Operando Surface Characterization of InP Nanowire p–n Junctions

Sarah R. McKibbin, Jovana Colvin, Andrea Troian, Johan V. Knutsson, James L. Webb, Gaute Ottnes, KaiDirscherl, Hikmet Sezen, Matteo Amati, Luca Gregoratti, Magnus T. Borgström, Anders Mikkelsen, and Rainer Timm*

ABSTRACT: We present an in-depth analysis of the surface band alignment and local potential distribution of InP nanowires containing a p–n junction using scanning probe and photoelectron microscopy techniques. The depletion region is localized to a 15 nm thin surface region by scanning tunneling spectroscopy and an electronic shift of up to 0.5 eV between the n- and p-doped nanowire segments was observed and confirmed by Kelvin probe force microscopy. Scanning photoelectron microscopy then allowed us to measure the intrinsic chemical shift of the In 3d, In 4d, and P 2p core level spectra along the nanowire and the effect of operating the nanowire diode in forward and reverse bias on these shifts. Thanks to the high-resolution techniques utilized, we observe fluctuations in the potential and chemical energy of the surface along the nanowire in great detail, exposing the sensitive nature of nanodevices to small scale structural variations.

KEYWORDS: InP nanowire, pn-junction, surface potential, KPFM, STM, SPEM

Semiconductor nanowires (NWs) offer previously unimagined flexibility in heterostructure design thanks to the breadth of possible material combinations and dopants, which has fostered their use in a diverse range of applications with growing technological importance.1−5 Since III–V semiconductor NWs can be grown directly on a silicon substrate without dislocations, they are highly promising candidates for both nanostructured photovoltaics6,7 and optoelectronic components with optimized power consumption and color rendering indexes.5 Their low dimensionality allows one to understand the relationship between surface structural properties and electrical behavior down to the atomic scale.

We focus our investigations on InP nanowire p–n junctions, which have demonstrated record current densities and solar cell efficiency and thus show great promise for reducing the cost of high efficiency nanostructured solar cells.8,9,10,11 Previously, we investigated either p-doped or n-doped InP NWs by using scanning tunneling microscopy/spectroscopy (STM/S) and X-ray photoemission spectroscopy (XPS), thereby correlating chemical composition with surface band alignment and electron affinity.12 In addition, we mapped the doping profile and the vacuum ionization levels along InP NWs with n-type and undoped (nominally intrinsic, i) segments using synchrotron-based photoemission electron microscopy (PEEM), obtaining a picture of the n–i–n junction band bending.13

Here, we present a detailed investigation of the p–n junction within InP NWs. We employ a complementary combination of scanning probe techniques with synchrotron based spatially resolved photoemission microscopy to form a complete understanding of the structural, electronic, and chemical properties of the NW p–n junction and directly compare neighboring NW segments with different doping types. Kelvin
probe force microscopy (KPFM) was used to map the surface potential drop along the NW p–n junction. STM/S was used to obtain both structural and electronic properties of the NWs with down to atomic-scale precision. Core level photoelectrons were applied for imaging with surface chemical sensitivity as well as for spatially resolved spectroscopy using synchrotron scanning photoelectron microscopy (SPEM)\textsuperscript{14} and spectromicroscopy of InP NWs in a device configuration. All three techniques are very sensitive to local changes in the surface doping level, which would shift the position of the measured surface potential within the semiconductor band gap. In this way, we can form a complete detailed picture of the surface chemistry, structure, and composition of the p–n junction while simultaneously applying a bias across the NWs and directly correlating these properties with the surface band alignment and potential distribution under operational conditions.

InP NWs were grown on InP(111)B wafers in a metal–organic vapor phase epitaxy (MOVPE) reactor, using Au particles to catalyze growth, defined on the growth substrate as discs of about 180 nm diameter by nanoimprint lithography.\textsuperscript{15} Trimethylindium (TMIn) and phosphine (PH\textsubscript{3}) were used as precursor gases with diethylzinc (DEZn) for p-type doping and hydrogen sulfide (H\textsubscript{2}S) for n-type doping. The dopant precursors switched halfway through the growth process, resulting in NWs with an axial p–n junction in the center. Nanowire tapering was controlled by in situ etching using HCl gas to maintain a constant diameter.\textsuperscript{16} More details on growth conditions as well as a scanning electron microscopy image of the grown NW sample can be found in the Supporting Information, S1. After growth, the NWs were mechanically transferred onto different carrier substrates\textsuperscript{17,18} to perform STM/S, KPFM, and SPEM measurements.

We used atomic force microscopy (AFM) combined with KPFM to reveal information on the built-in potential of InP nanowires while simultaneously recording the overall topography of the NW. This technique has been used before to directly probe individual NWs and map changes in doping or NWs containing complex heterostructures.\textsuperscript{19} The contact potential difference between the sample and the probe is defined as the energy difference between the vacuum level and the Fermi energy, even in the case of a semiconductor. Accordingly, the contact potential difference amounts to \( V_{\text{cpd}} = (\phi_s - \phi_t)/e \), where \( \phi_s \) is the work function and \( e \) is the electron charge. Here, an area of the sample with a deposited NW was scanned and the contact potential difference was mapped (see the Supporting Information, S2 for details about the method and the used KPFM setup). It is important to point out that this signal is very surface sensitive, meaning that a map of the relative surface potential distribution is obtained, which is expected to differ significantly from bulk values inside the NW due to surface states, oxides, and other sources of surface band-bending.

In Figure 1a, we present a topographic AFM scan, confirming that the NW is 2.5 \( \mu \)m long and about 200 nm wide/high. The Au particle used to seed the NW growth can be observed at the left side of the image, followed by the n-doped and then the p-doped regions to the right. The blue and green lines on this image indicate the position of individual line scans taken for Figure 1b, the latter showing morphological variations of up to 20 nm in height on the top surface of the NW.

Figure 1c shows an KPFM overview image of the nanowire and the surrounding substrate, and the color bar legend indicates the measured surface potential. Both the image and an individual potential line scan shown in Figure 1d show a lower contact potential difference at the top end of the NW, corresponding to a higher Fermi level. This potential increases abruptly about 0.8 \( \mu \)m away from this end, revealing the switch between n-type and p-type doping. The bulk of this potential drop occurs over an approximately 100 nm wide region indicating the position of the depletion region. However, it should be noted that this width of 100 nm can only be seen as an upper limit of the surface depletion width, as this corresponds roughly to the lateral resolution of the KPFM potential measurement. For example, the physically instantaneous transition between the potential level of the substrate and the NW side wall occurs gradually over a distance of about 80 nm in the KPFM image (not shown). The obtained potential difference between the n-type and p-type segment of 0.3 eV is obviously much smaller than the band gap of InP of 1.34 eV at room temperature, and also significantly smaller than the open circuit voltages \( V_{\text{OC}} \) of 0.6 to 0.9 eV that have been reported for similar InP NWs.\textsuperscript{5,11} Here one has to take into account the surface sensitivity of the KPFM measurements, indicating that potential differences due to different doping inside the n-type and p-type segments of the NWs are significantly weakened at the surface due to its native oxide, surface states, or defects, and the resulting surface band-bending and Fermi-level pinning.\textsuperscript{12} Even stronger surface
band-bending effects have been reported for a KPFM study of a GaN NW p–n junction, where a potential difference of only 0.15 eV was obtained.\textsuperscript{22}

We can also see some variations in the measured surface potential within each segment. In general, the signal fluctuates locally by less than 0.1 V. These fluctuations represent the measurement noise of the potential signal of approximately 0.03 V root-mean-square, as has been calculated from the variations in the otherwise constant potential signal of the sample substrate. In addition, an increase of the surface potential by about 0.1 eV over a distance of 1 μm can be seen along the p-doped NW segment, followed again by a small drop toward the end of the NW. The presence of these small variations in potential, besides the larger monotonic change over the space charge region at the interface location, may suggest either nonuniform doping or nonuniform electrical activation of dopants within the host NW crystal.

There are several artifacts that can influence the surface potential as measured by the KPFM tip, which may come into play here and make interpretation difficult. Notably regions where the probe tip must traverse a large height differential on the sample, such as the ends of the NW, may not allow for accurate potential mapping. In these cases, the probe tip not only senses the surface potential with its ending point but also with its side flanks. However, by comparing the line scans in Figure 1b,d we can exclude topographical changes along the NW as the dominating property for the electrical characteristics measured by KPFM. In addition, due to a relatively large tip-to-sample distance the tip probes the surface potential of a larger area than indicated by the pixel location, which limits the resolution of the map of the NW space charge region.

One additional feature from our KPFM image is that the depletion region and dopant interface occur closer to the Au particle, instead of being exactly halfway along the NW as the growth conditions would indicate. This asymmetry may be due to a different behavior of the Zn p- and S n-dopants during InP NW growth; Zn has a much higher solubility in Au than S, which can lead to a reservoir effect of Zn atoms in the Au particle.\textsuperscript{23} Zn is also known for other types of memory effects during NW growth,\textsuperscript{24} including carry over from Zn precursor species absorbed to the MOVPE reactor walls.\textsuperscript{11} A recent study based on nano-X-ray fluorescence mapped Zn dopant concentrations across nominally abrupt p–i–doping interfaces in InP NWs, finding an exponential decay of the Zn concentration over several hundred nanometers.\textsuperscript{25} Therefore, this junction asymmetry may indicate a delayed transition from p-type to n-type doping due to unwanted Zn incorporation in the NW even after switching of the dopant precursor.

To investigate the atomic scale structure and electrical properties of the p–n junction interface more carefully, we also examined the InP NWs with STM/S. For these experiments, InP NWs were transferred onto an InP(111)B substrate and cleaned in ultrahigh vacuum (UHV) by being exposed to atomic hydrogen at 2 × 10^{-6} mbar and annealed to 400 °C, which has been found previously to remove surface oxides.\textsuperscript{12,26} The cleaned NWs were investigated under UHV conditions using an Omicron XA STM operated at room temperature, using electrochemically etched and Ar\textsuperscript{+} sputtered W tips. An overview STM image of an entire InP NW is shown in Figure 2a. The spherical gold droplet at the top of the NW is again clearly visible by the bright contrast region at the left of the image, followed by the n-type S-doped region and the p-type Zn-doped region. A close up of the interface region where we observed by KPFM that the doping type switches from n to p is shown in Figure 2b(i). The surface morphology of the NW side facets shows a zinc-blende (Zb) structure with twinning defects and relatively narrow flat terraces, interrupted by one atomic layer high surface steps. Interestingly, the Zb structure is even found at the n region close to the interface, as confirmed by the atomic rows of the (110) surface visible in the close up image of Figure 2b(ii), although the chosen growth conditions and the S dopants are expected to result in a wurzite structure of the n-type region.\textsuperscript{12}

High-resolution STS mapping was performed on this region, and the positions where each STS spectra are taken are indicated in Figure 2b (these positions were chosen such as to avoid tunneling through a defect or terrace edge, which might strongly impact the measurement). Each I–V curve was measured with a maximum tip–sample bias of ±3 V. The current I is plotted as a color map on a logarithmic scale as a function of voltage V and is positioned along the p–n junction.
in Figure 2c. The dashed line denotes the Fermi level, which is always set to zero bias during STS. The solid lines mark the approximate position of the valence and conduction band edges, as recognized by the onset of measured tunneling currents, which show that the transition between p- and n-type segments occurs over only 15 nm. This very short surface transition region cannot be the same as the depletion region of the p–n junction inside the NW, since a depletion width of only 15 nm would correspond to unrealistically high doping levels. However, since the energy shift between p- and n-doped segments at the NW surface is much smaller than the built-in potential inside the NW (as will be discussed below), this potential drop can also occur across a much shorter area at the surface as compared to the transition layer inside the NW. The n-type side of the NW on the left of the map in Figure 2c is identified due to the Fermi level being closer to the conduction band (CB) edge. The average of the observed valence band (VB) and CB onsets for the n-doped region are $-1.1$ and $0.5$ eV, respectively. For the p-doped region, we then see an average onset of $-0.8$ and $1.0$ eV for the VB and CB, respectively. These correspond to apparent band gaps of 1.6 and 1.8 eV for the n-doped and p-doped regions, respectively, which is larger than the literature bulk band gap of InP of 1.34 eV. This discrepancy can partly be explained by tip-induced band bending.18,27 In addition, the absolute band gap may be slightly overestimated by $I−V$ data obtained by STS, because the tunneling current close to the band edges can become very small. It is worth mentioning that in the right part of Figure 2c, the Fermi level position is found nearly in the middle between CB and VB edges, contrary to what would be expected for the p-doped region. However, this behavior is in agreement with previous STM/S studies of p-doped InP NWs with Zb crystal phase, where it was explained by strong Fermi-level pinning due to surface states localized at step edges.12

In Figure 2d, we show STS measurements averaged over the outermost nine sweeps of the map shown in Figure 2c, (the positions of these spectra are marked there by green and pink arrows), that is, about 20 nm away from the surface depletion region at the n- and p-doped sides of the junction. Here we can clearly see that the onset of both the VB and the CB is shifted between these two regions. A linear fit of the VB and CB edges for very low measured currents results in a shift of 0.4 ± 0.1 eV for the VB and 0.6 ± 0.1 eV for the CB edge. In addition, very small current contributions can be observed within the band gap, which can be interpreted as tunneling into empty acceptor states (p-doped region, between 0 and 1 eV) and out of filled donor states (n-doped region, between $-1.3$ eV and $-0.5$ eV).28 Since the crystal structure is the same in both regions, we can exclude different sizes of the band gap and the existence of a type-II band alignment as has been observed by STS for wurzite/zinc-blende interfaces previously.18 Taking into account the uncertainties in the VB and CB edge determination, we conclude that the energy shift between the surfaces across the p–n junction amounts to 0.5 eV. This value is still significantly smaller than the InP band gap or typical $V_{oc}$ measured for these type of NWs,4,11 so it is smaller than the expected doping-induced built-in potential in the inside of the NW but it is 0.2 eV larger than the shift observed by the KPFM measurements. Here we note that for STM/S investigations it is necessary to remove surface oxides which was not the case for KPFM. This suggests a substantial effect of surface pinning due to In and P oxides of up to 0.2 eV. This is in line with previous observations that the oxides lead to substantial negative doping of the surface, which may be suppressing the change in the measured potential on the p-doped side of the nanowire.29,30

Scanning photoemission microscopy combines the chemical and electronic sensitivity of XPS with high spatial resolution, therefore it can be used to provide complementary detailed information on the doping of nanowires along the growth axis.25,30 We have performed SPEM and nanofocus XPS at the ESCA Microscopy beamline of the Elettra synchrotron facility in Trieste, Italy,11,14 where the sample was scanned under UHV conditions through the focused X-ray beam with a spot size of 130 nm. The sample plate was further equipped with two electrical contacts connected to an external power supply in order to perform operando measurements. A photon energy of 671 eV was chosen, which allowed detection of In 4d, P 2p, Au 4f, In 3d, and O 1s core levels. Further details about the experimental setup can be found in the Supporting Information, S3. We have used SPEM measurements to investigate the difference in surface chemical and electrical properties from doping of the InP NWs to first compare these results to the KPFM and STM/S measurements as well as to examine the p–n junction behavior in a device configuration. This allows us to explore the potential role of surface oxides on device behavior and to observe changes in local band alignment during electrical operation. For these measurements, InP NWs were transferred via clean room paper onto a prefabricated device structure containing a physical trench and two metal contacts so that either end of the NW is contacted electrically, as shown in Figure 3. The electrical contacts are formed by electron beam lithography and thin film evaporation of 120 nm Ti with a 2–5 nm Au capping layer onto a Si/SiO2 substrate.32 The NWs then lay across two electrodes which are physically separated by a 1.5 μm wide gap. The device layouts show a single NW for simplicity but in reality there were a number of NW candidates crossing the insulating gap, meaning that multiple NWs may be connected in parallel with the NW presented. Therefore, accurate determination of the current flowing through individual NWs during this experiment is not possible, and the behavior of individual NWs will be the subject of future investigations.

Individual NWs resting with their p- and n-type segments on opposite contacts were first identified by optical microscopy for our detailed SPEM studies. Such optical micrographs are shown in Figure S3 of the Supporting Information for that NW that can also be seen in the SPEM images of Figure 3. By selecting a material appropriate kinetic energy for the analyzer and taking a series of SPEM maps we could navigate on the sample with respect to micrometer-scale markers and position these NWs in the nanofocus X-ray beam. For the operando measurements, the contact to the electrode below the n-type segment of the NW was grounded, while a bias was applied to the opposite contact.

The sample is placed on an x/y scan table in the SPEM setup, allowing us to take chemically sensitive spatially resolved maps of the NW. Figure 3b–e shows the maps taken for the Au 4f, In 3d, P 2p, and In 4d core level spectra for electron binding energies centered at 83.5, 444, 129, and 17.5 eV,
respectively. Each pixel of the maps corresponds to a spectrum over an energy window centered at the previously mentioned binding energy, and its intensity is obtained by integrating the spectra. For Au 4f and In 4d, this energy window was 3.9 eV, and for the P 2p and In 3d maps it was 7.8 eV. However, the presence of core levels is not the only source of contrast in the images. For example, in the P 2p map the electrical contacts also appear bright, not because they contain P or another core level in the chosen energy window but because of the high inelastic background scattering arising from the Au 4f peak. This is not the case for the In 4d map because the binding energy window for this map lies below the Au 4f core level.

In addition, because each pixel in the maps is a spectrum, one can obtain more detailed information on the effect of the doping along the NW. It is in fact possible to select within the energy window two energy bands corresponding to two specific binding energies and calculate the corresponding integrals. Images showing the ratio of these integrals highlight the different spectra contributions and their spatial distribution (see ref 33 for details). Figure 3f shows the In 4d map by selecting appropriate energy windows, so that we can visualize the surface potential drop along the p–n junction. The top part of the NW appears brighter demonstrating that the precise energy of the In 4d peak changes depending on the position along the NW.

We then examine both the built-in potential of the NW and how this is affected by an applied external bias by probing the In 4d and P 2p core levels locally on either end of the NW (corresponding to the n-type and p-type regions). These results are shown in Figure 4a for forward bias, (b) for zero bias, and (c) reverse bias. (i) Diagrams of the expected behavior of a p–n device in each case, showing how an external bias (V_{ext}) would affect CB and VB edges (E_C and E_V) as well as the binding energy (E_B) of the core levels (CL) such that the built-in in potential of the device (∆E) is either suppressed under forward bias or enhanced under reverse bias. (ii) and (iii) In 4d and P 2p spectra. For each bias condition, the shift in core level peak maxima ∆E_{p–n} between n- and p-type spectra is indicated. Fitting of the spectra results in one large bulk (In–P) doublet (blue) and two smaller components for each core level, whose origin is discussed in the text.
Figure 5. (a) In 3d 2D map of a NW, overlaid with the positions where individual high-resolution In 3d spectra were taken, to show the approximate positions for the forward (red crosses), zero (yellow circles), and reverse bias data sets (blue triangles). (b) In 3d core level spectra at equidistant locations to map in detail the built-in potential due to doping along the NW and observe the core level shifts under zero bias conditions. Spectra are colored green, blue, and pink to highlight n-doped, depletion region, and p-doped areas, respectively. (c) The relative shifts of the fitted In 3d core level peak position along the NW. We see an enhancement of the energy shift between the n- and p-doped regions when the device is operated in reverse bias and suppression for forward bias.

bias (showing the surface built-in potential); and (c) for reverse bias. The bias applied across the NW amounts to ±0.3 to 0.4 V, as evaluated from XPS spectra taken at the upper and lower Au contacts (see the Supporting Information, S4 for more details). The expected behavior of the change in binding energy of core levels across a p–n junction under each bias condition is illustrated by the diagrams shown in Figure 4a–c(i); the built-in potential, due to the different doping across the p–n junction, not only results in a shift of the CB and VB edges but also in an equally large shift of the binding energy of any core level of the NW. Applying a forward (backward) bias to the junction should decrease (increase) the observed energy shift. In Figure 4a–c(ii,iii), we then present the detailed In 4d and P 2p core level spectra, respectively (shown after Shirley background subtraction) for both the n-doped and p-doped regions, and their measured shifts during device operation in each bias case. The lower part of the NW visible in the maps (shown in Figure 3) consistently occurs at a lower binding energy than the upper end of the NW, confirming this is the type end of the NW and the upper part is the n-type doped region. Under zero bias, the observed core level energy shift due to the NW doping ΔEP–P (based on the position of the peak maxima) was 0.48 eV for the In 4d core level and 0.47 eV for the P 2p peak. This provides our direct observation of the built-in potential of the p–n junction at the NW surface. These shifts were suppressed slightly to 0.43 eV for In 4d and 0.40 eV for P 2p when the NW was operated in forward bias case and enhanced to 0.65 eV for In 4d and 0.59 eV for P 2p when the NW was operated in reverse bias case.

The built-in potential of 0.5 eV obtained here equals the value measured by STS and is significantly larger than the potential difference seen by KPFM. We want to point out that although different individual NWs were studied by the different techniques, all NWs were taken from the same growth substrate. SEM images confirm a high homogeneity of the NW sample, as shown in Figure S1 of the Supporting Information. Furthermore, the trends for the shift in surface potential measured by KPFM, STS, and SPEM have been seen for several NWs measured by each technique. Although the SPEM measurements have been performed under UHV conditions, the same as the STM/S experiment, the NWs have not been cleaned from their native oxide, in contrast to the STM/S case. Thus, we should still see the effect of the oxide on surface band-bending, principally resulting in a smaller surface potential shift. The fact that the shift observed by SPEM is larger than that seen in KPFM might indicate that a water film on the sample surface, which can be expected for the KPFM measurements, but not in the UHV setup, could induce additional surface band-bending and Fermi-level pinning. Another important factor should be the surface sensitivity of the measurements: while KPFM measures the electrostatic potential above the surface and STS measures the local density of states at the position of the probe tip, that is, roughly 1 nm above the surface atoms, the inelastic mean free path of the photoelectrons measured in our SPEM experiments amounts to about 0.8 nm for the In 3d core level, 1.5 nm for the P 2p core level, and 1.7 nm for the In 4d core level. Thus, SPEM is still a surface-sensitive method, even though it probes slightly deeper inside the NW than KPFM and STS. Because surface band-bending usually extends several nanometers or rather tens of nanometers into the NW, the slightly larger probing depth of SPEM should only marginally compensate such surface band-bending effects as compared to KPFM and STS. Another effect that needs to be discussed is a surface photocurrent induced by the X-rays. Exposing a p–n junction to an X-ray beam can excite electron–hole pairs, where the resulting electrons and holes in the depletion region will be accelerated into opposite direction, inducing a photocurrent, which in turn can reduce the measured built-in potential. Nevertheless, the effect of this X-ray-induced surface photovoltage should be of similar size for no external bias and for a small forward or reverse bias; therefore it might affect the measured built-in potential but not significantly the change of the built-in potential under applied bias.

Fitting was performed on the In 4d and P 2p core level spectra to investigate the main components of the n-doped and p-doped regions (the full fitting procedures, parameters, and results are explained in the Supporting Information, S5). We can see from these spectra that despite the native oxide residing on the surface of these NWs we do not observe large In–O and P–O components in the spectra when compared to previous XPS investigations on InP NWs. Our experiments were performed at a higher photon energy and thus we are able to better penetrate the typically 1–2 nm thick native oxide on the NW surface. In addition, we noted slightly smaller oxide components after applying a bias across the NW, possibly due to better penetration of the X-rays into the NW. Nevertheless, the effect of this X-ray-induced surface photovoltage should be of similar size for no external bias and for a small forward or reverse bias; therefore it might affect the measured built-in potential but not significantly the change of the built-in potential under applied bias.
to Joule heating of the NW and resulting oxide reduction. We are able to observe two individual surface related components for the P 2p peak shifted to higher binding energies by ∼0.95 eV (red component in Figure 4) and ∼3.5 eV (orange) compared to the bulk component (blue). According to literature, the component with the larger chemical shift can be interpreted as P in a +5 oxidation state (as e.g., in InPO4), and the component with the smaller shift as P0.37. For our In 4d measurements shown in Figure 4a–c(ii), we observe a small component (orange) shifted to 0.6 eV higher binding energy than the bulk component (blue), which may arise from an oxide component.43 However, we can also see an additional component at 0.75 eV lower binding energy in the In 4d spectra (red), principally on the upper end of the nanowire (n-doped region). This may indicate the presence of metallic In or some In/Au alloy species43 either arising from the In enriched Au particle at the top of the nanowire25 or some alloying of the In of the NW with the Au-covered electrodes.

We also measured In 3d core level spectra, which provide a higher energy resolution than In 3d SPEM maps at equidistant locations (roughly equivalent to the 130 nm resolution of the X-ray beam) along the entire InP NW to observe in more detail the energy difference of the p–n-doped regions and the space charge region of the NW while the device is in operation. Figure 5a shows a chemically sensitive map of the InP NW for the In 3d peak, overlaid with the positions where each spectrum was taken according to the x/y scan table. The positions with respect to the x/y scan table varied slightly due to drift but a small map was taken at each new location to ensure the NW was centered for the measurement. These spectra were taken for no externally applied bias (yellow data points), −0.3 V reverse bias (blue), and 0.4 V forward bias case (red). The error bars indicate the likely sampled region given the 130 nm spot size of the X-ray beam.

These high-resolution In 3d 5/2 core level spectra for the 0 V case are plotted in Figure 5b. The spectra are shifted for clarity and colored to indicate the n-type side of the NW (green) and the p-type side (pink). We observe a drop in intensity for the first and last measurements in each data set confirming the locations for each end of the NW. We can see lower energy for the p-type side which is consistent with the observed reduction in binding energy discussed previously. The surface built-in potential that we observe in between the extremities of the NW is about ∼0.4 eV when the nanowire is unbiased.

In Figure 5c, we plot the shift in core level position for each of the spectra data sets with respect to the n-type side of the nanowire for the different applied biases. After background subtraction (a combination of Shirley and a constant offset), these spectra were fitted with a Voigt line shape to identify the precise peak position. The change in binding energy between the n-doped and p-doped region is enhanced for the reserve bias case to ∼0.6 eV and suppressed for the forward bias measurement to ∼0.2 eV. For an ideal p–n junction, we would expect a constant binding energy for each dopant type and a gradual shift over the depletion region of the NW. However, in addition to small variations in the potential along the NW, we see a slight shift toward the n-type end of the NW to a lower energy and a prolonged drop in potential along the p-type end of the NW. Excluding the absolute measurements at the extremities of the NW, the qualitative nature of the core level shifts follows similar behavior to that observed in the KFPM measurements (Figure 1), supporting the observation of a Zn dopant memory effect during NW growth.

At the extremities of the NW, we observe additional binding energy shifts which we think are unlikely to be accounted for purely by dopant diffusion. These may be due to a combination of several factors including NW geometry and the device architecture which may influence these operando measurements. First, we observe a substantial drop in peak intensity in the first and last measurements due to a drop in the number of core level electrons coming from the NW as it moves out of range of the X-ray beam. This may affect the accuracy of the corresponding fitted peak positions. In addition, we see a substantial shift for the last data point taken for the end of the p-doped region, which corresponds to the part of the NW which has been broken off from the growth substrate. There may therefore be a contribution to the signal arising from an uneven cleavage surface with many steps, which would result in an energy shift relative to the otherwise probed (110) side facet. The device structure may also play a role in these topmost and bottommost core level shifts. Each end of the NW is in physical contact to the underlying electrode, but since four terminal contact resistance measurements are not possible the quality of these contacts is unknown. From the chemical map we cannot be certain that the NW is lying completely flat on the Ti/Au contacts. If the NW is bending up slightly away from the electrode, we may observe some additional contribution due to charging of the NW or point contact formation. It is also well established by several studies on electrical transport through III–V NWs that forming a high quality contact to p-doped InP is a challenge compared to the highly n-doped material due to difficulties in achieving a high doping density with Au-seeded nanowires and surface Fermi-level pinning of the conduction band.44,45 However, from the chemically sensitive maps in Figure 3, it is likely in our case that the Au particle has broken off the NW making it more difficult to achieve high quality electrical contact without removal of the surface oxides. The presence of two thin Schottky-like contacts at the extremities of the NW might also explain the additional band bending to lower energies we observe.

Our SPEM results combined with scanning probe results provide a complete set of quantitative values for surface composition of chemical, electrical, and structural components across the NW junction, which are highly relevant for correlating the performance of nanoscale devices. This technique is neither limited to InP or other III–V semiconductor material systems nor to the nanowire geometry, and it has thus great potential for both in situ and operando studies to monitor changes in electrical and photovoltaic behavior arising from cleaning and reoxidation processes, passivation, or functionalization of nanostructure surfaces.

In conclusion, we have presented a detailed examination of the surface doping and band bending on individual InP p–n junction NW devices. We have used a combination of scanning probe techniques to measure a surface built-in potential of 0.3 eV for the oxidized surface and 0.5 eV after native oxide removal, and a depletion region at the surface which can be resolved down to 15 nm by scanning tunneling spectroscopy. We observe additional fluctuations in the active doping profile along the surface of the NW within each dopant region by changes in surface potential in both Kelvin probe force microscopy and scanning photoemission microscopy measurements. We attribute these surface variations to Zn dopant
memory effects during NW growth. The use of nanofocus XPS allowed us to detail complex band bending phenomena along an individual NW during operando studies and to see the effect of operating the device under zero bias and forward/reverse bias conditions. This study shows the added value of applying complementary surface characterization techniques, and it demonstrates the potential of SPEM and nanofocus XPS for operando surface studies of nanostructure devices.

■ ASSOCIATED CONTENT

1 Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.9b03529.

Nanowire growth details, Kelvin probe force microscopy, scanning photoelectron microscopy, operando XPS measurements, calibration of the electrical bias applied to a nanowire, details of XPS fitting (PDF)

■ AUTHOR INFORMATION

Corresponding Author
Rainer Timm — Lund University, Lund, Sweden; orcid.org/0000-0001-8914-5924; Email: Rainer.Timm@sljus.lu.se

Other Authors
Sarah R. McKibbin — Lund University, Lund, Sweden
Jovana Colvin — Lund University, Lund, Sweden
Andrea Troian — Lund University, Lund, Sweden
Johan V. Knutsson — Lund University, Lund, Sweden
James L. Webb — Lund University, Lund, Sweden
Gaute Otnes — Lund University, Lund, Sweden; orcid.org/0000-0002-4241-5234

Kai Dirscherl — Danish National Metrology Institute, Horsholm, Denmark

Hikmet Sezen — Elettra – Sincrotrone Trieste S.C.p.A. di Interscienza Nazionale, Trieste, Italy; orcid.org/0000-0002-5438-3305

Matteo Amati — Elettra – Sincrotrone Trieste S.C.p.A. di Interscienza Nazionale, Trieste, Italy

Luca Gregoratti — Elettra – Sincrotrone Trieste S.C.p.A. di Interscienza Nazionale, Trieste, Italy

Magnus T. Borgström — Lund University, Lund, Sweden; orcid.org/0000-0001-8061-0746

Anders Mikkelsen — Lund University, Lund, Sweden

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acs.nanolett.9b03529

Author Contributions
Measurements were performed by S.R.M., J.C., A.T., H.S., M.A., L.G., and R.T. (SPEM), J.C., K.D., and R.T. (KPFM), and J.V.K. (STM/S). G.O. and M.T.B. grew the NW sample. S.R.M. and J.L.W. processed the NWs for operando experiments. S.R.M., J.V.K., and K.D. analyzed the data. S.R.M., A.M., and R.T. planned and supervised the experiments. S.R.M. and R.T. wrote the manuscript with contributions from all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was performed within the NanoLund Center for Nanoscience at Lund University and was further supported by the Swedish Research Council (VR), the Swedish Foundation for Strategic Research (SSF), and the European Research Council as well as the European Commission under the European Union’s Seventh Framework Programme, Grant Agreements 259141 and 608153. Part of the work presented here has been funded by the Danish Ministry of Higher Education and Science.

■ REFERENCES

(1) Barrigón, E.; Heurlin, M.; Bi, Z.; Monemar, B.; Samuelson, L. Chem. Rev. 2019, 119, 9170–9220.
(2) Wernersson, L.-E.; Thelander, C.; Lind, E.; Samuelson, L. Proc. IEEE 2010, 98, 2047–2060.
(3) Ottes, G.; Borgström, M. T. Nano Today 2017, 12, 31–45.
(4) Wallentin, J.; Anttu, N.; Asoni, D.; Huffman, M.; Åberg, I.; Magnunsson, M. H.; Siefier, G.; Fuss-Kailuweit, P.; Dimroth, F.; Witzigmann, B.; Xu, H. Q.; Samuelson, L.; Deppert, K.; Borgström, M. T. Science 2013, 339, 1057–1060.
(5) Nguyen, H. P. T.; Zhang, S.; Cui, K.; Han, X.; Fathololoumi, S.; Couillard, M.; Botton, G. A.; Mi, Z. Nano Lett. 2011, 11, 1919–1924.
(6) Deng, M. T.; Valtoköivas, S.; Hansen, E. B.; Danon, J.; Lejinse, M.; Flensberg, K.; Nygård, J.; Krogstrup, P.; Marcus, C. M. Science 2016, 354 (6319), 1557–1562.
(7) Persson, O.; Webb, J. L.; Dick, K. A.; Thelander, C.; Mikkelsen, A.; Timm, R. Nano Lett. 2015, 15, 3684–3691.
(8) Robertson, J.; Guo, Y.; Lin, L. J. Appl. Phys. 2015, 117 (11), 112806.
(9) Wu, J.; Babadi, A. S.; Jacobsson, D.; Colvin, J.; Yingman, S.; Timm, R.; Lind, E.; Wernersson, L.-E. Nano Lett. 2016, 16, 2418–2425.
(10) van Dam, D.; van Hoof, N. J. J.; Cui, Y.; van Veldhoven, P. J.; Bakkers, E. P. A. M.; Gomez Rivas, J.; Haverkort, J. E. M. ACS Nano 2016, 10 (12), 11141–11149.
(11) Ottes, G.; Barrigón, E.; Sundvall, C.; Svensson, K. E.; Heurlin, M.; Siefier, G.; Samuelson, L.; Åberg, I.; Borgström, M. T. Nano Lett. 2018, 18 (5), 3038–3046.
(12) Hjort, M.; Wallentin, J.; Timm, R.; Zacharov, A. A.; Håkanson, U.; Andersson, J. N.; Lundgren, E.; Samuelson, L.; Borgström, M. T.; Mikkelsen, A. ACS Nano 2012, 6 (11), 9679–9689.
(13) Hjort, M.; Wallentin, J.; Timm, R.; Zacharov, A. A.; Andersson, J. N.; Samuelson, L.; Borgström, M. T.; Mikkelsen, A. Appl. Phys. Lett. 2011, 99, 233113.
(14) Abyaneh, M. K.; Gregoratti, L.; Amati, M.; Dalmiglio, M.; Kiskinova, M. e-J. Surf. Sci. Nanotechnol. 2011, 9, 158–162.
(15) Ottes, G.; Heurlin, M.; Graczky, M.; Wallentin, J.; Jacobsson, D.; Berg, A.; Maximov, I.; Borgström, M. T. Nano Res. 2016, 9 (10), 2852–2861.
(16) Borgström, M. T.; Wallentin, J.; Trägårdh, J.; Ramvall, P.; Ek, M.; Wallenberg, R.; Samuelson, L.; Deppert, K. Nano Res. 2010, 3, 264–270.
(17) Timm, R.; Hjort, M.; Fian, A.; Borg, B. M.; Thelander, C.; Andersson, J. N.; Wernersson, L.-E.; Mikkelsen, A. Appl. Phys. Lett. 2011, 99, 222907.
(18) Hjort, M.; Lehmann, S.; Knutsson, J.; Timm, R.; Jacobsson, D.; Lundgren, E.; Dick, K. A.; Mikkelsen, A. Nano Lett. 2013, 13, 4492–4498.
(19) Minot, E. D.; Kelkensberg, F.; van Kouwen, M.; van Dam, J. A.; Kouwenhoven, L. P.; Zwiller, V.; Borgström, M. T.; Wunnicke, O.; Verheijen, M. A.; Bakkers, E. P. A. M. Nano Lett. 2007, 7 (2), 367–371.
(20) Lysov, A.; Vinaji, S.; Offer, M.; Gutsche, C.; Regolin, I.; Mertin, W.; Geller, M.; Prost, W.; Baker, G.; Tegade, F.-J. Nano Res. 2011, 4, 987–995.
(21) Minj, A.; Cros, A.; Auzelle, T.; Pernot, J.; Daudin, B. Nanotechnology 2016, 27 (38), 385202.
(22) Sun, X.; Wang, X.; Wang, P.; Sheng, B.; Li, M.; Su, J.; Zhang, J.; Liu, F.; Rong, X.; Xu, F.; Yang, X.; Qin, Z.; Ge, W.; Shen, B. Opt. Mater. Express 2017, 7 (3), 904–912.
(23) Li, N.; Tan, T. Y.; Go, T. Appl. Phys. A: Mater. Sci. Process. 2008, 90 (4), 591–596.
(24) Goto, H.; Nosaki, K.; Tomioka, K.; Hara, S.; Hiruma, K.; Motohisa, J.; Fukui, T. Appl. Phys. Express 2009, 2, 035004.
(25) Troian, A.; Otnes, G.; Zeng, X.; Chayanun, L.; Dagyte, V.; Hammarberg, S.; Salomon, D.; Timm, R.; Mikkelson, A.; Borgström, M. T.; Wallentin, J. Nano Lett. 2018, 18, 6461–6468.
(26) Hjort, M.; Knutsson, J. V.; Mandl, B.; Deppert, K.; Lundgren, E.; Timm, R.; Mikkelson, A. Nanoscale 2015, 7, 9998–10004.
(27) Knutsson, J. V.; Lehmann, S.; Hjort, M.; Lundgren, E.; Dick, K. A.; Timm, R.; Mikkelson, A. ACS Nano 2017, 11, 10519–10528.
(28) Feenstra, R. M.; Yu, E. T.; Woodall, J. M.; Kirchner, P. D.; Lin, C. L.; Pettit, G. D. Appl. Phys. Lett. 1992, 61, 795–797.
(29) Jabeen, F.; Rubini, S.; Martelli, F.; Franciosi, A.; Kolmakov, A.; Gregoratti, L.; Amati, M.; Barinov, A.; Goldoni, A.; Kiskinova, M. Nano Res. 2010, 3 (10), 706–713.
(30) Fanetti, M.; Ambrosini, S.; Amati, M.; Gregoratti, L.; Abyaneh, M. K.; Franciosi, A.; Chia, A. C. E.; LaPierre, R. R.; Rubini, S. J. Appl. Phys. 2013, 114, 154308.
(31) Amati, M.; Barinov, A.; Feyer, V.; Gregoratti, L.; Al-Hada, M.; Locatelli, A.; Mentes, T. O.; Sezen, H.; Schneider, C. M.; Kiskinova, M. J. Electron Spectrosc. Relat. Phenom. 2018, 224, 59–67.
(32) Webb, J. L.; Persson, O.; Dick, K. A.; Thelander, C.; Timm, R.; Mikkelson, A. Nano Res. 2014, 7, 877–887.
(33) Gregoratti, L.; Barinov, A.; Benfatto, E.; Cautero, G.; Lacovig, P.; Lonza, D.; Kiskinova, M.; Tommasini, R.; Mahl, S.; et al. Rev. Sci. Instrum. 2004, 75, 64–68.
(34) Yeh, J. J.; Lindau, I. At. Data Nucl. Data Tables 1985, 32, 1–155.
(35) Renault, O.; Morin, J.; Tchoulfiian, P.; Chevalier, N.; Feyer, V.; Pernot, J.; Schneider, C. M. Ultramicroscopy 2015, 159, 476–481.
(36) Soudi, A.; Hsu, C.-H.; Gu, Y. Nano Lett. 2012, 12, 5111–5116.
(37) Vogt, P.; Frisch, A. M.; Hannappel, T.; Visbeck, S.; Willig, F.; Jung, C.; Follath, R.; Braun, W.; Richter, W.; Esser, N. Appl. Surf. Sci. 2000, 166 (1–4), 190–195.
(38) Adam, S.; McGinley, C.; Riedler, M.; Moller, T. Conf. Proc. - Indium Phosphide Relat. Mater. Conf., 14th, Stockholm, Sweden, 2002; pp 601–604.
(39) Palmgren, P.; Priya, B. R.; Niraj, N. P. P.; Göthelid, M. J. Phys.: Condens. Matter 2006, 18 (48), 10707–10723.
(40) Robert-Goumet, C.; Monier, G.; Zefack, B.; Chelda, S.; Bideux, L.; Gruzza, B.; Awitor, O. K. Surf. Sci. 2009, 603 (19), 2923–2927.
(41) Borgström, M. T.; Norberg, E.; Wickert, P.; Nilsson, H. A.; Trägårdh, J.; Dick, K. A.; Statkute, G.; Ramvall, P.; Deppert, K.; Samuelson, L. Nanotechnology 2008, 19 (44), 445602.
(42) van Weert, M. H. M.; Wunnicke, O.; Roest, A. L.; et al. Appl. Phys. Lett. 2006, 88, 043109.