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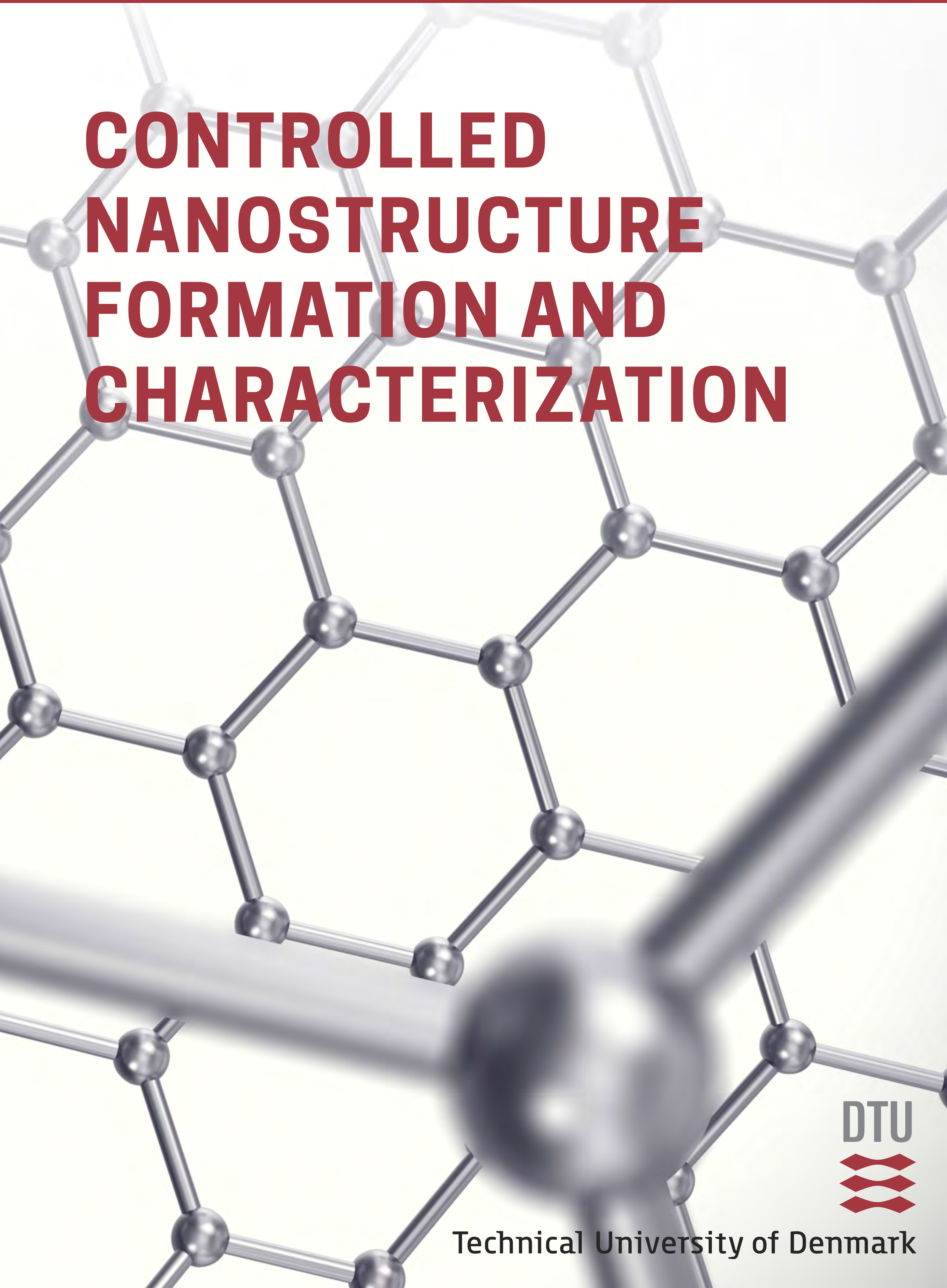

CONTROLLED NANOSTRUCTURE FORMATION AND CHARACTERIZATION

DTU
Technical University of Denmark

Controlled nanostructure formation and characterization

Professor Jakob Birkedal Wagner, Head of Nanocharacterization Section at DTU Nanolab, Technical University of Denmark, provides an in-depth look at controlled nanostructure formation and characterization and how these can be looked at with electron beam based microscopy and spectroscopy

Nanoscale fabrication and nanoscale characterisation are entangled to a large degree. Nanofabrication allows for the synthesis and formation of tailor-made materials and structures with properties not necessarily found naturally on Earth, bringing value to the society in terms of higher energy efficiency, higher sustainability, increased living standards via advanced tools for medical treatment to name a few.

The fabrication or synthesis of nanostructured materials relies on top-down or bottom-up processes. In order to gain control of such processes, the individual steps have to be closely monitored.

The National Centre for Nano Fabrication and Characterization at the Technical University of Denmark (DTU Nanolab) embraces both the state-of-the-art fabrication of micro- and nanostructures, as well as characterisation of the said structures by means of electron beam based microscopy and spectroscopy. DTU Nanolab operates and maintains advanced processing equipment within 1350 m^2, class 10-100, ISO 9001-certified, open access, pay-per-use cleanroom facilities. In a separate specially constructed building, the center operates eight state-of-the-art electron microscopes, among them four transmission electron microscopes (TEM) and a Dual Beam Scanning Electron Microscope (FIB-SEM).

The fabrication part of DTU Nanolab is built as a versatile micro- and nanofabrication platform to shape a wide range of materials with structures down below 20 nanometres on substrates up to 8 inches in size. This includes a comprehensive and expanding selection of state-of-the-art process equipment for lithography, etching, thermal processing, thin film deposition, wafer cleaning, advanced packaging and characterisation.

The characterisation part of DTU Nanolab has established world-class expertise within material characterisation. Our state-of-the-art equipment includes a FEI Titan Analytical 80-300ST and a FEI Titan E-cell Transmission Electron Microscope (TEM). The analytical TEM is capable of forming very fine electron probes and is used primarily for high spatial resolution chemical analysis.

The E-cell TEM has a differential pumping system, allowing imaging of samples in gaseous environments up to pressures of 1000 Pa and temperatures of 1000°C (depending on gas composition). Dynamic events at the atomic level can thus be recorded in real time.

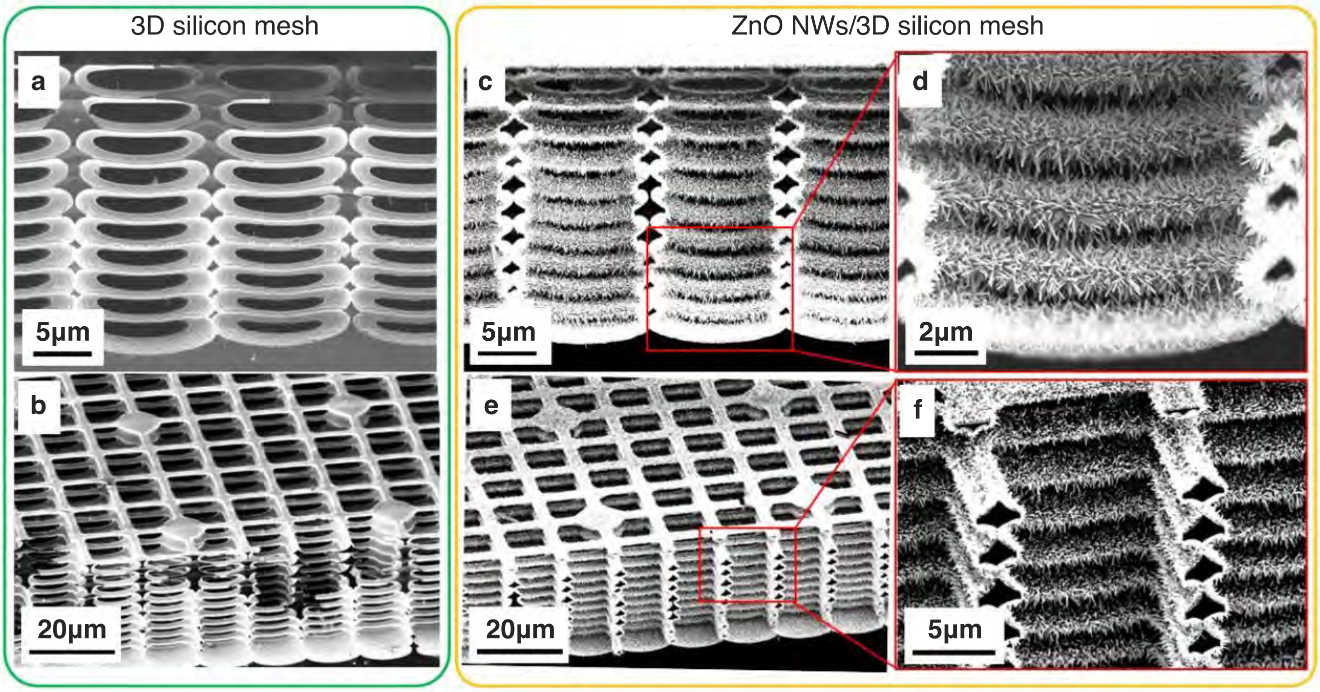

Figure 1: Scanning electron micrographs of ZnO NWs/3D silicon structure. a) -b) 3D silicon structure before the growth of ZnO NWs. c) -f) 3D silicon structures integrated with ZnO nanowires, the formed ZnO nanowires are approximately 1 μm in length and 60nm in diameter.

The combined facility has currently around 100 staff members and over 450 registered users, active in research, education, analysis, material characterisation, development, prototyping and small scale production. DTU Nanolab's scientific staff is pushing the state-of-the-art in characterisation and fabrication by conducting research on new electron beam based microscope techniques and new micro- and nanofabrication technologies. Engineers and technicians repair and maintain the equipment and train and help the various users to achieve their respective goals.

The interplay between the fabrication and characterisation parts of DTU Nanolab results in a deeper understanding of the at times extraordinary structure-functionally relations found at the nanometre scale, helping to bring the fundamental research into applications.

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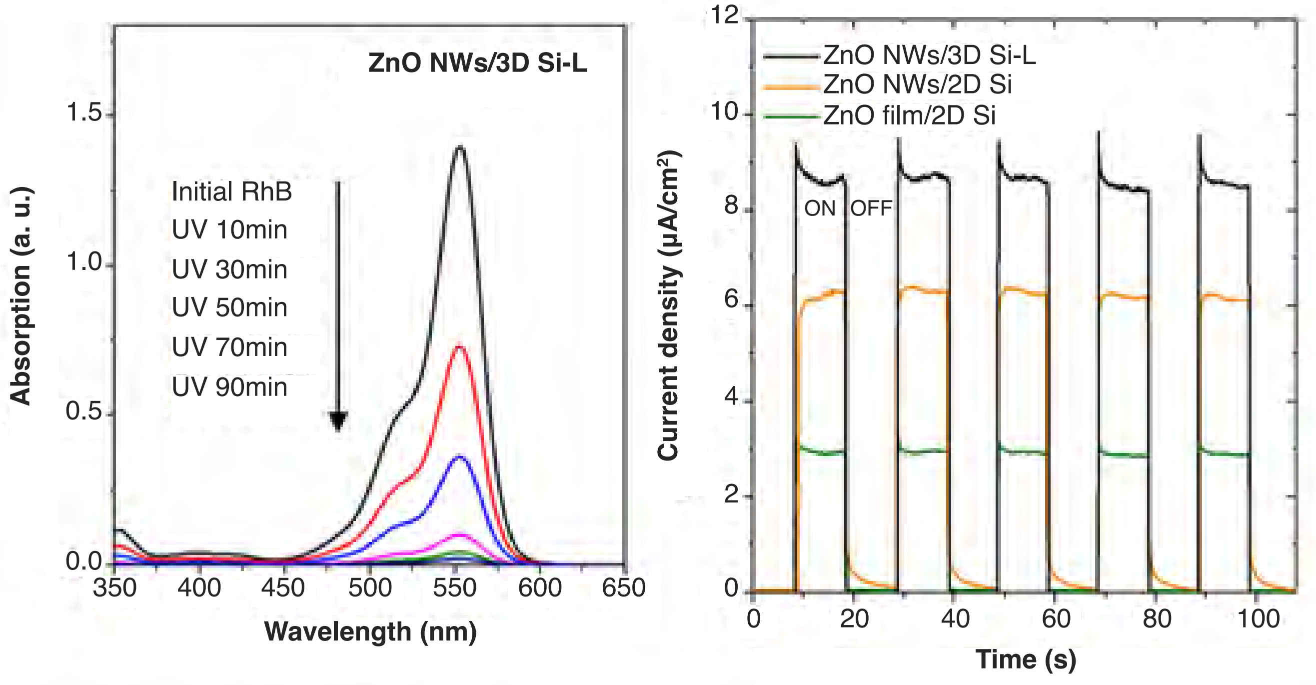

Figure 2: Left: UV-Vis absorption spectra of an aqueous solution of an organic dye (RhB), when ZnO NWs/3D Si is used as photocatalyst for degradation. The decreasing absorption peak of the RhB dye (at 554nm) during extended UV exposure indicates the photocatalytic degradation process. Right: Photocurrent response of ZnO NWs/3D Si structures illuminated by UV light on/off cycles at a bias of 0.5 V vs. saturated calomel electrode.

DTU Nanolab is located on DTU's main campus in Lyngby, 15 km north of the centre of Copenhagen, Denmark around 30 minutes from Copenhagen Airport Kastrup.

The integration of low-dimensional nanomaterials with hierarchical three-dimensional microstructures opens for the realisation of novel properties or improved functionalities. **Figure 1** shows an example of such kind of integrated structures. Heavily doped silicon has been fabricated into a highly ordered 3D micro-mesh structures by standard photolithography followed by a modified plasma etch process[1]. The density of the integrated zinc oxide nanowires into the mesh is increased by approximately an order of magnitude in comparison with a more traditional 2D substrate. The increased density of ZnO nanowires results in an increased performance of photocatalytic degradation and photocurrent generation **(Figure 2)**.

To exploit the application of gold thin films within plasmonics, metamaterials, 2D materials and nanoelectronics, efficient adhesion of gold layers on dielectric or semiconductor substrates is of the highest importance. The general downscaling in nanoscience and technology brings the dimensions of the thin metal layers to be similar to the adhesion layer. This implies that the interplay and structural relationship between the substrate, adhesion layer and metallic film needs further understanding and control for efficient application.

The fabrication of such layered structures by e-beam evaporation and strong monitoring by means of characterisation at the sub-nanometre scale brings a better understanding of the interdiffusion, as well as the structural behaviour of the evaporated layers[2] **(Fig. 3)**. More insight into the nature of the adhesion enhancement guaranteed by the adhesion layers can also be obtained

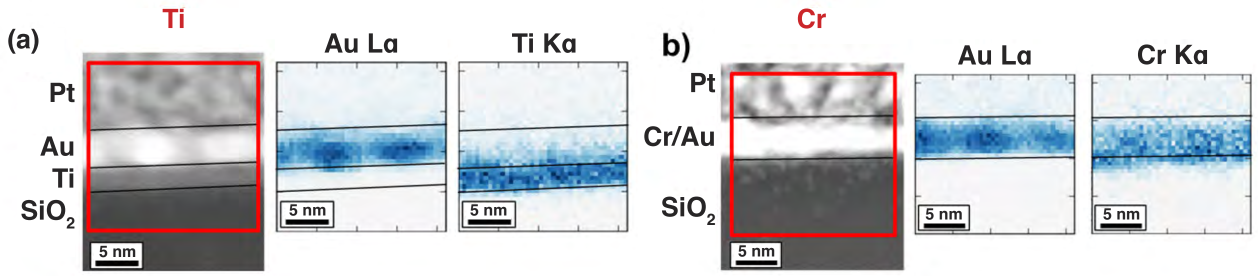

Figure 3: STEM-EDX maps of (a) 2nm-Ti/2nm-Au sample and (b) 2nm-Cr/2nm-Au sample. Au Lα signal is acquired at 9713 eV, Ti Kα signal at 4510.9 eV and the Cr Kα signal at 5414.7 eV. The measurement at the Ti/Au interface shows the presence of a continuous Ti layer below the Au layer, while the analysis of the Cr/Au sample shows instead of the presence of Cr throughout the whole thickness of the Au layer, suggesting a strong inter-diffusion between the layers.

using spectroscopic techniques, which permit to analyse the chemical composition at the interface of the multilayer with nanometre resolution **(Fig. 4)**.

The density of integrated electronic components in the semiconductor industry continues to increase, resulting in shrinking dimensions of individual devices. Many different semiconductor materials are synthesised in the nanowire (NW) form. NWs are structures with length from few hundred nanometres to microns and thickness significantly smaller compared to its length. The cross section of a NW can be round, hexagonal or polyhedron, according to the crystallography of the used material. **Figure 5** shows scanning electron micrographs (SEM) for Si and GaN NWs, having different geometries.

Semiconductor NWs are employed as building blocks for high-performance nanoscaled devices because they impart various benefits to electronic and photovoltaic devices compared to their thin film counterparts. For instance, they can be grown with no crystal defects and they can accommodate large lattice mismatch strain, enabling new heterostructure material combinations with atomically sharp interfaces[3].

One of the major challenges towards nanometre-size scaling of electronic devices based on semiconductor NWs, is achieving controlled doping of NWs at the atomic level. Doping is the intentional addition of atomic

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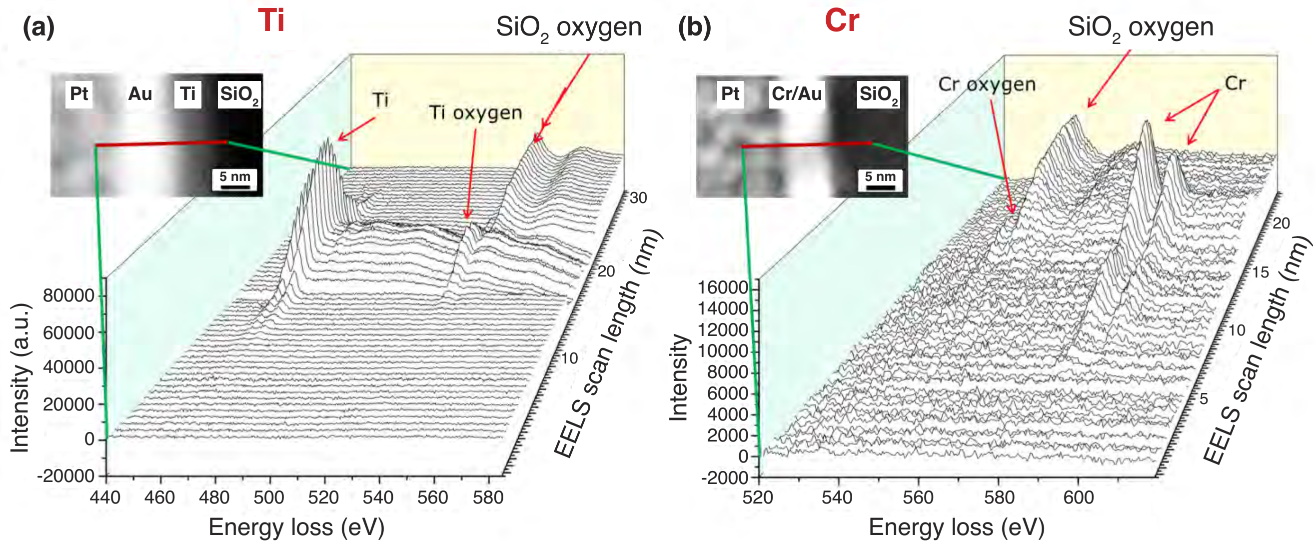

Figure 4: (a) STEM-EELS linear scan of 2nm-Ti/2nm-Au sample, showing the presence of oxygen in the Ti layer. (b) STEM-EELS linear scan of the 2nm-Cr/2nm-Au sample, which shows the presence of oxygen that is bounded to Cr and Cr diffusion into the Au layer.

impurities in a material to produce positive (p-type) or negative (n-type) semiconductors. This is done to accurately manipulate the electrical, optical and magnetic properties. For silicon, elements, such as P, As and Sb are donors as they have one more valence electron than silicon and make the silicon n-type. Likewise, elements, such as B, Al and Ga are acceptors and make the silicon p-type. Typical methods of doping semiconductors are ion implantation, in-situ doping where the dopants are introduced into the NWs during growth and chemical approaches/ such as chemical vapor deposition (CVD) and spin-on doping (SOD).

The doping in NW can be measured by different methods, including photoluminescence and conductivity, four-point probe resistivity, Raman spectroscopy, secondary ion mass spectrometry and atom probe tomography. At DTU Nanolab we can use off-axis electron holography to measure the doping in nanowires. Off-axis electron holography is a transmission electron microscopy (TEM) technique that measures a spatially resolved phase contrast from a specimen due to an electrostatic potential. This technique enables to detect active dopants and provide direct visualisation of doping distribution and p-n junctions at the atomic scale.[4-6]

An example of a holographic measurement across an in-situ doped core-shell GaAs NW is shown in **Figure 6**. Cross-sectional specimens for off-axis electron holography are prepared perpendicular to the growth direction of the NWs using focused ion beam (FIB) milling, which is a technique also available at DTU Nanolab. The amplitude image **(Figure 6 (a))** is equivalent to a conventional TEM image, whereas the phase image **(Figure 6 (b))** is sensitive to the presence of electrostatic potentials inside the NW caused by active dopants. The active dopants show a remarkable azimuthal distribution, which is attributed to preferred incorporation along 3-fold symmetric truncated facets of the NWs during growth[4]. These results reveal an unexpected doping mechanism that has not been predicted nor observed previously.

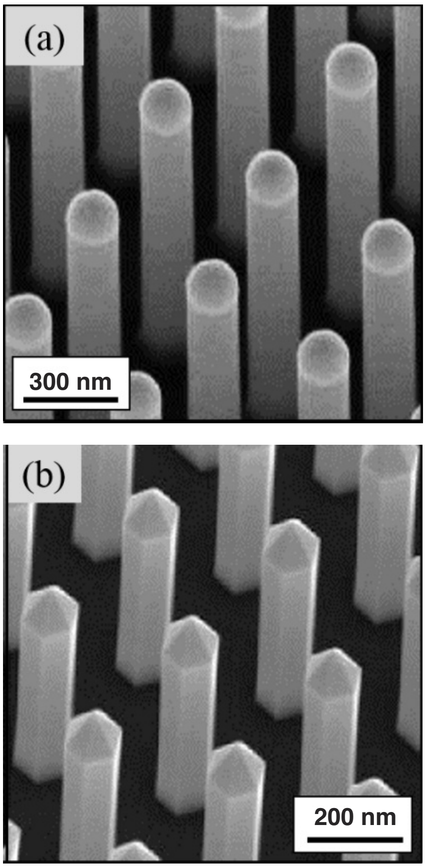

Figure 5: SEM images of (a) Silicon and (b) Gallium Nitride nanowires.

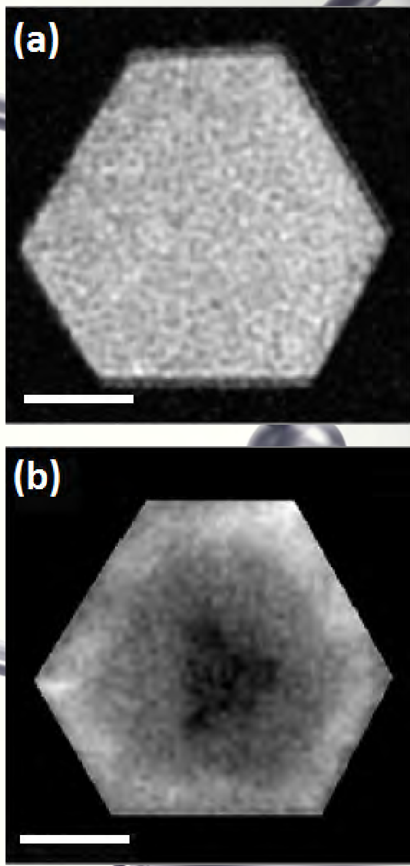

Figure 6: (a) Amplitude and (b) phase images measured using off-axis electron holography. The scale bar is 100 nm.

References

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National Center for Nanofabrication and Characterization

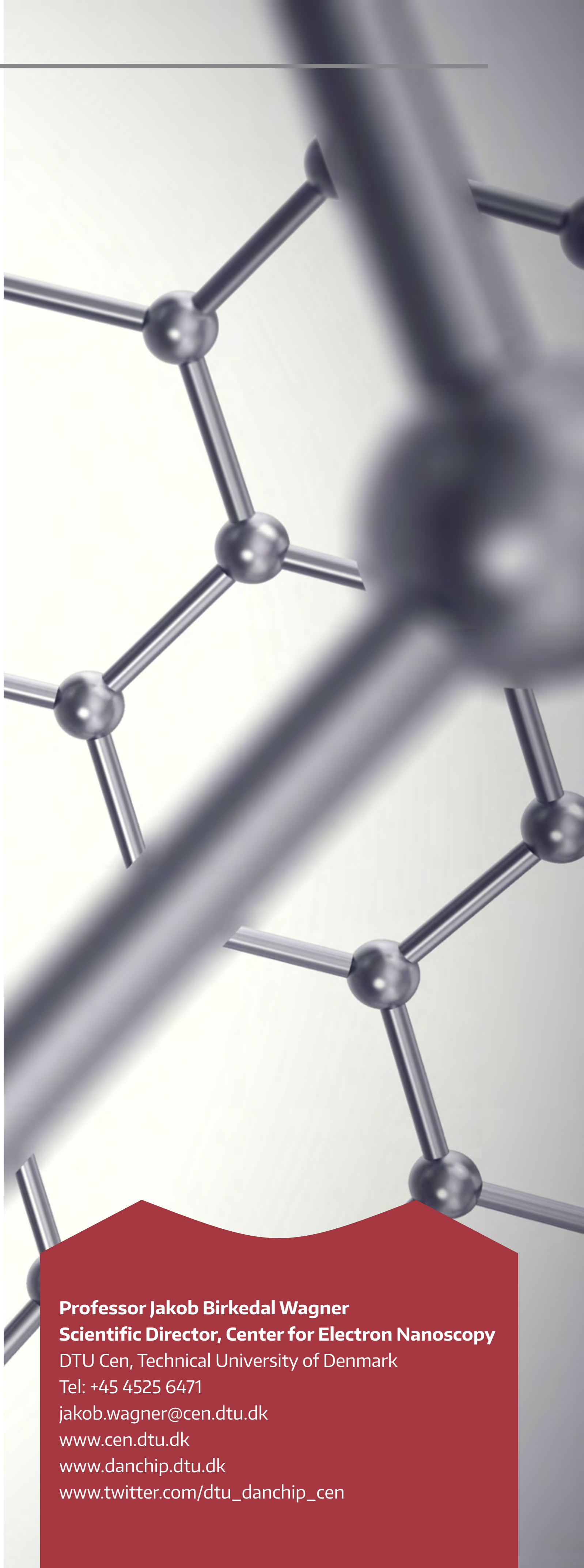
High-end research infrastructure for electron microscopy based characterisation and analysis at Technical University of Denmark

Following a generous donation from the A. P. Møller and Chastine Mc-Kinney Møller Foundation, the Center for Electron Nanoscopy at the Technical University of Denmark (DTU Cen) was inaugurated in 2007. The center has now changed name to the National Center for Nanofabrication and Characterization (DTU Nanolab), but the center continues with high end nanocharacterization. The center was established as a state-of-the-art electron microscopy (EM) facility with a suite of microscopes housed in a high specification building that only a handful of other labs worldwide could rival. The broad aim of the center is to ensure a balance between advanced research, teaching and training, and fostering collaborations with national and international partners. Now, a decade after the official inauguration of DTU Cen, the microscopy center employs 17 researchers (including PhD students and post docs.) as well as 7 technical and administrative staff. Over the years, the activities of the center have been expanding as DTU Nanolab attracts funding from both Danish and European funding agencies.

Access for academic and industrial scientists to DTU Nanolab's electron microscopes supports existing research and results in the creation of new research fields and in the

sharing of knowledge for the development of materials, processes, technologies, techniques and instrumentation. The list below gives an idea of the broad research areas that the center is currently pursuing:

- In situ characterization of individual nanoparticles under controlled atmosphere;
- Nanostructures for Plasmonic sensing;
- Magnetic materials;
- Pore structures in minerals and soil;
- (pseudo) 1-dimensional semiconductor heterostructures for solar cells and quantum computing;
- Growth and characterization of 1D and 2D materials;
- Grain boundary mapping and phase transitions of alloy materials.



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