Nanoscale characterisation of semiconductors by cathodoluminescence

K Thonke, I Tischer, M Hocker, M Schirra, K Fujan, M Wiedenmann, R Schneider, M Frey and M Feneberg

1 Universität Ulm, Institut für Quantenmaterie / Gruppe Halbleiterphysik, DE-89081 Ulm, Germany
2 Otto-von-Guericke-Universität, Institut für Experimentelle Physik, Magdeburg, Germany

E-mail: klaus.thonke@uni-ulm.de

Abstract. Cathodoluminescence measurements carried out either in a scanning secondary or a transmission electron microscope allow a direct correlation of structural features with the emission spectra. Applied to semiconductors, numerous material and electronic properties can be determined on a length scale down to 10 nm in favourable cases. In this tutorial, we discuss the nature of the most important light emission processes in semiconductors, and what kind of information can principally be derived. Several examples for the application of this method in studies on bulk and nanocrystalline semiconductor materials are discussed.

1. General
This manuscript is the summary of a tutorial presented at the EMAS 2013 workshop and addresses material scientists working on other classes of materials than semiconductors, or using other electron microscope based methods than cathodoluminescence like EDS, etc. It is not meant as a comprehensive review of all latest achievements, but tries to show some typical cases starting from features and defects in 3D samples, and continues with examples of the analysis of lower dimensional systems. For a broader discussion, the reader is referred e.g., to the book of Yacobi and Holt 0, or for review articles like Refs. [2-8]. A more theoretical analysis of the optical excitation processes can be found in Ref. 0. An overview over data processing procedures and noise reduction of “hyperspectral” CL images can be found in Ref. 0.

Here, we first want to discuss the nature of different electron-hole recombination processes in semiconductors to understand what information these potentially can carry, and then shortly look at some experimental considerations, before we consider several examples and extensions of the method.

2. Luminescence processes in semiconductors

2.1. Fundamentals of radiative recombination processes
To understand what kind of information can be drawn from cathodoluminescence (CL) spectra, we first take a look at the possible radiative recombination processes in semiconductors with so-called direct bandgap, i.e., those with both the valence band maximum and conduction band minimum at the same \(k\)-value (figure 1). In this type of material, electrons and holes can recombine and – in fortunate
cases – emit a photon without any phonon being involved in the process, which in indirect semiconductor is needed to fulfill the **dispersion relation** of the single particle electron states in a semiconductor. The band gap separates mostly occupied states in the valence band (VB) from the mostly unoccupied states in the conduction band (CB). In direct semiconductors (like gallium arsenide, GaAs), the maximum of the VB and the minimum of the CB are both at the same **k**-value, typically **k** = 0, whereas in indirect semiconductors (like silicon, Si) these are shifted. Recombination requires then a phonon to be involved, what makes the process less probable by some 3 or 4 orders of magnitude as compared to the direct case.

Process “a)” is a direct band-band recombination from an electron in the conduction band with a hole in the valence band, which is typically the dominant process at room temperature for defect-free direct semiconductor materials. The emission band starts at the (temperature dependent) band gap energy **Egap** and extends to higher energies. It is governed in its line shape by the combined density of states **D(E)** in both bands involved, and the occupation probability, which for not too highly doped or highly excited semiconductors can be approximated by a Boltzmann distribution.

At low temperatures, these charged particles (e,h) form electron-hole pairs called excitons (“X”), before they recombine (process “b)” in figure 2). This lowers the emission energy by the exciton binding energy, which is typically in the range of some 5 meV to 50 meV, depending on the effective mass of the particles involved and the dielectric constant of the material.

In the next step, these excitons can diffuse through the crystal and attach by exchange interaction to neutral shallow dopant impurities, forming excitons bound at donors (D⁰,X) or acceptors (A⁰,X). Depending on the band structure, also binding to ionized impurity cores ((D⁺,X), (A⁻,X)) might be possible. In direct semiconductors, the **k** selection rule leads to relatively sharp excitonic emission lines (ΔE ≈ 1 meV) with hydrogen-like excited states, since the **k**-value of the photon emitted is negligible compared to the **k** values of the electron and hole states involved.

**Figure 1.** *E(k)* dispersion relation of the single particle electron states in a semiconductor. The band gap separates mostly occupied states in the valence band (VB) from the mostly unoccupied states in the conduction band (CB). In direct semiconductors (like gallium arsenide, GaAs), the maximum of the VB and the minimum of the CB are both at the same **k**-value, typically **k** = 0, whereas in indirect semiconductors (like silicon, Si) these are shifted. Recombination requires then a phonon to be involved, what makes the process less probable by some 3 or 4 orders of magnitude as compared to the direct case.
Figure 2. Possible radiative recombination processes in semiconductors in a simplified band model. “e” and “h” stand for free electrons and holes, respectively. “D°” and “A°” are neutral donors and acceptors, i.e., shallow dopants, which still have (at low temperature) their excess particle bound. “X” marks electron-hole pairs, so-called excitons.

Processes involving again shallow dopants, but no excitons, are the free electron $\rightarrow$ acceptor ($e$,A°) transition or their counterpart, the donor $\rightarrow$ free hole ($D^\circ$,h) transition. Since free particles are involved, their density of states and thermal energy distribution is mirrored in the emitted line shape. These bands start at a lower threshold energy ($E_{gap}$ - $E_A$) or ($E_{gap}$ - $E_D$), respectively.

For certain doping ranges, transitions between neutral donors ($D^0$) and neutral acceptors ($A^0$) become observable, leading to series of lines merging to broad bands due to Coulomb interaction of the charged donor ($D^+$) and acceptor ($A^-$) cores in various distances left over after recombination.

Finally, internal transition between levels localized at point or extended defects might occur. Examples for point defects are transitions in the d-shell of transition metals or the f-shell of rare earth atoms. Extended defects like dislocations often just act as non-radiative sinks for excited particles showing up as dark regions in the sample (like in GaAs), but might also lead to specific (broad) emission bands below the bandgap energy like the D$_1$-D$_4$ lines in silicon, or the basal plane stacking fault related emission bands in gallium nitride [12, 13].

Generally, all these transitions are affected by several broadening mechanisms. Thermal broadening by shortening the lifetime of the initial or final state of the transitions leads to Lorentzian type line shapes. Broadening by statistical fluctuations of strain in the material, or the influence of charged impurities arranged around statistically, alloy fluctuations in composed materials, etc., lead typically to Gaussian type line broadening. If free particles are involved, their thermal distribution also affects the line shape by introducing exponential high energy band tails.
2.2. Which semiconductor property can be measured via which emission type?

In this section we want to discuss, what kind of information can be drawn from which spectral feature, which might be measurable in advantageous cases. It is clear, that several prerequisites have to be fulfilled to be in a position for getting out interesting information. First of all, the overall luminescence signal level should be high enough to record low noise spectra and low noise “wavelength maps”, i.e., charts which show, which signal can be excited on which spot. Unlike optical microscopy, the CL method does not detect where the light is coming from, but where it can efficiently be excited. If for the distinction of close lying narrow lines high spectral resolution is necessary, a monochromator with a long enough focal length and a sensitive detector are required, since in this case the entrance slit of the monochromator has to be set quite narrow. The sample should not spatially drift during the spectra recording, and not pile up charges, which distort the image. Let us first look at local properties of bulk semiconductors.

From the emission energy of either the band-band (e,h) transition (process “a)” in figure 2) or the free exciton X (process “b)” in figure 2), the bandgap energy can be evaluated (in the latter case the exciton binding energy must be known). For simple materials like elemental or binary III-V or II-VI semiconductor crystals (like GaAs, ZnSe), any deviation from the literature value (at a given sample temperature) contains information about the local strain in the sample. For most semiconductors of technical interest, the deformation potentials describing the change in bandgap energy as a function of the strain components are known. If the strain situation is clear – what means that the relative contributions of axial and shear strain is known – the shifted bandgap energy gives a direct measure for the strain.

The situation becomes more complicated, when alloys of semiconductor are under investigation. In the case of ternary crystals like (Al,Ga)As, a local determination of the composition can be undertaken – if the strain situation is known. For the case of more complex materials like quaternary compounds (e.g., (In,Ga,Al)P used for red LEDs), some additional input from other methods (like EDS or EELS) is required to separate the individual atomic ratios.

For indirect semiconductors, the band-band or excitonic recombination is only allowed with an additional phonon involved, as mentioned above. In the case of alloys from elemental indirect semiconductors like the technologically important Si$_x$Ge$_{1-x}$, additional information can be drawn from the “phonon replicas” of the transitions, i.e., those spectral lines, which are shifted from the bandgap or free exciton energy by characteristic phonon energies. For mixed SiGe crystals, different modes of Si-Si, Ge-Ge, and Si-Ge vibrations can couple to the electronic transition and lead to multiple low-energy sidebands. From the relative intensity of these, also information on the local composition can be drawn. In principle, minor shifts of the phonon energies also give a measure of the local strain – but this is very hard to access for these broader lines.

Another important issue for semiconductor devices is the local dopant concentration. The presence of shallow dopants leads to the occurrence of bound excitons in the spectra (process “c)” in figure 2), which are found at slightly lower energy (some meV) in the spectra than the free excitons. For moderate dopant concentrations, the associated lines are rather sharp, but are becoming broader for high concentrations. Either from their ratio relative to the free exciton or the line shape, the dopant concentration can be estimated. For most semiconductors, different dopants lead to different well separated emission lines –allowing for the simultaneous determination of compensating dopant concentrations.

The information contained in the free-to-bound transitions (processes “d”),”e)” in figure 2) is mostly less pronounced, since these lines are broader due to the thermal distribution of the free carriers, and are mostly weaker than the bound exciton lines in the spectra. Nevertheless, there are some examples in literature, where from these bands acceptor energies of (deeper) defects in ZnO or GaN were determined.
The donor-acceptor pair band \((D^0,A^0)\) is often observed for crystals with minor quality, e.g., GaAs substrate material. If the binding energies of the two shallow dopants involved are known, the concentrations of the more abundant dopant can be estimated from the energy position of the emission band maximum.

But also if the defects of interest do not emit light, but just act as efficient non-radiative recombination centres, CL studies reveal the presence of these point-like or extended defects as dark points or lines on an otherwise luminescent background. For not too high defect densities, this allows statistics on the density of such defects.

When it comes to low-dimensional semiconductor structures like quantum wells (2D), quantum wires (1D), and quantum dots (0D), the locally and spectrally resolved CL allows gathering information on quantized states and – in best cases – even their spatial extension. These quantized states lead to maxima in the emitted spectra, which might be compared to model calculations. The local variation of the emission of quantum dots with statistically varying size, embedded in a matrix with higher bandgap, is a typical application of CL.

CL can also provide valuable information on optical resonator structures built from semiconductors or patterned hetero-layer systems from these. When the detection system is set to a characteristic allowed wavelength of the resonator, spatial mapping yields a landscape, on which spots of the structure excitation is more or less efficient, i.e., where are the maxima and the nodes of the resonant mode electric field distribution. This way, e.g., “whispering gallery modes” in tapered ZnO nanopillars were analysed or of coupled ultraviolet standing waves in ZnO pillars with only \(\approx 100\text{ nm diameter}\) 0. Vice versa, fixing the excitation spot to a point of interest, an emission spectrum should result which mirrors the full spectral resonator characteristics.

3. Experimental considerations

3.1. Experimental setup

For spatially resolved CL, two basic types of equipment are of interest: either the implementation in a scanning secondary electron microscope (SEM-CL) – what is the most popular version –, or in a scanning transmission electron microscope (TEM-CL). Whereas in the case of the SEM-CL simultaneous recording of the surface structure can be combined with CL emission maps, in the TEM-CL case one tries to combine a “look through the sample” with emission charts. Both methods have their specific advantages, disadvantages, and experimental requirements. For the SEM version, classically there has to be made a choice between eventually higher image resolution as obtainable with field-emitter-type cathodes at the cost of lower beam current, or higher e-beam brightness as available with LaB\(_6\) cathodes at the cost of reduced image quality. For the newest generation of field emitter type microscopes, this conflict is now overcome with new electron optics providing simultaneously high current (~ 100 nA) and excellent image quality. For most practical cases, a beam current of 0.1 nA … 1 nA is high enough.

For spectroscopy on semiconductors, it is advantageous to have a low temperature cryostat available. Typically, the signal level increases for low temperatures by reducing the efficiency of competing non-radiative recombination channels. Any shallow bound states e.g., like bound excitons, which carry information on doping, are observable only at sufficiently low temperatures, what could mean in cases like donor bound excitons in GaAs temperatures below 10 K. Practically all emission spectra broaden with higher temperature either by thermal filling of states proportional to \(k_B T\) (like in the case of quantum wells, locally varying bandgaps in inhomogeneous materials, or free excitons in indirect semiconductors), or by lifetime broadening as a consequence of thermal activation of competing recombination channels. The latter process might even affect sharp intra-3d or 4f transitions in transition metals and rare earth atoms. If one is interested in determining the real radiative lifetime of radiative recombination processes by time-resolved CL, one has good chances to do so at low temperatures.
Although numerous CL investigations can be carried out successfully at room temperature, a liquid nitrogen cooled sample stage, or even better a liquid helium cooled cryostat opens the path for more detailed investigations. But these cooling devices introduce the problem of vibrations – caused by the evaporation of the cooling liquid in the tubes - and special care must be taken in the microscope cryostat design. Also, additional drift problems due to thermal expansion/contraction have to be faced. In any case of cooling, the vacuum system of the electron microscope has to be absolutely oil free, since otherwise the sample – as the coolest spot in the system – will be contaminated rather fast.

### 3.2. Coupling out the light

In both cases of SEM-CL or TEM-CL, one of the key questions is which way to couple out the light efficiently, without disturbing and shadowing the signal on the electron (or other like X-ray) detectors.

Commercial setups for SEM-CL mostly use a scheme, where an elliptic (or parabolic) mirror is placed between the last electron lens and the sample stage (figure 3). A small hole (Ø < 1 mm) drilled into this mirror allows the electrons to pass. The acceptance solid angle can be made quite large (some 60 % of 2π), but at the cost of losing secondary electron (SE) signal on the typical SE detector placed horizontally apart. Any in-lens detector for backscattered electrons placed in the electron column cannot be used efficiently with this arrangement. Since for high spatial resolution the primary electron energy has to be quite low (e.g., E ≈ 2 keV for 50 nm in GaN), the working distance WD (i.e., the distance between the pole piece and the sample) has to be reduced to ≈ 3 mm for most electron optics. This cannot be realized with mirror optics squeezed in between. Some minimum height of such mirrors is around 6 mm, and their focal length on the object side ≈ 3 mm. This means that on the detection side a largely magnified light spot is created with typically ≈ 0.5 mm diameter including the blur circle. As long as only low spectral resolution is required, the signal can pass through the entrance slit of the monochromator, but not so if higher spectral resolution is needed.

![Figure 3. Typical arrangement for SEM-CL: The light is coupled out via an ellipsoid mirror. A small hole allows the electrons to pass. The sample is in one of the focal points of the ellipsoid, and the detection system entrance at the other.](image)

Alternatively, the CL detection system can be attached to an electron probe microanalyser (EPMA) with built-in mirror optics, which collects the light from a certain angle on top and then couples it out sideward into the detection system 0, or to collect the light via a reflecting microscope objective mounted laterally from a sample holder tilted by 45° (see figure 4 and Refs. [10, 18]). In both cases, the collection efficiency is reduced compared to the larger mirror used in the figure 3, but shielding of other detectors is avoided, and perfect electron images, collection of X-rays, etc. are available. The better image quality of this type of optics allows focusing the collected light onto a small (i.e., diameter of ≈ 25 µm 0) spot at the entrance slit of the monochromator.
A further alternative for coupling out the light is to use a glass fibre 0, which is approached from the side under a low angle close to the excited spot (figure 5). For a fibre with 100 µm diameter approached to 50 µm distance, the numerical aperture value is still $\approx 0.7$ and thus quite reasonable. The advantage of the latter mentioned setups is that all the electron and X-ray detectors can be used with almost the same signal level as without CL addition – even the in-lens detector. The disadvantage of the fibre approach is that an additional moving part has to be carefully handled, and that not all directions of the emitted light are captured.

For the TEM-CL case, the light collection mirror could either be mounted on top of the sample in a similar way as described above, or just underneath the sample to couple out again the light sideward, and also with a hole to let the electrons pass to the rest of the TEM lenses and electron image detector.
3.3. Spatial resolution

The achievable spatial resolution in CL is governed by three main factors: (i) the beam diameter, (ii) the volume, where the electron energy is deposited and (e,h) pairs are generated, and (iii) the diffusion length of minority carriers and excitons. Besides these, vibrations of the sample mounted to a cold finger might be a serious problem.

The beam diameter in modern field-emitter SEMs is \( \approx 1 \ldots 2 \text{ nm} \) and not limiting the resolution. From the Bohr-Bethe energy-loss relation, phenomenological models for the stopping range \( s_0 \) as a function of electron energy \( E \) in the form \( s_0 = kE^\alpha \) were derived, valid in the energy range 5 - 25 keV. For SEM-CL, the average depth \( z_D \) the electrons reach in the sample (i.e., the centre of the scattering ellipsoid) is \( z_D = \frac{2s_0}{1+\sqrt{1}} \left( 1 - \exp \left( -\frac{E}{Z} \right) \right) \), with the atomic number \( Z \). As an example, a rough estimate for ZnO and 2 keV electron energy gives an excited ellipsoid-shaped region with approximate half-axes of \( a = 39 \text{ nm} \) and \( b = 32 \text{ nm} \) with \( z_D = 13 \text{ nm} \). Another approximation for the penetration depth \( z_D \) of a sphere-shaped excited region was given by Kanaya and Okayama as \( R = \left( \frac{K}{\rho} \right) E^\alpha \), with \( K \) a material specific constant \( \sim Z^{8/9} \), \( \rho \) the material density, and \( \alpha = 1.67 \ldots 1.75 \).

There are also several Monte-Carlo type simulation programmes available [25, 26]. The major problem for these is the estimation of the scattering cross-sections and the energy loss at low energies. A simulation for the excited range in GaN for electrons with 2 keV primary energy is shown in figure 6. We find most of the scattering events concentrated in a rather small volume, and an overall range of about 50 nm diameter for 90% of the events for this specific case.

![Figure 6. “Scattering bulb” for 2 keV electrons in GaN calculated by a Monte Carlo simulation using the “continuous slowing down approximation”. The colour scale encodes the number of inelastic scattering events per volume. (From M. Hocker, Diploma Thesis, University of Ulm, 2012).](image-url)

The third parameter influencing the resolution, the diffusion length of minority carriers and excitons, is rather material and sample specific. In direct semiconductors like GaN it is at low temperatures in the range of 50 - 100 nm, but can become very large for indirect semiconductors like silicon. For highly doped or defect-rich material this length might be shortened to some few nm. Also high surface recombination rates suppress the diffusion process. Drift movement of excited (e,h) pairs by built-in electrical fields should not be a critical factor, since these fields separate the pairs (or they even can crack excitons), and this way suppress radiative recombination. Our practical experience on ZnO nanostructures or bulk samples with defects is that the scattering bulb diameter gives the right estimate for the characteristic length found for CL contrast changes. We were able to record spectra from GaN structures for energies down to 0.4 keV, what should allow for lateral and depth resolutions on the 20 nm range. Donolato has shown in his calculations on a uniformly excited sphere, that the excess carrier density outside this sphere falls off very steep (faster than exponential) – what means, that the carrier-redistribution by diffusion should not play a big role in most situations.
For STEM-CL, the situation is different, since the very sharply focused high energy (60 - 300 keV) beam mostly penetrates through the very thin (≈ 50 nm) sample prepared for TEM, exciting (e,h) pairs primarily just in a cone shaped volume with ≈ 1 nm diameter on the top. The spread \( d_b \) (μm) of the beam at the bottom of the sample is given by

\[
d_b = 6.25 \left( \frac{Z}{E} \right)^{1/2} \left( \frac{\rho}{A} \right) \frac{t^{3/2}}{}
\]

with the atomic number \( Z \), \( E \) the electron energy in keV, \( \rho \) (in g/cm³) the material density, \( A \) the atomic weight in (g/mol), and the sample thickness \( t \). The excess carriers are mainly concentrated in the central region. Carrier diffusion then also might broaden the excited range, but since the next surface acting as an efficient recombination sink is never far, this broadening effect is expected to be marginal. Actually, there are reports of STEM-CL on nanostructures with ≈ 10 nm lateral resolution [32, 33]. Practically, the preparation necessary for TEM investigation requires sample thicknesses between 50 nm and 100 nm. This creates a defective surface layer on both sides of typically > 30 nm thickness, which has high non-radiative recombination rates. Therefore, additional steps are required for TEM-CL to remove these defects and to get light out of the sample – a rather delicate task. For as-grown nanostructures with suited thicknesses this step is not necessary. Since STEM-CL requires high electron energies, much faster defects in the sample might be created by the electrons.

3.4. Detection system issues
In the simplest case, a photomultiplier tube or any other relatively fast detector suitable for the wavelength range under investigation is enough to record so-called “panchromatic” CL maps. When appropriate colour filters are added, such maps can be recorded wavelength-selective. When complete spectra should be recorded, a monochromator with a grating optimized for the specific task (i.e., the best suited resolving power and grating blaze) has to be inserted. For very efficient collection, a multi-channel detector like a cooled CCD camera is advantageous. This way, for each point of the sample complete spectra may be recorded during the scan forming a so-called “hyperspectral image”. These data can then be processed for monochromatic CL images etc. externally. Problems arise with this technique, when large sample drifts or charge pile up occurs during the recording time, or when the sample degrades under the electron bombardment. Alternatively, a single channel detector might be used to record sequentially spectral maps for each wavelength – synchronously with SEM micrographs. To get rid of drifts occurring between the scans, correlation of the SEM micrographs helps to shift the CL maps correctly over each other. For time resolved CL spectroscopy, a fast beam blanker (or a photocathode hit by a pulsed laser) is required on the excitation side, and a fast detection system like a photon counting PMT or a streak camera.

4. Examples of SEM-CL
In this chapter we will take a look at several examples of CL spectra of semiconductors recorded in scanning electron microscopes, either from the top or on cross-sections. For SEM-CL, the samples do normally not need special treatment besides cleaving for access to the desired cross-section.

4.1. Cross-section of a thick GaN layer: hidden defect structures
In figure 7 an example of a cross-section of an epitaxial layer of AlGaN grown on sapphire is shown. The Al content in this layer is slightly below 20 %. Whereas in the secondary electron micrograph no special features are visible, the CL map recorded on the same region clearly shows the traces of several defects, which appear as non-emitting dark horizontal lines in the lower part. In the upper Si-doped range, the emission is shifted to slightly longer wavelength, but relatively homogeneous.
4.2. Non-planar sample with quantum wells: local change of composition

The example shown in figure 8 comprises InGaN quantum wells emitting in the visible range on top of “inverse pyramid” GaN structures. The depressions are approximately 5 µm deep. Whereas in the SE image (left) just a few point-like defects close to the ridges are visible, the colour-coded CL map (right) shows distinctively different emission colours from different facets. Obviously, already minor changes in the orientation of the surface lead to clear changes in the growth rate and composition of the quantum wells, which then change their quantized state energies and emission wavelengths. Remarkable in this example is also the very large depth of focus of the electron and CL image, which allows recording changes in emission wavelength with very high lateral resolution.
4.3. Defect identification in semiconductors: stacking faults in GaN; direct correlation with TEM

Numerous CL studies in literature are dedicated to the local detection of point or extended defects in semiconductors. As an example, we take a look at high-resolution CL spectra recorded on the cross-section of triangular GaN stripe structures (figure 9). Low-temperature CL finds here highly localized horizontal stripes, from which the dominant defect bands at 3.41 eV and 3.32 eV are emitted. Then a thin cross-section lamella was cut out just at the same position, which was then analysed by HR-TEM to localize the exact position and type of stacking faults present there. This way a direct correlation revealed that the band at 3.32 eV is introduced by type I$_2$ stacking faults, which electronically act as fcc structure GaN quantum wells embedded in hexagonal structure GaN barriers.

4.4. Spectroscopy on V-pit defects in InGaN/GaN

Another example of defect identification by correlation of changes in emission and defect structures visible in SEM micrographs was recently presented by Bruckbauer et al. On the surface of c-plane InGaN quantum wells embedded in GaN barriers, they see the typical “V-pits” with diameters in the range of 50 - 100 nm present in high densities, plus chains of such pits and trench-like features. In a detailed room temperature CL investigation over the diameter of typical pits, they found a pronounced change of emission energy and intensity with changes on a scale of 10 - 20 nm, see figure 10. It is not straightforward to distinguish between changes in In-concentration, in strain, quantum well thickness or changes in piezo-field based on CL maps alone, and correlation with data from other methods like TEM, EDS or other is required.

4.5. Local determination of dopant concentration: ZnO nanowires

A CL setup based on a field-emitter SEM (FESEM-CL) allows to record in one synchronous run very detailed images of the nanostructures under investigation together with emission maps. As discussed above, setting the electron excitation spot to a specific region of interest, also spectra with high energy resolution can be recorded, when a larger monochromator and a sensitive detector like a liquid-N$_2$ cooled CCD camera are attached.
Figure 9. Left: Schematic drawing of GaN stripes with triangular cross-section grown by selective epitaxy on sapphire substrate. By FIB a slice was cut out for high-resolution TEM studies. Right: emission bands at different energies originate from highly localized emission spots and stripes. (Reprinted with permission from 0; copyright American Physical Society).

Figure 10. Details of pits in InGaN/GaN quantum well samples. a) SEM micrograph of a region with different defects like isolated pits, agglomerates of pits, and trenches; b) CL energy map derived from fits to room temperature CL spectra recorded at 5 kV on this area; c) related CL intensity map; d and e) CL line scans through trench-like features with pits and an isolated pit. (From 0; reprinted with permission from Applied Physics Letters; copyright AIP Publishing LLC.).
For the case of high quality ZnO, the half width of the bound exciton emission lines at low temperature can be below 100 µeV. To distinguish different donor dopant species like Ga or In emitting close-lying sharp lines, a spectral resolution of \( \approx 200 \) µeV is required. We carried out such measurements on single ZnO pillars on sapphire substrate in side view under \( \approx 45^\circ \) tilt 0. Indeed, significant changes in the dopant concentration and emission intensity mirroring the crystal quality can be found from bottom to top. Seemingly, a certain amount of Al diffuses from the sapphire substrate into the lower part of the pillar as evidenced by the Al bound exciton (line “I6” in figure 11). The crystal quality becomes best just below the tip (spot #4), whereas it degrades again at the very tip (spot #5), where eventually parts of the catalytic alloy drop, which governed the growth, resides.

**Figure 11.** FE-SEM micrograph of single ZnO pillars on sapphire substrate, and low temperature high resolution CL spectra recorded on the marked spots. “I6” corresponds to the aluminium bound exciton, and “I8” to excitons bound to gallium donors. (Reprinted with permission from 0; copyright American Institute of Physics).

4.6. Resolution test for SEM-CL on layered heterostructures

A very nice example to check the resolution of a SEM-CL system was published by Norman 0 (figure 12). He was looking at the cross-section of GaAs quantum wells embedded in AlGaAs barrier layers. There were stacked different sequences on top of each other with well and barrier thicknesses decreasing from 40 nm to 10 nm. When this stack of layers is mapped at 2 keV electron energy, a CL intensity modulation can clearly be seen for the 30 nm structures, and partially still for the 20 nm period ones. Of course, due to the change of quantisation energies in the quantum wells of different thickness, also the emission energy must increase when moving the e-beam to thinner wells. Eventually, the resolution could be even improved applying lower electron beam energy.
5. Examples for STEM-CL

Principally, the resolution limit imposed by the volume excited by the electron beam can be made much smaller in STEM-CL, and resolution down to 10 nm has been reported. A 1:1 correlation with high resolution TEM micrographs would be the ideal goal, but is hard to reach due to the vibrations the sample is subject on a cold finger sample holder typically required.

5.1. Triangular III-nitride nanowires

STEM-CL studies on III-nitride core-shell nanowires were reported by Lim et al. They obtained a lateral resolution of 20 nm, and recorded either local spectra with a multichannel detector, or monochromatic CL maps at 110 - 300 K sample temperature (see figure 13). Selective area electron diffraction (SAED) patterns recorded on the areas of interest allow to classify the crystal structure and growth direction. Dark-field STEM images were recorded simultaneously with the CL spectral maps.

5.2. Quantum discs in a nanowire

Recently, Zagonel et al. have published a study on a nanowire with ≈ 50 nm diameter and a sequence of thin AlN/GaN heterolayers with a period length of ≈ (3 nm (AlGaN) + 1 - 3 nm (GaN)) incorporated, covered by a thin (5 - 10 nm) AlN shell. The structure is shown in figure 14a. The emission wavelength shifts along the wire, what is ascribed to the slowly changing diameter and strain. The authors claim a lateral resolution of 1 nm, what might be correct for the high angle annular dark field (HAADF) signal recorded in parallel, but is not obvious for the CL maps shown in figures 14c-e. A line scan along the NW axis shows clear modulation in the HAADF intensity, and is just resolvable at some spots for the 6 nm periods in the CL signal (see figure 15).
Figure 13. Direct correlation between structural and optical properties on the cross-section of a GaN/InGaN/GaN/AlGaN SQW nanowire. a) Bright-field TEM image and SAD pattern taken along the [11-20] zone axis (scale bar = 300 nm). b) Dark-field STEM image showing weakly the InGaN SQW (scale bar = 100 nm). c) EDS line scan profiles of Al, Ga, and In along the yellow arrow in (b). d) Cross-section schematic drawing of the SQW nanowire. e) Dark-field STEM image of the same SQW nanowire during the CL measurement (scale bar = 300 nm). f) 110 K CL spectrum of the SQW nanowire. g and h) Monochromatic images. (Reprinted from 0; permission from Nano Letters; copyright American Chemical Society).

Figure 14. TEM-CL study on a GaN/AlN nanowire with 20 quantum discs embedded. The images have a size of 256x64 pixels with 0.6 nm / pixel, and a colour depth of 256 pixels, $\Delta \lambda = 2$ nm/pixel, recorded within $\approx$ 6 min. a) HAADF image, where GaN appears whiter, AlN darker, scale bar is 20 nm. b) HAADF acquired simultaneously with the CL, scale bar 20 nm. c) Wavelength position. d) Intensity, and e) FWHM of the most intense peak. Some individual spectral features can be correlated to some individual quantum disks, as emphasized by the black dashed rectangles (E = 60 kV, T = 150 K). (Reprinted with permission from Ref. 0; copyright American Chemical Society).
5.3. Time-resolved CL

Time resolved CL measurements are possible, when the beam can be blanked and a fast enough detection system like a PMT in photon counting mode or streak camera is used. Electronic beam blanking allows for variable excitation pulse width and repetition rates, and allows for time resolution on the scale of 35 psec. Even shorter times, but at fixed repetition rate and pulse length are accessible by using a photocathode for the electron emitter excited by a short pulse laser system to produce electron pulses on the 10 psec time scale. Figures 16 and 17 show the scheme of the setup, and time resolved spectra recorded with the streak camera on InGaAs/AlGaAs pyramid structures. From the 10 keV electron energy, we would estimate the lateral resolution to be on the order of 100 - 200 nm.
6. Investigation of resonator modes

The CL method can also be utilized to excite specific modes in optical resonator structures made from semiconductors or isolators – or even plasmon modes on metal-nano-antennas. Schirra et al. 0 looked at the coupled modes for UV light occurring in very thin ZnO nanowires with ≈100 nm diameter and a few µm length. Nobis et al. 0 recorded along thicker tapered hexagonal ZnO rods with diameters around 1 µm whispering gallery modes of different order. In a recent publication, Sapienza et al. 0 tested the local density of optical states (LDOS) in a photonic crystal cavity (here in Si₃N₄) on the 30 nm scale using the electron beam as a local point source. They were able to resolve the spatial mode structure at a so-called “H1 defect” photonic crystal cavity (see figure 18).

![Figure 17. CL signal from InGaAs/AlGaAs pyramids recorded with a streak camera. The sample comprises different quantum structures like quantum dots (QD) on top, vertical quantum wires (VQWR), lateral quantum wires (QWR), vertical quantum wells (VQW), and quantum wells (QW) on the facets of the pyramid (E = 10 keV, T = 90 K). (Reprinted by permission from [35]; copyright Macmillan Publishers Ltd.).](image17)

![Figure 18. a) SEM image of a photonic crystal membrane with a hole defect (H1 cavity) with a lattice constant a = 330 nm and a hole diameter of 230 nm. b) LDOS image of the cavity in the centre part of a) at a wavelength of 650 nm, with a bandwidth of 9 nm. (Reprinted by permission from [36]; copyright Macmillan Publishers Ltd.).](image18)
7. Extension: combined CL characterisation + E-beam lithography (CLL)

By covering the sample with a thin e-beam photoresist, the CL setup can be used in a combined mode for first selecting a region of interest by the emitted CL signal, and then using the e-beam for a writing process (figure 19). Gschrey et al. recently suggested and applied this procedure to create well-isolated single quantum dots (QDs) from InGaAs QDs embedded in a GaAs matrix, densely grown in statistical order by the Stranski-Krastanov-Method. For thin PMMA layers, the semiconductor structures underneath can still be excited and their (visible range) emission detected.

![Figure 19. Process steps for combined CL and e-beam lithography: a) Spin coating of the sample by PMMA; b) Selection of an InGaAs QDs by means of the CL signal emitted through the PMMA layer; c) e-beam lithography + dry etching to create sub-µm mesas; d) mesas with single quantum dots result. (Picture courtesy of S. Reitzenstein, TU Berlin).](image)

After having localized special bright spots, the e-beam is used to pattern the PMMA layer. After development of the resist and final dry etching, pre-selected, well isolated QDs embedded in mesa structures are created. Optical experiments on these (by µ-PL) indeed show perfect quantum dot single emitter behaviour.

8. Summary

In this tutorial article, we discussed first the fundamentals of different recombination processes in semiconductors and what information they carry, and looked at some basic experimental considerations. Some typical examples of studies on nanosized defects in bulk samples and on nanorods illustrate the possibilities (and difficulties) of SEM- and TEM-based cathodoluminescence. Extension like time-resolved CL and in-situ e-beam lithography show some further perspectives of this rather powerful method, which can yield very rich information especially when combined on the same sample with methods capable of atomic resolution like TEM.

Acknowledgements

The authors thank the group of Prof. Scholz (Univ. of Ulm, Inst. of Optoelectronics) for the loan of several samples presented here. Anton Reiser, Günter M. Prinz, Tobias Röder and Manfred Madel (Univ. of Ulm, Inst. of Semiconductor Physics, and Inst. of Quantum Matter) grew the ZnO-nanopillars presented. A part of this work was supported by the Deutsche Forschungsgemeinschaft (DFG) in the frame of the SFB 569, and the “PolarCon” research group.
References

[1] Yacobi B G and Holt D B 1990 *Cathodoluminescence microscopy of inorganic solids.* (New York: Plenum Press)

[2] Christen J, Grundmann M and Bimberg D 1991 *J. Vac. Sci. Technol. B: Microelectron. Nanometer Struct.* 9 2358-2368

[3] Petrov V I 1992 *physica status solidi (a)* 133 189-230

[4] Gustafsson A, Pistol M-E, Montelius L and Samuelson L 1998 *J. Appl. Phys.* 84 1715-1775

[5] Gustafsson A 2008 *Scanning* 30 317-323

[6] Dierre B, Yuan X and Sekiguchi T 2010 *Sci. Technol. Adv. Mater.* 11 043001

[7] Edwards P R and Martin R W 2011 *Semicond. Sci. Technol.* 26 064005

[8] Stowe D 2011 *physica status solidi (c)* 8 1423-1426

[9] Garcia de Abajo F J 2010 *Rev. Mod. Phys.* 82 209-275

[10] Edwards P R, Jagadamma L K, Bruckbauer J, Liu C, Shields P, Allsopp D, Wang T and Martin R W 2012 *Microsc. Microanal.* 18 1212-1219

[11] Sauer R, Weber J, Stolz J, Weber E R, Küsters KH and Alexander H 1985 *Appl. Phys. A* 36 1-13

[12] Liu R, Bell A, Ponce F A, Chen C Q, Yang J W and Khan M A 2005 *Appl. Phys. Lett.* 86 021908

[13] Tischer I, Feneberg M, Schirra M, Yacoub H, Sauer R, Thonke K, Wunderer T, Scholz F, Dieterle L, Müller E and Gerths D 2011 *Phys. Rev. B* 83 035314

[14] Nobis T and Grundmann M 2005 *Phys. Rev. A* 72 063806

[15] Schirra M, Feneberg M, Prinz G M, Reiser A, Röder T, Thonke K and Sauer R 2009 *Phys. Rev. Lett.* 102 073903

[16] Nakaji D, Grillo V, Yamamoto N and Mukai T 2005 *J. Electron Microsc.* 54: 223-230

[17] see a scheme at http://ssd.phys.strath.ac.uk/index.php/File:CL_system.gif

[18] see scheme of P Edwards and Rt Martin at http://nano.strath.ac.uk/local/2009-11/Edwards_Nanometrology_Nov09.pdf, page 8

[19] Hoenk M E and Vahala K J 1989 *Rev. Sci. Instrum.* 60 226-230

[20] Everhart T E and Hoff P H 1971 *J. Appl. Phys.* 42 5837-5846

[21] Werner U, Koch F and Oelgart G 1988 *J. Phys. D* 21 116

[22] Schirra M, Reiser A, Prinz G M, Ladenburger A, Thonke K and Sauer R 2007 *J. Appl. Phys.* 101 113509

[23] Kanaya K and Okayama S 1972 *J. Phys. D: Appl. Phys.* 5 43-58

[24] Donolato C 1978 *Optik* 52 19-36

[25] Drouin D, Couture A, Joly D, Tastet X, Aimez V and Gauvin R 2007 *Scanning* 29 92-101

[26] Demers H, Poirier-Demers A R, Joly D, Guilmain M, de Jonge N and Drouin D 2011 *Scanning* 33 135-146

[27] Hocker M (University of Ulm) private communication

[28] Tischer I, Feneberg M, Schirra M, Yacoub H, Sauer R, Thonke K, Wunderer T, Scholz F, Dieterle L, Müller E and Gerths D 2011 *Phys. Rev. B* 83 035314

[29] Bruckbauer J, Edwards P R, Wang T and Martin R W 2011 *Appl. Phys. Lett.* 98 141908

[30] Schirra M, Reiser A, Prinz G M, Ladenburger A, Thonke K and Sauer R 2007 *J. Appl. Phys.* 101 113509

[31] Norman C E 2002 *Microsc. Analys.* 16(2): 9-12

[32] Lim S K, Brewster M, Qian F, Li Y, Lieber C M and Gracdecak S 2009 *Nano Letters* 9 3940-3944

[33] Zagonel L F, Mazzucco S, Tencel M, March K, Bernard R, Laslier B, Jacopin G, Tchernycheva M, Rigutti L, Julien F H, Songmuang R and Kociak M 2011 *Nano Letters* 11 568-573

[34] Bertram F, Christen J, Dadgar A and Krost A 2007 *Appl. Phys. Lett.* 90 041917
[35] Merano M, Sonderegger S, Crottini A, Collin S, Renucci P, Pelucchi E, Malko A, Baier M H, Kapon E, Deveaud B and Ganière J-D 2005 *Nature* **438** 479-482

[36] Sapienza R, Coenen T, Renger J, Kuttge M, van Hulst N F and Polman A 2012 *Nature Mater.* **11** 781

[37] Gschrey M, Gericke F, Schüßler A, Schmidt R, Schulze J-H, Heindel T, Rodt S, Strittmatter A and Reitzenstein S 2013 arXiv:1304.3631v1 [cond-mat.mes-hall], April 2013