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Fabrication and characterization of abrupt TiO$_2$–SiO$_x$ core-shell nanowires by a simple heat treatment

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Three dimensional hierarchical metal oxide nanostructures, like TiO$_2$ nanowire arrays, have attracted great attention for electrochemical energy conversion and storage applications. The functionality of such devices can be further enhanced by adding a nanowire shell with a different stoichiometry or composition compared to the core. Here, we report an approach with a facile heat treatment at 1050 °C, which allows the fabrication of rutile TiO$_2$–SiO$_x$ core-shell nanowire arrays on silicon substrates. Our detailed electron microscopic investigation shows that this method is able to cover hydrothermally grown rutile TiO$_2$ nanowires with a uniform shell of several nanometers in thickness. Moreover, the treatment improves the quality of the rutile TiO$_2$ core by removing lattice defects, introduced from the hydrothermal growth. Electron energy loss spectroscopy reveals that the homogeneous shell around the TiO$_2$ core consists of amorphous SiO$_x$ and does not form any intermediate phase with TiO$_2$ at the interface. Thus, the properties of the TiO$_2$ core are not affected by the shell, while the shell suppresses undesired electron back transfer. Latter leads to performance losses in many applications, e.g., dye sensitized solar cells, and is the main reason for a fast degradation of devices incorporating organic materials and TiO$_2$. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license.

TiO$_2$ nanowires (NWs) combine the versatility of TiO$_2$ with the unique properties of 1D nanostructures, e.g., directed electron path and large surface area. Thus, TiO$_2$ NWs are a promising material for solar cells, photocatalysis, photocatalytic pollutant degradation, gas sensing, and UV shield. Most applications rest upon the UV-absorption and its associated charge generation and separation. However, these charges might be unintentionally transferred in opposite direction to the band alignment. This electron back transfer can lead to efficiency losses and a short life time of the device. To avoid photo degradation of functional organic materials and high recombination rates in, e.g., hybrid solar cells, the interfacial recombination dynamics have to be suppressed. Hence coating of TiO$_2$ nanomaterials by an insulating material, e.g., Al$_2$O$_3$ or SiO$_2$, has attracted a lot of interest.

SiO$_2$ coatings on TiO$_2$ are usually obtained by a sol-gel process. This process is suitable to coat the TiO$_2$ with a uniform shell, but the shells are 20-200 nm thick. In the last years, other synthesis methods for the SiO$_2$ coating, such as chemical vapor deposition and hydrothermal flow reaction, have been developed. Another possibility to produce TiO$_2$–SiO$_x$ core-shell NWs is the heating of multilayered substrates, but the resulting NWs are not well aligned and the shell is thick and rough.

In this study, TiO$_2$–SiO$_x$ core-shell NW arrays were prepared by a heat treatment of TiO$_2$ NWs, which were hydrothermally grown on Si substrates. Uniform coating of TiO$_2$ NWs with a 3-4 nm thick shell is achieved by this simple and facile approach. The core-shell NW is investigated by electron microscopy to study the morphological changes, the structure of the shell and the local changes across the TiO$_2$–SiO$_x$ interface.

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Polycrystalline rutile TiO$_2$ films that act as seed layers for the hydrothermal NW growth were obtained by a direct current sputter deposition process. 40 nm Ti was deposited on a polished, boron-doped, p-type (100) silicon with a native oxide layer and then oxidized in a rapid thermal processing oven at 850 °C for 2 h. For the growth of the NW arrays, these films were placed in a Teflon liner filled with a mixture of 20 ml 14.5% HCl and 350 μl titanium(IV) butoxide and autoclaved for 3 h in an oven at 180 °C. The as-prepared NW arrays were annealed at 1050 °C in an evacuated (p ≈ 1.6 mbar) rapid thermal processing oven for 2 h.

The morphology of the NW arrays was investigated by scanning electron microscopy (SEM) with a Zeiss CrossBeam 1540XB field emission SEM operated at 5 kV using an in-lens detector. Detailed information about the atomic structure and the elemental distribution of TiO$_2$–SiO$_x$ core-shell NWs was obtained by transmission electron microscopy (TEM). Conventional bright field TEM and selected area electron diffraction was performed with a Phillips CM20 operated at 200 kV. An aberration-corrected FEI Titan Themis 60-300 TEM operated at 300 kV was used for scanning TEM (STEM) and, in combination with energy dispersive X-ray spectroscopy (EDS) or electron energy loss spectroscopy (EELS), for elemental analysis with high spatial resolution.

SEM images in Fig. 1 show that the morphology of the NWs changes during the heat treatment, but the thickness of the NW is constant within the error bar (as-grown: 130 ± 27 nm, annealed at 1050 °C: 137 ± 27 nm). These NWs grow along the [001] direction and the {110} surfaces are the main facets, as it was also observed in a previous study. Significant changes occur at the NW top and at the surfaces of the NW. The NW top in the as-grown state has a fibrous structure, which is typical for hydrothermally grown rutile TiO$_2$. For our synthesis conditions, this fibrous structure is caused by a V-shaped defect cascade and was recently identified as recombination source. The origin of the fibrous structure for our NWs is different to the one reported for branched TiO$_2$ rutile mesocrystals. The latter were formed by self-assembly of nanofibers which were precipitated in solution in the initial stage. The heat-treatment performed in the present work removes the nanofiber structure and forms a uniform NW tip with pyramidal faceted shape. The facet type and the core-shell structure itself cannot be identified by SEM. The steps on the surfaces parallel to the [001] growth direction of the NW, which are visible in the as-grown state, are also removed after the heat treatment and new ones form perpendicular to the original ones. The resulting NWs have smooth {110} surfaces, which are connected by small {100} surfaces. The corresponding cross-sections of the heat-treated NW parallel to the {110} and {001} planes are shown in the pictograms in Fig. 1(b). The heat-treated NWs are much closer to the thermodynamical equilibrium shape proposed by Goldschmidt than the as-grown NWs. Deviating from this ideal shape, steps perpendicular to the growth direction occur.

TEM investigations confirm these changes in morphology and give insight into which facets were formed. Figure 2(a) is a bright field TEM image of a heat-treated NW and the selected area electron diffraction pattern of the NW, which corresponds to rutile TiO$_2$ acquired along the [1-10] zone axis, confirming the [001] growth direction. Thus, no phase transformation takes place during the annealing. This is in good agreement with the phase diagram of bulk TiO$_2$, which reveals that rutile

![FIG. 1. Top view SEM image of (a) as-grown TiO$_2$ NW array and (b) TiO$_2$ NW array after the heat treatment at 1050 °C in vacuum. The pictograms next to the images show a simplified cross-section of the NW parallel (upper one, {110} cutting plane) and perpendicular (lower one, {001} cutting plane) to the NW growth direction.](image-url)
is the thermodynamically most stable crystal modification.\textsuperscript{14} In comparison to as-grown NWs and NWs annealed at lower temperatures (e.g., 500 °C),\textsuperscript{15} the TiO\textsubscript{2} core of the NWs annealed at 1050 °C is free of lattice defects and does not incorporate any voids or other structural defects. The bright field STEM image in Fig. 2(b) shows that the \{110\} surfaces parallel to the [001] growth direction and close to the NW tip are interrupted by several steps. These steps are faceted and represent the \{111\} surface. At the NW top, the \{111\} surfaces built the pyramidal tip, which is slightly rounded. Similar morphologies have been observed for other rutile TiO\textsubscript{2} nanostructures.\textsuperscript{16} From the bottom to the top, the NW is covered by a 3.7 ± 1.6 nm thick, amorphous shell [Fig. 2(c)]. Moiré patterns in bright field STEM image prove a complete encapsulation of the NW by the shell [Fig. 2(b)]. The shell even covers defects at the \{110\} surface of the rutile TiO\textsubscript{2} core (highlighted in S1 of the supplementary material). As shown in the elemental map, obtained by EDS analysis [Fig. 2(d)], the shell consists of Si and O, indicating the formation of SiO\textsubscript{x}. The core is pure TiO\textsubscript{2} (Ti:Si 1:0.15), as the amount of Si detected corresponds to the 3-4 nm thick SiO\textsubscript{x} shell that homogenously covers the NW and thus also contributes to the EDS signal. We estimated the relative amount of oxygen in the shell using the EDS data, although the value is prone to a large error due to the low fluorescence yield of light elements and the absorption of low energy X-rays in the detector and the sample. Assuming TiO\textsubscript{2} stoichiometry for the core and the same error in the analysis of oxygen for the shell, the Si:O ratio is roughly 1:1.7.

The interface between the rutile TiO\textsubscript{2} core and the amorphous SiO\textsubscript{x} shell is analyzed by EELS. For the core (9.8-2.2 nm away from the interface), the Ti-L\textsubscript{2,3} and the O-K edge show the typical energy loss near edge structure (ELNES) of rutile TiO\textsubscript{2}.\textsuperscript{17} The peaks of the Ti-L\textsubscript{2,3} split into a duplet of t\textsubscript{2g} and e\textsubscript{g} because of the tetragonal distortion of the [TiO\textsubscript{6}]\textsuperscript{8-} octahedra in rutile TiO\textsubscript{2}. This t\textsubscript{2g}-e\textsubscript{g} splitting also affects the O-K edge, which has a duplet with two main peaks at 531 eV and 534 eV. This duplet arise from the hybridization of the O 1s orbitals with the Ti 3d orbitals. The broad peak at
537-546 eV is formed by three bands, which correspond to transitions from the hybridized orbitals of the O 2p orbitals with the s and p orbitals of the bonding partner (e.g., 4s and 4p for Ti). The Ti-L$_{2,3}$ edge changes close to the interface between the core and the shell (the outer 2.2 nm of the TiO$_2$). The edge onset is shifted to lower energy losses, the peak width is decreased, and no t$_{2g}$-e$_g$ splitting is resolved. These changes arise from substoichiometric TiO$_x$. At the surface, as the Ti-L$_{2,3}$ edge of as-grown NWs shows the same changes at the surface (see S2 of the supplementary material), these changes are independent of the heat treatment and shell formation. The intensity of the Ti-L$_{2,3}$ edge decreases close to the surface, but the intensity ratio between the Ti-L$_{2,3}$ peak and the O-K duplet remains constant (see S3 of the supplementary material). Thus, no extended area (>1 nm) comprising a TiO$_2$–SiO$_x$ solid solution with Ti–O–Si bonds is formed in the interface region. In the shell, no Ti can be detected and the shape of the O-K edge changes significantly. The duplet (531 eV and 534 eV) disappears and the edge-onset is shifted to higher energy losses. The O-K edge for the shell has an edge onset of 534 eV and decays faster compared to the broad peak (537-546 eV) of the O-K edge in the TiO$_2$ core.

The Si-L edge (see S4 of the supplementary material) is detected all over the nanowire, as it is completely covered by the shell, but has a higher intensity in the outer region where the TiO$_2$ core is absent. Neither the edge-onset nor the ELNES of the edge changes at the interface. Figure 3(d) exemplarily shows an EEL spectrum of the Si-L edge, which was taken from the shell without the TiO$_2$ core. Starting with an edge onset of 103.8 eV, the edge consists of three distinct energy loss regions. In the ELNES two sharp and a broad peak arise. The sharp peaks result from Si 2p $\rightarrow$ 3s and Si 2p $\rightarrow$ 3d transitions. The delayed maximum starts at higher energy losses. It results from inner well resonances and appears frequently in Si compounds that are tetrahedrally coordinated by strong electronegative ligands like O. The extended energy loss fine structure starts above 150 eV.

![Image](image_url)
but its oscillations are weak and overlap with the Si-L\textsubscript{1} edge, which has a maximum at 157.2 eV. The second edge shown in Fig. 3(d) is a reference spectrum of amorphous SiO\textsubscript{2}. All features are visible for both edges, but the first peak in the ELNES, which arises from a 2p $\rightarrow$ 3s transition, has much lower intensity in the shell. In the literature, such shape of the Si-L\textsubscript{2,3} edge is assigned to the native oxide formed on Si-wafers under ambient conditions.\textsuperscript{23} It is proposed that the native oxide is amorphous SiO\textsubscript{x}, whereas our EDS measurements on the shell show a SiO\textsubscript{1.7} stoichiometry. Thus, the reduced intensity in the first peak, indicating less 2p $\rightarrow$ 3s transitions, might result not only from a slight oxygen deficiency but also from additional electrons in the 3s states.

Our results show that a high temperature treatment of hydrothermally grown TiO\textsubscript{2} NWs on a Si substrate is suitable to produce TiO\textsubscript{2}–SiO\textsubscript{x} core-shell NWs with a single-crystalline, defect-free, rutile TiO\textsubscript{2} core. Such 1D TiO\textsubscript{2} has advantages compared to the as-grown TiO\textsubscript{2} NWs, which have numerous defects and tend to split up in nanofibers.\textsuperscript{9} The originally present free space between these fibers (around 14% of the NW volume) is compensated by the faceting, which gradually thins the NW towards the top of the annealed NW. The volume loss of the annealed NWs is around 13%, which matches with the free volume between the nanofibers. Our analysis indicates that the removal of the defects in the TiO\textsubscript{2} core occurs first and is completed before the shell covers the upper, faceted part of the NW. Otherwise, one would expect cracks in the shell next to the kinks or SiO\textsubscript{x} inclusions in the TiO\textsubscript{2} core. Neither can be detected in the TiO\textsubscript{2}–SiO\textsubscript{x} core-shell NWs. This conclusion is in accordance with previous results, which showed that the defect removal in TiO\textsubscript{2} NWs happens within seconds, as soon as a critical temperature is reached.\textsuperscript{15}

After the changes in the TiO\textsubscript{2} core, the SiO\textsubscript{x} shell is formed. As the vacuum in the heating chamber is not low enough to evaporate Si at 1050 °C,\textsuperscript{25} the shell has to be formed by diffusion of Si along the sidewalls of the NWs. High mobility of Si at temperatures far below the Si melting point was shown before.\textsuperscript{26} Si atoms of the substrate pass the TiO\textsubscript{2} seed layer most likely through the grain boundaries and diffuse along the contamination free sidewalls of the NW by a surface diffusion process. Due to the small concentration gradient we expect slow diffusion and the velocity of the shell growth is slow. The high temperature during the process is sufficient to avoid the formation of Ti–O–Si bonds\textsuperscript{27} and consequently, the Si atoms are free to move, which enables formation of a uniform shell. The SiO\textsubscript{x} is formed after removing the samples from the oven in a process similar to the formation of native oxide layers on Si wafers.\textsuperscript{28}

In summary, we presented a method to cover TiO\textsubscript{2} NWs uniformly with a 4 nm thick SiO\textsubscript{x} shell by a thermal treatment at 1050 °C. Besides the shell formation, this treatment heals all defects present in the TiO\textsubscript{2} core of the as-grown NWs. The formed material is a core-shell material without intermixing between both materials. Therefore, the functionality of TiO\textsubscript{2} is preserved, while unwanted surface reactions, like recombination in solar cells or degradation of organic material, can be minimized. In future, this procedure can be adopted to other photoactive metal oxides such as ZnO, and it can be used to produce Si shells around, e.g., TiO\textsubscript{2}, if the material is handled in an oxygen-free atmosphere.

See supplementary material for detailed experimental descriptions, additional images and EEL spectra.

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