Zn₃As₂ nanowires and nanoplatelets: Highly efficient infrared emission and photodetection by an earth abundant material

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KEYWORDS: Nanowire, nanoplatelet, II-V, semiconductor, MOVPE, crystallography, optoelectronics

ABSTRACT: The development of earth abundant materials for optoelectronics and photovoltaics promises improvements in sustainability and scalability. Recent studies have further demonstrated enhanced material efficiency through the superior light management of novel nanoscale geometries such as the nanowire. Here we show that an industry standard epitaxy technique can be used to fabricate high quality II-V nanowires (1D) and nanoplatelets (2D) of the earth abundant semiconductor Zn_3As_2 . We go on to establish the optoelectronic potential of this material by demonstrating efficient photoemission and detection at 1.0 eV, an energy significant to both photovoltaics and optical telecommunications. Dynamical spectroscopy reveals this superior performance as resulting from a low rate of surface recombination combined with a high rate of radiative recombination. These results introduce nanostructured Zn_3As_2 as a high quality optoelectronic material ready for device exploration.

The explosion in demand for electronic goods has placed increasingly unsustainable pressure on a variety of scarce materials used in their production.¹ Of particular concern are many current generation optoelectronic and photovoltaic (PV) technologies designed around semiconductor materials of low earth abundance. While silicon is of high earth abundance, the indirect nature of its bandgap is often disadvantageous for such roles. In contrast to silicon, the majority of commercialized direct bandgap semiconductors including members of the III-V family, cadmium telluride and copper indium selenide/sulfide (CIGS) contain elements of low earth abundance. As a result, there is an ongoing need for alternate semiconductor materials combining superior optoelectronic performance with earth abundance. Promising examples include Zn_3P_2 ,^{2, 3} copper zinc tin sulfide (CZTS)^{4, 5} and more recently the organic-inorganic perovskites.^{6, 7}

Relatively unexplored, the II-V family of semiconductors holds appeal for a diverse range of applications. Examples range from the highly earth abundant Zn_3P_2 which is an attractive material for PVs,^{2, 3} to materials of lesser abundance such as Zn_4Sb_3 which is among the most efficient of thermoelectric materials^{8, 9} and Cd_3As_2 which was recently identified as one of the few known examples of a three-dimensional topological Dirac semimetal.^{10, 11} Less well studied, Zn_3As_2 is an earth abundant semiconductor with a band gap around 1.0 eV^{12, 13} and the potential to realize high hole mobilities.^{14, 15, 16} Of key importance for possible optoelectronic applications, the band gap may be tuned across the infrared through alloying with Cd_3As_2 (semimetal) and Zn_3P_2 (1.5 eV).^{17, 18} The epitaxial integration of Zn_3As_2 with established III-V materials is also possible due to their close structural similarity and, in the case of InP, a lattice mismatch of only 0.5%.^{19, 20}

In parallel with the development of earth abundant materials, efficiency gains in optoelectronic and PV devices may also be realized through improved light management. Novel nanoscale geometries are promising in this role as they offer a route to superior optical performance particularly in regards to light trapping and guiding in synthetic structure. Gains have recently been demonstrated in nanowire (NW) PV devices where light trapping has been shown to exceed the ray optics limit applicable to planar devices.^{21, 22, 23, 24} The NW geometry is furthermore a useful platform for achieving relevant heterostructures such as the epitaxial integration of high mobility, optically active III-V materials with silicon.^{25, 26} Single photon emission and photon number resolved detection using NWs have also been shown.^{27, 28, 29} One key theme of nanowire research to date has been crystal phase perfection and the elimination of planar defects.³⁰ Similarly strong research interest has recently centered on 2D-like materials from the atomically thin³¹ to nanosheets and nanoplatelets.^{32, 33} Two-dimensional nanostructures have proven a

particularly useful basis for nanoscale optoelectronic devices including photovoltaic cells, phototransistors/detectors and lasers.^{34, 35, 36}

Here we use standard sources in a metal organic vapor phase epitaxy (MOVPE) reactor compatible with commercial production of III-V materials to grow both NWs and nanoplatelets of the earth abundant II-V semiconductor Zn_3As_2 . To date there have been relatively few reports of Zn_3As_2 synthesis,^{18, 19, 20, 37} among which only a couple have described nanoscale Zn_3As_2 .^{16, 38} In both of the latter two cases the authors employed thermal evaporation techniques. Such techniques lack the control and reproducibility of MOVPE growth while also limiting possibilities for heterostructure definition and commercial integration. A comprehensive optoelectronic assessment of nanoscale Zn_3As_2 moreover remains lacking from the literature. Through detailed structural analysis we demonstrate that our nanostructures are single crystalline and free from planar defects. Efficient emission and clear photoabsorption are then shown at 1.0 eV establishing the optoelectronic potential of this material for a broad range of future applications in the near infrared.

Zn_3As_2 nanowires and nanoplatelets were grown via horizontal flow MOVPE (Aixtron 200/4) on semi-insulating GaAs(110) which had been pre-treated with 50 nm colloidal Au. (Ted Pella, Inc.) Growth was performed at 10 kPa under a total flow of 15 standard liters per minute using the precursors AsH_3 and diethylzinc (DEZn) at molar fractions of 4.8×10^{-3} and 4.8×10^{-6} respectively to give a V/II ratio of approximately 1000. The growth time was 30 minutes. Subsequent investigation by both scanning electron microscopy (SEM) and transmission electron microscopy (TEM) was performed utilizing a FEI Helios 600 NanoLab Dualbeam (FIB/SEM) operated at 10 kV and a JEOL 2100F TEM operated at 200 kV respectively. (Representative SEM images are

shown in supporting Figure S6.) Samples for TEM investigation were prepared by mechanical dispersion on holey carbon copper grids.

Figure 1. Structure and morphology of the Zn_3As_2 NWs and nanoplatelets: (a) $\langle 221 \rangle$ axis bright field TEM image of a NW; (b) $\langle 221 \rangle$ axis HRTEM image of the NW / seed particle interface; (c) Fourier transform of (b) revealing $\langle 110 \rangle$ type growth direction; (d) $\langle 201 \rangle$ axis TEM image of the NW tip; no planar defects are apparent; (e) $\langle 221 \rangle$ axis HRTEM image of the nanoplatelet / seed particle interface; (f) Fourier transform of (e) showing that the growth direction is rotated 60° relative to (b); (g) $\langle 221 \rangle$ axis bright field TEM image of the entire nanoplatelet (h) $\langle 221 \rangle$ axis diffraction pattern (i) $\langle 201 \rangle$ axis diffraction pattern (j) $\langle 241 \rangle$ axis diffraction pattern (k) $\langle 111 \rangle$ axis diffraction pattern (l) simulation of $\langle 221 \rangle$ diffraction from α' Zn_3As_2 (m) simulation of $\langle 201 \rangle$ diffraction from α' Zn_3As_2 (n) simulation of $\langle 241 \rangle$ diffraction from α' Zn_3As_2 (o) simulation of $\langle 111 \rangle$ diffraction from α' Zn_3As_2 (p) atomic model of the Zn_3As_2 NW shown in top view with facet directions marked (q) top view SEM image of a Zn_3As_2 NW (scale bar 100 nm) (r) atomic model of the Zn_3As_2 NW shown in side view with facet directions marked (s) Schematic model of α' Zn_3As_2 as reported by Pietraszko³⁹ (t) atomic model of the Zn_3As_2 nanoplatelet shown in top view with facet directions marked (u) SEM image of a Zn_3As_2 nanoplatelet (scale bar 500 nm) (v) atomic model of the Zn_3As_2 nanoplatelet shown in side view with facet directions marked.

Bright field TEM images typical of the two distinct free-standing nanostructure geometries obtained are presented in Figures 1(a,b,d,e,g). Each micrograph excepting 1(d) depicts the same major zone axis, later determined to be $\langle 112 \rangle$. The apparent length of the nanostructures was maximized in this zone axis indicating that the major geometrical axis of each nanostructure lies in the plane of these images. Examining the low magnification images, Figures 1(a,g), the two geometries may be described as NW and nanoplatelet-like respectively. The NW is somewhat longer than the nanoplatelet, being approximately $11.5 \mu\text{m}$ in length and almost taper free, ranging from 75 to 150 nm in diameter from tip to base. In contrast, the nanoplatelet is approximately $8.5 \mu\text{m}$ long and its width increases from 50 nm at the tip to a maximum of $1.3 \mu\text{m}$ near the base to give a necktie-like silhouette. From SEM imaging (supporting section S2) the thickness of these nanoplatelets was found to be in the range of 50-100 nm, approximately equal to the diameter of the seeding particle.

Considering the high-resolution images, (Figures 1 (b) and 1(e)) and their Fourier transforms, (Figures 1 (c) and 1(f)), this difference in morphology is seen to arise from a difference in growth direction. With reference to the expected pseudocubic structure of Zn_3As_2 ,^{39, 40} as is later confirmed, the NW may be said to have grown along the equivalent cubic direction $\langle 110 \rangle$ and nanoplatelet $\langle 112 \rangle$. While these directions differ from the usual $\langle 111 \rangle$ VLS growth direction, conditions favoring non- $\langle 111 \rangle$ growth have been widely reported in other material systems.⁴¹ Concomitant changes in geometry are also common and may be related to changes in the symmetry of the growth axis.^{41, 42, 43}

That both nanostructures presented here are single crystalline and appear free from planar defects is clear from the images presented in Figures 1(a-g) along with similar images from a variety of zone axes (see supporting sections S1.1 - S1.3) and representative selected area electron

diffraction patterns (SADP) from each of these zones axis (Figures 1(h-k)). Interestingly, an absence of planar defects has also been widely noted for NWs propagating along non- $\langle 111 \rangle_B$ growth directions.^{43, 44, 45}

X-ray energy dispersive spectroscopy (XEDS) (see supporting Figure S7) analysis of the nanostructures identified only zinc and arsenic in an approximate atomic ratio of 3:2 as quantified by the standardless Cliff-Lorimer method using calculated k -factors. This ratio is consistent with Zn_3As_2 , one of two line compounds in the arsenic-zinc binary system. Zn_3As_2 is known to be tetragonal at room temperature before transforming into a cubic structure at 651°C.⁴⁶ The room temperature phase α as investigated by both X-ray diffraction^{39, 47} and neutron diffraction⁴⁰ techniques has been described by a 160-atom unit cell. This cell consists of a distorted face centered cubic As sublattice interpenetrating a 75% filled simple cubic Zn sublattice. In this arrangement each arsenic atom is surrounded by six zinc atoms and two zinc vacancies and each zinc atom is surrounded by four arsenic atoms. A small alteration in the symmetry of the zinc vacancies produces the α' phase at 190°C.^{39, 46}

Figure 1(h-k) presents four zone axis SADPs obtained from the NW structure presented in Figures 1(a-c, g) which are representative of those obtained from all the nanostructures investigated. A clear pseudocubic symmetry is again apparent. Using the *jems* software package (Pierre Stadelman), we simulated the expected diffraction patterns of various reported α and α' Zn_3As_2 structures.^{39, 40} The experimental SADPs were best replicated by the α' Zn_3As_2 ³⁹ phase which is expected to be the most stable phase at the growth temperature. Shown in Figure 1(l-o) with the same orientation and scale as the experimental patterns, the α' simulations are seen to replicate all experimentally observed diffraction spots. In contrast, simulation of the α Zn_3As_2

phase³⁹ showed a space group absence of $h=k$, $l=4n$ and a lattice absence of $h+k+l=2n+1$, spots observed in the experimental $\langle 221 \rangle$ and $\langle 102 \rangle$ axis diffraction patterns. (The α phase simulation is presented in supporting section S4.) In all cases the seed particle could be indexed to β' AuZn and exhibited a clear orientational relationship to the Zn_3As_2 nanostructures. (See supporting section S1.4 for full details.)

Under most imaging conditions electron diffraction is known to be strongly dynamical, which greatly complicates the analysis of the relative diffracted intensities.⁴⁸ We did however observe the intensity of the 204 type spot to be systematically greater than that expected from modeling. One explanation for this difference could be a variation in zinc ordering. Variation from the expected structure^{39, 40} has previously been deduced from Raman spectroscopy and is expected to occur with relative ease.⁴⁹ An understanding and control of zinc ordering is moreover expected to be crucial in realizing the thermoelectric potential of the Zn-V compounds.⁸

The Zn_3As_2 α' unit cell is shown in Figure 1(s) with atomic models of the NW and nanoplatelet structures constructed from this basis shown in Figures 1(p,r) and (u,v), respectively. Figures 1(q) and (p) illustrate the diamond shaped cross-section of the NW with a top view SEM image of a NW looking along the $\langle 102 \rangle$ growth axis being inset into a top view of the atomic model with labeled plane normals. Confirmed by both SEM imaging and TEM measurement of apparent diameter at varying tilts, this shape is formed by the primary sidewall facets of the NW which are $\{112\}$ type or in equivalent cubic terms, $\{111\}$ type. The vertices of this diamond are blunted by small strips of $\{102\}$ type (equivalent cubic $\{110\}$) and to a lesser extent, $\{100\}$ type sidewall facets. A similar pattern of faceting has previously been reported for several other NW systems growing along the cubic $\langle 110 \rangle$ direction including oxide assisted silicon,⁵⁰ Au seeded

germanium,⁵¹ and Pd seeded InAs⁴⁵. Figure 1(s) shows the same atomic model in a side profile similar to the orientation of the NW in Figure 1(a).

In contrast to the 1D geometry found for the $\langle 112 \rangle$ growth direction in many other material systems,^{51, 52} Zn_3As_2 growing along $\langle 112 \rangle$ was here found to form 2D-like nanoplatelets. Figures 1(t-v) illustrate this geometry with an atomic model of the platelet structure shown from the side (Figure 1(v)) and the top (Figure 1(u)) with a top view SEM image of a platelet inset (Figure 1(t)). Through a combination of SEM imaging and TEM tilting studies similar to those undertaken for the NW, the major facet or face of the nanoplatelet was determined to be $\{112\}$ type or in equivalent cubic terms, $\{111\}$ type. The shorter sidewalls perpendicular to the $\langle 112 \rangle$ viewing direction in Figure 1(g) were thus identified as $\{122\}$ type or in equivalent cubic terms $\{112\}$ type. The longer sidewalls meeting at the apex defined by the seed particle are more complex and were observed to vary in angle with the length of the nanoplatelet. (High resolution images of these sidewalls are shown in supporting section S1.5 where it is observed that this longer sidewall is actually a combination of $\{122\}$ and $\{110\}$ facets.) Interestingly, the geometry found here is somewhat similar to that reported by Kouklin *et al.*³⁷ for platelets millimeters in length and microns in thickness grown by thermal evaporation.

Figure 2. Temperature dependant PL of Zn_3As_2 nanostructures: (a) Temperature dependant PL spectra from an ensemble of Zn_3As_2 nanostructures showing fits (dashed lines) to the high energy tails of the spectra. The fitted bandgap and broadening are also shown. (b) Fitted bandgap and broadening (error bars) as a function of temperature for an ensemble of Zn_3As_2 nanostructures (squares), a single Zn_3As_2 NW (circles) and a single Zn_3As_2 platelet (triangles). A fit of the Varshni equation to the ensemble data is also shown (dashed line). Results obtained by transient Rayleigh scattering and photocurrent spectroscopies (see Figures 3 and 4 respectively) are shown for completeness. An SEM image of the Zn_3As_2 NW investigated is inset.

Having established that our nanostructures were of high crystalline quality we then investigated their optoelectronic performance. Micro-photoluminescence (PL) measurements employed a 50x/0.55NA NIR objective lens (Leica HCX PL Fluotar) with excitation from a 830 nm continuous-wave laser (Topica DL100) delivering between 1 μW and 8mW at the focal spot. The PL was passed through an 830 nm edge filter and then a spectrometer (Horiba T64000) fitted with a 150 lines/mm diffraction grating before being collected on a liquid nitrogen cooled InGaAs array detector. Temperature dependant photoluminescence measurements were

conducted between 77 and 570 K under nitrogen in a liquid nitrogen cooled cryostat. (Linkham TS1500) Both the Zn_3As_2 NWs and nanoplatelets were found to emit a strong photoluminescence (PL) signal in the near-infrared across this temperature range. Figure 2(a) shows typical spectra which in this case were obtained from an ensemble of nanostructures over the temperature range of 90 to 330 K. Power- and temperature-dependent data for single NWs and platelets can be found in supporting sections S5.2, S5.3 and S5.7. A single peak is observed to narrow and blueshift from 1.0 eV at room temperature to 1.1 eV at 80K. These energies correspond well to what has previously been described as the band edge emission of bulk Zn_3As_2 .^{12, 19} The integrated intensities of PL emission are maximum near room temperature (see supporting section S5.4) decreasing relatively slowly with decreasing temperature (activation energy 21.5 meV) and quite quickly (85.3 meV) with increasing temperature. This is in contrast with previous studies of planar Zn_3As_2 where this peak was not observed below 100K but was instead replaced with various lower energy peaks (0.7 – 1.0 eV).^{12, 19} The authors of these previous works attributed the absence of band edge emission at lower temperatures to an indirect bandgap as suggested by previous pseudo-potential modeling¹⁴ of the band structure. The nature of the bandgap in this system is however contentious as other experimental results have shown the transition to be direct.^{13, 53} We suggest that some of these discrepancies arise from variation in material quality and that in our case the VLS growth method may act to reduce impurity incorporation.⁵⁴ We also recall the planar defect-free nature of our nanostructures.

In order to quantify both band gap and effective spectral broadening the high energy tail of each PL spectrum was fitted with a line shape describing band-to-band emission.⁵⁵ (see supporting sections S5.5 and S5.6 for details of the fit form and plots of the model parameters as a function of lattice temperature) As plotted in Figure 2(a), the fits, the extracted band gap and the extracted

effective broadening (first standard deviation of the modeled Gaussian distribution) are seen to reproduce both the data and trends discussed. The extracted carrier temperatures (supporting Figure S13(b)) are furthermore close to the measured lattice temperatures indicating equilibrium between carriers and thermal phonons. Interestingly, a step in the extracted carrier temperature is noted around 150K, the same point as there is an apparent increase in PL intensity. This temperature equates well with the exciton binding energy as calculated using the hydrogenic approximation (see supporting section S5.8) and represents a topic for future research.

In Figure 2(b) the fitted bandgap energy and its effective broadening is plotted as a function of lattice temperature for a single NW (SEM shown inset), a single platelet (SEM shown in supporting Figure S15) and the same ensemble of nanostructures studied in Figure 2(a). Little variation is observed between datasets with a fit of the Varshni equation to the ensemble data in the temperature range of 80 to 570 K returning the coefficients; $E_g = 1.094$ eV, $A = 5.087 \times 10^{-4}$ eV/K and $B = 170.7$ K. This fit and the underlying data is in good agreement with the behavior of bulk Zn_3As_2 .^{12, 53} As discussed later, the fit also anticipates our low temperature measurements by both Rayleigh scattering and energy dependant photocurrent measurements.

Figure 3. Transient Rayleigh scattering spectroscopy of a single Zn_3As_2 NW: (a) Time dependant photo-modulated polarization response showing fitted bandgap. (b) Measured electron hole plasma density and fit extracting non-radiative lifetime and radiative recombination rate coefficient. (c) Plot of radiative and non-radiative recombination rates and the extracted internal quantum efficiency.

In order to further understand and quantify the efficiency of emission as observed by PL we performed transient Rayleigh scattering spectroscopy (TRS) experiments on single Zn_3As_2 nanostructures using a method previously described.⁵⁶ Briefly, a pump-probe (550 nm; 900-1200 nm) setup is used to measure the time dependant photo-modulated polarization response of scattered light from a single NW following photoexcitation.⁵⁶ By modeling this response parameters such as the band gap energy, background carrier concentration and minority carrier lifetime may be extracted. Figure 3(a) presents a typical contour plot of the pump-induced variation in the photo-modulated polarization response, $\Delta R'/R' = \Delta(R_{\parallel} - R_{\perp})/(R_{\parallel} + R_{\perp})$, as a function of incident photon energy and time following photoexcitation. A strong response with a decay extending beyond 1 ns is immediately apparent in the energy range between 1.05 and 1.25 eV. As this measurement represents a derivative form at later times, the zero crossing point (dashed line, Figure 3(a)) of approximately 1.10 eV marks the band edge of these nanostructures. Using simple band-to-band transition theory to determine the carrier-dependent complex index of refraction, fits to the TRS spectral line shapes were made for given times following photoexcitation. (See supporting section S6.1 for these line shapes and fits) The fundamental band gap was thus determined to be at 1.108 eV at 10K with an effective broadening of 30 meV (FWHM). This energy and effective broadening correspond well to the PL results presented in Figure 2 and previous low temperature investigations of Zn_3As_2 .^{13, 19, 53} Fits to the TRS lines shape required a free hole density of $2 \times 10^{17} \text{ cm}^{-3}$ in the valence band, a concentration similar to that previously found from optical absorption and Hall measurements of nominally undoped Zn_3As_2 at low temperature.^{19, 53, 57} Figure 3(b) shows the extracted photoexcited carrier concentrations as a function of time following photoexcitation. (The temperature decay is presented in supporting Figure S17). These values are seen to decay from approximately 4×10^{18}

to 4×10^{17} in around 1 ns. Observed on the logarithmic axis, the non-linear nature of this decay at earlier times is suggestive of significant radiative recombination. Fitting this decay to bimolecular recombination which includes a linear non-radiative loss term, we find the lifetime of non-radiative decay to be 730 ps and the bimolecular recombination coefficient, B, to be $0.6 \times 10^{-9} \text{ cm}^3/\text{s}$.

The non-radiative lifetime found here is significantly longer than that measured previously for unpassivated GaAs NWs and approaches values measured for InP NWs.^{58, 59} Given the NW geometry, such a long non-radiative lifetime is indicative of a low surface recombination velocity. The radiative recombination coefficient, B, is furthermore similar to that of direct bandgap semiconductors and likely incompatible with a phonon assisted transition. Taken together these two factors lead to a high IQE and may be considered responsible for the observation of a strong PL signal. Figure 3(c) plots the instantaneous non-radiative and radiative decay rates and their corresponding internal quantum efficiency (IQE) as a function of time following photoexcitation. Beginning at around 60%, the IQE is observed to decrease towards a background level of 8% as determined by the background carrier concentration.

Figure 4. Characterization of single Zn_3As_2 nanostructure metal-semiconductor-metal photodetector devices. (a) Room temperature dark I-V characteristic and fit of a single platelet device. (b) Room temperature and low temperature dark I-V characteristics of a single NW device showing a fit to the room temperature data. (c) Photocurrent normalized by incident power as a function of excitation energy for the single NW device imaged by SEM and illustrated schematically in (d) and (e) respectively.

In order to realize the optoelectronic potential of our Zn_3As_2 nanostructures we fabricated single NW and single nanoplatelet metal-semiconductor-metal photoconductor devices. The nanostructures were first dispersed from solution onto a highly doped silicon substrate with a thermal oxide thickness of 300 nm. Photolithography followed by the deposition of Ti (20 nm) / Al (500 nm) and lift off was used to define contacts at either end of nanowires. The devices were wire bonded and mounted in an optical cryostat (attocube) for low temperature photocurrent measurement. Photocurrent measurements were performed using a tunable pulsed light from a super continuum photonic crystal fiber. The laser light was focused onto the nanowire with 50X/0.5NA long working objective and a fixed bias of 5 V applied across the nanowire. We

acquired the photocurrent data using a standard lock in technique involving chopping of the laser light. Cooling was provided by a continuous flow of liquid helium. Figures 4(a-b) present dark I-V characteristics of a single platelet device at room temperature and a single NW device at both room and low temperature respectively. These IV curves show that both Ti-Al contacts to the NWs and nanoplatelets form Schottky barriers. To quantify the background carrier concentration of each device we adopted the approach of Zhang *et al.*⁶⁰ in modeling these IV curves. Briefly, the devices were modeled as a three element equivalent circuit consisting of an ohmic resistance in series with Schottky barriers described by thermionic emission under forward bias and thermionic field emission⁶¹ under reverse bias. (For full details see supporting section S7.1). Fits to the IV curves using this analysis are shown for the room-temperature plots, with the background carrier concentration of the NW determined to be $1.67 \times 10^{18} \text{ cm}^{-3}$, and the platelet $7.41 \times 10^{18} \text{ cm}^{-3}$. Although high, these values are consistent with previous studies which have found Zn_3As_2 to possess a significant p-type background^{19, 62, 63} which has been related to shallow-level¹⁵ native defects.²⁰ Compensation of this p-type character has previously been successfully achieved by doping with In.⁵⁷ In the case of the related semiconductor material, Zn_3P_2 , a similar p-type background has been related to the formation of charged phosphorus interstitial defects.⁶⁴ Despite significant background hole concentrations, high room temperature hole mobilities of between 200-300 cm^2/Vs have previously been determined for Zn_3As_2 .^{16, 63}

All the Zn_3As_2 MSM devices investigated were found to be photosensitive demonstrating useful photodetection down to approximately 1.0 eV. (A comparison of light and dark I-V curves is presented for a NW device in supporting Figure S19) As shown in Figure 4(c), the photocurrent versus excitation energy at low temperature displays a clear onset at approximately 1.13 eV. This energy is consistent with the band gap found by transient Rayleigh scattering spectroscopy and

extrapolation of the Varshni fit to the PL data and may thus be related to the same transition. It also accords well with previous measurements of the absorption edge at low temperature which were assigned to a direct bandgap transition.^{13, 65, 66}

In summary, we have reported on the growth of Zn_3As_2 NWs and nanoplatelets using standard MOVPE sources and demonstrated the significant optoelectronic promise of these nanostructures. Both geometries were found to be single crystalline, free from planar defects and to emit a strong room temperature PL signal at around 1.0 eV. Through direct measurement of the photoexcited carrier lifetime we were able to quantify the high efficiency of this emission and relate it to both a low surface recombination velocity and high coefficient of radiative recombination. In order to further demonstrate the optoelectronic potential of this material we fabricated single nanostructure MSM photoconductor devices which showed photosensitivity in the near-infrared and visible ranges.

As an earth abundant semiconductor exhibiting efficient 1.0 eV emission and photodetection, Zn_3As_2 presents a range of intriguing opportunities for nanotechnology. The use of MOVPE to synthesize Zn_3As_2 nanostructures introduces these opportunities to an existing community of researchers and brings the highest levels of control and reproducibility to growth. Beyond binary Zn_3As_2 , the door is now open for the MOVPE/MBE synthesis of nanostructured II-V semiconductor materials, II-V alloys and novel II-V / III-V heterostructures for applications encompassing optoelectronics, thermoelectrics, high speed nano-electronics and topological physics.

ASSOCIATED CONTENT

Supporting Information. Additional TEM images of the NW and nanoplatelet presented in Figure 1; images and zone axis patterns of a NW that grew in the $\langle 110 \rangle$ direction; HRTEM, FFT and SADP of seed particles; TEM images of a platelet's sidewalls; SEM of NWs and platelets; EDX studies; simulation of electron diffraction from the α phase; temperature dependant PL of an ensemble of Zn_3As_2 nanostructures and fits; temperature dependant PL of a single NW and fits; temperature dependant PL of a single platelet and fits; a description of the PL lineshape fitting procedure; the temperature dependence of parameters extracted by fitting the PL; the power dependence of PL; discussion of the exciton binding energy; SEM of the single platelet studied; transient Rayleigh scattering spectra and fits; electronic temperature decay; a discussion of the Schottky barrier fitting procedure; the material parameters used for fitting the Schottky barriers; the room temperature photoresponse of an MSM device. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

T.B. and P.C. conceived the idea for the research and performed the material growth. T.B and Y.G. performed the microscopy and structural analysis. T.B. performed the PL experiments and analysis. Y.W. performed the TRS experiments and analysis. B.B. fabricated the MSM devices and performed the electrical and photoconductance measurements. B.B., T.B. and L.M.S. analyzed the IV results. P.C., L.M.S., H.H.T. and C.J. supervised T.B. and participated in discussions throughout the work. L.M.S and

H.E.J supervised Y.W. and B.B and also participated in discussions throughout the work. The manuscript was prepared with contributions from all authors.

Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

T.B., P.C., Y.G., H.H.T. and C.J acknowledge the Australian Research Council. T.B., P.C., Y.G., H.H.T. and C.J thank the Australian National Fabrication Facility for access to the growth and microscopy facilities and Centre for Advanced Microscopy and Australian Microscopy and Microanalysis Research Facility for access to microscopy facilities used in this work. Y.W., B.B., H.E.J and L.M.S. acknowledge the financial support of the National Science Foundation through grants DMR-1105362, 1105121 and ECCS-1100489.

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