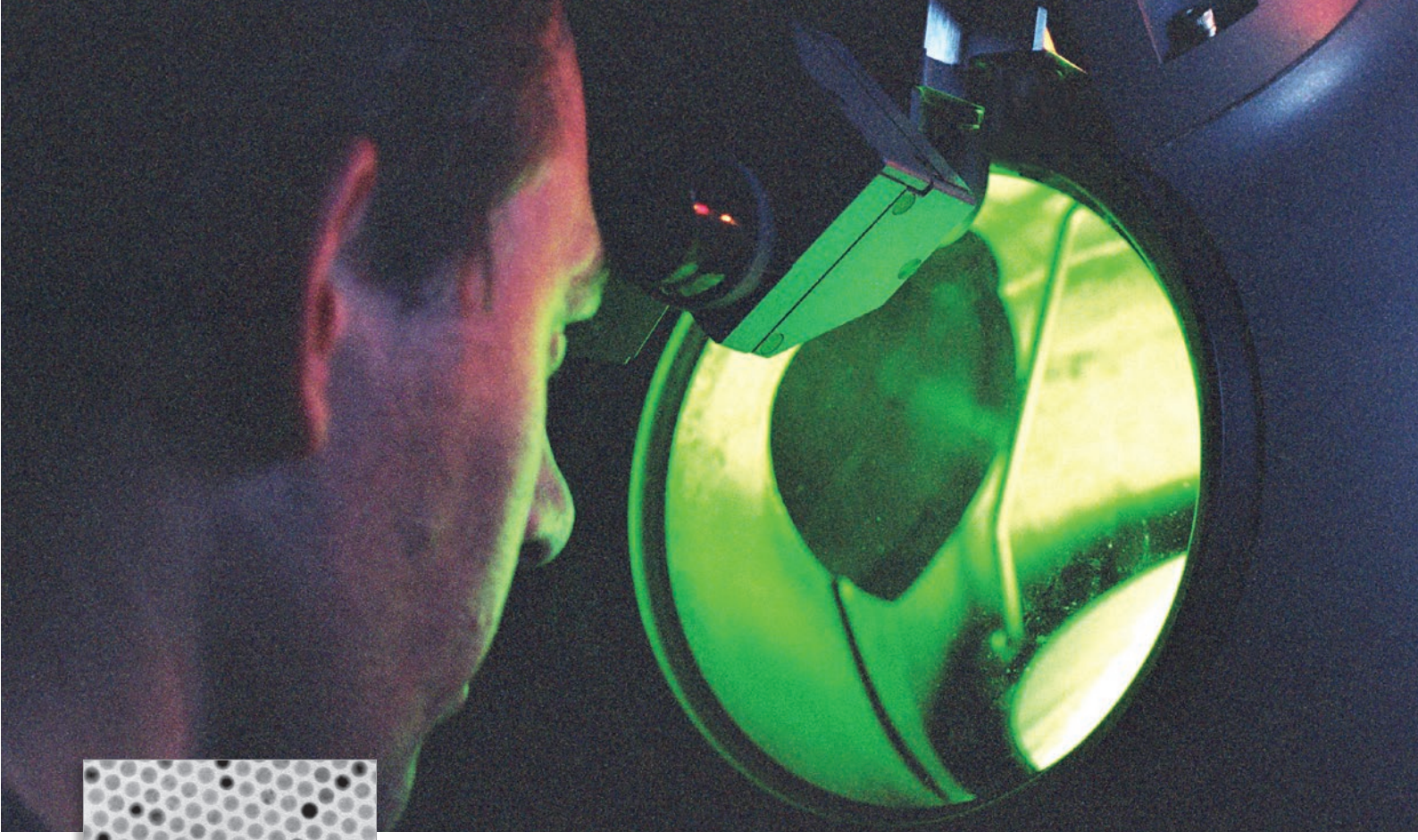

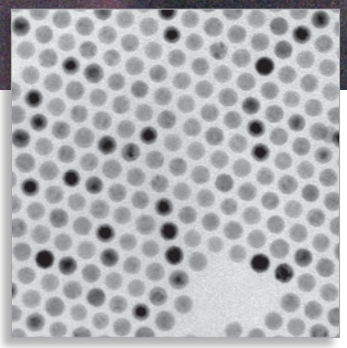

Transmission Electron Microscopy

(TEM)

- atomic resolution
- morphology
- crystal structure
- element mapping
- composition profiling
- 3-D morphology

Transmission Electron Microscopy (TEM) is a well known technique for imaging solid materials at atomic resolution. Structural information can be acquired both by (high resolution) imaging as well as by electron diffraction. Additional detectors allow for elemental and chemical analysis down to this sub-nanometer scale.

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Basic principles

The design of a transmission electron microscope (TEM) is analogous to that of an optical microscope. In a TEM high-energy (>100 kV) electrons are used instead of photons and electromagnetic lenses instead of glass lenses. The electron beam passes an electron-transparent sample and a magnified image is formed using a set of lenses. This image is projected onto a fluorescent screen or a CCD camera. Whereas the use of visible light limits the lateral resolution in an optical microscope to a few tenths of a micrometer, the much smaller wavelength of electrons allows for a resolution of 0.2 nm in a TEM.

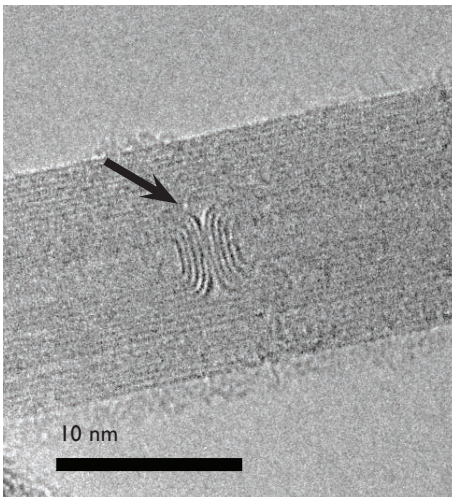


Fig. 1: High resolution TEM image of a multi-walled carbon nanowire. The wire consists of segments, bounded by inner segment boundaries, see arrow.

Imaging

Image contrast is obtained by interaction of the electron beam with the sample. Several contrast effects play a role. In the resulting TEM image denser areas and areas containing heavier elements appear darker due to scattering of the electrons in the sample. In addition, scattering from crystal planes introduces diffraction contrast. This contrast depends on the orientation of a crystalline area in the sample with respect to the electron beam. As a result, in a TEM image of a sample consisting of randomly oriented crystals each crystal will have its own grey-level. In this way one can distinguish between different materials, as well as image individual crystals and crystal defects. Because of the high resolution of the TEM, atomic arrangements in crystalline structures can be imaged in large detail (figure 1).

Electron diffraction

In case of a crystalline material, electron diffraction will only occur at specific angles, which are characteristic for the crystal structure present. As a result, a diffraction pattern of the irradiated area is created that can be projected onto the CCD camera. In this way, electron diffraction can provide crystallographic information from thin films (see figure 2), bulk materials as well as from nanometer sized particles.

Chemical analysis

As a result of the interaction of the electron beam with the specimen, some energy is transferred from the electrons to the sample. The excitation and de-excitation of atoms and molecules in the sample allow (local) chemical analysis.
This analysis can either be performed using the broad beam used for normal imaging, or by focusing the beam size down to 0.2 nm. The combination of Scanning TEM (STEM), a mode in which this narrow beam scans a selected area of the specimen, with chemical analysis techniques such as Electron Energy Loss Spectroscopy (EELS) and Energy Dispersive X-Ray analysis (EDX) allows for mapping of the lateral distribution of elements with high spatial resolution.

Electron Energy Loss Spectroscopy (EELS)

When travelling through the sample the electrons may lose energy due to (multiple) inelastic scattering events. The amount of energy that is transferred from the incident electron to the sample is dependent on the composition of the sample. Because the primary beam of electrons has one well-defined energy, the spectrum of the electrons that have passed the sample contains chemical information on the irradiated area. This principle is used in both EELS and Energy Filtered TEM (EFTEM).
Using EELS an energy loss spectrum is acquired, such as shown in figure 3. Quantification of the spectrum enables determination of (local) concentrations of elements. The fine structure in the EELS spectra provides information on the chemical binding of the atoms involved. The combination of EELS and STEM allows for 1-D and 2-D mapping of the lateral distribution of elements.

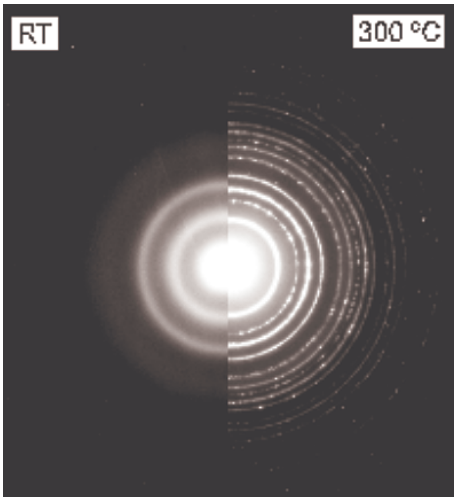


Fig. 2: Electron diffraction patterns of an as-deposited (room temperature) and an annealed (300 °C) Al-Ge film. The left part shows a set of a few, broad rings, characteristic of an amorphous film. The right part shows a large number of sharp rings. The diameters of these rings are characteristic for the crystal structure present. In this case a mixture of crystalline Al and crystalline Ge.

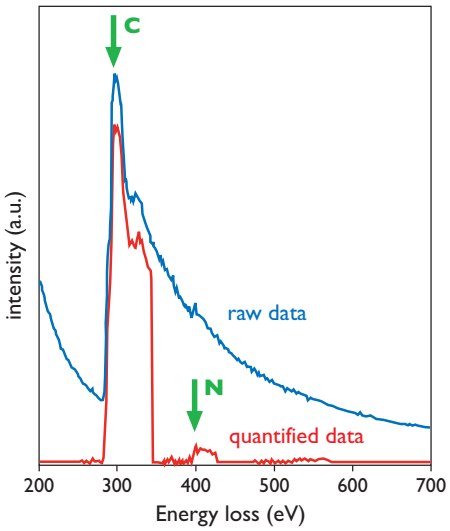


Fig. 3: EELS spectrum acquired from the segment-boundary shown in figure 1. Quantification yielded 5-7 atomic % of N in this segment boundary, whereas in the outer walls only 1-3 % of N is present.

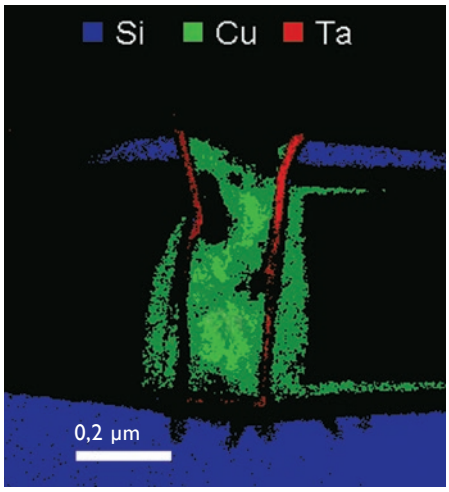


Fig. 4: A color map, combining EFTEM images acquired at the characteristic energy losses of Si, Cu and Ta. Here, a cross-section of a copper line is shown that is running perpendicular to the plane of view. The result of electro-migration is visible: due to electrical stress copper has migrated through the Ta barrier layer into the neighboring areas.

Energy Filtered TEM (EFTEM)

A special filter on the TEM allows for selection of a very narrow window of energies in the EELS spectrum. Using the corresponding electrons for imaging, EFTEM is performed. The resulting image is formed by electrons with one element-specific energy loss. As a result, a qualitative elemental map is obtained. (see figure 4). EFTEM is the only chemical analysis procedure in the TEM that does not use a scanning beam. As a consequence, it is much faster.

Energy Dispersive X-ray analysis (EDX)

As a result of the interaction of the incident electron beam with the sample, X-rays are emitted. Their energies are characteristic for the atoms present in the volume that is probed. The detection and analysis of these X-rays is called Energy Dispersive X-Ray analysis. The X-ray spectrum that is obtained allows for quantification of the elemental composition of the irradiated area. The combination of EDX and STEM allows for mapping of the lateral distribution of elements. A typical example is shown in figures 6 and 7.

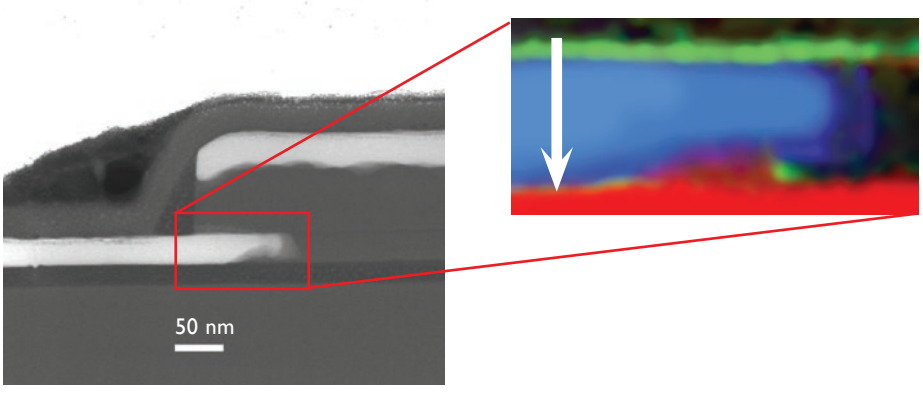
HAADF

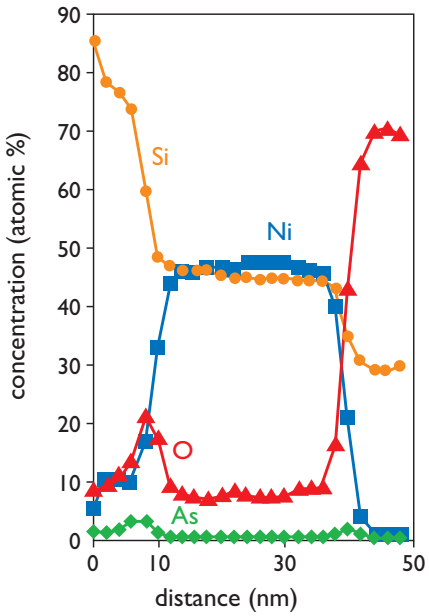
Another way of obtaining compositional as well as structural information using TEM is High Angle Annular Dark Field (HAADF) imaging. For this application a dedicated detector is used that only collects electrons that are elastically scattered over large angles by the specimen. The intensity that is detected is dependent on the average atomic number Z present in the irradiated area: $I \sim Z^2$. In combination with STEM, mass contrast images can be acquired down to atomic resolution. (see figure 5).

Fig. 5: HAADF image of a MOS transistor on SOI. Due to Z-contrast the SiO_2 , silicon and NiSi areas appear dark grey, light grey, and white respectively.

Fig. 6: A color map displaying the elemental distributions of O (red), Ni (blue) and As (green) within the red box in figure 5. In each of the 1250 pixels of 2×2 nm² the compositions were determined quantitatively by EDX.

Fig. 7: Graph displaying the elemental concentrations of As, O, N, and Si along the line in figure 6.





	(HR)TEM	EELS / EFTEM	EDX	HAADF
Spatial resolution:	Atomic resolution (0.2 nm)	EELS: 0.5 nm EFTEM: 1 nm	1 nm	Atomic resolution (0.2 nm)
Detectable elements:	-	All	B and heavier elements	No unique Z assignment
Detection limits:	-	0.1 %	0.1 %	2 %
Issues:		- Elaborate sample preparation (very thin and clean sample needed) - Very sensitive for light elements	Due to limited energy resolution some high Z elements have overlapping spectra	Sample thickness variations and voids may complicate interpretation
Samples:	Solid materials (amorphous and crystalline): bulk, thin film, aqueous dispersions and powders. The area of interest should be thinner than 0.1-0.2 µm. For most samples, this implies sample preparation.			
In-house sample preparation:	Focussed Ion Beam (FIB), mechanical (tripod) polishing, dimple grinding, ultramicrotomy, ion-milling, TEM-windows, vitrification of aqueous samples.			

Table 1: overview of characteristics of the various TEM techniques

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Tomography

TEM tomography involves the acquisition of a large series of images at many tilt angles of the sample with respect to the electron beam. In analogy to the CT scanner used in medical diagnostics, the acquired tilt-series is reconstructed into a 3-D representation. This technique is especially useful in case of studies on 3-dimensionally shaped objects, such as layers in small pores and 3-D shapes of small objects (see figure 8).

Cryo-TEM

Using dedicated equipment, it is possible to freeze 0.1 µm thick water films and study these films at -170°C in the TEM. This enables imaging of the natural shape of organic bilayer structures (such as liposomes and polymersomes) in their aqueous environment (see figure 9). Also, agglomeration processes in a dispersion can be studied. In addition, the application of cryogenic conditions facilitates studies of beam-sensitive samples.

Applications

- (Epitaxial) growth of thin layers and multilayers
- Morphology studies in (IC) device structures
- Composition profiling in multilayers
- Crystal structure determination of precipitates, minority phases and nanowires
- Morphology of liposomes, polymersomes and other particles in aqueous dispersions
- 3-D morphological studies of complex heterogenous structures
- In-situ heating experiments to study phase transitions

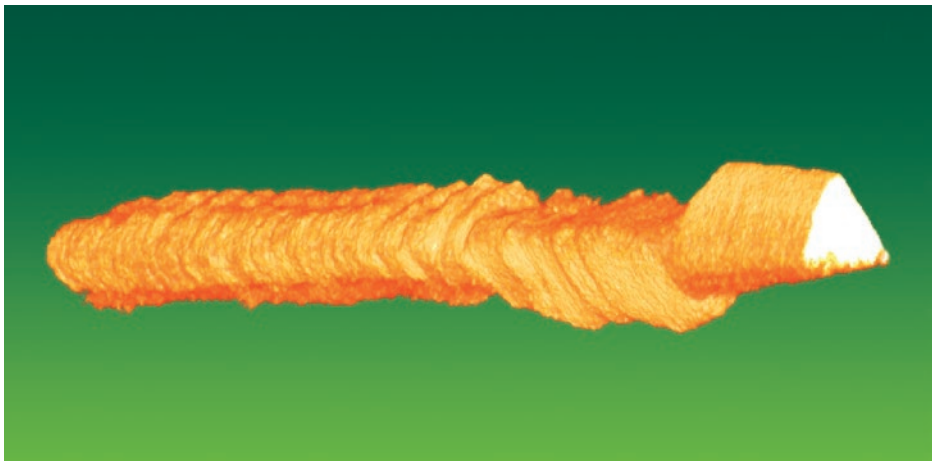

Fig. 8: The 3-dimensional reconstruction of the morphology of a part of a GaP-GaAs hetero-structured nanowire with 40 nm diameter.

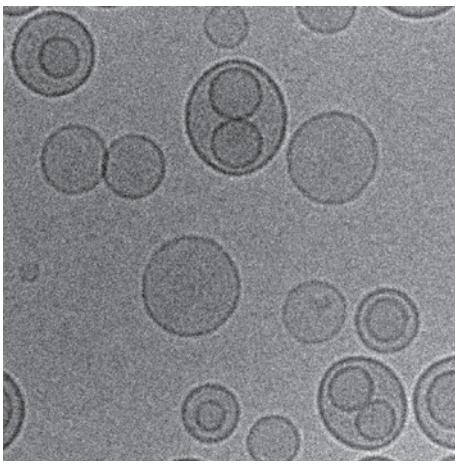

Fig. 9: cryo-TEM images of single-walled and double-walled liposomes in water.