanowires on InP was challenging as the substrate would readily decompose in the presence of Sn to form In or Sn/In droplets. We could observe a higher prevalence of only Sn-catalysed growth at lower particle deposition temperatures. However, this was not an issue for growth on Si (111) substrates as are much more stable. The parameter window for growth on Si (111) substrates greatly overlapped with that observed for In-catalysed on InP (111)A/B substrates, which significantly facilitated this study as we had an excellent starting point. The growth behaviour in this case was slightly more stable than In-catalysed with changing growth conditions, as we did not observe significant morphology changes despite large changes in e.g. the V/II precursor relative pressures. Representative electron microscopy images of Sn-catalysed  $Zn_3P_2$  nanowires on Si (111) are shown in Figure 2. The nanowires could grow with very high density, producing highly optically absorbing samples, as shown in Figure 3.

A peculiar feature we noticed, as shown in Figure 2a, is that the Sn-catalysed nanowires have five facets in a pseudo-pentagonal cross-section rather than the expected previously observed square or hexagonal cross-sections. Conventional crystallography and group theory does not allow a five-fold symmetry in conventional crystals (not including quasi-crystals). Some metal nanostructures have shown pentagonal cross-sections achieved through penta-twinning. However, this type of defect would not make sense to form in  $Zn_3P_2$  due to its tetragonal structure, making standard twinning unlikely. This was recently confirmed by a collaborator (ICN2, Spain) who performed cross-sectional transmission electron microscopy analysis of these samples, showing that there was no penta-twin or other defect responsible for this morphology. Together with another international collaborator (Ruhr University Bochum, Germany) specialising in density functional theory (DFT) simulations we are looking into the surface energies to determine the exact formation mechanism. The current working theory is that the three-fold symmetry of the initial growth on Si (111) results in a triangular top facet. This can often lead to the growth of twin-plane superlattices where you have oscillating triangular cross-sections, which has been previously observed. However, what happens instead in this case is that one of the facets formed along the sides of the triangle is a  $\{101\}$  type facet (the most stable facet for zinc phosphide) that was perpendicular to the growth direction instead of with an inclination, which is needed for

twin-plane superlattice formation. However, the remaining two facets for a triangular cross-section would be  $\{211\}$  facets, which would be higher energy for  $\text{Zn}_3\text{P}_2$  (according to initial calculations, final calculations still underway. What happens then is that each of the  $\{211\}$  facets split into two separate facets, one being  $\{100\}$  while the other is  $\{111\}$ . The splitting of these two facets into four results in the observed pseudo-pentagonal cross section, rather than the conventional square or hexagonal cross-sections observed in other nanowires. Further characterisation and potential integration of these samples in devices is currently underway together with additional international collaborators (AMOLF, Netherlands and University of Manchester, UK). The previously mentioned partners at ICN2, Barcelona are also investigating the epitaxial relation between  $\text{Zn}_3\text{P}_2$  and Si as well as investigating potential defect formation.



**Figure 3.** Representative images of  $\text{Zn}_3\text{P}_2$  nanowire samples using a) In as a catalyst and b) Sn as a catalyst.

There are currently two manuscripts under preparation based on the results from this project, with the potential of more originating in follow-up studies. The results have so far been presented at two international conferences (ICMAT23, Singapore and EUROMAT23, Frankfurt), and will be presented as part of an invited talk at the European Materials Research Society's 2024 Spring Meeting.