Interfaces in nanoscale photovoltaics
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Citation for published version (APA):
Au-Cu$_2$O core-shell nanowire photovoltaics

The electrical properties of semiconductor nanowires strongly depend on the realized junction and electrode geometry (axial vs. radial). For radial charge carrier extraction the required minority carrier diffusion length is on the order of 10-100 nm and therefore strongly relaxed compared to bulk solar cells. To this end, we study metal-semiconductor core-shell nanowires, which have been predicted to show even better optical absorption than solid semiconductor nanowires, with the additional advantage of a local metal core contact for radial charge carrier extraction. We fabricate and analyze such a geometry using a single Au-Cu$_2$O core-shell nanowire photovoltaic cell as a model system. Spatially-resolved photocurrent maps reveal that although the minority carrier diffusion length in the Cu$_2$O shell is less than 1 µm, the radial contact geometry with the incorporated metal electrode still allows for photogenerated carrier collection along an entire nanowire. Current-voltage measurements yield an open-circuit voltage of 600 mV under laser illumination and a dark diode turn-on voltage of around 1V. This study suggests the metal-semiconductor core-shell nanowire concept could be extended to low-cost, large-scale photovoltaic devices, but stresses the importance of careful interface engineering.
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Figure 2.1: Schematic drawing of the metal-semiconductor core-shell geometry. Two devices are electrically connected to electrodes and a laser beam (bright blue) is incident on one of them. The Au electrode contacts the Au core while a Ti electrode contacts the Cu$_2$O shell (red) only at the end (top left) or along most of the length via an additional thin Ti pad (center). The inset shows a cross section of the device geometry. The incident light creates electron-hole pairs (e-, h$^+$), which are extracted via the shell and the core, respectively.

2.1 Introduction

2.1.1 Cu$_2$O as photovoltaic material

Cuprous oxide (Cu$_2$O) is an earth abundant and non-toxic semiconductor that can be grown using many different fabrication methods including evaporation and sputtering. Its direct band gap of $\sim$2.0 eV provides the potential to reach power conversion efficiencies of up to 20%. This combination of abundance, simple fabrication and efficiency potential has therefore made Cu$_2$O a popular choice for thin-film solar cell research since the early days of photovoltaics.[29][30] Assuming that excellent surface passivation can be achieved, thin-film solar cells can in general even reach higher open-circuit voltage ($V_{oc}$) values than their bulk counter parts due to shorter charge carrier extraction paths and hence reduced bulk recombination.[31] Cu$_2$O has a band gap that is close to the ideal value for a silicon-based tandem solar (1.7-2.0 eV), making it a candidate for high efficiency photovoltaics.[32–34] Recently, several groups have focused on the interface properties of Cu$_2$O and were able to increase the $V_{oc}$ up to 1.2 V by using interfacial layers, such as Ga$_2$O$_3$ and ZnO, combined with transparent conductive oxides (TCOs) as top contacts.[35–43]
2.1.2 Metal-semiconductor core-shell nanowire

Here we utilize a metal-semiconductor core-shell geometry to fabricate a single horizontally aligned Au-Cu$_2$O nanowire photovoltaic cell. Such a structure has several potential advantages. The thin semiconductor shell in direct vicinity of the metal core electrode allows for facile extraction of photogenerated carriers, even in materials with short minority carrier diffusion lengths. The radial core-shell geometry has already proven useful in semiconductor nanowire photovoltaics and we expect even better charge carrier extraction in our geometry where photocarriers are injected into the metal immediately.[44–47] Another previously demonstrated advantage of semiconductor nanowires is their high absorption cross section, which can exceed the geometrical one.[23, 48, 49] The metal-semiconductor core-shell structure can lead to even higher absorption, while further reducing the amount of semiconductor.[50] Several research groups have already utilized metal-semiconductor core-shell nanospheres or rods for plasmon mediated charge carrier dynamics for photovoltaics and photocatalysis. In these examples however, semiconductor materials were not used for the visible light absorption or materials were suspended completely in solution.[51–57] Here we fabricate and test a single metal-semiconductor core-shell nanowire photovoltaic cell, utilizing Au for the core and Cu$_2$O for the shell.

2.2 Results

To fabricate the core-shell nanowires, we followed a procedure developed by Sciaccia et al. for solution-based synthesis of metal (Ag, Au or Cu) core Cu$_2$O shell nanowires.[58] The metal nanowires were synthesized using the polyol process and subsequently coated with a Cu$_2$O shell at room temperature in aqueous solution, adapting a protocol originally developed for core-shell nanoparticles.[59, 60] This specific Cu$_2$O synthesis route was chosen over other methods to produce Cu$_2$O nanowires because it allowed for epitaxial growth on metal nanowires suspended in solution.[61, 62] Photoluminescence (PL) measurements showed a peak near 1.9 eV, similar to what has been observed in pure-phase, bulk Cu$_2$O.[58, 63]

Figure 2.1 shows a schematic of a single nanowire photovoltaic cell illuminated by a laser beam. As can be seen in the drawing, the Cu$_2$O shell has two contacts: one that collects photogenerated holes and one that is selective for photogenerated electrons. One simple and effective method for inducing this carrier selectivity is to use metal contacts with different work functions such that one metal makes an Ohmic contact to the Cu$_2$O and the other a Schottky junction.[19]

Here we have chosen Au as the metal nanowire core because it has a large work function (~ 5.4 eV; similar to that of Cu$_2$O) and makes an Ohmic contact to Cu$_2$O. Furthermore Au has a high chemical stability, low lattice mismatch with Cu$_2$O (~ 4%) and a simple nanowire synthesis route.[58, 64–67] As the Schottky contact we have chosen Ti, which has a low work function (~ 4.3 eV), excellent adhesion to many materials and a stable surface oxide.[68]
Figure 2.2: Single nanowire photovoltaic with radial charge carrier collection.
(a) False-colored SEM image of a nanowire (yellow) connected between Ti (blue) and Au (red) contacts. (b) Optical reflection image. (c) Photocurrent map with an incident laser power of 42 $\mu$W, polarization perpendicular to the nanowire axis, a spot size of $\sim 1 \mu$m, and illumination wavelength of 405 nm. The local photocurrent collection next to the Ti contact is clearly visible.

To fabricate such samples, we started with Si$_3$N$_4$ covered Si substrates with evaporated Au electrodes. The core-shell nanowires were contacted using electron beam lithography and metal evaporation. The optical characterization was conducted with a tunable laser source in the range of 405 nm - 750 nm. The light was focused through an objective lens to a spot size of $\sim 1 \mu$m onto the electrically connected single nanowire photovoltaic cells. The details of the device fabrication and characterization can be found in the supporting information.

Figure 2.2(a) shows a colored scanning electron microscope (SEM) image of a typical single nanowire photovoltaic cell (yellow). The reflection map in Figure 2.2(b) shows the diagonal orientation relative to the parallel contact pads. Figure 2.2(c) shows photocurrent generation of up to 350 pA under 42 $\mu$W laser illumination at $\lambda = 405$ nm. The localized charge carrier collection only occurs near the Ti contact finger, where the Schottky junction induces a built-in electric field, such that the minority charge carriers do not have to travel long distances to get extracted. Due to the optically thick Ti contact we do not expect any substantial contribution to the photocurrent from the Cu$_2$O regions under the contact. This photocurrent collection localized only close to the Ti contact suggests that the minority carrier diffusion length is less than or equal to the beam spot size of $\sim 1 \mu$m, consistent with reported values for Cu$_2$O synthesized by different methods.[69, 70]

Despite the excellent crystallinity and epitaxial shell growth in these core-shell nanowires, the high surface and contact areas could lead to even shorter minority carrier diffusion lengths, as these are known to be sources of increased non-radiative recombination in bulk solar cells.[19] Future studies involving thin interfacial spacing layers and surface passivation are needed to quantify the importance
2.2 Results

![Figure 2.3: Extended radial charge carrier collection.](image)

(a) Schematic of single nanowire with employed Ti pad. (b) Colored SEM image of a nanowire connected between Ti (blue) and Au (red) contacts and partially covered by a 10 nm thin Ti pad (blue). (b) Reflectance map. (c) Photocurrent map with an incident laser power of 7 µW, polarization perpendicular to the nanowire axis, a spot size of 1 µm, and illumination wavelength of 405 nm. The photocurrent collection is extended by the presence of the Ti pad.

of these effects and our single core-shell nanowire geometry provides a perfect platform for such studies.

To directly probe the importance of the radial built-in field and carrier collection mechanism, we have compared the above results to the case where a 10 nm thin Ti pad covers approximately 2/3 of the nanowire (Figure 2.3(a)). This arrangement is closer to a realistic large-scale device, where the whole nanowire would be covered with an additional contact (either a transparent conductive oxide or a continuous thick metal layer with illumination through a transparent substrate). Figure 2.3(b) shows a false-colored SEM image of the device, with a Ti pad (blue) on top of the nanowire (yellow), which is connected between a Ti (blue) and an Au (red) contact. Figure 2.3(c) shows the reflection image and Figure 2.3(d) the respective photocurrent map under 7 µW laser illumination at λ = 405 nm, which reveals photocurrent collection from an extended elongated area. This photocurrent profile demonstrates charge carrier collection from the nanowire along the entire length covered by the Ti pad. This supports the idea that charge carriers generated by light passing through the 10 nm Ti pad can be separated and collected at the metal core and the Ti top contact. The maximum photocurrent is around 25
Figure 2.4: Spectral response of single nanowire. (a) Reflectance map of the nanowire at 405 nm. (b-e) Responsivity maps at laser wavelengths of (b) 405 nm, (c) 520 nm, (d) 620 nm and (e) 700 nm. The responsivity was obtained by first subtracting the background values and subsequently dividing by the incident laser power, to facilitate comparison. In all cases the laser polarization was perpendicular to the nanowire axis. The spatial shift of the photocurrent with increasing wavelengths is due to chromatic aberration of the objective lens and drift in the mechanical stage.

...times smaller than in the axial collection case shown in Figure 2.2, which can be attributed to the reduction in incident power from 42 to 7 μW and the substantially reduced absorption in the wire due to the Ti pad. The responsivity (photocurrent after background subtraction divided by the incident laser power) is only lowered by a factor of four by the Ti pad. These results prove the utility of this concept: photocurrent collection can take place along the whole length of the nanowire, even with materials that have very short minority carrier diffusion lengths.

To investigate the core-shell nanowire spectral response, we map the responsivity under 405 nm, 520 nm, 620 nm and 700 nm laser illumination (Figure 2.4(b)-2.4(e), respectively). The polarization was perpendicular to the nanowire axis for all
measurements, which is the polarization that supports plasmon resonances. In the other polarization we observed weaker currents. Currently, we can not distinguish between charge carrier generation due to band-to-band absorption in the Cu₂O and plasmon-mediated transfer mechanisms, such as resonance energy transfer, direct energy transfer and hot carrier injection.[51, 71–75]

The strong reduction in photocurrent for $\lambda = 700$ nm is consistent with the literature value of the optical band gap (1.95 eV or 635 nm) and our own single nanowire PL measurements.[58, 76] However, absorption in the Ti pad as well as variations in the optical resonances must be taken into account to quantitatively explain the observed results. Finally, we show single nanowire current-voltage (I-V) measurements in the dark and under laser illumination (Figure 2.5). This nanowire device, which did not contain an extended Ti pad showed clear rectification behavior with a turn on voltage of 1 V in the dark. Under laser illumination with 42 µW power at 405 nm, an $I_{sc}$ of -300 pA and a $V_{oc}$ of 600 mV were observed.

These results clearly demonstrate that single metal-semiconductor core-shell nanowires function as photovoltaic cells. The photocurrent increases at higher reverse voltages and reaches reverse break down before saturating. We attribute this slope to a higher photogenerated carrier collection efficiency at larger reverse bias voltages due to an increased depletion region. Furthermore, we observe a substantial charge carrier extraction barrier and hence s-shaped I-V curve, which is a well-known phenomenon that can be attributed to accumulated space charges at the material interfaces or a non-ideal Ohmic contact.[77–80] This observation
can be explained by the non-optimized metal-semiconductor interfaces, which are likely to induce recombination-active trap states and accumulated space charges. We note that the photocurrent under the AM 1.5G spectrum was below the detection limit (≈5 pA) of the source measure unit used and therefore did not allow the measurement of our devices under the full solar spectrum. The low photocurrent can partially be explained by the localized Schottky region close to the optically thick Ti contact which is mostly inaccessible for the incident light. Only a small fraction at the edge of the contact can contribute to the photocurrent.

2.3 Conclusions

We have realized for the first time a single metal-semiconductor core-shell nanowire photovoltaic cell. We measured photocurrent maps on individual Au-Cu$_2$O core-shell nanowires, showing charge carrier collection via a Schottky Ti contact on the surface, with the Au core being utilized as an Ohmic contact. The spectral response is consistent with a band gap of ≈2 eV. We show that a $V_{oc}$ of 0.6 V and $I_{sc}$ of 300 pA can be achieved without any detailed contact optimization, however only at a very high illumination intensity. By depositing a thin (10 nm) Ti layer over the wire, we clearly demonstrate that two conductive radial metal contacts allow for radial photogenerated carrier collection in semiconductors with short minority carrier diffusion lengths <1 μm.

We observe a strongly s-shaped I-V curve, which is indicative of a charge carrier extraction barrier at one of the two metal interfaces. As also reported in previous literature, it is possible that a redox reaction under the Ti contact converts the Cu$_2$O to TiO$_2$ and Cu at the interface.[81] Furthermore, the direct vicinity of a metal and a semiconductor is well known to cause metal-induced band gap states in the semiconductor which can lead to mid-bandgap Fermi level pinning and hence extraction barriers.[19]

Therefore, we would expect better performance if appropriate interfacial passivation layers could be incorporated, as already demonstrated not only with Cu$_2$O but also other material systems, such as silicon in Chapter 3 of this thesis.[38, 82, 83]

 Furthermore, we would expect a further improvement in the device performance for a reversed contact geometry, allowing for a Schottky/metal-insulator-semiconductor junction along the whole length of the metal core. However, the solution growth of a passivating insulator between the metal and the semiconductor and a core-shell structure with a low work function core metal have not been realized so far.[58]

While the limitations discussed above explain the overall low photovoltaic performance of our device, they do not present insurmountable obstacles on the way to high efficiency metal-semiconductor core-shell nanowire solar cells. We note that the metal-semiconductor core-shell nanowire geometry is not limited to the materials used for this proof-of-concept study. An ideal structure would employ low cost metals with appropriate interfacial layers, replacing Au and Ti.
2.4 Supplemental information

2.4.1 Fabrication

Au-Cu$_2$O core-shell nanowires were prepared in solution as described in detail by Sciacca et al.[58] The nanowires had a Au core diameter of ~ 50 nm and a Cu$_2$O shell thickness of ~ 30 nm and were then dropcast onto 3 x 3 mm$^2$ low-stress LPCVD-Si$_3$N$_4$ (~ 300 nm) covered Si chips with evaporated Au electrodes (~ 150 nm). The core-shell nanowires were contacted using a 2 or 3 - step electron beam lithography and metal evaporation scheme. The Cu$_2$O shell was locally etched for 1-2 min with 0.1 mM sulfuric acid prior to Au evaporation (~ 200 nm) for the core contact, while the Ti contact (~ 200 nm) was directly evaporated on the Cu$_2$O shell. For the experiments with the 10 nm thin Ti pad, an additional resist exposure and evaporation step was conducted prior to the thick Ti shell contact finger formation. For the multi-step electron beam lithography process, pre-patterned alignment markers on the substrates were used to align subsequent exposure patterns to the correct nanowire and electrode locations.

2.4.2 Characterization

The optical characterization was conducted with a home-built laser setup. A super-continuum laser (Fianium WL-SC390-3) was sent through an acousto-optic tunable filter (Fianium AOTF-V1-N1) to select wavelengths in the range of 410 nm - 750 nm. The polarization was controlled with a $\lambda/2$ plate (Thorlabs) before the light was focused through an objective lens (Mitutoyo M PLAN APO NUV 50X) to a spot with waist $w_0$ ~ 600 nm on the electrically connected single nanowire photovoltaic cells. The substrate was mounted on and wire bonded to a custom designed printed circuit board to facilitate the electrical connections. Then the substrate was scanned relative to the focused beam position with a 3-axis piezoelectric stage (Piezosystem Jena Tritor 400 CAP). The photocurrent was measured with an Agilent B2902A source-measure unit, while simultaneously recording the reflected and incident beam power (both measured with Thorlabs amplified photodiodes model PDA100A) to correlate the current with the position of the laser spot and to normalize to variations in the laser power during a single measurement. The absolute beam power was measured using a calibrated silicon photodetector (Newport model 818-UV-L). The I-V curves were also measured with the source-measure unit (Agilent B2902A).