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Advanced Analysis of Modern Nanostructured Materials by Means of Transmission Electron Microscopy

For advanced materials particular properties can be tailored by designing internal structures of reduced dimensions down to nanometer scale (10^{-9} m). Such nanostructured materials comprise all classes of materials, i.e., metals, alloys, ceramics, semiconductors, polymers, biomaterials, etc. The specific materials behaviour is essentially controlled both by the intrinsic structure and chemistry of these nanoscopic objects. Therefore, the quantitative information about microstructure and composition on a nanometer scale is indispensable getting a thorough understanding of structure-property relationships of nanostructured materials. Nowadays, transmission electron microscopy (TEM) is an analytical tool providing local information with high resolution (spatial resolution: sub-Å, energy resolution: sub-eV) about both structure and chemistry.

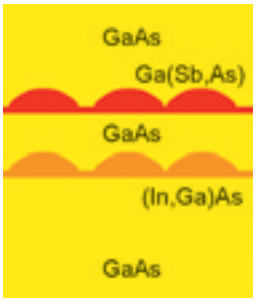


Fig. 2
Configuration of QD sample.

In general, the following main approaches are applied to characterize structure and composition of nanostructured materials: microscopic imaging, diffraction and spectroscopy. The big advantage of analytical TEM is that these approaches can be carried out subsequently in a modern analytical transmission electron microscope. The combined facilities for obtaining electron microscopic images, diffraction patterns, and spectroscopic images from the same specimen area investigated in the various types of modern microscopes (TEM, STEM – scanning TEM) offer numerous possibilities for investigating and characterizing the physical, chemical, and crystallographic nature of crystalline and non-crystalline materials. TEM is a destructive solid-state analysis technique. It requires special and very often time-consuming specimen preparation techniques in order to obtain electron-transparent specimen regions of a thickness smaller than 100 nm. Image formation in a TEM consists of two main processes: The electron-optical imaging due to the action of the electron lenses as imaging elements and the physical interaction process between the electron radiation and the matter under investigation. The interaction process may be either elastic or inelastic. Both scattering processes may be utilized for the materials analysis.

The tailoring of nanostructures needs the profound knowledge about structure, chemistry, and strain state around and within the nanostructures. Various electron microscopic techniques can be applied to gain the information required (Fig 1).

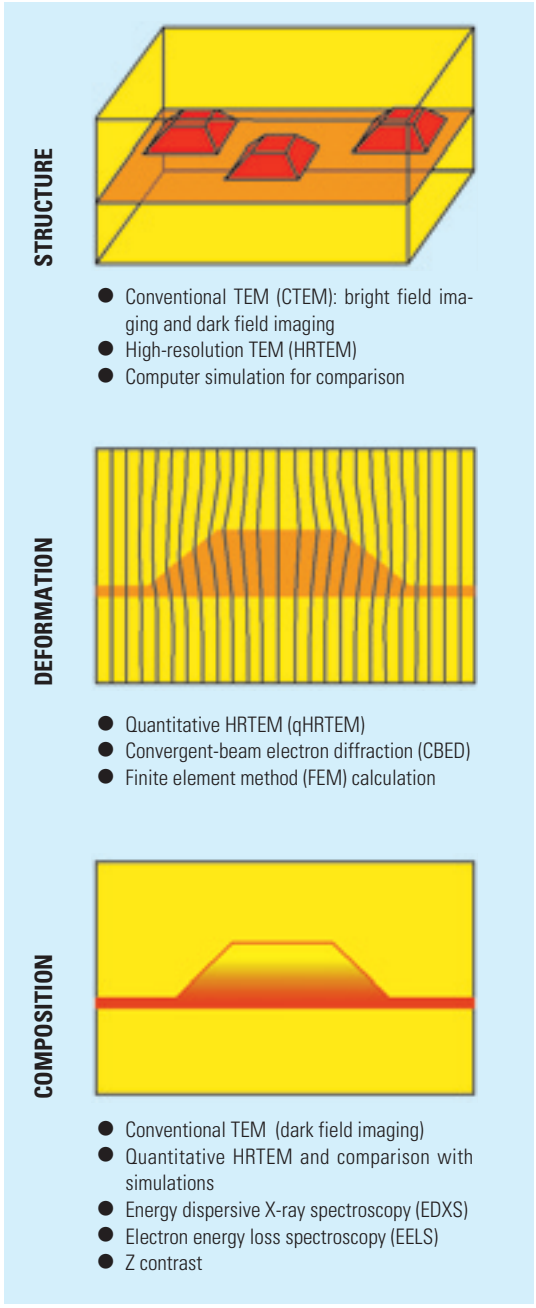


Fig. 1
Methods of transmission electron microscopy for investigation of specific properties of nanostructured materials.

Charakterisierung moderner nanostrukturierter Materialien mittels elektronenmikroskopischer Verfahren
Die Entwicklung moderner nanostrukturierter Materialien mit definierten, maßgeschneiderten physikalischen und chemischen Eigenschaften stellt neue Anforderungen an die festkörperphysikalischen und festkörperchemischen Untersuchungsmethoden. Die modernen elektronenmikroskopischen Verfahren nehmen insbesondere bei der Aufklärung des Zusammenhanges zwischen Struktur und Eigenschaften von Nanostrukturen eine herausragende Stellung ein. Sie bieten Möglichkeiten der direkten Abbildung von Struktur und Morphologie im nm-Bereich mit atomarer Auflösung. Informationen über die Ideal- und Realstruktur können einerseits direkt aus der elektronenmikroskopischen Abbildung bzw. aus dem Elektronenbeugungsdiagramm gewonnen werden. Zum anderen besteht durch die Kombination von abbildenden und spektroskopischen Verfahren die Möglichkeit einer quantitativen chemischen Analyse der nanostrukturierten Materialien bei gleichzeitiger Beobachtung des interessierenden Objektbereiches. Die Leistungsfähigkeit der verschiedenen elektronenmikroskopischen Methoden wird anhand ausgewählter Beispiele demonstriert.

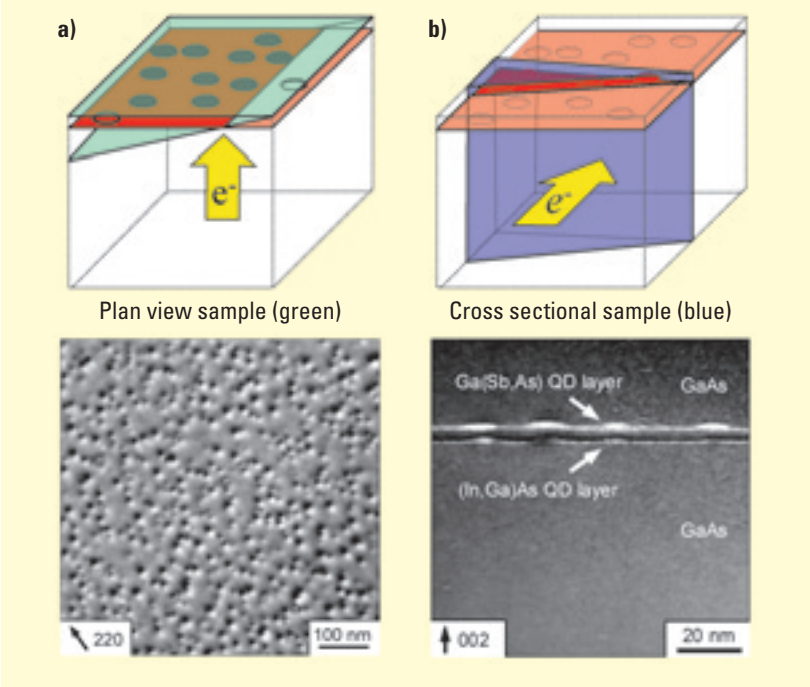


Fig. 3
Two different projections for imaging of epitaxially grown samples; above: schemes of sample cut out for plan-view (left) and cross-sectional investigation (right), below: corresponding TEM diffraction contrast micrographs.

The diffraction contrast imaging techniques of conventional TEM (CTEM) provide information on the size, shape, arrangement, and under certain conditions also quantitatively on the chemical composition of the nanostructures. In order to get an insight of the structure and composition of the nanostructures even on an atomic scale high-resolution TEM (HRTEM) has to be applied. In general, the direct interpretation of HRTEM images is not possible due to the complexity of both the scattering and the imaging process. Therefore, the image simulation and the trial-and-error matching techniques are the indirect way of structure retrieval (see e.g. [1]). The other possibility of structure retrieval is the determination of the scattered wave function at the exit surface of the crystalline specimen by electron holography or focus series reconstruction techniques [2, 3].

In order to extract quantitative information on atomic structure, elastic strain, and chemical composition from high-resolution TEM micrographs different methods and program packages of quantitative HRTEM (qHRTEM) have to be applied [4].

Furthermore, the chemical composition can be determined by electron energy loss spectroscopy (EELS) and energy-dispersive X-ray spectroscopy (EDXS). Moreover, dedicated sub-techniques are used to image the element distribution along a line (EDXS profile, series of EEL spectra) or two-dimensionally (X-ray mapping, energy-filtered TEM) at a lateral resolution of some nanometers (EDXS) or even on the sub-nm scale.

Semiconductor quantum dot structures

Nanostructured semiconductor materials, particularly quantum structures are of great interest because the dimensionality on the nanometer scale may drastically change the density of electronic states and the optoelectronic properties. The state of the art of growth, characterization and application of self-organized quantum dot (QD) structures is reviewed by Bimberg et al. [5]. The optoelectronic properties of QD devices such as quantum dot lasers are a function of size, shape, arrangement, and chemical composition of the QDs.

For various semiconductor systems of low dimensions including multilayers, island structures, and QDs the potential applicability of TEM was demonstrated [6, 7]. As one example QDs of (In,Ga)As and Ga(Sb,As) were epitaxially grown on GaAs separated by a GaAs spacer layer and finally capped by GaAs. A sketch of the sample configuration is given in Fig. 2.

In general, two main viewing projections of interfaces are utilized. On the one hand, plan-view samples permit imaging with projection parallel to the growth direction and thus perpendicular to the interfaces (cf. Fig. 3a). The sketch gives the layer of interest in red and the volume of the TEM sample in green where the wedge-shape of the sample is owing to the final step of preparation by ion beam milling. From TEM diffraction contrast images of such samples information can be extracted on area density and on lateral arrangement of the QDs as well as on presence of structural defects inside the QDs. Every black-white spot in the diffraction contrast image of the lower part of Fig. 3a corresponds the a double stack of QDs. In addition, it can be concluded from the image given in Fig. 3a that there are no crystal defects (e.g. dislocations or stacking faults). Additionally, dark-field imaging of the plan-view sample provides information on the extension of the strain field surrounding the QDs perpendicular to the growth direction. Comparing experimental images with simulated diffraction contrast ones some hint can be obtained to the shape of the QDs.

On the other hand, inspection of the QDs perpendicular to the growth direction and hence along the interfaces to the underlying material is realized by cross-sectional samples as schematically represented in blue in the upper part of fig. 3b. Inspecting those samples by diffraction contrast techniques, the height of single QDs as well as the width of its basal plane can be detected. The brightness of the cross sectional image predominantly depends on the chemical composition of the semiconductor compound material because of using a so-called »chemically sensitive reflection« for dark-field imaging. Contrary to this, strain sensitive reflections provide the strain state of the system.

Z contrast imaging as a particular dark-field imaging in STEM mode utilizes the angular distribution of scattered electrons being directly proportional to the mean atomic number of the material hit by incident electrons. The electron beam constricted to a diameter smaller than 1 nm is scanned across the sample and

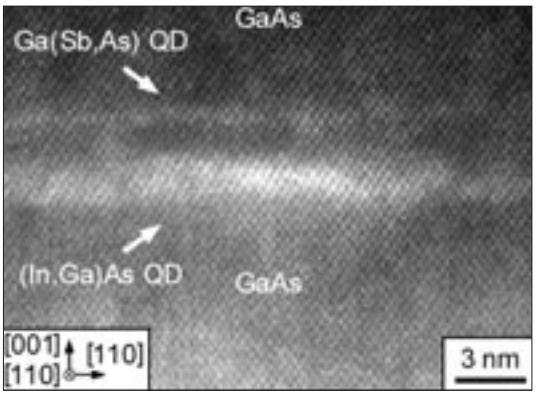
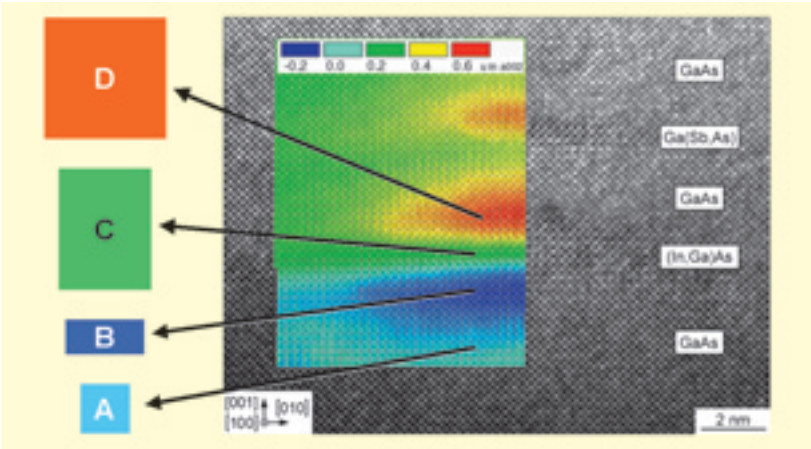


Fig. 4
Z contrast image of the QD structure in cross section.

consecutively the number of electrons registered by a high-angle annular dark field detector is visualized as intensity at the actual beam position. Fig. 4 gives a corresponding Z contrast image of a stack of two QDs where the QDs can be identified by the higher brightness due to the higher mean atomic number of (In,Ga)As and Ga(Sb,As) compared to that of GaAs.

In order to gain quantitative information on, e.g., the strain field surrounding the QDs qHRTEM has to be applied. As a result of the different lattice parameters of the deposited materials the distance varies between the positions of the atomic columns visible as bright spots in the HRTEM image of Fig. 5. The analysis is realized by comparing the lattice parameter parallel to the growth direction [001] for every individual lattice plane with that of a reference region defined well underneath the (In,Ga)As QD. The reference area is given in light blue and the corresponding arrow points to a square marked by A representing the strain free GaAs with the crystal lattice having cubic symmetry. Approaching the QD GaAs undergoes a tetragonal distortion of the unit cell as indicated by dark blue and the rectangle marked with B. Owing to the higher lattice parameter of the above (In,Ga)As the GaAs unit cell is tensely strained. On the other hand, the GaAs matrix causes compressive strain to the QD material as indicated by the rectangle C. At the topmost region of the QD partial relaxation results in a cubic unit cell for (In,Ga)As (cf. square D). The Ga(Sb,As) QD is located exactly above the (In,Ga)As QD confirming the validity of the seed layer concept.

Fig. 5
Quantitative image analysis of a cross-sectional HRTEM micrograph of the QD structure. Analysis reveals colour coded information on strain state parallel to the growth direction,
A: GaAs substrate – non strained,
B: GaAs substrate – tensely strained,
C: (In,Ga)As QD – compressively strained,
D: (In,Ga)As QD – elastically relaxed.



Strain compensation and chemical composition of semiconductor layers

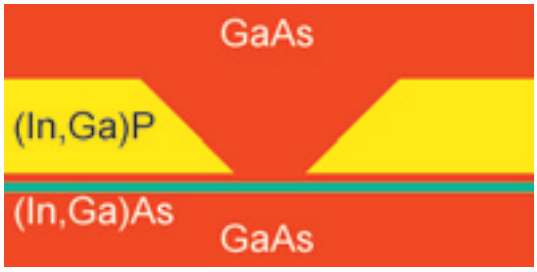
In semiconductor device structures strain plays an important role, especially, when causing undesired defects. Crystal defects can decrease the efficiency and even the lifetime of devices. Thus, one main interest of fundamental research in device fabrication focuses on strain minimization.

In order to get a thorough understanding of the strain compensation phenomenon the growth of a GaAs cap layer was performed. A schematic drawing of a semiconductor device structure in cross section is shown in Fig. 6.

In addition to HRTEM image analysis the convergent beam electron diffraction (CBED) can be utilized for visualization of strain fields in crystalline structures. Applying large-angle CBED (LACBED) the diffraction pattern provides information about both the lattice geometry as well as structural peculiarities of the sample in one and the same experiment (Ronchigrams). For this experiment the area between two V-grooves was looked at.

In general, a stack of materials having different lattice parameters introduce transitions of strain state from compressive to tensile and vice versa. A shift of the line position while crossing an interface due to gradual change of lattice parameters indicates this variation of strain. In Fig. 7 the different kind of bending while crossing the interfaces allows the determination of the strain state.

Fig. 6
Configuration of V-grooved sample after overgrowth for strain compensation.



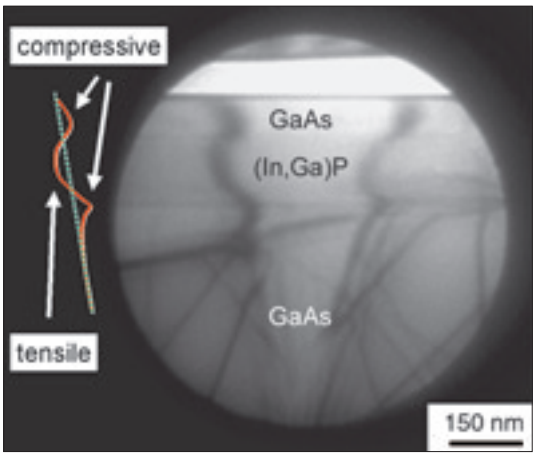


Fig. 7
Large-angle CBED pattern of the region between two V-grooves. Dark lines (schematically represented by the red line) are bent due to strain.

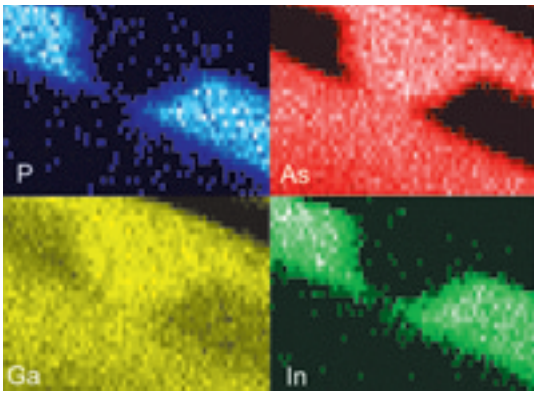
The different layers of the sample can be visualized by an analytical TEM method sensitive to the chemical composition like EDXS. An EDX spectrum provides qualitative and quantitative information on the composition of the sample.

In fig 8 a set of elemental maps and for comparison a scanning dark-field TEM (STEM DF) image are presented. The V-grooved $In_{0.48}Ga_{0.52}P$ layer is clearly observable in both the P and the In map whereas the filling with GaAs can easily be realized from the As map. The Ga distribution shows higher intensity in the GaAs region compared to the (In,Ga)P layer which can be explained by the higher Ga content of 50 atom% for GaAs compared to about 26 atom% for (In,Ga)P.

Magnetic materials

Local magnetic structures of nanosized materials can be imaged by Lorentz microscopy and electron holography.

In electron holography [2] the electron wave is split into a reference beam passing through vacuum and a beam transmitting the sample. The beams are superimposed in the image plane, where an interference pattern is recorded. In this way the technique gives access to phase information, which is hidden in normal TEM operation. Knowledge about the phase shift of the electron wave in the specimen is especially precious when imaging electric and magnetic fields. An electron wave suffers a phase shift, when it passes a magnetic vector potential (Aharonov-Bohm effect). Electron holography utilizes this effect for direct imaging of magnetic fields. Fig. 9a shows the phase map



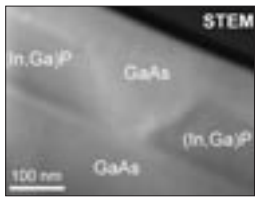


Fig. 8
Elemental distribution of the V-groove area in cross section as gained by EDXS. For comparison a STEM dark-field image of the same region is given.

of a cobalt sample with micro domains in antiparallel in plane magnetisation. The sample is sufficiently thick to shift the electron phase several multiples of 2π, leading to »phase jumps«, the contour in Fig. 9a. Intuitively these contours can be identified as magnetic lines of flux. In Fig. 9b the phase jumps are unwrapped. Finally, in the derivative of the phase shift (Fig. 9c) the magnetic domains can be easily identified. The method is quantitative, i.e., the local magnetization can be determined if the sample thickness is known.

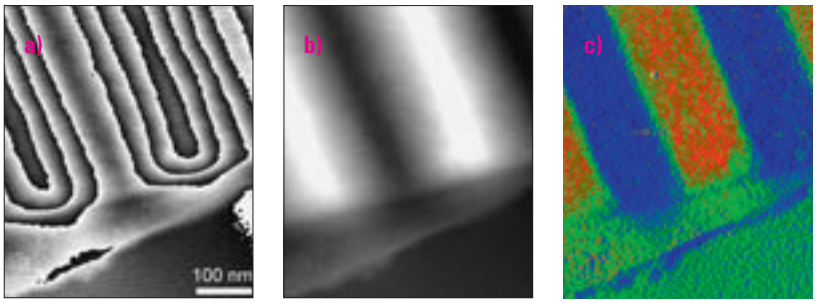


Fig. 9
Electron holography investigation of cobalt sample exhibiting magnetic domains; a) phase map, b) unwrapped signal, c) derivative of phase shift visualizing the two different domains represented in red and blue.

References

[1] *Möbus, G./Schweinfest, R./Gemming,T./Wagner, T./Rühle, M.*: J. Microscopy, 190 (1998) 109.
[2] *Lichte, H./Lehmann, M.*: Adv. in Imaging and Electr. Physics, 123 (2002) 225.
[3] *Thust, A./Coene, W. M. J./Op de Beeck, M./Dyck, D. van*: Ultramicroscopy, 64 (1996) 211.
[4] *Kret, S./Ruterana, P./Rosenauer, A./Gerthsen, D.*: phys. stat. sol (b), 227 (2001) 247.
[5] *Bimberg, D./Grundmann, M./Ledentsev, N.N.*: Quantum dot heterostructures, John Wiley & Sons, Chichester, 1998.
[6] *Neumann, W.*: Materials Chemistry and Physics 81, (2003) 364.
[7] *Neumann, W./Kirmse, H./Häusler, I./Otto, R./Hähnert, I.*: J. of Alloys and Compounds (2004) in print.

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