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Electron microscopy of quantum dots

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Summary

This brief review describes the different types of semiconductor quantum dot systems, their main applications and which types of microscopy methods are used to characterize them. Emphasis is put on the need for a comprehensive investigation of their size distribution, microstructure, chemical composition, strain state and electronic properties, all of which influence the optical properties and can be measured by different types of imaging, diffraction and spectroscopy methods in an electron microscope.

Quantum dot systems

Definition

Quantum dots are artificial nano-structures of semiconductors wherein the charge carriers, that is, electrons, holes or electron-hole pairs – so-called excitons – are confined in all three spatial dimensions. As a result, such systems behave electronically, and therefore also optically and electrically, like point-like dots with zero-dimensional density of states.

Colloidal quantum dots

Colloidal quantum dots are quantum dots that have been synthesised by chemical reactions from solutions wherein small semiconductor crystals can precipitate out by dropping the temperature, changing the pH value or adding other chemicals. In order to avoid aggregation into larger crystals, which could eventually transform the material into a polycrystalline solid, the surfaces of the nano-particles need to be saturated by functional organic groups ('functionalised') that make the nanoparticles photostable (Gaponik *et al.*, 2002) and generate a steric hindrance to further compaction (Yin & Alivisatos, 2005). Often the surfaces of the nano-crystallites formed are covered by shells of other semiconductors of a larger band-gap to ensure the core material still confines the charge carriers without loosing them to surface-bound states that could act as nonradiative centres, which can thus be avoided in such core-shell structures (Klimov *et al.*, 2007). As a result, colloidal quantum dots are readily available as suspensions. Due to their luminescent properties they are used as fluorescent markers that can be attached to antibodies in the study of specific components of viruses, bacteria, living cells (Jaiswal *et al.*, 2003) and even living animals (Ballou *et al.*, 2004). Colloidal quantum dots are also tested as antireflective coatings for luminescent displays (Jacobsson & Edvinsson, 2012) or solar cells (Tsai *et al.*, 2012; Ingenhoven *et al.*, 2013).

According to the above definition, metallic nano-particles would not be considered quantum dots because they lack single localised charge carriers. The free electrons typically found in metals are here responsible for low-energy surface plasmons, however, that are intricately linked to the particle sizes (Alvarez *et al.*, 1997) and geometries, that is, faceting, (Nelayah *et al.*, 2009) and often yield resonances in the optical frequency range so that such systems are also interesting for applications as optical waveguides, in nanophotonic devices and as sensors (Hutter & Fendler, 2004). The basis of such plasmonics remains, however, fundamentally different from quantum confinement in semiconductor quantum dots.

Epitaxial quantum dots

Epitaxial quantum dots, on the other side, are crystalline quantum dots that have been grown epitaxially by physical methods (molecular beam epitaxy, pulsed laser deposition, sputtering or liquid phase epitaxy) or chemical methods (chemical vapour phase epitaxy, metal-organic chemical vapour deposition) onto single crystalline substrates. They can be either free-standing on the surface or incorporated into the bulk by epitaxial overgrowth (the repetition of which can then be employed to generate stacks with multiple layers of embedded quantum dots, thereby enhancing the total number of dots per surface area). In order to confine both electrons and holes within the quantum dots their band-gap must be smaller than that of the surrounding barrier material and the bands be aligned in a type-I structure, with conduction and valence band offsets anticorrelated. In type-II structures, steps in the

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conduction and in the valence band are positively correlated, that is, point in the same direction, so that electrons and holes are spatially separated by confinement on opposite sides of the interfaces formed. The band-gap of semiconductors generally shrinks with expanding lattice constant, which can be understood in terms of the energy dependence of the wavelength of the quantum mechanical Bloch waves that describe the eigenstates of the crystal. Thus, the lower band-gap material forming the quantum dot usually has an increased lattice constant compared to the substrate (and the surrounding barrier material), which implies it will be under compressive strain. This is technically important as the so-called Stranski–Krastanow growth mode, which describes the transition from flat layer-by-layer epitaxy to three-dimensional island growth, is a strain-relief mechanism typically found in strained layer epitaxy of compressively stressed films. Films under tensile stress often simply crack instead. Stranski–Krastanow growth on planar semiconductor substrates yields a spontaneous, random self-assembly of quantum dots in the form of small islands, typically with island densities up to several 10^{10} cm^{-2}, upon a very thin so-called wetting layer. This phenomenon, originally observed for ionic crystals grown from liquid solutions (Stranski & Krastanow, 1938), has successively been found in the 1990s to be applicable also to the epitaxy of metals (Gautier & Stoeffler, 1991), elemental semiconductors (Hansson *et al.*, 1992; Knall & Pethica, 1992) and compound semiconductors (Leonard *et al.*, 1994; Berti *et al.*, 1996). Overgrowth of such islands by a cap layer of a semiconductor with higher band-gap often takes more than 8 nm without annealing before a completely flat surface is recovered (Joyce *et al.*, 2002; Liew *et al.*, 2007; Suseendran *et al.*, 2009; Krause *et al.*, 2014). The capping leads to flattening of the islands and some lateral diffusion of the larger atomic species from the buried islands into the surrounding barrier material (Steimetz *et al.*, 1998; Bischoff *et al.*, 2000; Chen *et al.*, 2008), which will be enhanced by subsequent annealing (Qiu *et al.*, 2010a,b). The flattening changes the dot geometry, with a reduction in height leading to higher carrier confinement energies and thus a blue-shift. Lateral interdiffusion or intermixing changes the chemical composition of the dot, with a correlated reduction in strain and lattice parameter leading to a further blue shift. Thus both size and chemistry of the quantum dots need to be carefully controlled in order to engineer the optical emission wavelength of the quantum dots to a desired wavelength. As the carrier confinement in quantum dots is stronger than in thin films or quantum wells made of the same material, optical emission is often more efficient. This is the basis of many modern light-emitting diodes (LEDs) and laser diode devices. A detailed review of the optoelectronic properties of quantum dot systems has been compiled by Yoffe (2001).

If growth proceeds on nonplanar substrates that have been patterned by ultraviolet (Grützmacher *et al.*, 2007), X-ray (Buso *et al.*, 2009), electron beam (Chu *et al.*, 1994; Gourgon *et al.*, 1994) or focused ion beam (Gray *et al.*, 2006; Zhang *et al.*, 2013) lithography or by nano-imprinting (Cheng *et al.*, 2011), arrays of periodic quantum dots can be produced which have potential applications in microcavities and as photonic crystals.

Microscopy studies of quantum dots

Optical ellipsometry and photoluminescence

The collection of light integrated over a certain region, the size of which is diffraction limited (i.e. of the order or the wavelength of the light, or larger), yields average optical properties of ensembles of quantum dots: ellipsometry measures the rotation of the polarisation of incident polarised light, photoluminescence the optical emission spectrum upon excitation with a higher energy laser line and photoluminescence excitation spectroscopy certain resonance features in the quantum dots when the incident laser wavelength is varied. These techniques are described in almost all textbooks on optical materials.

Optical microscopy of individual quantum dots

The diffraction limit of lens-based optical microscopes lies in the region of half the wavelength of the light used for illumination and is thus usually too large to investigate individual structures on the scale of a few nm to several 10nm, such as typical quantum dots. If, however, the distances between adjacent quantum dots are larger than about 500nm, or a single quantum dot is positioned in a microcavity (Peter *et al.*, 2005) or the microscopy is performed in near-field mode and a mask is used to cover all other adjacent quantum dots but one, which effectively selects a quantum dot at a specific position (Makhonin *et al.*, 2013), imaging and spectroscopic investigation by microphotoluminescence of selected single quantum dots are possible.

Scanning probe microscopy

Atomic force microscopy measures the topography of samples and is now routinely used to determine the areal density, heights and lateral widths of free-standing epitaxial quantum dots (i.e. without any cap layer). If the tip is conductive, this can be directly combined with scanning tunnelling microscopy (STM), cf. Tanaka *et al.* (1999). STM can easily achieve atomic resolution at cryogenic temperatures and in addition allows the user to also image the surface reconstruction, distinguish between filled and empty states and thus distinguish atoms/ions from different groups of the periodic table in compound semiconductors, which can be used to measure surface diffusion lengths of each type of atoms. Employing a stationary probe and varying the bias can be used to determine the band-gap, integrated over the area where the tip interacts with the surface, at intermediate energy resolution (Ebert

et al., 1996). STM imaging has also been performed on cleaved samples of layers of quantum dots, yielding cross-sectioned views of these (Eisele *et al.*, 1999), or at elevated temperatures during epitaxial growth in standard plan-view geometry (Voigtländer, 2001).

Scanning electron microscopy

Secondary electron imaging in a scanning electron microscope exhibits strong topographic contrast and can thus be used to measure size distributions of quantum dots on exposed surfaces if a field-emission source with a corresponding small source width is used. Due to the directional dependence of the signal upon the position of the detector, such images can provide three-dimensional impressions of the surface topography. In contrast to scanning probe methods, it is usually difficult to accurately calibrate the height information from exposed islands or quantum dots. Backscattered electron detectors can provide additional chemical contrast as heavier atoms scatter more strongly and can emerge from deeper regions within the specimen, enabling the imaging of quantum dots that have been covered by other thin material, however, such images are generally noisier and more difficult to quantify. Direct chemical analysis based on energy-dispersive or wavelength-dispersive X-ray spectroscopy of quantum dots on surfaces suffer from the extent to which the electron beam penetrates the sample and thereby creates an interaction volume from which X-rays are generated that is often orders of magnitudes larger than individual quantum dots. Reimer (1998) wrote a textbook that provides a comprehensive overview of imaging and microanalysis in a scanning electron microscope (SEM).

Cathodoluminescence

As it is relatively easy to cool the sample stage in an SEM down to very low temperatures using liquid nitrogen or even liquid helium, low-temperature cathodoluminescence (CL) studies can be performed if the electron beam excites bound electrons from the valence to the conduction band. If an optical spectrometer or a light-sensitive detector is incorporated into the electron microscope, CL spectroscopy and pan-chromatic imaging of single quantum dots can be performed (Williams *et al.*, 1991). Combining a pulsed electron emitter with a streak camera, time-resolved CL can be recorded to study excitation and relaxation dynamics (Merano *et al.*, 2005). Incorporation of CL into a scanning transmission electron microscope (STEM) is more difficult because both cooling of the sample and efficient collection of the light emitted are tricky to achieve, but as the sample is a thinned section, the interaction volume with the higher energy electron beam is smaller and the spatial resolution can be better (Pennycook *et al.*, 1980) if it is not limited by the diffusion length of charge carriers within the sample or on its surfaces. Successful applications to quantum dot systems have only rather recently been described (Zagonel *et al.*, 2011).

The decay of an excited atomic state can generally occur via emission of either visible light or of Auger electrons. If an electron energy analyser is incorporated, a so-called scanning Auger electron microscope (SAM) is formed (MacDonald & Waldrop, 1971), the lateral resolution of which has over the decades been decreased sufficiently to in principle also enable imaging with a resolution sufficient for the study of quantum dots (Venables *et al.* 1976; Hembree & Venables, 1992), although no such study on quantum dots has yet been reported.

Bright- and dark-field transmission electron microscopy

Bright- and dark-field electron microscopy in transmission geometry is routinely applied to characterise colloidal or epitaxial quantum dots. The latter can be studied in plan-view geometry, looking down onto the surfaces covered, or in cross-sectional geometry. In plan-view, the quantum dot density can be easily measured, and an estimate of the size distribution and geometry can be obtained, although for the latter strain effects have be taken into account as it has been shown that typically lens-shaped strained islands of cubic materials can exhibit an apparent square symmetry in top-view and features related to specific crystallographic directions (Zou *et al.*, 1999). Resolution is typically in the range of 0.3–0.5 nm, depending on the primary electron voltage and size of the objective aperture used, which is sufficient to clearly observe shape transitions in quantum dot systems *in situ* during epitaxial growth and capping (Ross *et al.*, 1998).

High-resolution electron microscopy

High-resolution electron microscopy can be performed with either planar illumination (HR-TEM) or by raster scanning an area with a focused electron beam (HR-STEM) at high magnification. If the resolution of the instrument is sufficient, lattice planes reveal the underlying crystal structure so that extended defects, such as dislocations, stacking faults, twins, inversion domains, antiphase domains and grain boundaries can be studied. In particular, the mechanism for dislocation generation in compressively strained small islands is important for the understanding of the formation of epitaxial quantum dots, their partial strain relaxation and the role of dislocations as non-radiative defects. It has been shown that the first dislocations in compressively strained islands usually form at the sides of the often facetted islands, as the local strain is highest here (Cullis *et al.*, 1995). The strain in the underlying buffer and its relaxation may be measured directly from lattice fringe displacement fields (D'Anterroches *et al.*, 1987; Rosenauer *et al.*, 1997), however, care has to be taken to estimate thin foil relaxation effects in cross-sectioned samples which can introduce

severe artefacts (Mallard *et al.*, 1991; Walther & Humphreys, 1995; Tillmann *et al.*, 2000).

Electron holography

Holography measures phase shifts from interference of at least one diffracted with a reference wave, and there are several different possibilities to implement this technique in a transmission electron microscope (Cowley, 1992). As phase shifts in reciprocal space directly correlate to displacements in real space, even tiny local displacements of atomic columns, which can be due to in-built static crystal potentials and doping (Rau *et al.*, 1999) or piezoelectric fields (Barnard & Cherns, 2000) or to strain fields (Hytch *et al.*, 2008; Cooper *et al.*, 2011), can be visualised and measured.

Energy-filtered transmission electron microscopy

If a transmission electron microscope is equipped with a two-dimensional detector behind an imaging energy filter, of which different designs exist (electrostatic Henry–Castaing type, single magnetic prism type or multiple electromagnetic type), then a slit in the energy-dispersive plane can be used to restrict the detected signal to electrons that have undergone specific energy losses. Varying this energy-loss systematically (which is most often performed by adjusting the primary electron energy and retaining the set-up of all postspecimen lenses to minimise aberration) series of energy-filtered images can be recorded (Reimer, 1995; Walther *et al.*, 1995). If this is performed around the plasmon loss, a distribution map of the local plasmon loss energy can be recorded, which may be material specific, so that the chemical composition in projection (Kong *et al.*, 2012) or the material-specific effective electron mass (Gass *et al.*, 2004) can be mapped. If an ionisation edge is investigated instead and the background routines that are typically used in electron energy-loss spectroscopy (see next paragraph) are applied to whole image series, then jump-ratio maps for qualitative phase imaging (Brydson *et al.*, 1995), elemental maps for semiquantitative compositional imaging (Liao *et al.*, 2002) or fully quantitative elemental concentration maps (Walther *et al.*, 2001a,b) of cross-sectioned quantum dots can be recorded with sub-nm spatial resolution.

Electron energy-loss spectroscopy

If a one- or two-dimensional detector is placed behind an energy-dispersive element, which can be magnet, a transverse electrical field or a combination thereof, then the intensity distribution of the electrons can be recorded as function of energy-loss. Such an electron energy-loss spectrum (EELS) consists of the zero-loss peak, phonons, inter- and intraband transitions that allow inference of the local band-gap by so-called valence EELS (Howie & Walsh, 1991) if the band-gap is large enough not to be swamped by the massive tails of the intense zero-loss peak (van Benthem *et al.*, 2001; Schamm & Zanchi, 2002), which can be reduced by monochromation (Erni & Browning, 2005; Walther & Stegmann, 2006), and if Cherenkov radiation effects (Gu *et al.*, 2007; Stöger-Pollach & Schattschneider, 2007) and surface guided modes (Erni & Browning, 2008) are negligible. At higher energy losses, plasmons of bulk, surface or interface type are observed and finally atomic ionisation edges on an almost exponentially decaying Bremsstrahlung background. The intensity of the ionisation edges (core losses) is proportional to the product of incident beam intensity, inelastic scattering cross-section and atomic areal density of the corresponding element (Krivanek *et al.*, 1991) so the latter, or the corresponding elemental concentration, can be determined with quasi-atomic spatial resolution. EELS has been used to measure lateral segregation of Ge atoms across SiGe islands, which are considered precursors of quantum dot structures (Walther, 2000).

Energy-dispersive X-ray spectroscopy

If the ionisation measured by the electron energy-loss is the primary excitation event then the radiative emission of an X-ray when an electron from a higher shell jumps into a lower energy shell to fill the hole due to the previous ionisation is the secondary event. As all shells in atoms have discrete energy levels given by the rules of quantum mechanics, their differences are also discrete. Such transitions hence yield sharp, element-specific X-ray emission peaks, so-called characteristic lines, on top of a low and broad background of Bremsstrahlung. The integrated peak intensity is proportional to the product of X-ray fluorescence probability of an atom, absorption within the sample, detector window transmissivity, detector efficiency and chemical concentration (Williams & Carter, 1996). X-ray spectra can thus be used to measure the chemical composition at certain points, and mapping allows fully compositional distribution maps to be obtained easily. However, as the energy resolution of X-ray detectors is poor (typically 50–140 eV for Si:Li solid state or Si drift detectors, depending on energy range and pulse processor setting, down to at best 2–8 eV for a microcalorimeter for low-voltage SEM; Wollman *et al.*, 1997, 2000) compared to electron energy-loss spectrometers (typically 0.3–2 eV for field-emission cathodes, down to now 0.03–0.05 eV with the most recent monochromators; Essers *et al.*, 2010; Krivanek *et al.*, 2013), no direct chemical information is usually available in this mode, making it at least very difficult to distinguish bonding in different materials, for example, silicon in Si compared to SiO_2.

Electron diffraction

Kikuchi patterns from back-scattered electrons in SEM or selected-area diffraction patterns in TEM can both be used to distinguish amorphous from crystalline quantum dot structures, and if the quantum dots are single crystalline their

crystal structure (crystallographic point group, hexagonal wurtzite vs. cubic sphalerite) can be determined as well.

The problem of reliable size measurements

Although electron microscopy is a standard tool to measure size distributions of colloidal and epitaxial quantum dot systems (cf. Rice *et al.*, 2013), the microscopist should be aware of some potential pitfalls related to the above imaging, mapping or diffraction methods.

SEM, particularly if no field-emission gun is available, often has insufficient spatial resolution to image the very smallest quantum dot systems that can be only a few nanometres in width.

TEM based mapping approaches based on CL, EELS or EDXS spectral data are only meaningful if both statistically significant count rates are obtained and a high enough sampling (i.e. fine enough pixel size) is chosen for the maps. For a given dose, both criteria basically exclude each other, which means that long acquisition times will be needed that may finally induce drift or lead to beam damage or even particle disintegration. Using the EFTEM approach, it has been shown for the example of gold nanoparticles on titania support (i.e. not a quantum dot system in the strict sense, as outlined above, but related) that the particle detection limit of $\sim$1 nm was ultimately limited by surface diffusion of the smaller particles on the support during the extended exposure, rather than by electron optics (Walther & Mader, 1999).

HREM and HR-STEM can both yield atomic resolution images, but the detection probabilities for small colloidal particles will depend very much on the medium of support and the chemistry of the particles themselves. Although particles with diameters $>>2$ nm that yield sufficient phase contrast are generally rather well visible, smaller particles will be more difficult to detect under bright-field conditions, which can be due to geometrical overlap problems (Bescond *et al.*, 2014) or weak scattering in the presence of stronger scattering from a polycrystalline support or other uneven background (Gontard *et al.*, 2011). If one carefully compares size measurements by HREM and ADF-STEM, then the results for particles >5 nm in diameter typically agree very well, whereas similar measurements for smaller particles can disagree significantly: HREM tends to overlook some of the particles <2 nm in diameter (if tiny crystals are oriented off Bragg conditions, or the particles are amorphous, their phase contrast can be minute), and this will distort the apparent size distribution (Walther, 2004). In summary, transmission electron microscopy can be used to calculate particle size distributions, but the histograms may be somewhat truncated for particle diameters <2 nm in case of weakly scattering objects or due to beam damage, surface diffusion during extended exposures or simple detection issues.

Finally, the Scherrer formula to determine average particle sizes from the broadening of diffraction peaks, which was originally developed for X-ray diffraction (Patterson, 1939) but equally applies to electron diffraction, only yields numerically exact data for round colloidal nanoparticles or small isotropic polycrystals. For highly elongated colloidal particles, various empirical form factors need to be taken into account, and epitaxial quantum dots are usually not dense enough to yield any meaningful measurements by this method.

Tomography and the projection problem

All micrographs and local measurements with a focused beam of any structures in transmission geometry are thickness-integrated projections (In the case of electron beam channelling (Howie, 1966) and, in particular, highly focused electron probes with small depths of focus (Dwyer & Etheridge, 2003), the influence from sections at different depths may not be weighted equally. Although this is generally not a problem for colloidal quantum dots as long as they are dispersed evenly on a suitable carbonaceous support grid so that each quantum dot can be imaged individually, the problems in interpreting data from epitaxial dot or island structures that have either been cross-sectioned at unknown depths or are embedded in barrier material can be significant: the chemical composition and sometimes even the structure along the electron beam direction is no longer constant along the electron beam path. In particular the situation where small dots are more or less completely surrounded by other material, which will broaden the electron beam by multiple (mainly elastic) scattering and thereby increase the interaction volume, makes it difficult to assess quantitatively the concentrations of chemical elements within the dots. Raw measurements hence often underestimate concentrations of minority elements considerably (Walther *et al.*, 2014), and modelling of the electron beam-solid interaction will be required to reconcile experiment and theory, as has been demonstrated by, for example, Crozier *et al.* (2003). In such cases, tomographic approaches or simply projections from different directions near major zone axes, may help to elucidate the interplay between shape, lattice structure, strain and local composition.

Summary

Quantum dot systems are relevant for optical, biomedical and optoelectronic applications. Their main feature is the intensity of their spectral emission. This optical property depends critically on a number of parameters, such as size, shape, crystallographic structure, defects, strain and local chemical composition, that are themselves linked in a complicated way. Microscopy, in particular electron microscopy with its high spatial resolution, holds the key to measure these parameters for individual quantum dots, and different microscopy techniques can be combined to address the rather complicated interplay between the above mentioned parameters.

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