Imaging the influence of oxides on the electrostatic potential of photovoltaic InP nanowires

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ABSTRACT

Nanowires require surface passivation due to their inherent large surface to volume ratio. We investigate the effect of embedding InP nanowires in different oxides with respect to surface passivation by use of electron beam induced current measurements enabled by a nanoprobe based system inside a scanning electron microscope. The measurements reveal remote doping due to fixed charge carriers in the passivating $\text{PO}_x/\text{Al}_2\text{O}_3$ shell in contrast to results using SiO_x . We used time-resolved photoluminescence to characterize the lifetime of charge carriers to evaluate the success of surface passivation. In addition, spatially resolved internal quantum efficiency simulations support and correlate the two applied techniques. We find that atomic-layer deposited $\text{PO}_x/\text{Al}_2\text{O}_3$ has the potential to passivate the surface of InP nanowires, but at the cost of inducing a field-effect on the nanowires, altering their electrostatic potential profile. The results show the importance of using complementary techniques to correctly evaluate and interpret processing related effects for optimization of nanowire-based optoelectronic devices.

KEYWORDS

InP nanowires, oxides, MOVPE, electron beam induced current (EBIC), time-resolved photoluminescence (TRPL), field-effect

1 Introduction

Nanowire (NW) solar cells have the potential to reach similar or even higher efficiencies as thin-film solar cells while at the same time only using fractions of the expensive III-V semiconductor materials [1]. Furthermore, these low dimensional material building blocks enable a facile combination of materials with different lattice parameters [2, 3] and the possible integration in flexible polymers after peel-off [4, 5]. Due to the high research interest in NW solar cells, several reviews on this topic have been published recently [6–9].

However, the reduced dimensions of the NWs pose new challenges. One of those is the high surface-to-volume ratio that can lead to unfavorable surface recombination of charge carriers. It is thus of great importance to passivate the surface of most III-V NWs, and different passivation strategies have been presented based on wet chemical treatment [10], epitaxial shell growth [11, 12] and dielectric layers [13–15]. Even though InP has a relatively low surface recombination velocity V_{SR} [16], we have recently observed that using different insulation layers strongly affects device performance [17]. It is challenging to passivate InP because no obvious high bandgap, lattice-matched passivating material is available to be grown *in-situ*. Alternatively, atomic layer deposition (ALD) of amorphous oxides such as a stacked layer of $\text{PO}_x/\text{Al}_2\text{O}_3$ has been shown to increase the photoluminescence decay lifetime of nominally intrinsic, selective area grown wurtzite InP NWs from 1.8 to

5.4 ns [14]. On the other hand, it has been shown, that passivation is necessary but may not be sufficient to optimize NW devices, as fixed charges in a passivation layer can influence the electrostatic potential of the p–n junctions in the NW solar cells due to a field-effect [18]. A fixed positive (negative) charge at the interface between the semiconductor NW and the dielectric insulation layer increases the electron (hole) density and induces n-type (p-type) behavior. Up to now, on a single NW level, this has only been simulated [18].

Electron beam induced current (EBIC) measurements have been proven to be a successful tool to investigate p–n junctions of both single NWs [17, 19–22], and processed NW solar cells [23–25]. Using this technique, single NWs are contacted in a scanning electron microscope (SEM) equipped with a piezo-controlled tungsten probe, enabling to measure EBIC and IV-characteristics. Time-resolved photoluminescence (TRPL) is often used to study photovoltaic materials [26, 27] and especially the surface passivation thereof [14, 15]. Both EBIC and TRPL enable to obtain information about the photovoltaic quality of NWs rapidly without the need of any time-consuming processing.

In this work, we investigated photovoltaic InP NWs with p–i–n junctions by use of EBIC to determine the influence of insulating oxides on the electrostatic potential. The nanowires were measured as-grown after synthesis, and again after depositing SiO_x [17] or a $\text{PO}_x/\text{Al}_2\text{O}_3$ stack [14]. We detected a field-effect on the electrostatic potential when the NWs were

capped with $\text{PO}_x/\text{Al}_2\text{O}_3$. We then prepared uniformly doped nanowires using the same dopant molar fractions during synthesis as in the respective segments of p–i–n junctions to characterize and compare the mobile charge carrier lifetimes of nominally intrinsic, p- and n-type InP NWs by use of TRPL. Additionally to as-grown NWs, surface passivated NWs using the same oxides were measured. The dependence of both doping and V_{SR} on EBIC measurements was calculated with the help of spatially resolved internal quantum efficiency (SIQE) [28] modelling. The simulations agree with the experimental data and demonstrate the influence of surface passivation and dopant concentrations on the electrostatic potential of NWs with p–i–n junctions thus helping to understand the correlation of TRPL and EBIC measurements. An EBIC signal along the full NW is desired for optimal short circuit density [17, 28], but a possible change of the EBIC signal after oxide deposition has been ignored. We show that with EBIC the displacement of a p–n junction due to a field-effect can be measured. Understanding the effect of the use of different oxides on the electrostatic potential of semiconductor NWs is crucial, as many nanowire-based devices, especially NW solar cells with axially defined junctions [17, 29, 30], employ insulation layers to prevent electric short circuits.

2 Experimental details

Periodic arrays of gold seed particles were prepared by nanoimprint lithography, metal evaporation and lift-off on 2" InP (111)B wafers [31] that were diced into 9 mm × 11 mm substrate pieces after patterning. InP nanowires were grown using the vapor liquid solid growth mode [32] by use of a laminar flow Aixtron 200/4 MOVPE reactor at 100 mbar using hydrogen as a carrier gas in a total flow rate of 13 L·min⁻¹. After a low-temperature pre-annealing nucleation step to preserve the periodic pattern (molar fraction of trimethylindium (TMIn) $\chi_{\text{TMIn}} = 8.91 \times 10^{-5}$, and of phosphine (PH_3) $\chi_{\text{PH}_3} = 6.92 \times 10^{-3}$) [31], the substrate was annealed at 550 °C ($\chi_{\text{PH}_3} = 3.46 \times 10^{-2}$), after which growth was initiated by introducing TMIn and reducing the PH_3 molar fraction at 440 °C ($\chi_{\text{TMIn}} = 5.94 \times 10^{-5}$, $\chi_{\text{PH}_3} = 6.92 \times 10^{-3}$). Hydrogen chloride (HCl) was used to prevent tapering *in-situ* ($\chi_{\text{HCl}} = 1.23 \times 10^{-4}$) [33]. The resulting NWs were 2 μm long and 200 nm in diameter. The crystal structure of similar NWs has been investigated by the use of transmission electron microscopy [34]. Diethylzinc (DEZn) and tetraethyltin (TESn) were used for p- and n-doping respectively ($\chi_{\text{Zn}} = 1.11 \times 10^{-5}$, $\chi_{\text{Sn}} = 4.29 \times 10^{-5}$) [35]. In order to compensate the n-type background doping of nominally intrinsic InP [36, 37], the doping level of the middle segment of p–i–n junctions was varied between samples from $\chi_{\text{Zn}} = 0$ (nominally intrinsic) to $\chi_{\text{Zn}} = 2.64 \times 10^{-7}$, which resulted in slightly n- and p-type material, respectively, as determined by the EBIC peak position [17, 21].

Two different oxides were deposited by ALD. SiO_x was deposited in a Veeco/CNT Savannah ALD chamber at 255 °C and a base pressure of 100 mbar. Tris(*tert*-butoxy)silanol (TTBS) and trimethylaluminum (TMAI) were used as precursors of which TTBS was heated to 90 °C. 18 cycles were deposited, and each cycle consisted of one 0.06 s TMAI pulse and three 3 s TTBS pulses. The resulting thickness of SiO_x on the NWs was 30 nm and contained a low Al content [38]. The $\text{PO}_x/\text{Al}_2\text{O}_3$ was deposited on other samples in a Veeco/CNT Fiji ALD chamber at 50 °C at a base pressure of 80 mbar. Trimethyl phosphate (TMP) and TMAI were used as precursors. First PO_x was deposited by 100 cycles of 2 s TMP pulses each terminated by a 5 s O_2 plasma oxidation step. Then, Al_2O_3 was deposited using 133 cycles of 0.08 s TMAI pulses and 5 s

oxidation by use of O_2 plasma. The resulting thickness of $\text{PO}_x/\text{Al}_2\text{O}_3$ on the NWs was 12 nm.

All of the TRPL experiments were performed in a dry nitrogen atmosphere and at room temperature. A Ti:Sapphire 770 nm 100 fs pulsed laser (Spectra-Physics, Tsunami) with a repetition rate of 81 MHz was used for sample excitation. The laser beam was focused on the sample with an angle of 70°, which is close to the Brewster angle of InP. The PL emission from samples was collected via two lenses with a focal length of 50 mm, and focused on a spectrograph (Chromex) having a 50 lines·mm⁻¹ grating. Then, the output of the spectrograph was sent into the streak camera (Hamamatsu C6860) set at a slit width of 20 μm. In the data processing, background subtraction, shading and spectral sensitivity corrections of the PL decay images were utilized with a calibrated standard lamp (Ocean Optics, LS-1-CAL). Efforts were taken to keep the alignment of the experimental set-up the same for all the samples studied.

EBIC was measured in a Hitachi SU8010 SEM by a Point Electronic EBIC amplifier. Samples were cleaved and glued on a 90° stub such that the NW axis was perpendicular to the electron beam. A Prober Shuttle from Kleindiek Nanotechnik was used to contact single NWs with a tungsten probe. At least four NWs were measured per sample. In order to contact the gold alloy particle of the coated NWs, the oxide was scratched away at the tip of the NWs using the tungsten probe while taking care to avoid charging of the oxide layer under the electron beam of the SEM. All measurements were conducted using 5 kV acceleration voltage and a beam current in the order of tens of pA.

A three-dimensional drift-diffusion model was employed to simulate the carrier distribution and splitting process in InP nanowire. The technical equation and simulation parameters were stated in Ref. [28]. In the SIQE simulation, a cubic box with a side length of 10 nm was placed on the surface of the nanowire. In the box, an initial carrier density of $1 \times 10^{21} \text{ cm}^{-3}$ was fixed and the current was calculated with this initial condition at a short circuit situation. The ratio between the number of carriers in the current and the number of carriers in the box is defined as SIQE which shows the ability to split electron-hole pairs at this local position. In the band diagram simulation, an oxide shell was added to the nanowire and the contact was extended from the tip of the nanowire to the sidewall. Thus the surface of the oxide shell has the same electrical potential as the top contact. The oxide was simulated as a very high bandgap semiconductor (9 eV [39]) with type I band alignment between InP and oxide shell.

3 Results and discussion

3.1 Time-resolved photoluminescence

Figure 1(a) shows an SEM image of our NW arrays and Figs. 1(b) and 1(c) show schematics of as-grown and coated NW arrays respectively. The electrostatic potential of nanowires is strongly influenced by doping and V_{SR} . Therefore, to deepen the understanding of EBIC measurements of capped NWs, we firstly investigated the passivation effect of SiO_x and $\text{PO}_x/\text{Al}_2\text{O}_3$ on nominally intrinsic and intentionally doped as-grown InP NWs with TRPL. A constant dopant flow was used during synthesis, but it should be noted that the doping efficiency can vary with the length of NWs [40–42]. Subsequently, TRPL was measured on the same NWs coated by the two aforementioned oxides. As the passivation by $\text{PO}_x/\text{Al}_2\text{O}_3$ is expected to improve over time or after a thermal annealing step [14], these NW samples were thermally annealed for 1 min at 250 °C in N_2

Figure 1 (a) SEM image with 30° tilt of epitaxially vapor–liquid–solid grown InP NWs with gold seeds. Schematics of (b) as-grown and (c) oxide coated InP NW arrays. (d) TRPL decay of nominally intrinsic nanowires coated by different insulation layers.

atmosphere after characterization and then re-measured.

In order to extract the charge carrier lifetime of nominally intrinsic NWs, a bi-exponential decay was fitted to the TRPL measurements in Fig. 1(d). We observed that coating the nominally intrinsic InP NWs with any oxide reduced the charge carrier lifetime. In particular, at an excitation flux of 3×10^{12} photons·cm⁻²·pulse⁻¹ the charge carrier lifetime decreases from 650 ps for as-grown NWs to 507 ps for SiO_x covered NWs and 474 ps for PO_x/Al₂O₃ covered NWs (see Table S1 in the Electronic Supplementary Material (ESM)). These results show significantly lower lifetimes than those reported by Black et al. [14], possibly because a different characterization tool using a different time range was studied. It should be pointed out that in this study a streak camera was used that has a much shorter (ca. two orders of magnitude) instrument response function than time-correlated single photon counting (TCSPC), allowing to resolve the dynamics of PL at short time scales, which could be completely missed by TCSPC. Indeed, when measured with TCSPC, our samples exhibit lifetimes ranging from 4 to 7 ns, as shown in Fig. S1 in the ESM.

We observed that nominally intrinsic NWs exhibit the longest lifetimes. Some strategies have been presented to produce doping-free NW solar cells based on carrier-selective contacts [43], but generally and especially for two-terminal multi-junction solar cells, doping is used. Therefore, NWs with the same dopant molar fractions used in the respective segments of p–i–n junctions were grown and characterized by TRPL. The measurements of uniformly doped NWs are shown in Fig. 2. The carrier lifetime decreases when doping is introduced. Interestingly, using small amounts of DEZn for compensation doping decreases the lifetime more than heavy p-doping. Though the exact origin is unclear, one explanation could be that outdiffusing Zn forms a thin ZnO layer after exposure to air which has been reported to passivate InP [44]. The same figure includes the measurements performed of the samples with the different passivation schemes. While the lifetime of the doped NWs decreases after deposition of SiO_x, both n- and p-doped nanowires covered with PO_x/Al₂O₃ have longer lifetimes than as-grown NWs (see Table S1 in the ESM). The passivation is further improved after annealing (for 1 min at 250 °C under N₂ atmosphere), indicated by increased amplitudes of the longer decays.

3.2 Electron beam induced current measurements

It has been shown that fixed charges of an insulation layer can induce a radial change of the carrier density and thus affect the performance of NW solar cells [18]. In order to validate if the used oxides show a field-effect on InP NW samples, a series of InP NWs with p–i–n junctions using the same dopant molar fractions as for the uniformly doped nanowires (Fig. 2) were grown. The doping of the middle segment was

Figure 2 TRPL decays of (a) n-doped, (b) compensation doped, and (c) p-doped InP NW arrays at an excitation flux of 3×10^{12} photons·cm⁻²·pulse⁻¹. The scatter plot shows the measured data points, while the solid line is a bi-exponential fit to the data. After deposition of SiO_x (blue) the optical properties of as-grown InP NWs (black) degrade. After an annealing step, the PO_x/Al₂O₃ (green) improves the photoluminescence.

varied by increasing the DEZn molar fraction in the middle segment from $\chi_{\text{Zn}} = 0$, to $\chi_{\text{Zn}} = 0.3 \times 10^{-7}$, to $\chi_{\text{Zn}} = 2.6 \times 10^{-7}$. This corresponds to a nominally intrinsic, compensation doped, and overcompensation doped middle segment respectively, as depicted in Figs. 3(a)–3(c). Figure 3(d) shows a representative composition image of the greyscale SEM image and EBIC measurement for an as-grown NW from Fig. 3(c).

We observe that the metallurgical p–n junction of as-grown NWs is located at the p–i interface for NWs with nominally intrinsic middle segments (Fig. 3(a)), but at the i–n interface for NWs with compensation doped middle segments (Figs. 3(b) and 3(c)) [17, 21]. The latter is advantageous because due to strong light absorption in the NWs most charge carriers are generated at the tip of the NWs [28]. Generally, a flat EBIC profile is desired to maximize charge carrier generation and short-circuit current [21].

The measurements after oxide deposition reveal that the oxides have a strong effect on the peak position and width of the EBIC signal. We observe that if the EBIC profile of as-grown

Figure 3 Representative EBIC profiles along the NW axes including the Au particle. The DEZn molar fraction in the middle segment is increased from (a) $\chi_{Zn} = 0$, to (b) $\chi_{Zn} = 0.3 \times 10^{-7}$ to (c) $\chi_{Zn} = 2.6 \times 10^{-7}$. $\text{PO}_x/\text{Al}_2\text{O}_3$ induces an n-type field-effect that moves the peak position of the EBIC signal for all samples. SiO_x decreases the EBIC signal in the middle segments, but increases the EBIC signal in the p-segment of the NWs. (d) Composition image of SEM (greyscale) and EBIC (colorbar) signal of the as-grown NWs from (c).

NWs is flat due to a compensation doped middle segment, the EBIC profile before and after SiO_x deposition looks similar. For a n- as well as for a p-type middle segment, the EBIC signal in the middle segment decreases and the peak gets much sharper. The question remains whether this SiO_x induces a field-effect or not since the position of the EBIC signal is not significantly moved in any direction.

The use of $\text{PO}_x/\text{Al}_2\text{O}_3$, on the other hand, leads to an n-type field-effect which moves the position of the junction closer towards the bottom p-segment of the NWs. The nominally intrinsic middle segment (Fig. 3(a)) already shows n-type behavior of but the position of the EBIC signal peak is still moved even closer to the substrate because of the n-type field-effect on the p-segment. In the case of an overcompensated p-type middle segment (Fig. 3(c)), the field-effect of the oxide counteracts the intended doping and the EBIC signal flattens out (i.e., moving towards a the ideal p-i-n case with a uniform EBIC profile along the NW). If the middle segment is compensation doped (Fig. 3(b)), the use of $\text{PO}_x/\text{Al}_2\text{O}_3$ leads to a peak at the p-i interface in addition to the signal at the i-n interface. This double-peak can be explained by a field-effect caused by fixed charges in the shell. In Fig. S2 in the ESM, it can be seen how the potential of fixed charges in the oxide provokes band bending at both the p-i and i-n interface. As the EBIC signal peaks at the p-i interface we deduce that the field-effect leads to an inversion of the middle segment from slightly p-type to slightly n-type.

In order to get a better understanding of the different EBIC profiles, simulations for the SIQE of InP NW p-i-n junctions with different doping in the middle segment and varying V_{SR} have been calculated and are shown in Fig. 4. The carrier lifetime is inversely proportional to V_{SR} in the model used for calculations and therefore short lifetimes are represented by fast V_{SR} .

The SIQE of Fig. 4(a) (n-type middle segment) and 4(b) (p-type middle segment) with a V_{SR} of $10^4 \text{ cm} \cdot \text{s}^{-1}$ resembles the measured EBIC profiles of as-grown NWs from Figs. 3(a) and 3(b) respectively. Further simulations (see Fig. S3 in the ESM) show, that the measured EBIC profile of as-grown NWs from Fig. 3(c) with increased χ_{Zn} cannot be explained by only increasing the dopant concentration. The measured EBIC profile is better resembled by the simulation using an increased V_{SR} in the order of $10^5 \text{ cm} \cdot \text{s}^{-1}$.

For nominally intrinsic NWs we did not observe any improvement on the passivation by either oxide (Fig. 1(d)) with TRPL. Accordingly, for p-i-n junctions with nominally intrinsic middle segments, both oxides decrease the EBIC signal and the profiles match with simulations for increased V_{SR} . For compensation doped NWs, SiO_x showed the shortest lifetimes in TRPL (Fig. 2). That is why the EBIC measurements

Figure 4 Simulated SIQE for InP NW p-i-n junctions with different surface recombination velocities (V_{SR}). The dopant concentration for both the bottom p-segment (400 nm) and the top n-segment (100 nm) is 10^{18} cm^{-3} . (a) The middle segment is slightly p-doped (10^{17} cm^{-3}). (b) The middle segment is slightly n-doped (10^{17} cm^{-3}).

after SiO_x deposition are sensitive to the doping level of the middle segment as seen in Fig. 3.

After deposition of $\text{PO}_x/\text{Al}_2\text{O}_3$ we did not observe significantly improved lifetimes with TRPL for compensation doped NWs. Therefore, we attribute the flattened EBIC profile of NWs with a p-type middle segment in Fig. 3(c) to the field-effect of $\text{PO}_x/\text{Al}_2\text{O}_3$ and not to a decrease in V_{SR} . Instead, we believe that due to fixed positive charges in the oxide the electron concentration is increased towards the interface between NW and oxide which compensates the overcompensation of Zn. Another indication for this hypothesis is that for the double peak EBIC profile with a lower χ_{Zn} the highest signal is detected at the p-i interface suggesting an inversion of the middle segment from p-type to n-type.

4 Conclusions

By measuring TRPL on nominally intrinsic and doped InP NWs, we showed that the influence of insulation layers is doping dependent. Then, we measured EBIC on a similar set of InP NWs capped with insulation layers to characterize the effect of the dielectric layer on the electrostatic profile of the nanowires and show the importance of such layers in the performance optimization of NW solar cells. Indeed, a field-effect can be induced by embedding the nanowires in the oxides, that can change the electrostatic potential of the NWs and even invert the polarity due to fixed charges in the oxide layer. This is especially the case for $\text{PO}_x/\text{Al}_2\text{O}_3$ due to the n-type field effect as indicated by the EBIC measurements. All EBIC measurements

could be reproduced and explained by simulated SIQE for varied dopant concentrations and V_{SR} . By comparing the simulations to the measured EBIC profiles and considering the passivation properties obtained from TRPL, we demonstrate that neither a change in surface passivation nor a change in dopant concentration alone can explain the measurements. Instead, both effects have to be recognized and kept in mind for device optimization.

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