Incorporating few-layer 2D phosphorus–arsenic alloys (PAs) into optoelectronic devices requires a synthesis technique that allows control of the alloy composition while producing volumes of material suitable for application development such as photodetectors, solar cells, and lasers. With that goal in mind, high-energy ball milling allows production of both orthorhombic (o-PAs) and trigonal (t-PAs) alloys by reacting red phosphorus and metallic arsenic powders. The synthesis follows a two-step process in which arsenic rapidly reacts with red phosphorus to first produce t-PAs followed by a slower phase transformation into o-PAs; synthesis time and overall conversion rate are slightly enhanced by the presence of arsenic. Optical measurements on exfoliated alloys at the few-layer atomic limit of the 2D PAs reveal emission spanning from the visible (≈1.9 eV) into the near-infrared region, covering a broad application space. Rapid powder synthesis within a closed system for stochiometric control of the solid-solution PAs alloys combined with solution-based exfoliation opens up opportunities for a whole new class of optoelectronic devices based on PA nanomaterials.

1. Introduction

In pursuit of 2D materials for use in optoelectronics, binary alloys of pnictogens (group V semiconductor elements) at the few-layer limit have promising optical properties. While the orthorhombic structure of pure black phosphorus (BP) has a layer-dependent direct-bandgap spanning 0.3–2.0 eV, orthorhombic phosphorus–arsenic (o-PAs) alloys have narrower bandgaps, near 0.15 eV, in the bulk. Theoretically, o-PAs alloys also have layer-dependent widening of the direct bandgaps of up to 2.1 eV at the monolayer limit.1–3 Pure orthorhombic arsenic has an indirect bandgap (0.73 eV) at the monolayer but becomes direct (0.52 eV) at two layers with the gap decreasing with increasing number of layers.4,5 Experimentally, infrared spectroscopy on bulk o-PA samples determined an optical gap between 0.15 and 0.3 eV as a function of composition.6–9 Similarly, naturally occurring trigonal gray arsenic exhibits a layer-dependent bandgap ranging from 2.3 eV for monolayer, 0.37 for bilayer, and undergoes a transition to semimetallic behavior in the bulk.10–12 Alloying with phosphorus to produce trigonal PA-layered crystals (t-PAs) may enable bandgap tuning, thereby opening opportunities for optoelectronic devices in the vis–IR spectrum.13 Anticipated applications of layered o-PAs and t-PAs alloys include transistors,14–15 photodetectors,6,7,16–18 saturable absorbers,19 solar cells,20 gas sensing,20 lithium batteries,21 lasers,22 thermoelectrics,23 and light radars.6

Synthesis of PA compounds is challenging. The methods include high pressure (HP),14,24–26 mercury (Hg),27,28 epitaxial growth on InP wafers,14 and mineralizer-assisted chemical vapor transport (CVT).6,29–32 Direct thermal heating of mixtures of red phosphorus and arsenic inside sealed silica tubes can produce o-PA alloys when the arsenic content is greater than 50 at% matching results from the 1940s that used steel cans.33–34 Direct synthesis of o-PAs alloys on silicon wafers without metallic seed layers (which quench optical properties) at moderate temperatures is lacking. Solution-based additive manufacturing of 2D materials onto silicon wafers may provide a viable route to optoelectronic devices as long as the 2D materials can be produced by an industrially scalable method.35–38 Herein, we demonstrate high-energy ball milling (HEBM) as a synthesis route for o-PA and t-PA alloys using a planetary ball mill at ambient temperature and pressure in a relatively short time.

HEBM, also referred to as mechanical alloying (MA), is a unique route for the production of BP.19–21 MA exploits the rapid far-from-equilibrium thermomechanical condition which exists within compressed powders trapped in the collisions

S. V. Pedersen, F. Muramutsa, C. Greseth, J. Eixenberger, D. Estrada, and B. J. Jaques*
between media and the vessel wall. These impact conditions provide sufficient energy in the form of pressure and localized heat to enable the red-to-BP phase transformation.\textsuperscript{[39–41]} MA avoids formation or use of toxic vapors, promotes control of stoichiometry of high vapor pressure elements, and avoids catalysts for alloy formation. While metal-rich phosphides have been explored by MA, studies are lacking in the literature for the solubility limits and possible phases that can be produced by ball milling red phosphorus with other pnictogens, such as arsenic.\textsuperscript{[42,43]}

This work demonstrates HEBM synthesis of the o-PA (1–70 at\% arsenic) and the t-PA (70–90 at\% arsenic) alloys. The resulting powders are characterized using X-ray diffraction (XRD), Raman spectroscopy (Raman), and transmission electron microscopy (TEM). Compositions and bonding behavior are analyzed using energy-dispersive spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS).

2. Results and Discussion

The kinetics of the conversion process and estimated rate constant are compared with pure BP synthesis and show slightly faster conversion kinetics. The faster kinetics appear to be enabled by the rapid conversion of red phosphorus into the t-PA phase. The slowest step is the gradual conversion of the t-PAs into o-PAs. The overall conversion rate is therefore limited by this slower transformation. Photoluminescence (PL) and UV–vis absorption (UV–vis) measurements on ultrasonic probe tip exfoliated\textsuperscript{[44]} few-layer solutions containing flakes from o-PAs, and t-PAs show an optical gap around 1.8–2 eV for all compositions. Both Pas’ solid-solution alloy series exhibit emission in the visible and near-IR, making them promising for a wide range of optical applications.

The layered orthorhombic (\textit{Cmca}) o-PAs alloys and layered trigonal (\textit{R\textsubscript{3}m}) t-PAs alloys were successfully synthesized via HEBM, as shown by the XRD patterns and Raman spectra in Figure 1. The structural transition from the o-PAs to t-PAs occurs near 70 at\% arsenic composition and is discerned by the appearance of two peaks of the trigonal phases that appear at 44° and 49° in Figure 1a. Powder XRD Rietveld refinement of the 70 at\% arsenic sample indicated that \textapprox{}5 wt\% of the o-PA phase was present, while 95 wt\% of the sample was the t-PA phase, as shown in Figure S1, Supporting Information. The narrow diffraction angle range in the nonnormalized data in Figure 1b helps to reveal the peak shift to lower angles of the strong peaks (040 and 110 planes) near 34°, while also showing the relative intensity increase, which is consistent with the expansion of the unit cell with increasing arsenic content due to the larger atomic radius of arsenic.

Raman spectra in Figure 1c show vibrational modes related to As–As, As–P, and P–P bonding. The peak positions and relative intensities of the HEBM-synthesized o-PA alloys qualitatively match the results for CVT-grown o-PA single crystals or thin films.\textsuperscript{[45]} The Raman spectra for the t-PA alloys with 70+ at\% arsenic spectra exhibit multiple broad peaks at 190–260 cm\textsuperscript{−1}, which implies bonding of phosphorus into the trigonal structure and qualitatively matches the expected wavenumber range for trigonal arsenic (\textapprox{}200, \textapprox{}255, and \textapprox{}366 cm\textsuperscript{−1}).\textsuperscript{[46]} Table S1, Supporting Information, presents the crystallographic details.
and vibrational modes of the orthorhombic and trigonal phases of phosphorus and arsenic along with reference phases from the Inorganic Crystal Structures Database (ICSD).[45]

**Figure 2** shows that the o-PAs alloys obey a Vegard-like linear trend in the lattice parameters $a$, $b$, and unit cell volume, $V$ (obtained from XRD Rietveld refinements, as shown in Figure S10, Supporting Information), which follow the relationship in Equation (1)

$$A_{P_{1-x}As} = (1-x)A_P + xA_{As}$$

where $A_P$ is the parameter of interest.[46] The Rietveld refined cell parameters for each ball-milled composition agree with the values obtained from CVT and mercury flux-synthesized single crystals and polycrystalline powders including the apparent deviation from linearity for the $c$ lattice parameter.[29] Figure 2 includes refinement results on a purchased pure BP single crystal that was ground into powder, denoted (SC).

Figure S2, Supporting Information, shows the low arsenic (0–10 at%) XRD and Raman spectra more clearly; even at low arsenic concentrations, the peak shifts are apparent. In Figure S3, Supporting Information, Gaussian fits to the Raman peaks for arsenic compositions from 0 to 30 at% show a linear trend in the peak shifts of $A_{1g}$, $B_{2g}$, and $A_{2g}$ modes from 0 to 10 at% with deviation from linearity beyond 10 at% arsenic. The weakly affected $A_{1g}$ mode only shifts 2.5 cm$^{-1}$ between the 0 and 10 at% samples, whereas the strongly affected $A_{2g}$ mode shifts 7.9 cm$^{-1}$. Multiple new modes at lower wavenumbers and severe peak distortion of the original three pure BP modes occur above 10 at% arsenic, indicating new phonon mode forms.

A milling study on the synthesis kinetics of the o-PA composition with 50 at% arsenic shows slight improvement in the synthesis time, but more importantly, the study reveals different mechanistic steps as compared with the pure BP production using identical milling parameters.[39] Unlike pure BP milling which undergoes an amorphous-to-crystalline pressure-induced phase transformation, addition of arsenic makes this process similar to a binary reaction between two elements. **Figure 3a** shows the XRD patterns from the time study on the PA 50 at% arsenic composition, while Figure 3b shows the estimated phase fraction for the same time intervals. From Figure 3c, linear regression gives the rate constant, $k$ [min$^{-1}$], from the logarithm of the unconverted phase fraction versus time plot.[39,47] The conversion at 600 rpm is comparable with pure BP with minor deviation from linearity from 0 to 30 wt% portion which is also observed in the pure BP trials. Within the first 5 min, all of the red phosphorus reacts with arsenic to produce the mostly single-phase t-PA powder. Subsequent impacts transform the t-PAs into the o-PAs phase. The rate constant for o-PAs 50 at% is slightly faster at 3.4 $\times$ 10$^{-2}$ min$^{-1}$ versus pure BP at 2.5 $\times$ 10$^{-2}$ min$^{-1}$ under identical milling conditions.[39]

Scanning electron microscopy (SEM) on powders loosely adhered to carbon tape shows a plate-like morphology for all

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**Figure 2.** Vegard behavior of lattice parameters and unit cell volume of o-PAs alloys. a–c) Ball mill-synthesized o-PA alloys show linear behavior in the $a$ and $b$ lattice parameters and show the same deviation in the $c$ lattice parameter as observed for literature values of CVT and mercury-fluxed o-PA single-crystal alloys, as obtained by XRD Rietveld refinement. d) The linear trend in the unit cell volume is clearly observed for all datasets.
compositions. In Figure 4a, large plates up to ≈100 μm in lateral extent are intermixed with smaller irregular particles produced by comminution from grinding media inside the steel vessel. The EDS spectra for the PA alloys in Figure 4b show the expected relative intensity changes for the phosphorus K line and arsenic L line for the target compositions. Overall, each composition from 1 to 90 at% arsenic was successfully produced with minor variations, as shown in Table S2, Supporting Information.

XPS show covalent bonds between phosphorus and arsenic based on the binding energy of the arsenic 3d core-level and phosphorus 2p core-level peak positions, as shown in Figure 5, for the o-PA alloys with low arsenic content. Using orthorhombic arsenic as a reference, the arsenic 3d peak resides near 41.6 eV.[21,35,48,49] At low levels (<10 at%), arsenic forms a covalent bond with phosphorus and acts as a charge transfer element within the BP lattice, resulting in a shoulder sub-band at ≈40.2 eV for the arsenic 3d spectrum and at ≈128.6 eV for the phosphorus 2p spectrum. The electronegativity difference between phosphorus and arsenic is about 0.01; phosphorus is slightly more electronegative and will tend to pull electrons away from arsenic. At low concentrations, arsenic may act as an n-type dopant at low concentrations but further electrical characterization is necessary to elucidate effects on carrier concentrations.

TEM results in Figure 6 show uniform arsenic distribution within crystalline flakes obtained by wet ball mill exfoliation of the o-PA 20 at% alloy. TEM results on the o-PA 60 and t-PA 80 at% arsenic samples are included in Figure S4 and S5, Supporting Information. The selected-area electron diffraction (SAED) pattern in Figure 6a shows bright rings (corresponding to the 040 and 111 planes, that is, overlapped peaks near 34° in the XRD patterns) highlighting the polycrystalline structure of the flakes shown in Figure 6b. The SAED pattern corresponds to the majority of the flakes within Figure 6b as the beam spot size is ≈200 nm diameter. The scanning transmission electron microscopy (STEM) map scans in Figure 6c,d show uniform distribution of phosphorus and arsenic atoms and no unreacted arsenic powders. The one-to-one correspondence of phosphorus and arsenic elemental maps suggests complete atomic mixing between the starting red phosphorus and gray arsenic powders producing a solid-solution alloy. Lattice fringes from overlapped flakes shown in Figure 6e also confirm the crystallinity of the flakes after wet ball mill exfoliation in isopropanol. Within this representative sample, flake lateral sizes ranged from about 50 to 500 nm. Previous particle size analysis on ball mill-synthesized pure BP exfoliated using the same wet ball milling method gave a similar size distribution from 100 to 1000 nm.[39] Particle size analysis in Figure S6, Supporting Information, on ultrasonic probe tip-exfoliated samples was done to produce the PL and UV–vis o-PAs and t-PAs suspensions show comparable size distributions for all compositions. The exfoliated polydisperse suspensions contain a distribution of flake thicknesses that need to be size and thickness separated using advanced sorting techniques such as centrifugation with density gradients.[50,51] Synthesis of monodispersed solutions with a specific layer thickness with narrow lateral size distributions would improve integration into optoelectronic devices. As noted in Figure S6, Supporting Information, in ultrasonic probe tip-exfoliated samples was done to produce the PL and UV–vis o-PAs and t-PAs suspensions show comparable size distributions for all compositions. The exfoliated polydisperse suspensions contain a distribution of flake thicknesses that need to be size and thickness separated using advanced sorting techniques such as centrifugation with density gradients.[50,51] Synthesis of monodispersed solutions with a specific layer thickness with narrow lateral size distributions would improve integration into optoelectronic devices. As noted in Figure S6, Supporting Information, the size distribution tends to increase to larger flake diameters with increasing arsenic content; presumably, the higher-arsenic alloys will require more energy to cleave the individual layers apart from the stronger interlayer metallic bonding from arsenic.[55] Nonetheless, similar particle size distributions were observed for both the o-PAs and t-PAs alloys. Further optimization of exfoliation by ultrasonic...
Figure 4. SEM of PA-alloyed powders. a) The ball-milled PA alloy powders for all compositions exhibit large 100 μm plates intermixed with smaller irregular-shaped particles as an outcome of the high-pressure impacts and continuous grinding within the steel vessel. b) Representative energy spectra of the PA samples show relative changes in the phosphorus K and arsenic L peak intensities as a function of alloy composition.

Figure 5. XPS for PA alloys generated by mechanochemical alloying: a) Arsenic 3d and b) phosphorus 2p core-level spectra for increasing amounts of arsenic show covalent bonding. At 41.6 eV, arsenic is configured in an orthorhombic form. At low arsenic concentration (<10 at%), the covalent arsenic acts as a charge transfer element within the host orthorhombic structure, producing a new shoulder sub-band at ≈40.2 eV for the arsenic 3d spectrum and at ≈128.6 eV for the phosphorus 2p spectrum.

Figure 6. TEM on exfoliated flakes of o-PAs 20 at% alloy: a) electron diffraction shows strong ring patterns (040, 111 planes) confirming the crystallinity of the exfoliated flakes and their match to the orthorhombic crystal structure, b) exfoliated flake sizes range from 50 to 500 nm, c,d) STEM map scans for phosphorus and arsenic show uniform distribution throughout the flakes, and e) lattice fringes reveal the crystallinity of the flakes. The circle and square outlines the regions from which the diffraction patterns and lattice fringes were obtained, respectively.
probes. The optical emission and absorption spectra on an ultrasonic tip-sonicated few-layer PA alloys reveal optical bandgaps within the visible spectrum, as shown in Figure 7a and S7, Supporting Information, respectively. The exfoliated alloys were drop-cast onto high-purity electrically fused quartz slides and encapsulated with a thick poly(methyl methacrylate) (PMMA) layer to prevent oxidation and degradation during exposure to the 532 nm excitation laser. The drop-cast solutions were polydispersed and contained presumably monolayer and thicker flakes, as determined by TEM. The optical transitions of the PA alloys cover the visible (one-layer) to at least the long-wavelength edge of the InGaAs detector (1700 nm). The weak, narrow peaks at 1.54 and 1.95 eV are artifacts from the 532 nm laser (808 nm pump) and from a strong PMMA or residual isopropanol Raman mode that appears at 630 nm when excited with a 532 nm laser source. Figure 7b presents the experimental PL and UV–vis estimate for the optical transition for each composition and compares them to literature predictions for the monolayer electronic and optical bandgap. Several theoretical works used density functional theory (DFT) and the GW approximation which takes into account the interaction of the single particle self-energy using Green’s function, $G$, and the screened Coulomb interaction, $W$, to more accurately calculate the exciton binding energies. The ball-milled PA alloys have transitions nearer the electronic gap, indicating a low exciton binding energy presumably due to a self-screening effect as the PL was performed on clumps of multilayer PAs. The dielectric constants of PA alloys are comparable with pure silicon, resulting in a small exciton binding energy ($\lesssim$100 meV). These PA results contrast with other reports in the literature, which use silicon dioxide substrates and thin pure BP material (≈nanometers) that results in a redshift of the PL peak due to larger exciton binding energy on these substrates (300 meV). While the majority of the existing literature focuses on the monolayer case for select compositions (0, 25, 50, 75, 83 at% arsenic), new theoretical and experimental work should accurately predict (i.e., GW approximation) and measure the bandgap of two-layer and thicker o-PAs and t-PAs alloys.

Figure S8, Supporting Information, shows the near-infrared PL obtained with a thermoelectrically cooled InGaAs detector using a 532 nm laser for illumination. Like pure BP, the PA alloys also exhibit PL response in the near-infrared with broad overlapped peaks near 0.8 eV (1500 nm). Due to the polydispersity of the exfoliated solutions, submicrometer flake sizes, and nanostructured grains with rough surfaces obtained from ball mill-synthesized powders, no attempt to obtain the layer-by-layer PL response was made. Figure 6e shows that the flakes are polycrystalline with individual grains fused together through the repeated media impacts within the planetary milling vessel. Nonetheless, PL from the exfoliated samples demonstrates the promising visible and NIR optical properties of few-layer o-PAs and t-PAs alloys.

The HEBM synthesis of multigram-scale quantities of PA alloy powders for use in solution-based additive manufacturing technologies (inkjet, aerosol, roll to roll, dipping, and spray-deposition, etc.) may enable high-volume device fabrication and transform the optoelectronic industry. HEBM of PA alloys provides a convenient source of stock powders for additive manufacturing, and better understanding of the milling kinetics is paramount for commercial scale-up. In the initial stages of milling of the o-PA 50 at% arsenic sample, red phosphorus and arsenic rapidly react to produce the t-PA phase. Milling at a lower milling intensity (e.g., 300 rpm, not shown) resulted in the formation of this phase within only 30 min. Visually, the powder charge in the steel vessel appeared as a dull matte black, indicative of the complete consumption of the red phosphorus prior to the formation of any o-PAs as shown by XRD. Only after 15 min of ball milling at the highest milling intensity (i.e., 600 rpm) (or longer at lower rpm) did the o-PA phase appear within the XRD characterization, as shown in Figure 3a. This result is counterintuitive based on the CVT work by Osters et al. They noted that o-PAs would form when the arsenic content was below 83 at% and they also calculated that the energy stability and thermodynamic free energy of the o-PA phase
was in all cases more favorable than the t-PA phase below 70–83 at% arsenic.[20] Likewise, the recent vapor-phase synthesis of o-PA and t-PA alloys indicated a preference for o-PA when the arsenic content was less than 70 at%.[13] As phosphorus and arsenic allotropes both share the same orthorhombic (Cmca) and trigonal (R3m) crystal structures (see Table S1, Supporting Information), have the same electron valency, similar electronegativity, and atomic radii are within 15%, the formation of substitutional solid-solution alloys is expected.[60] Presumably, the addition of trigonal arsenic may stabilize the high-pressure trigonal phase of phosphorus. Insights gained from in situ XRD and Raman studies on pure BP during high-pressure experiments suggest that the trigonal phase may be more readily formed chemically but is not as stable as orthorhombic BP upon decompression.[61] Adding arsenic may increase the stability of the trigonal phase and allow it to be retained at ambient pressure during the initial short milling times. As the milling continues, successive high-energy impacts then drives the system toward the kinetically hindered, but more thermodynamically stable, orthorhombic structure.

The transition from orthorhombic to trigonal PAs is observed near 70 at% arsenic, as shown in Figure 1a. Recent room-temperature HP experiments on pure black arsenic showed an irreversible phase transition from o-As to t-As upon decompression from the transition pressure regime (3.4–5.4 GPa), which is likely reduced when factoring in temperature and shear strain effects.[62–68] Inside a planetary ball mill, media collisions can produce localized pressure and temperature near 6 GPa and 200°C, respectively.[42] Presumably, the high-pressure collisions may push the solubility limit to lower arsenic content (70 vs. 83 at%) as the trigonal structure is favored at higher pressures. The transition at 70 at% arsenic observed in this work resides between the reported lower solubility near 60 at% arsenic as determined by HP[24–26] trials and the upper solubility limits of 74 at% (mercury flux)[28] or 83 at% (CVT).[6]

The overall reaction mechanism appears to consist of two steps: (fast step 1) alloying of amorphous red phosphorus and crystalline gray arsenic to form the trigonal PAs structure (slow step 2) and pressure-induced phase transformation of trigonal PA alloys into the orthorhombic PA alloys. The limiting step is the slower phase transformation (from t-PAs to o-PAs), which took up to 2 h of milling for the synthesis of five grams of o-PAs 50 at% arsenic at the maximum milling intensity evaluated (600 rpm).

Application of the deterministic impact model by Delogu and Cocco to that of phase transformations and binary reactions during mechanochemistry was used to estimate the rate constant and obtain a metric for comparing different synthesis conditions.[57,69–72] Although the process has two mechanistic steps, the majority of the synthesis time (>90%) reflects the second slower phase transformation of t-PAs to o-PAs. Therefore, fitting the conversion data while excluding the initial (<5 at%) and final (>95 at%) phase fractions using an exponential model is a reasonable approximation. The rate constants between pure BP and o-PA 50 at% arsenic are 2.5 \times 10^{-2} and 3.4 \times 10^{-7} min^{-1}, respectively, which is an increase in \approx 33%. At 50 at% concentration, arsenic provides a modest conversion rate enhancement. Additional studies on the amount of arsenic needed for accelerating the conversion are warranted as well as a systematic study on the conversion kinetics of the t-PA alloys.

The nonuniform lattice expansion observed in the XRD results in Figure 2 and the nonuniform Raman shifts in Figure S3, Supporting Information suggest arsenic may preferentially locate at specific sites within the o-PAs crystal lattice. From Figure S3, Supporting Information, the unit cell is defined with the lattice parameter a along the zigzag direction, b along the stacking direction, and c along the armchair direction. Similarly, the directions of atomic movement corresponding to the main vibrational modes of BP are also denoted in Figure S3, Supporting Information. The \( A_{1g} \) mode (stretch along the armchair direction) shows the greatest peak shift while the c lattice parameter grows larger than that predicted by uniform lattice expansion. Arsenic may reside at site locations that stretch the unit cell along the armchair direction and these sites may possibly dampen the highest frequency mode \( (A_{1g}\) at 460 cm\(^{-1}\) more so than other modes. Further studies using atomistic modeling of vibrational mode sensitivity to arsenic occupancy may better help reveal the atomic occupancies for low-arsenic-content o-PA alloys.

As predicted by several theoretical works on the layer-dependent bandgaps of o-PAs alloys,[1–3] the PL on HEBM-synthesized o-PAs and t-PAs powders exfoliated into few-layer flakes indicates a large optical transition near \( \approx 1.9 \) eV (corresponding to an emission centered near 650 nm). The main feature here is the exciton binding energy which is known to vary significantly for monolayer BP depending upon the substrate. The exciton binding energy of freestanding monolayer BP is near 0.8 eV; it is reduced to 0.3 eV on thick (90+ nm) SiO\(_2\) on silicon, and it is further reduced to 0.1 eV on silicon with a 10 nm SiO\(_2\) native oxide.[52,58] The measurements here were performed on thick noncentrifuged polydispersed drop-cast samples encapsulated with PMMA. Visually, under 100× optical magnification, the clumps appeared to be large agglomerates of multilayer BP while TEM imaging revealed some fraction that likely consisted of monolayer flakes, possibly with turbostratic stacking. That is, the dielectric environment of the present monolayer PAs is most likely that of other monolayers, or thicker flakes of PAs, such that the exciton binding energy is negligible or less than 0.1 eV. This is due to the fact that BP and PAs have similar dielectric constants as silicon. The PL results here show a relatively constant peak near 1.8–2.0 eV for all compositions, which is in line with theoretical predictions.

In addition, the PL from exfoliated few-layer trigonal PA alloys shown in Figure 7a matches the predicted and observed energy gaps for few-layer trigonal arsenene; although the reports are inconclusive if the gap is direct or indirect.[12,19,51–76] Presumably, adding 10–30 at% phosphorus into the trigonal arsenic crystal may result in a direct gap or at the very least, an optical transition that is readily observed at room temperature. A future study with detailed atomistic modeling of the effect of phosphorus alloying on the few-layer optical and electronic band structure of arsenene would be of great benefit.

From the data collected here, the optical transitions at 1.8–2.0 eV are inferred to be from monolayer o-PAs or t-PAs, assuming a negligible exciton due to the surrounding BP self-screening the monolayer from the quartz substrate. The claim of monolayer is tentative as atomic force microscopy measurements were confounded by the nanoscale lateral dimensions and rough surfaces of the exfoliated flakes. Nonetheless, the PL results here agree with GW approximations for monolayers.
Arguably, optical transitions from thick flakes with higher-order transitions are generally unresolved at room temperature. An outstanding question is if the addition of phosphorus into the trigonal arsenic structure expands the layer-dependent bandgap range, such that three- or four-layers would also have a narrow bandgap before the onset of semimetal behavior. Confirmation of visible and NIR emission in both alloy series extends the wavelength regime from medium-wavelength infrared into the vis–NIR spectrum. While recent literature emphasizes the mid-IR applications of orthorhombic black arsenic alloys, emission within the visible spectrum suggests applications such as biomedical photothermal treatment, facial recognition, visible lasers, and detectors. Coupling the low-cost direct synthesis of PA alloy powders by HEBM with solution-based centrifugation methods for isolating specific flake sizes and thicknesses may enable scalable optoelectronic device fabrication based on 2D nanomaterials.

3. Conclusion

In summary, we have demonstrated high-energy planetary ball milling as a direct route to produce orthorhombic and trigonal PA solid-solution alloys and investigated the optical behavior at the few-layer limit. The industrially scalable ball-milling synthesis route provides relatively large amounts of PA alloy powder in a short period of time within an enclosed system at ambient temperature and pressure. The rate limiting step in the conversion process is the slow transformation of t-PAs into o-PAs; the synthesis time is comparable with pure BP synthesis. An enhanced solubility of phosphorus into the trigonal PAs alloy is observed. The exfoliated flakes contain crystalline domains within an amorphous matrix and arsenic and phosphorus are uniformly distributed within the crystals. Emission in the visible and NIR regimes from both orthorhombic and trigonal PA alloys suggests an optical gap comparable with pure BP but a layer-by-layer study could help to delineate the layer dependency. More studies, both theoretical and experimental, are required to discern the layer-by-layer behavior of PA alloys. High-volume synthesis of commodity-grade PA alloyed powders is a step forward toward nanomaterials in commercial optoelectronic devices.

4. Experimental Section

In the milling experiment, for the synthesis of the PA alloys from 1 to 90 at% arsenic, stoichiometric amounts of red phosphorus (0–1 g) (Alfa Aesar, 97% purity, –60 mesh) and gray arsenic (0–1 g) (Alfa Aesar, 99.99% purity, –200 mesh) amounting to 1 gram of powder charge and stainless steel media (10 mm diameter, 100 g) were weighed and loaded into a stainless steel vessel (250 mL) inside an argon atmosphere glovebox (PO2 < 0.1 ppm) and sealed under argon (90–95 kPa) at room temperature. The ball-to-powder mass ratio was 20:1. All milling experiments were conducted with the PM100 planetary ball mill (Retsch, Germany) with pauses in the milling cycles (15 min on, 30 min off) to prevent overheating of the unit and switch the direction of flywheel rotation (promotes better mixing). Milling conditions (rpm and duration) were held constant at 600 rpm and 34 h of milling. For the kinetic study, stoichiometric amounts of red phosphorus and gray arsenic were added to produce 50 at% composition for 5 gram powder charge for comparison with a pure BP kinetic study under identical milling conditions (5 g, 600 rpm, 250 mL vessel, 30 stainless steel grinding spheres of 10 mm diameter) with XRD samples collected as described previously.[39]

To obtain few-layer PA suspensions, the converted powder (0.1 g) was solvent-exfoliated in isopropanol (30 mL) using a high-energy mixer mill (Spex 8000) with small (1 mm diameter) chrome steel ball media sealed inside a steel vessel (50 mL) for 12 h at ~1000 cycles per minute. These solutions were used for TEM characterization. Exfoliation with anaerobic conditions with an ultrasonic probe tip sonicator with a cooling ice bath was used to obtain few-layer suspensions in IPA.[51] These solutions were drop cast onto high-purity electrically fused quartz slides (to eliminate the silicon peak in PL measurements). UV–vis measurements were performed on ultrasonic tip probe-exfoliated solutions with optical densities between 0.3 and 1.0 and measured with a quartz cuvette using the Spectrovis Plus spectrometer (Vernier, USA).

Powder XRD data was obtained in the Bragg–Brentano geometry (Cu Kα, Rigaku MiniFlex 600, Japan) on powder (0.165 g) sealed inside a polyimide dome within an argon glovebox to prevent ignition with air during X-ray measurements. The internal standard method using NIST Silicon 640D powder (ICSD #51688) was added in trace amounts to enable correction for vertical displacement errors with the polyimide dome X-ray accessory (Rigaku, accessory 23928101). Rietveld refinement was performed using the GSAS-II software and the crystal information file of the P3,4,5A5.5 compound (ICSD #611147) with occupancies set to the nominal composition of each sample. Refined factors included phase fraction, sample displacement, preferred orientation, unit cell parameters, strain, and crystallite size.

Raman spectroscopy (Raman) data was obtained (Horiba LabRam HR Evolution, Japan) on densely packed powder samples (0.01 g) prepared inside an argon glovebox that were sealed inside a custom-built enclosure with a sapphire window to prevent oxidation and ignition during measurements. A 50 mW 532 nm laser source (Nd:YAG) was used to generate spectra collected with a Si charged-coupled device (CCD). Spectra were obtained at 20× objective with repeat acquisitions for 60 s at ten random locations throughout the bulk surface using the 1800 lines mm−1 grating. PL measurements were obtained using two detectors for visible and infrared measurements. Exfoliated PAs samples were drop cast in three locations onto electrically fused quartz slides, followed by immediate (~1 min) PMMA encapsulation using a 200 °C bakeout for 10 min to cure the PMMA film. Each PA spot was measured at least three times, resulting in an average of nine measurements per composition. A Princeton Aston spectrometer coupled with a silicon CCD (visible) and NIRvana InGaAs (NIR) thermoelectrically cooled array and an excitation wavelength of 532 nm at 40 mW was used to obtain the visible and infrared spectra. Data were collected for 5 s using a 100× near-infrared objective.

SEM was performed on samples pressed onto carbon tape and imaged at 5000x magnification and intermediate accelerating voltages using a FEI Teneo LoVac, model 1 068 566, FE-SEM. XPS was performed on samples prepared inside an argon glovebox by pressing PA powders into indium foil and transferred to the XPS with transfer chamber. XPS spectra were collected using a Physical Electronics Versaprobe system with a monochromated Al Kα X-ray source utilizing a beam diameter of 100 μm and 25 W of power. For general survey scans, a pass energy of 117.4 eV and an energy step size of 0.8 eV was used. For higher-resolution core-level scans, a pass energy of 23.5 eV and an energy step size of 0.2 eV was used. TEM was performed using a JEM-2100, (Jeol, Japan), with Orius SC1000 CCD camera; samples were drop cast onto lacey carbon grids and transferred into the vacuum chamber within 5 min. A low accelerating voltage of 100 keV was used with minimal dwell times roughly 30 s for imaging to prevent the amorphization of the flakes.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

C. Husko and J. Wood are equity holders in Iris Light Technologies.

Data Availability Statement

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

Keywords

arsenides, ball milling, black phosphorus, mechanochemistry, photonics

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