The path towards 1 \( \mu \)m monocrystalline \( \text{Zn}_3\text{P}_2 \) films on InP: substrate preparation, growth conditions and luminescence properties

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Abstract
Semiconductors made with earth abundant elements are promising as absorbers in future large-scale deployment of photovoltaic technology. This paper reports on the epitaxial synthesis of monocrystalline zinc phosphide (\( \text{Zn}_3\text{P}_2 \)) films using molecular beam epitaxy with thicknesses up to 1 \( \mu \)m thickness on InP (100) substrates, as demonstrated by high resolution transmission electron microscopy and x-ray diffraction. We explain the mechanisms by which thick monocrystalline layers can form. We correlate the crystalline quality with the optical properties by photoluminescence at 12 K. Polycrystalline and monocrystalline films exhibit dissimilar photoluminescence below the bandgap at 1.37 and 1.30 eV, respectively. Band edge luminescence at 1.5 eV is only detected for monocrystalline samples. This work establishes a reliable method for fabricating high-quality \( \text{Zn}_3\text{P}_2 \) thin films that can be employed in next generation photovoltaic applications.

1. Introduction

The adverse impact of global energy consumption on the environment necessitates a massive shift in energy production toward more sustainable and non-fossil energy sources. A prominent part of a multicomponent solution is the large-scale deployment of photovoltaic (PV) energy production, which can be facilitated using semiconductors made of earth-abundant elements [1–3]. However, many earth-abundant semiconductors suffer from narrow growth windows, thermodynamic instability, coexistence of multiple phases and long term degradation among other factors [4–8], affecting the performance of PV devices. A common challenge with many of these materials is the inclusion of a cation with multiple oxidation states, which, especially in high oxidation states, is likely to switch to lower oxidation numbers [9]. \( \alpha - \text{Zn}_3\text{P}_2 \), on the other hand, is a candidate material with promising advantages, such as the simplicity of Zn–P system phase diagram [10–12] and thermodynamic stability thanks to the singular oxidation state of zinc. It demonstrates high absorption of more than 10\(^4\) cm\(^{-1}\) in the visible range of the electromagnetic spectrum [13, 14], reported bandgap close to the optimal value of the Shockley–Queisser limit [12, 15], carrier diffusion length in the range of 5 – 10 \( \mu \)m [16] and passive grain boundaries [17], which in turn could improve the performance of PV devices based on this material.

Epitaxial growth of high-quality \( \text{Zn}_3\text{P}_2 \) is inherently difficult, in part because of its very large tetragonal unit cell [18], with \( a = 8.089 \) Å and \( c = 11.45 \) Å [19], making it challenging to find commercially available substrate for epitaxial growth. \( \text{Zn}_3\text{P}_2 \) tends to grow in the (001) direction [20]. In this orientation, the P sub-lattice of the tetragonal unit cell exhibits a low lattice mismatch with the group V elements of (001).
oriented InP and GaAs (2.4% and 1.3% respectively). Still, monocrystalline layers have been limited to a thickness of 150 nm on GaAs(100) [17]. The other difficulty in the growth of high-quality Zn$_3$P$_2$ thin films stems from its high thermal expansion coefficient. For instance, this coefficient is $14 \times 10^{-6}\text{K}^{-1}$ at room temperature for Zn$_3$P$_2$ [21] in comparison to $6 \times 10^{-6}\text{K}^{-1}$ and $3 \times 10^{-6}\text{K}^{-1}$ for GaAs and Si, respectively. Upon cooling down, the mismatch in coefficient of thermal expansion results in formation of cracks in the thin films grown at high temperatures [22]. A recent solution that overcome these challenges corresponds to growth on graphene substrates by van der Waals epitaxy [23]. In addition, restricting the interface with the substrate to nanoscale regions via the creation of nanowires or selective area epitaxy are also being investigated as potential solutions [23–26]. To the best of our knowledge, to date none of these strategies has yet provided large area monocrystalline structures.

In this work, we report on the growth requirements to achieve monocrystalline Zn$_3$P$_2$ thin films on InP(100) substrates using molecular beam epitaxy (MBE). Growth parameters such as substrate temperature, ratio between P and Zn fluxes (V/II ratio) and substrate preparation are varied, resulting in amorphous, polycrystalline and monocrystalline thin films. A range of characterization techniques including Raman spectroscopy, x-ray diffraction (XRD), (scanning) transmission electron microscopy (S/TEM) and electron energy loss spectroscopy (EELS) have been employed to shed light on the differences between thin films obtained in different conditions. As a key parameter, we find that substrate surface preparation by effectively removing the native oxide is essential for obtaining monocrystalline layers. Finally, the optical properties of the thin films are investigated using photoluminescence (PL) spectroscopy and the differences between the characteristics of polycrystalline and monocrystalline Zn$_3$P$_2$ thin films are demonstrated.

### 2. Results and discussion

We start by exploring the role of the V/II ratio calibrated using a beam flux monitor and the manipulator temperature on the crystalline quality of the thin films. Substrate preparation includes two steps of sample degassing for 2 h each at 150 °C and 300 °C in ultra-high vacuum, and a third step under P$_2$ flux $> 1 \times 10^{-4}$ Torr at a manipulator temperature of 580 °C to fully remove surface contaminants and the native oxide. The effects of duration of the last annealing step are discussed further down. Figures 1(a) and (b) depict cross-sectional scanning electron microscopy (SEM) images of typical amorphous and polycrystalline thin films, grown with V/II = 0.83, $T = 280$ °C and V/II = 0.48, $T = 265$ °C, respectively. The thin film in figure 1(a) shows a continuous and smooth structure, while in figure 1(b) one finds a granular structure, denoting the polycrystalline nature of the film. In this case, the cross-section SEM indicates that growth starts by forming small grains that gradually merge into larger grains as growth continues. Room temperature Raman measurements have been conducted on the samples to assess their crystalline quality. Figure 1(c) displays the Raman spectra for thin films grown with V/II ratios between 0.43 and 1.37 and substrate temperatures between 250 °C and 290 °C. The characteristic spectrum of $\alpha$ - Zn$_3$P$_2$ is observed [27]. A dozen low-wavenumber peaks, dominated by Zn atom displacements, merge into the broad peak at approximately 93 cm$^{-1}$, while the high-wavenumber peaks, mainly dominated by P atom displacements, merge into a series of overlapping peaks in the range from 280 cm$^{-1}$ to 360 cm$^{-1}$ [27]. The spectra of thin films grown at high V/II ratios (1.35 and 0.95) are mainly featureless or with few broad peaks, suggesting that samples obtained at high V/II ratios are amorphous, as reported in [26]. This is also the case for thin films obtained at the highest temperature, 280 °C. For V/II ratios between 0.72 and 0.95 Raman spectra of thin films grown at 250 °C and 265 °C are consistent with crystallinity. Similar trends have been recently observed for growth of Zn$_3$P$_2$ on graphene [26].

To further improve the crystalline quality and reproducibility, effects of the third degassing step at 580 °C for different durations are investigated. Figure 2 shows representative SEM cross-section micrographs of thin films obtained for increased degassing durations, namely 10, 20, 30, 45, 60 and 75 min. We observe that for the identical growth conditions, increasing the degassing time renders the thin films less granular. In fact, the granular nature disappears for annealing periods of 30 min or higher. Raman studies indicate that these samples are crystalline. In addition, the top surfaces of the thin films get smoother. It is to be noted that while increasing this degassing time makes it possible to obtain monocrystalline samples in a reproducible manner, a few samples with degassing times of 10 min were also monocrystalline, as presented in figure 3. However, the occurrence of the monocrystallinity tends to be non-reproducible for samples with degassing times less than 20 min. In figure 2(g), we show representative Raman spectra of a monocrystalline and a polycrystalline thin film acquired at 12 K with an incidence wavelength of 532 nm. A lower material temperature increases the phonon lifetime. This decreases the uncertainty of the phonon energy, lowering peak width and thus the overlap between the multiple peaks. We find that the Raman spectra obtained in different spots on each sample consistent, indicating relatively homogeneous crystalline quality. However, changes in relative intensities of the peaks can be observed between the two samples. We attribute these
Figure 1. Effect of growth temperature and V/II ratios. (a) 20° tilted cross section image of an amorphous Zn₃P₂ thin film grown with V/II = 0.83 and T = 280 °C. (b) Tilted cross section image of a polycrystalline Zn₃P₂ thin film grown with V/II = 0.48 and T = 265 °C demonstrating the presence of grain boundaries. Scale bars are 1 µm. (c) Micro-Raman with 532 nm laser for samples grown at different growth temperatures and V/II ratios. Increasing the growth temperature and V/II ratio makes the films amorphous. All the samples reported in this figure have degassing time at 580 °C of 10 min and P flux of 4.3 × 10⁻⁷ Torr.

High-resolution (HR) TEM and aberration-corrected high-angle annular dark-field (HAADF) STEM are used to investigate the crystalline quality. Figure 3(a) corresponds to a HRTEM image of a thin film obtained with V/II = 0.72, T = 265°C and the degassing time of 10 min at 580°C. HRTEM indicates that this is a monocrystalline thin film. The diffraction pattern obtained on a larger area also corroborates the differences to changes in the concentrations of point defects such as interstitials/vacancies or grain boundaries, which affect different vibrational modes of the lattice in varying ways. A detailed study to identify the defects in Zn₃P₂ thin films with Raman spectroscopy is ongoing.
monocrystallinity, as shown in the inset of figure 3(a). Calculations of atomic distances based on the selective-area diffraction pattern demonstrates a lattice mismatch of 2% considering the pseudo-cubic structure of Zn₃P₂ and the growth direction of [001], consistent with previous studies [20, 25]. The HAADF-STEM image of this sample in figure 3(b) adds further details of the interface between the film and the substrate. Considering that the heavier atoms appear brighter in HAADF-STEM images due to Z-contrast [28–30], the constituting elements can be assigned across the interface,, The brightness of atoms at the interface, intermediate between the one observed for In in the substrate and Zn in the layer indicates the formation of a mixed Zn–In monolayer, as depicted in the blue inset of figure 3(b). The monolayer Zn–In intermixing establishes the epitaxial transition from the InP substrate to the Zn₃P₂ film. The red inset of this figure establishes that while monocrystalline, these films may still include some structural defects stemming from misalignment of the systematic vacant sites in c direction. Figure 3(c) probes the oxygen core-loss EELS signature at 532 eV across the interface of this sample, demonstrating a uniform absence of oxygen around this area. Figure 3(d) corresponds to a low magnification TEM image of a sample obtained at V/II = 0.48, T = 265°C and with a degassing time of 10 min at 580°C. The micrograph shows the polycrystalline nature with a clear pattern of columnar-structured grains. The HAADF-STEM image of this sample in figure 3(e) further highlights the difference between the polycrystalline and the monocrystalline thin films, as the area above the interface appears diffused as opposed to the sharp interface of the monocrystalline film. Moreover, in this micrograph one can notice the randomly oriented atomic fringes in the thin film. Figure 3(f) corresponds to the oxygen map by core-loss EELS of the interface area shown in figure 3(e). There is a clear oxygen signature at the interface. The presence of an oxide could be the reason for the lack of sharpness of the interface in the HAADF image. In summary, the increase in degassing time at 580 °C promotes the complete desorption of the substrate native oxide in a consistent manner, which in turn facilitates the formation of a monocrystalline thin film.

To further examine the crystalline quality of the thin films obtained under the different conditions, high resolution XRD was performed. Figure 4 compares the XRD pattern for bare InP substrate, amorphous, polycrystalline and monocrystalline Zn₃P₂ thin films. The growth conditions of each thin film are presented in the figure caption. The most intense peak, observed at 30.4°, corresponds to the (200) reflection of the InP substrate [31]. Dashed vertical lines are employed to highlight the location of the peaks stemming from the InP substrate. Some of these peaks are absent on the amorphous sample (with broad peaks of Zn₃P₂ in the Raman spectra). The main crystalline signature of Zn₃P₂, observed at 31.4° corresponds to the (004) reflection [32], and is observed on both polycrystalline and monocrystalline thin films. Multiple peaks corresponding to the higher index planes are observed for the polycrystalline thin film between 30° and 50°. These peaks are absent on the monocrystalline film, with only peaks corresponding to (002), (004) and (006)
directions of Zn$_3$P$_2$ being visible. This indicates that the growth direction of the monocrystalline film is [001], consistent with the HRTEM analysis.

Low temperature PL was performed to evaluate and compare the optical properties of the polycrystalline and monocrystalline samples. In general, we find that the emission spectrum from polycrystalline samples strongly depends on the growth parameters. In figure 5, representative PL measurements for one polycrystalline and one representative monocrystalline sample measured with an excitation wavelength of 488 nm at 20 K are shown. In addition, the emission spectrum of a bare InP substrate is also included as a reference. The orange curve in figure 5 corresponds to the PL data of a typical polycrystalline sample. The emission spectra from polycrystalline Zn$_3$P$_2$ thin films consists of a single peak or a single set of overlapping peaks at energies lower than the direct bandgap energy [15, 33]. The low-energy emission was not expected to be so much stronger than the higher band-to-band-like transitions, based on previous reports [15]. Further work is ongoing to understand and quantify the different types of emission. Similar results have been observed in Zn$_3$P$_2$ and in other systems in the past and are attributed to defects [34, 35]. Other polycrystalline films, not shown in this figure, emit at slightly different energies, generally within a few dozen meV below 1.4 eV. The substrate emission is almost always observed, even though the film thickness is several times the penetration depth of the laser [15]. This could be due to the much larger radiative recombination efficiency of the InP substrate compared to Zn$_3$P$_2$ thin films or the diffusion of carriers from the film to the substrate. In addition to the differences in the optical properties of the different polycrystalline films, their emission shows minor variation based on the location, which could be due to the local variation of the properties such as density of defects across the thin film. If the probability of recombining through a
radiative path instead of a non-radiative path is different in the substrate and the film, any change in the diffusion and trapping of carriers may affect the relative intensities of the substrate and film emissions.

Our monocrystalline thin films exhibit a homogeneous emission spectrum over the whole sample. In figure 5, a representative photoluminescence spectrum of a monocrystalline sample is demonstrated by the black curve. The InP substrate emission is still measurable at 1.43 eV. For Zn$_3$P$_2$ we observe two peaks: a broad peak at lower energy, 1.3 eV and another at higher-energy centred around 1.52 eV. The latter is consistent with the direct bandgap of Zn$_3$P$_2$ [15]. The inset in figure 5 illustrates a magnified view of this peak. Although Kimball et al attributed the 1.3 eV emission to the indirect bandgap [15], we find it difficult to justify a higher emission intensity for an indirect transition. We think this emission may rather be linked to radiative recombination from defect levels below the bandgap. On the other hand, Briones et al assigned the transitions observed in their spectra in the range of 1.31–1.37 eV to donor–acceptor pair transitions [36].

### 3. Conclusion

In this study, we provide the main elements for the growth of monocrystalline Zn$_3$P$_2$ films with thicknesses up to 1 µm over areas up to a quarter of a 2" wafer on InP(100), ranging from the tuning of the growth conditions to the substrate preparation. While this study focuses on InP substrate, we believe the lessons learned can be relevant to other substrates. In particular, we highlight the long time necessary to completely desorb the native substrate oxide, key to obtain monocrystalline layers. We also provide the temperature and
II/V flux window that lead to stoichiometric and crystalline growth. Finally, we compare the luminescence between monocrystalline and polycrystalline layers. Luminescence from polycrystalline samples is dominated by emission below the bandgap. Monocrystalline samples also exhibit luminescence below the bandgap. Compared to the polycrystalline, the emission is considerably brighter and at lower energy. In addition, we observe band-edge luminescence, a sign of the high quality of the material. Further work is needed to identify the physical origin of the luminescence bands below the bandgap.

4. Methods

Zn$_3$P$_2$ thin films were grown using a Veeco GENxplor MBE system operating with separate Zn and P sources. The samples are obtained on InP(100) substrate. Substrate preparation includes two steps of degassing for 2 h at 150 °C and 300 °C and a third stage at 580 °C under P$_2$ equivalent beam pressures $>1 \times 10^{-6}$ Torr. Unless otherwise stated, the duration of this step is 10 min.

All the Raman measurements reported in figure 1 are done using confocal micro-Raman spectroscope operating with a 532 nm laser. The spectra offered is accumulation of 20 counts, each having the exposure time of 1 s and laser power of 9 µW.

The micro-Raman measurements shown in figure 2 have been acquired in back-scattering geometry at 12 K using the 532 nm line of a Coherent Sapphire SF laser for excitation. A microscope objective with a numerical aperture of 0.75 was used to focus the light onto the sample to a spot with a diameter of about 1 µm. The incident light is linearly polarized, while all the scattered light is collected regardless of the polarization. The signal was analysed using a TriVista triple spectrometer with 900, 900 and 1800 mm$^{-1}$ gratings in subtractive mode and a Princeton Instruments multichannel CCD PyLoN camera. The SEM images in figures 1 and 2 are acquired in a Zeiss Merlin field emission microscope. The TEM samples in figure 3 are prepared by Zeiss NVision 40 CrossBeam dual focused ion beam (FIB)/SEM with liquid Ga ion source. TEM images in figure 3 are captured by FEI Tecnai Osiris operating at 200 keV. The STEM images and EELS maps in figure 3 are captured by a FEI Titan Themis 60–300 kV, equipped with X-FEG, monochromator, Cs aberration (image and probe) correctors, and Gatan GIF Quantum ERS spectrometer, operating at 200 keV.

The XRD patterns in figure 4 are captured by a Panalytical Empyrean diffractometer operating in Gonio scan configuration with a Cu (K-α) x-ray source of 1.54 Å operating at 45 keV and 40 mA.

The micro-photoluminescence measurements, shown in figure 5, have been acquired in back-scattering geometry at 20 K using the 488 nm line of a Coherent Sapphire SF laser and an Andor iDus DV420A-OE.
detector. The spectra have been corrected for the response of the detector. A microscope objective with a numerical aperture of 0.75 was used to focus the light onto the sample to a spot with a diameter of about 1 μm. Radiant fluxes of approximately 470 μW, 470 μW, 0.47 μW and 1170 μW were used on the monocrystalline, polycrystalline 1, polycrystalline 2 and InP substrate samples. Hundred accumulations of 1 s, ∼0.01 s and ∼0.01 s were used on the first three samples, respectively, and one accumulation of ∼0.01 s was used to acquire the spectrum from InP.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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