Effective surface passivation of InP nanowires by atomic-layer-deposited Al2O3 with POx interlayer
Black, L.E.; Cavalli, A.; Verheijen, M.A.; Haverkort, J.E.M.; Bakkers, E.P.A.M.; Kessels, W.M.M.

Published in:
Nano Letters

DOI:
10.1021/acs.nanolett.7b02972

Published: 11/10/2017

Document Version
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

• A submitted manuscript is the author's version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

Citation for published version (APA):

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal

Take down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Download date: 20. Dec. 2018
Effective Surface Passivation of InP Nanowires by Atomic-Layer-Deposited Al₂O₃ with POₓ Interlayer

L. E. Black, A. Cavalli, M. A. Verheijen, J. E. M. Haverkort, E. P. A. M. Bakkers, and W. M. M. Kessels

Eindhoven University of Technology, Postbus 513, 5600 MB Eindhoven, The Netherlands
Philips Innovation Laboratories, High Tech Campus 11, 5656 AE Eindhoven, The Netherlands

Supporting Information

ABSTRACT: III/V semiconductor nanostructures have significant potential in device applications, but effective surface passivation is critical due to their large surface-to-volume ratio. For InP such passivation has proven particularly difficult, with substantial depassivation generally observed following dielectric deposition on InP surfaces. We present a novel approach based on passivation with a phosphorus-rich interfacial oxide deposited using a low-temperature process, which is critical to avoid P-desorption. For this purpose we have chosen a POₓ layer deposited in a plasma-assisted atomic layer deposition (ALD) system at room temperature. Since POₓ is known to be hygroscopic and therefore unstable in atmosphere, we encapsulate this layer with a thin ALD Al₂O₃ capping layer to form a POₓ/Al₂O₃ stack. This passivation scheme is capable of improving the photoluminescence (PL) efficiency of our state-of-the-art wurztite (WZ) InP nanowires by a factor of ∼20 at low excitation. If we apply the rate equation analysis advocated by some authors, we derive a PL internal quantum efficiency (IQE) of 75% for our passivated wires at high excitation. Our results indicate that it is more reliable to calculate the IQE as the ratio of the integrated PL intensity at room temperature to that at 10 K. By this means we derive an IQE of 27% for the passivated wires at high excitation (>10 kW cm⁻²), which constitutes an unprecedented level of performance for undoped InP nanowires. This conclusion is supported by time-resolved PL decay lifetimes, which are also shown to be significantly higher than previously reported for similar wires. The passivation scheme displays excellent long-term stability (>7 months) and is additionally shown to substantially improve the thermal stability of InP surfaces (>300 °C), significantly expanding the temperature window for device processing. Such effective surface passivation is a key enabling technology for InP nanowire devices such as nanolasers and solar cells.

KEYWORDS: Indium phosphide, semiconductor nanowires, surface passivation, atomic layer deposition, photoluminescence

II/V semiconductor nanostructures are the subject of increasing interest for device applications as researchers seek to overcome the intrinsic material limitations of Si while continuing device scaling and taking advantage of novel properties available at the nanoscale.¹⁻⁴ However, the high surface-to-volume ratio of such nanostructures makes effective surface passivation critical for many device applications, and passivation of III/V surfaces has historically proven far from trivial.⁵⁻⁻² In this work, we aim to address this problem for the case of InP, a technologically important III/V semiconductor with applications in a variety of electronic and optoelectronic devices. InP is notable for its high electron mobility and velocity, ease of integration with important ternary and quaternary III/V compounds (including In₀.₅₃Ga₀.₄₇As and In₀.₅₃Ga₀.₄₇AsP₀.₄₇), and direct bandgap of 1.34 eV which is ideal for photovoltaic applications. InP/dielectric gate stacks have been employed in InGaAs buried-channel field-effect transistors which are the first to outperform Si-based devices.¹⁻⁸ InP nanowires can be grown with good bulk material quality in both zinc-blende (ZB) and wurztite (WZ) crystal phases, and InP nanowire solar cells have achieved some of the highest conversion efficiencies among nanowire photovoltaic devices,⁹⁻¹⁰ while InP-based nanolasers hold promise as optical sources for silicon-integrated photonics.¹¹

Despite the widespread use of InP in devices, there exists no established method to stably and effectively passivate InP surfaces. It was early recognized¹² that (in contrast to GaAs) the native InP surface exhibits a relatively low surface recombination velocity (on the order of ~10²⁻¹⁰⁴ cm/s depending on dopant concentration¹³⁻¹⁷), and this is frequently cited as an advantage for device applications. However, this level of passivation is still limiting for many devices, and the native surface displays poor thermal...
More critically, this native surface passivation is generally not maintained following the deposition of standard dielectric layers (e.g., SiO\textsubscript{2} or Al\textsubscript{2}O\textsubscript{3}) on the InP surface,\textsuperscript{18,19} as required for the fabrication of many types of devices. More recent attempts to passivate InP nanowire surfaces have encountered similar difficulties. Wet chemical treatments have been shown to provide some degree of surface passivation,\textsuperscript{21,22} but this is generally not stable. Münch et al.\textsuperscript{23} found that atomic layer deposition (ALD) of HfO\textsubscript{2} significantly degraded surface passivation regardless of surface pretreatment or deposition conditions. Dhaka et al.\textsuperscript{24} reported similar surface degradation following ALD of Al\textsubscript{2}O\textsubscript{3}, AlN, TiN, GaN, and TiO\textsubscript{2} on InP nanowires and pillars. Some improvement was observed for very thin Al\textsubscript{2}O\textsubscript{3} films below a critical thickness of 2–3 nm, though carrier lifetimes remained well below 1 ns. Zhong et al.\textsuperscript{25} recently reported an increase in photoluminescence (PL) intensity and lifetime following plasma-enhanced chemical vapor deposition (PECVD) of SiN\textsubscript{x} on InP nanowires; however, they also observed a significant decrease in the open-circuit voltage of nanowire solar cells with the same films, making the significance of this result somewhat ambiguous. In sum, despite the acknowledged importance of surface recombination in InP nanowire devices, there remains no clearly established, stable, and effective surface passivation method for this material.

In attempting to devise an effective surface passivation scheme for InP nanowires, it is instructive to look back at historical work on the development of InP metal–insulator–semiconductor (MIS) devices. As noted above, early work showed that the deposition of standard dielectrics on InP tended to result in interfaces with poor electrical properties. It was conjectured that this might be linked to thermally induced degradation of the InP surface observed by various authors at temperatures ranging from 150 to 225 °C\textsuperscript{18–20} and thought to be linked to the desorption of surface P known to occur at least above 200 °C.\textsuperscript{26} Following this line of thought, or inspired by alternative structural considerations,\textsuperscript{27} a number of groups investigated the use of various P-rich layers, including deposition of P,\textsuperscript{28} PO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3},\textsuperscript{29} InP/PO\textsubscript{x},\textsuperscript{30} PN\textsubscript{x},\textsuperscript{31} or PO\textsubscript{N}N thin films (usually by PECVD),\textsuperscript{32} growth of P-rich anodic oxides,\textsuperscript{33,34} or deposition of other dielectrics in P over-pressure,\textsuperscript{35,36} to improve the interface characteristics of InP MIS structures. Such approaches appear to have been relatively successful, in most cases leading to significant improvements in MIS electrical characteristics. Since few of these groups employed PL characterization, it is not clear whether any of these approaches resulted in passivation improvements, or at least avoided degradation, relative to the native InP surface (those few who did perform such a comparison observed relative degradation\textsuperscript{31}), but such approaches nevertheless show significant promise as a path toward effective surface passivation of InP.

In this work, we adopt a novel approach inspired by this early work on InP MIS technology to develop an effective dielectric passivation scheme for InP nanowires. Specifically, we investigate the use of a deposited phosphorus oxide (PO\textsubscript{x}) film to passivate the InP surface. Since phosphorus oxides are known to be hygroscopic and consequently unstable under ambient conditions (indeed uncapped PO\textsubscript{x} films were observed to visibly degrade upon exposure to atmosphere), we encapsulate this layer with a thin ALD Al\textsubscript{2}O\textsubscript{3} capping layer to form a PO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3} stack. We deposit both layers in an ALD reactor at room temperature (25 °C) using a plasma-assisted process in order to avoid thermal degradation of the InP surface. Using this novel surface passivation scheme, we are able to increase the PL internal quantum efficiency and PL lifetime to levels representing unprecedented performance for undoped InP nanowires. The investigated passivation scheme displays excellent long-term stability and is additionally shown to improve the thermal stability of InP surfaces, significantly expanding the temperature window for InP device processing.

The InP nanowires studied in this work were grown by catalyst-free selective-area vapor-phase epitaxy on Zn-doped InP (111)A substrates using a SiN\textsubscript{x} mask patterned by nanoimprint lithography.\textsuperscript{37} Growth was performed at 750 °C from trimethyl indium (TMI) and phosphine (PH\textsubscript{3}) (PH\textsubscript{3}/ TMI molar ratio = 82) for 20 min. The wires were not intentionally doped. High-resolution transmission electron microscopy (TEM) showed that the wires were pure wurtzite phase, consistent with photoluminescence spectroscopy. The wires had a length of ~2.7 μm and a hexagonal cross-section with an average diameter of ~180 nm and were arranged in a square array with a 500 nm pitch. Figure 1 shows top-down and tilted SEM images of the nanowire array.

Deposition of the PO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3} thin film passivation stacks was performed in an Oxford Instruments FlexAL ALD reactor.

![Figure 1. (a) Top-view and (b) 30° tilt SEM images of as-grown WZ InP nanowire array. (c) Bright-field TEM image of single nanowire with PO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3} passivation layer. (d) Bright-field and (e) HAADF scanning TEM images taken around the center of the same nanowire, which show the bilayer structure of the deposited amorphous PO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3} stack. (f) Expanded partial view of panel e.](image-url)
Immediately prior to loading samples for deposition, they were immersed for 1 min in a 1% aqueous HF solution to remove the native oxide, followed by rinsing in deionized water. Phosphorus oxide (POₓ) deposition was performed at 25 °C by exposing the samples alternately to trimethyl phosphate (TMP), (CH₃)₃POₓ, and an O₂ plasma, with separating N₂ purges, in an ALD-like manner. The deposition of ALD Al₂O₃ capping layers was performed in situ immediately following POₓ deposition from trimethyl aluminum [TMA, Al(CH₃)₃] and O₂ plasma at the same temperature. More information on the deposition processes is given in the Supporting Information (SI). The use of a room-temperature deposition process was found to be critical to achieving the best passivation quality. Deposition of POₓ/Al₂O₃ stacks at higher temperatures (50 or 100 °C) resulted in consistently lower PL intensity and shorter PL lifetimes for both planar and nanowire InP samples compared to that obtained at room temperature (see SI). The thickness of the POₓ and Al₂O₃ layers was ∼5 nm and ∼16 nm, respectively (each process was run for 100 cycles), as determined by in situ spectroscopic ellipsometry on planar InP surfaces. The POₓ layer appeared to be transparent within the measured range (<5 eV) with a refractive index of 1.67 at 632 nm.

Figure 1 shows TEM images of an InP nanowire after deposition of such a POₓ/Al₂O₃ thin film stack. From the bright-field images the films appeared to be amorphous, as also indicated by X-ray diffraction measurements of similar film stacks on planar Si surfaces. The distinct bilayer structure of the passivation stack is clearly apparent in the contrast of the high-angle annular dark-field (HAADF) scanning TEM image. High-resolution TEM imaging of the POₓ/Al₂O₃ stack was unfortunately found to be impossible due to a pronounced beam sensitivity of the POₓ layer, which was observed to undergo rapid partial crystallization and delamination from the nanowire surface when exposed to higher fluences of the electron beam (see TEM images in SI). This also precluded accurate analysis of the composition profile by energy-dispersive X-ray spectroscopy (EDX).

To establish the composition of the deposited layers, depth-resolved (sputtered) X-ray photoelectron spectroscopy (XPS) measurements (Thermo Scientific K-Alpha system) were performed on POₓ/Al₂O₃ stacks deposited in parallel on HF-etched, polished (100) InP wafer substrates. Figure 2a shows the compositional depth profile determined from these measurements, while Figure 2b shows the main photoelectron peaks at several representative depths. Consistent with the TEM measurements, the profile exhibits a distinct bilayer structure. Beneath the capping Al₂O₃ there is a P-rich oxide layer, as expected. Surprisingly, however, this layer also appears to contain significant Al (Al/P−O ratio ≈ 0.5:1:4). This is despite the low deposition temperature and absence of postdeposition annealing which could promote Al diffusion. Near the substrate interface, indium oxides are also present in low concentrations, which can be attributed to the oxidizing effect of the O₂ plasma during the initial deposition cycles when the POₓ film is still nucleating. The carbon concentration in the phosphate layer was ∼0.7%, close to the detection limit. Note that the relative concentration of both In and Al in the POₓ layer is likely to be overestimated due to known selective sputtering of P with respect to both elements (this also accounts for the apparent nonstoichiometry of the InP substrate bulk: measurements of unspattered InP wafers both as-received and after HF etching showed stoichiometric composition using the same sensitivity factors—see SI).

The apparent composition of the phosphate layer, as well as the binding energy of the bulk P 2p oxide peak (135.2 eV), are most consistent with a phosphorus-rich aluminum polyphosphate structure Al[(POₓ)ₘ] analogous with In[(POₓ)ₘ], most likely incorporating excess oxygen in the form of OH groups (see SI for additional discussion of the XPS data). Steady-state and time-resolved photoluminescence (PL) measurements were performed to characterize the electrical and optical quality of the nanowires and the effectiveness of the surface passivation. In all cases the nanowires were measured as upright arrays on the growth substrate with excitation and detection parallel to the nanowire growth axis. A “positive aging” effect was noted for the passivated nanowire samples, whereby PL intensity and lifetime were observed to increase substantially over a period of weeks and months during sample storage under dark, ambient conditions. Such an effect has previously been noted for other semiconductor/dielectric interfaces, for example, Al₂O₃-passivated Si. It was found that this effect could be accelerated by postdeposition annealing at moderate temperatures. For instance, a 1 min anneal at 250 °C in N₂ shortly after POₓ/Al₂O₃ deposition was sufficient to increase the PL lifetime to a level similar to that obtained after months of aging at room temperature (see SI). Unless otherwise mentioned, the PL measurements of the POₓ/Al₂O₃-passivated nanowires reported below represent stabilized values measured more than 7 months after POₓ/Al₂O₃ deposition, without annealing.

The stabilized passivation layers were found to significantly enhance the PL efficiency of the nanowires. The integrated steady-state PL intensity at room temperature (295 K) was...
observed to increase by a factor of $\sim 10^{20}$ for the passivated wires compared to the as-grown wires depending on excitation intensity (Figure 3b), with the greatest increase observed at low excitation. The PL spectrum, shown in Figure 3a, is typical of pure WZ InP, with an emission peak close to 1.42 eV at room temperature. Interestingly, the dependence of PL intensity $I_{\text{PL}}$ on excitation intensity $I_{\text{exc}}$ for both as-grown and passivated wires closely follows a power law ($I_{\text{PL}} \propto I_{\text{exc}}^n$) over at least 7 orders of magnitude in PL intensity, with average exponents $n$ of 1.52 and 1.41, respectively [the local value of $n$ may be evaluated from the slope of log($I_{\text{PL}}$) vs log($I_{\text{exc}}$)]. These values can be considered as ideality factors in the one-diode equivalent circuit of the wires. While the physical interpretation of such apparent ideality factors should be treated with caution, increasing values in the range of $1 < n < 2$ are consistent with increasing nonradiative recombination associated with bulk or surface states.

In addition to the relative increase in PL efficiency apparent from Figure 3b, it is desirable to quantify the absolute PL internal quantum efficiency (IQE). This quantity relates directly to the efficiency potential of light-emitting devices and to the open-circuit voltage potential of photovoltaic devices. Yoo et al. have previously proposed that the PL IQE may be determined by fitting the room-temperature excitation-dependent PL intensity at high excitation levels with an idealized "rate equation" describing the recombination dynamics. Using this approach, Gao et al. have reported an IQE of $\sim 50\%$ for as-grown, undoped WZ InP nanowires of a similar diameter (200 nm) to our own, which constitutes the highest IQE reported for such structures. If we apply the same analysis to our own data at similar high excitation levels, we derive an IQE of 61% for the as-grown wires and 75% for the passivated wires (see SI for details). Gratifying as such values would be, they are clearly not reliable given the much larger (~10 times) relative difference in PL intensity between the same samples, and thus serve rather to highlight the general unreliability of this method for determining the PL IQE.

An alternative method of determining the PL IQE which is widely used in the literature is to take the ratio of integrated PL intensity at room temperature (295 K) to that at low temperature (10 K in our case). In this approach it is assumed that the efficiency of radiative recombination is 100% at low temperature, where nonradiative processes are strongly suppressed. This assumption, though not always justified, is supported in our case by the $n = 1$ power dependence of the integrated PL intensity on excitation at 10 K for both the as-grown and passivated nanowires (Figure 3b). This provides strong evidence that the PL IQE determined in this way (Figure 3c) is reliable in the present case. Resulting PL IQE values of 3.5% for the as-grown and 27% for the passivated
nanowires are obtained at the highest excitation levels. The latter represents an unprecedented level of performance for undoped WZ InP nanowires, taking into account differences in nanowire dimensions, as illustrated in Figure 3d.

Time-resolved PL (TRPL) measurements provide additional support for the effectiveness of the investigated surface passivation scheme. As shown in Figure 4a, PO$_x$/Al$_2$O$_3$ passivation resulted in a significantly longer PL decay, evidencing an enhanced carrier lifetime due to reduced surface recombination. As observed previously for InP nanowires, this decay is nonexponential. We therefore choose to take the time constant characteristic of the initial, most rapid portion of the TRPL decay, which we designate $\tau_{\text{min}}$, as a conservative measure of the excess carrier lifetime at the peak injection level of the measurement. This yields PL decay lifetimes of 1.8 and 5.4 ns, respectively, for the as-grown and passivated nanowires, indicating a 3 times increase in carrier lifetime due to passivation. Conversely, nanowires with only the Al$_2$O$_3$ layer (i.e., without the PO$_x$ interlayer) displayed a significantly reduced PL lifetime of 0.3 ns, showing the importance of the PO$_x$ layer for passivation. The PL decay characteristics were observed to be dependent on excitation intensity (Figure 4b). While such a dependence is expected, its exact form is rarely measured or reported. $\tau_{\text{min}}$ was observed to first increase then decrease with increasing excitation intensity, with a qualitatively similar excitation dependence for both as-grown and passivated wires, but a significantly increased (by a factor of $\sim 2$−3) lifetime for the passivated wires over the whole excitation range. Peak PL lifetimes of 1.9 and 5.4 ns were measured for the as-grown and passivated wires, respectively. It should be noted that the behavior of the TRPL decay at longer times, subsequent to the initial decay, deviated from this excitation dependence at the lowest excitation intensities, becoming longer as the excitation intensity was decreased (see SI), which may indicate the presence of trapping.

In Figure 4b we also show carrier lifetimes reported in the literature for undoped WZ InP nanowires of similar diameter to our own are shown for comparison.

Figure 4. (a) Room-temperature time-resolved PL decay at 870 nm of the nanowires as-grown and with either a surface-passivating PO$_x$/Al$_2$O$_3$ stack or Al$_2$O$_3$ only. Measurements were performed at an excitation intensity of $\sim 10^{12}$ photons cm$^{-2}$ pulse$^{-1}$. Dashed lines show graphically the extraction of the initial minimum PL decay lifetime $\tau_{\text{min}}$ from the data. (b) $\tau_{\text{min}}$ extracted from time-resolved PL measurements of the same as-grown and PO$_x$/Al$_2$O$_3$-passivated samples as a function of excitation intensity. Carrier lifetimes reported in the literature for undoped WZ InP nanowires of similar diameter to our own are shown for comparison.
observe that the highest values fall just below, but very close to, the data for our own as-grown wires. Since the dimensions of our wires are similar, this suggests that the bulk quality of these wires is comparable to the state-of-the-art. The large increase in lifetime observed for the passivated wires, however, shows that the lifetime of the as-grown wires is still significantly surface-limited. This is contrary to the conclusions of some authors that surface recombination is practically negligible for such wires. The lifetimes observed for the passivated wires appear to be the longest so far reported for InP nanowires by a significant margin. Li et al. have reported lifetimes of up to 7.4 ns for WZ InP micropillars; however, these had a diameter greater than 1 μm, which significantly reduces the influence of surface recombination. Given the significantly larger (micro-scale) dimensions of these structures we do not include this result in the comparison of Figure 4b.

It is desirable to quantify the contribution of surface recombination in the passivated and unpassivated wires. This is not straightforward, because the contribution from bulk recombination processes for such WZ InP nanowires is not known. For a cylindrical geometry (and when diffusion is not limiting), the effective surface recombination velocity \( S_{\text{eff}} \) is given by:

\[
S_{\text{eff}} = \frac{D}{4}(r_{\text{eff}}^{-1} - r_{S}^{-1})
\]

where \( D \) is the nanowire diameter, \( r_{\text{eff}} \) is the effective excess carrier lifetime, and \( r_{S} \) is the bulk lifetime due to radiative and nonradiative processes. An upper limit on \( S_{\text{eff}} \) may be derived by assuming that all recombination occurs at the nanowire surface (\( r_{S} = \infty \)). If we take \( r_{\text{eff}} \) as equal to the highest measured \( r_{\text{min}} \) for the passivated wires (6.5 ns, see Figure 5), we derive an upper limit to \( S_{\text{eff}} \) of 690 cm/s. For the as-grown wires (\( r_{\text{min}} = 1.9 \) ns), we similarly derive an upper limit to \( S_{\text{eff}} \) of 2.4 × 10^3 cm/s. A lower limit to \( S_{\text{eff}} \) for the as-grown wires may be derived by assuming that \( r_{S} \) is equal to the maximum measured lifetime for the passivated samples. This yields a lower limit of \( S_{\text{eff}} \) = 1.7 × 10^3 cm/s for the as-grown wires. This value is an order of magnitude higher than the value of 170 cm/s reported by Joyce et al. for WZ wires (see SI). Note that in general \( S_{\text{eff}} \) is expected to be dependent on dopant concentration.

The passivated nanowires were found to be significantly more thermally stable than the as-grown wires. As mentioned earlier, the InP surface is known to be unstable at elevated temperatures, undergoing P-desorption and associated electrical degradation at temperatures above at least 200 °C. In fact, time-resolved PL measurements, which are extremely sensitive to surface quality, show that the onset of electrical degradation occurs already between 100 and 150 °C for “bare” (native oxide only) nanowire and planar InP surfaces, as shown in Figure 5 for such samples annealed at various temperatures for 1 min in N_2. In contrast, the PL lifetime of PO/Al_2O_3-passivated samples was initially lower but was observed to increase with annealing temperature between 100 and 300 °C, reaching values significantly higher (up to 6.5 ns) than those of the unannealed, unpassivated samples. Although the lifetimes of the passivated samples also declined at temperatures above 300 °C, they remained higher than those of the unpassivated samples annealed at the same temperatures, indicating an improvement in the thermal stability of the surface. Figure 5 also shows that the lifetime of samples coated with the same Al_2O_3 film without a PO_2 interlayer remained well below those of the unpassivated surface regardless of annealing temperature up to 400 °C, emphasizing the critical role of the PO_2 interlayer to passivation. The fact that similar trends are observed both for the undoped WZ nanowires and for heavily doped n-type (100) ZB InP is a nontrivial result and suggests the effectiveness of the investigated passivation scheme for InP surfaces in general. The improved thermal stability of PO/Al_2O_3-passivated surfaces should allow the use of higher thermal budgets for InP device fabrication without compromising surface electrical properties, thereby expanding the temperature window for InP device processing.

Finally, we note that the fact that we obtain good passivation of InP with a P-rich interfacial oxide runs counter to some recent thinking on InP surface passivation. It is not uncommon in the more recent InP passivation literature to find studies in which the goal is the elimination of P oxides, ostensibly for the purposes of surface passivation. For example, on the basis of a comparison of capacitance–voltage and XPS measurements of Al_2O_3 and HfO_2 interfaces with InP, Galatage et al. concluded that the formation of P-rich oxides was probably harmful for InP passivation. Density functional theory studies have been interpreted in a similar light. Our results suggest that, on the contrary, P-rich oxides may be beneficial for InP surface passivation.

In conclusion, we have reported evidence of the effective surface passivation of InP nanowire and planar surfaces by PO/Al_2O_3 thin-film stacks deposited at room temperature. The application of this passivation scheme allows us to achieve PL internal quantum efficiencies and lifetimes significantly higher than previously reported for wurtzite InP nanowires of similar diameter. The passivation displays excellent long-term stability and is additionally shown to significantly improve the thermal stability of InP surfaces. Further improvements in passivation may be possible by optimizing the surface pretreatment and PO/Al_2O_3 film thicknesses in combination with postdeposition annealing conditions. Such passivation layers are a key enabling technology for InP nanowire device applications such as nanolasers and solar cells.

### ASSOCIATED CONTENT

5 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.7b02972.

Details of PO/Al_2O_3 deposition process and PO optical properties, instability of PO layers during TEM, XPS spectra of planar InP surfaces at various stages of the passivation process, further discussion of XPS profile results, experimental details of PL measurements, evolution of PO/Al_2O_3 passivation with storage time, influence of deposition temperature on passivation quality, details of PL IQE extraction according to the method of Yoo et al., calculation of expected diameter dependence of PL IQE, detailed excitation dependence of time-resolved PL decay at low excitation levels, extraction of \( S_{\text{eff}} \) from the data of Tedeschi et al. (PDF)

### AUTHOR INFORMATION

Corresponding Authors

*E-mail: l.e.black@tue.nl.
*E-mail: w.m.m.kessels@tue.nl.
The authors gratefully acknowledge E. Smalbrugge and C.A.A. van Helvoirt for technical assistance, J. Greil, L. Gagliano, S. Assali, and A. Dijkstra for advice and assistance with PL measurements, and B.W.H. van de Loo for feedback on the draft manuscript. TEM measurements were performed at a facility funded by Solliance and the Dutch province of Noord-Brabant.

■ ACKNOWLEDGMENTS

The authors declare no competing financial interest.

■ REFERENCES
