

Nanoplates and their suitability for use as solar cells

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ABSTRACT

The use of p-n junction nanowires as solar cells has received an increased amount of attention with results published on both individual silicon nanowires functioning as nano-solar cells and on larger surface areas covered with silicon nanowires. The results obtained using the nanowire geometry are promising and show a new direction towards a high efficiency/low cost solar cell.

Here we suggest the use of a different nanostructure geometry namely nanoplates which are fabricated using group III-V materials. The key properties of the InAs nanoplates are described and results from overgrowing them with a GaAs layer shown. Different ways to implement the nanoplate geometry into a solar cell are suggested and the very first results from the characterization of a single InAs-GaAs n-p junction nanoplate solar cell presented.

Keywords: nanoplates, nanowires, solar cell, n-p junction

1 NANOSTRUCTURE SOLAR CELLS

The classic silicon solar cell continues to be the dominant cell in the PV industry due to its combination of manufacturing simplicity, material cost and conversion efficiency. To counteract the increased demand for solar grade silicon and continue improving the €/Wp ratio several new PV designs have however been suggested like growing an epitaxial thin silicon film on an upgraded metallurgical grade silicon substrate [1] and the use of lift-off layers allowing reuse of the substrates [2]. In this article a novel approach towards a still lower €/Wp is suggested. It follows a logical evolution from the scheme originally investigated theoretically by Kayes *et al.* in 2005 [3] of using nanowires containing a radial p-n junction as light harvesting devices. The proposed scheme has since then to some extent been implemented with silicon nanowires [4,5,6]. Here we suggest a slightly different path towards the use of nanostructures as solar cells namely the use of nanoplates (NPs) [7] which we believe offers greater advantages like improvement in series resistance and intrinsic anti-reflection properties.

1.1 InAs nanoplates

InAs NPs are related to nanowires in the way that they are grown by means of a gold catalyst particle deposited or

formed on the substrate surface prior to growth. The NPs grow by a combination of the Vapor-Solid-Solid growth mechanism known from InAs nanowires [8] and standard epitaxial Vapor-Solid growth on their two arsenic terminated facets. The NPs grow perpendicular from a GaAs (100) substrate surface and offer excellent possibilities for systematic post growth processing and device manufacture due to a highly regular growth behavior over large surface areas. The thickness of the NPs is initially determined by the gold catalyst particle, NP width can be up to a micron however for the growth shown in figure 1a it is around 400 nm with a typical variation of less than 100 nm. Both thickness as well as width depends on the actual growth conditions used.

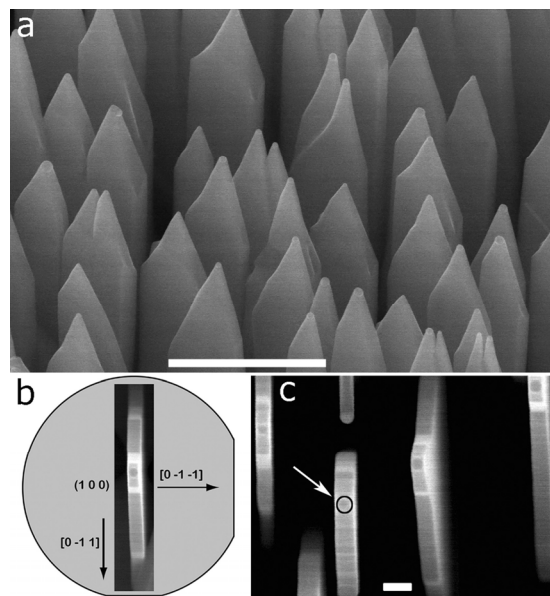


Figure 1 a, Forest of InAs nanoplates standing perpendicular from the surface of a (100) GaAs substrate. Scale bar, 1 μm . **b & c,** Images taken directly from above. The orientation of the nanoplates on a (100) EJ substrate, **b**. The plate thickness is determined by the diameter of the Au catalyst particle as indicated by the circle in **c**. Scale bar in **c**, 100 nm.

Figure 1a shows a forest of InAs NPs standing in the [100] crystal direction perpendicular to the (100) GaAs lattice mismatched substrate on which they are grown. All plates are oriented in the same way with the flat surfaces in

the [011] direction and every plate has a Au catalyst particle on top which initially determines its thickness. The shape at the top of the plate varies with no single preferred crystal direction but the sides of the lower part are close to the non-polar (0-11) and (01-1) surfaces. TEM investigations show that the NPs have a perfect zinc blende crystal structure. Only a small percentage of the TEM characterized plates displays defects, something which is also supported by X-ray diffraction [7].

The morphology of the substrate surface with the InAs NPs causes the surface to be highly anti-reflective. This is similar to intentionally fabricated silicon nanotip surfaces [9]. Visually the NP samples appear completely black and preliminary reflectance results indicate the anti-reflective properties – characterized in the 200–2200 nm wavelength regime – being perhaps as good as those of silicon nanotip surfaces [10].

With the NP geometry the surface to volume ratio is lower than for nanowires which can help minimize the negative effect of surface recombination. At the same time the increased cross section area, compared to the long thin nanowires, has a possibility for substantially reducing series resistance in each of the individual nano-solar cells.

2 NANOPlates AS SOLAR CELLS

The bandgap of InAs is ~ 0.36 eV which is insufficient for it to be useful as a stand alone solar cell material. Investigations regarding multiple exciton generation for single photon absorption have demonstrated that InAs is a particular well suited material with a carrier multiplication threshold close to two times the bandgap energy [11]. This has however been observed for nm sized quantum dots and it is dubious if it can be observed in the significant larger NP quantum wells.

In order for the excellent properties of the NP geometry to be utilized in solar cells a shift from low bandgap InAs to a high bandgap semiconductor, like GaAs, is needed. Future implementation of GaAs into the NP geometry includes changing the entire growth to being GaAs NPs on an inexpensive silicon substrate. The lattice mismatch between GaAs and silicon is very similar to that of InAs on a GaAs substrate. Another way to demonstrate the potential of the NP geometry is to use the already existing single crystal InAs NPs as templates for a subsequent GaAs crystal overgrowth.

For both of the implementations described above the growth conditions can after growth of the initial NP be changed such that growth also takes place on the side facets and surfaces of the NP. Having grown for instance an n-type InAs NP on an n-GaAs substrate the growth conditions can be changed and an undoped GaAs shell followed by a p-GaAs shell can be grown around the NP thereby generating a core-shell n-p junction where the n-side is contacted epitaxial through the substrate. In post growth processing steps the final PV device can be fabricated by filling the void between the NPs with a suitable material such that only the top of the NPs are exposed. By

depositing a top transparent contact on the filler, contact is made to the gold catalyst particles on the NP tops and hence to their outer shell. In this way a solar cell can be fabricated from billions of individual NPs each functioning as a small solar cell and all contacted in parallel. The only functions of the substrate will be as a growth platform and as contact to the inner core of the NPs; the only solar grade material necessary is the III-V materials used for NP growth. The amount of III-V material typically used to grow the NPs corresponds to less than $2 \mu\text{m}$ of bulk growth.

2.1 An InAs – GaAs solar cell

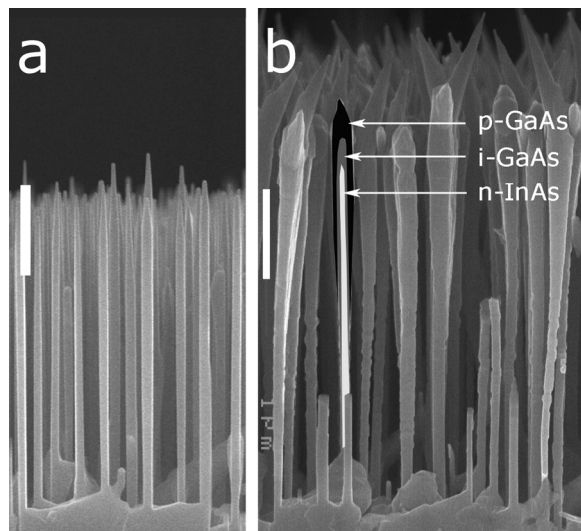


Figure 2 a. Forest of InAs nanoplates seen directly from their side. **b.** The same InAs growth recipe used as for the growth in **a** however followed by an i-GaAs and a p-GaAs growth step thereby forming an n-InAs – i-GaAs – p-GaAs core-shell structure. Because of the small spacing between the individual nanoplates the GaAs shell is only positioned on the upper part of the InAs nanoplates. Scale bars, $1 \mu\text{m}$.

We have realized the above mentioned implementation using the InAs NP as a template for overgrowth by GaAs. The n-InAs NPs were grown randomly positioned on an n-GaAs (100) substrate by means of Molecular Beam Epitaxy (MBE). A GaAs growth step was added immediately after finishing the InAs growth without removing the substrate from the MBE growth chamber. Because of differences on how gold catalyzed growth of InAs and GaAs takes place the addition of a GaAs growth step has for the growth conditions used caused the NPs to kink when GaAs growth was started.

Figure 2 shows results from two different growths. In figure 2a a standard InAs NP growth is shown seen directly from the side. In figure 2b the result from the same InAs NP growth procedure but followed by a GaAs growth step is shown. The GaAs growth step corresponded to approximately $0.5 \mu\text{m}$ of bulk growth and of this the first approximately two thirds were undoped GaAs and the last one third p-doped GaAs. It can immediately be seen that the

NP height as well as thickness have increased. The increase in thickness is however not uniform over the entire NP height. The non-uniformity is a consequence of the short distance between the individual NPs on the substrate together with the angle of more than 20° at which the Ga flux impinges on the substrate while it is rotated at 20 RPM. The bottom part of the InAs NPs because of this never gets covered with GaAs whereas the top part of the final NPs is pure GaAs.

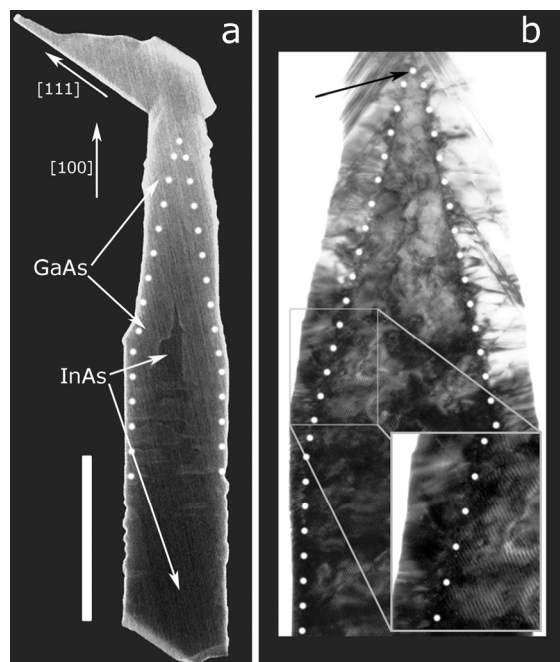


Figure 3 Both **a** and **b** are nanoplates from the growth shown in figure 2b. The white dotted lines are indicating how the InAs core is positioned under the GaAs layer. **a**, SEM image of a nanoplate removed from the growth substrate and placed on a SiO_2 surface. The GaAs (light gray color) can be seen to cover the nanoplate top and part of its sides. Scale bar, $1 \mu\text{m}$. **b**, Low resolution TEM image, the enlarged part clearly shows the Moiré interference pattern originating from the difference in lattice constants between InAs and GaAs.

When imaged with a Scanning Electron Microscope (SEM) the difference in contrast between GaAs and InAs made it possible to distinguish between parts of the NP covered with GaAs and parts without GaAs. In figure 3a an SEM image shows how the GaAs has grown on the top and the sides of the InAs NP, something which corresponds well with the known growth conditions described earlier.

Low resolution Transmission Electron Microscopy (TEM) on individual InAs NPs overgrown with GaAs revealed a Moiré interference pattern in areas where the InAs had been covered with GaAs. Moiré interference patterns appear when for instance two crystal lattices with different lattice constants are overlapping each other. In this case the lattice difference of 7 % between the InAs and

GaAs crystal lattices is what causes the Moiré interference pattern in the TEM image and hence shows the GaAs shell to be crystalline on the InAs NP surfaces.

3 CHARACTERIZATION OF INDIVIDUAL NANOPlates

We have chosen to investigate the properties of individual NP solar cells to obtain a thorough understanding of the individual building blocks before looking at large area solar cells.

The single InAs – GaAs core-shell NPs were harvested from their growth substrate by immersing it in isopropanol followed by a sonication for 15 s. A drop of the NP suspension was deposited on a highly doped Si substrate with a 500 nm insulating SiO_2 cap layer. The NPs were contacted with Ni/Au electrodes using an undercut bilayer resist patterned by electron beam lithography. To create a clean contact-nanoplate interfaces the devices were treated with 20 s of oxygen plasma ashing preceding metal evaporation. Care was taken to position the contacts such that the gold catalyst particle was covered with one of the contacts while the other contact was placed on the bottom InAs part of the NP. The final devices were characterized using a dc setup with a $1 \text{ M}\Omega$ resistance in series to protect the NP from damage due to excessive currents.

The inset in figure 4a is an SEM image of one of the characterized devices. The gold catalyst particle is covered with the Ni/Au contact together with a minimum amount of p-GaAs, the other contact is placed on the bottom n-type InAs part of the NP. Four devices were contacted in this way and all showed similar diode behavior in the dark as the device data shown in figure 4a. The photovoltaic properties of the NP diodes were characterized using a non-calibrated light source adapted from an optical microscope. The illumination was supplied by a 150 W halogen light bulb and through illumination light guides directed to the sample being characterized. The intensity of the illumination was varied from almost nothing and up to maximum intensity. How the illumination source compares with a standard 1-sun AM 1.5G illumination source has not been tested. I-V curves measured at different light intensities are plotted in figure 4b and show the I_{sc} and V_{oc} values increasing with increasing light intensity as expected. At maximum illumination the short-circuit current was 710 pA and the open-circuit voltage 52 mV. Plotting $\ln(I_{\text{sc}})$ vs. V_{oc} gives the expected linear relation for the four largest illumination intensities. All measurements were carried out with a $1 \text{ M}\Omega$ resistance in series.

The total NP area illuminated is approximately $1.2 \mu\text{m}^2$ while an estimate of the area containing the n-p junction is $0.5 \mu\text{m}^2$. Based on these values the maximum short-circuit current density is 142 mA cm^{-2} when using the estimated n-p junction size and 59.2 mA cm^{-2} using the size of the total exposed area. These large values should of course be seen with respect to the unknown intensity of the illumination source. The large values however indicate that the PV

properties of the core-shell InAs – GaAs NPs could become excellent if the open circuit voltage is improved.

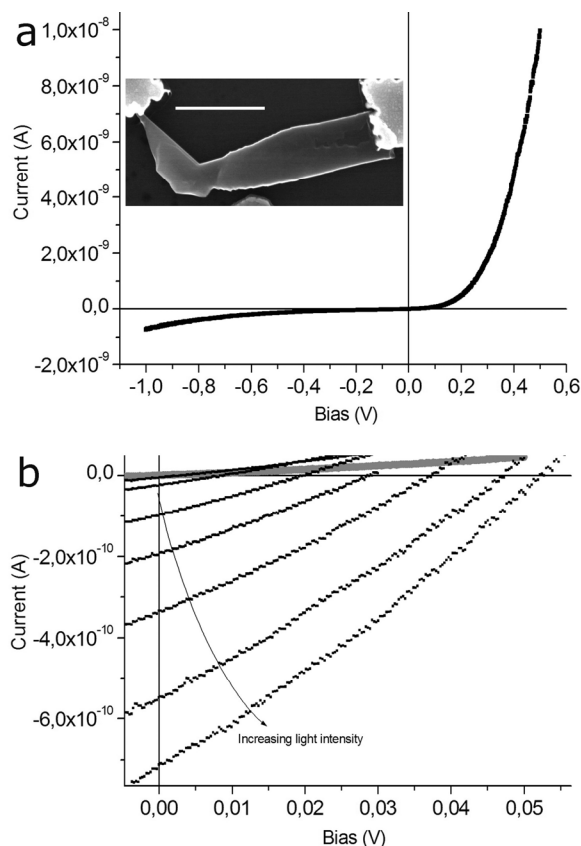


Figure 4 a, I-V characteristics measured in the dark on a nanoplate from the growth shown in figure 2b and 3. Inset: SEM image of the sample characterized, scale bar 1 μm . **b**, Current vs. bias measured for different illumination intensities, the gray curve is measured in the dark. The sample was illuminated using a non-calibrated light source. All measurements were done with a 1 M Ω resistance in series.

4 SUMMERY AND CONCLUSION

The NP geometry offers the possibility of perfect single crystal growth on non-lattice matched substrates. The substrate surface is intrinsically highly antireflective because of the NP geometry. In addition to the antireflective property each of the individual NP solar cells offer the advantage of a short distance from the point of exciton generation to exciton separation at the build in n-p junction. Compared to nanowire based solar cells the individual NPs furthermore have a possibility for an improvement in series resistance as well as in the surface to volume ratio which could minimize loss caused by non-radiative surface recombination. Furthermore the geometry of the NP growth with all NPs standing perpendicular from the (100) substrate surface – each with a gold particle on its top – makes the system highly suitable for post growth processing and sample fabrication.

We have demonstrated that it is possible to combine the InAs NPs with a crystalline GaAs layer. The very first measurements on individual n-InAs – p-GaAs NP core-shell structures show a significant PV effect scaling with illumination intensity.

Ongoing research is aimed at improving the open-circuit voltage by adding an n-GaAs layer immediately after the n-InAs growth thereby making a core-shell structure containing an n-p junction inside the GaAs. Further work will also focus on surface passivation by covering the n-p junction with an AlGaAs layer.

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REFERENCES

- [1] G. Beaucarne *et al.*, Epitaxial thin-film Si solar cells, *Thin Solid Films*, 511 – 512, 533 – 542, 2006.
- [2] J. J. Schermer *et al.*, Thin-film GaAs Epitaxial Lift-off Solar Cells for Space Applications, *Prog. Photovolt: Res. Appl.*, 13, 587–596, 2005.
- [3] B. M. Kayes, H. A. Atwater and N. S. Lewis, Comparison of the device physics principles of planar and radial p-n junction nanorod solar cells, *J. Appl. Phys.* 97, 114302, 2005.
- [4] B. Tian *et al.*, Coaxial silicon nanowires as solar cells and nanoelectronic power sources, *Nature*, 449, 885, 2007.
- [5] L. Tsakalakos *et al.*, Silicon nanowire solar cells, *Appl. Phys. Lett.*, 91, 233117, 2007.
- [6] M. D. Kelzenberg *et al.*, Photovoltaic Measurements in Single-Nanowire Silicon Solar Cells, *Nano Lett.*, 8, 710 – 714, 2008.
- [7] M. Aagesen *et al.*, Molecular beam epitaxy growth of free-standing plane-parallel InAs nanoplates, *Nature Nanotech*, 2, 761-764, 2007.
- [8] K. A. Dick *et al.*, Failure of the vapour-liquid-solid mechanism in Au-assisted MOVPE growth of InAs nanowires, *Nano Lett.* 5, 761-764, 2005.
- [9] Y. Huang *et al.*, Improved broadband and quasiomnidirectional anti-reflection properties with biomimetic silicon nanostructures, *Nature Nanotech*, 2, 770-774, 2007.
- [10] Measurements of the reflectance properties of an InAs nanoplate forest are presently being done at the National Yang Ming University in Taipei.
- [11] R. D. Schaller, J. M. Pietryga and V. I. Klimov, Carrier Multiplication in InAs Nanocrystal Quantum Dots with an Onset Defined by the Energy Conservation Limit, *Nano Lett.* 7, 3469-3476, 2007.