4 Experimental methods

4.1 Sample materials and preparation

For investigation dynamics and electrical activity of glide dislocations in typical compound semiconductor with zincblende and wurtzite lattice structure GaAs and ZnO bulk samples with low-index surface were chosen.

The GaAs bulk crystals were Si-doped n-type with carrier concentration about $5 \times 10^{17}$ cm$^{-3}$ and had $\langle 1\overline{1}1 \rangle \overline{1}$ B surface orientations.

The ZnO samples have been prepared from (0001) substrate wafer or from bulk crystal in form of hexagonal prisms that provide $(10\overline{1}0)$ and $(1\overline{1}20)$ planes as samples surfaces to be studied. The material was colourless and transparent by sight.

The ZnO materials were not doped, n-type with carrier concentration in the range of $10^{16}$ cm$^{-3}$. Both the GaAs and ZnO crystals showed low grown-in dislocation density less then $10^4$ cm$^{-2}$.

Figure 35. Low temperature cathodoluminescence spectra of undoped ZnO monocrystalline hexagonal prism.

Figure 35 shows representative CL spectra for the ZnO monocrystalline hexagonal prism used in experiments. As indicated, the two bands had peaks at 375nm and 530nm that were related to excitonic states and oxygen vacancies [stud98, van96] respectively.
Experimental methods

On properties of ZnO

Zinc oxide has attracted a significant amount of attention in the past several years since it is wide band gap the semiconductor finds a number of applications in catalysis, gas sensing, and the fabrication of varistors and other microelectronic devices. ZnO is appropriate for use as a transparent electrode in electronic and electric devices because of its transparency in the visible light region. Recently, ZnO-based optoelectronic devices, e.g. light-emitting diodes [ohn98] and lasers [oht00], have been developed. For the fabrication of such devices, high quality crystalline material with low defect density is necessary to achieve light emission with high efficiency.

ZnO single crystals are being grown in bulk by means of hydrothermal, melt, and seeded vapor phase (SVP) methods. Grown technique yields ZnO wafers having dislocation densities in the $10^4$-$10^5$ cm$^{-2}$ range and impurity level (causing n-type) in the $10^{16}$ cm$^{-3}$ range.

Regarding the ZnO WZ lattice structure the four low-index surfaces are of interest: non-polar (1010) and (1120) surfaces, and the polar (0001)-Zn and (0001)-O surfaces.

The enormous potential for use of ZnO in optoelectronic applications can be explained with reference to in Table 4-1 below which contains key properties of ZnO

<table>
<thead>
<tr>
<th>Type of lattice</th>
<th>WZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constants a and c / Å</td>
<td>a=3.2495, c=5.2066</td>
</tr>
<tr>
<td>Ratio (c/a)</td>
<td>6.137</td>
</tr>
<tr>
<td>Energy gap $E_g$ / eV</td>
<td>3.37 (RT)</td>
</tr>
<tr>
<td>Exciton binding energy / meV</td>
<td>60</td>
</tr>
<tr>
<td>Dielectric constant $\varepsilon$</td>
<td>8.75-10.8</td>
</tr>
<tr>
<td>Melting temperature $T_m$ / °C</td>
<td>2250</td>
</tr>
<tr>
<td>Vicker’s hardness / GPa</td>
<td>1.75</td>
</tr>
<tr>
<td>Young’s modulus / GPa</td>
<td>161-230</td>
</tr>
<tr>
<td>Shear Modulus / GPa</td>
<td>45.5</td>
</tr>
<tr>
<td>Poisson ratio</td>
<td>0.36</td>
</tr>
</tbody>
</table>

4.2 Fundamentals of cathodoluminescence mode in SEM

Cathodoluminescence (CL) is one of the interaction products originating from high-energy electron excitation of a non-metallic target (Figure 36) like semiconductor or insulating materials. CL represents the light emission associated with the materials excitation by the electron beam. CL radiation comes from the radiative recombination of non-equilibrium charge carriers such as electron–hole pairs excited in semiconductors by the impinging electrons. There are several luminescence channels in semiconductors. The recombination can be attained by various radiative transitions between the conduction band ($E_c$) and valence band ($E_v$) by excitons ($E_x$) or from donor ($E_d$) and acceptor ($E_a$) levels induced by dopants, impurities and point defects. Thereby, the energy of an emitted photon equals the difference between the initial and final energy levels of the captured excess electron.
Electron-hole pair recombination is also realized by nonradiative processes such as Auger effect or multiple-phonon generation. In many cases lattice defects can serve as non-radiative recombination centres. Particularly, dislocations may act as local non-radiative centres of carrier recombination.

The scanning electron microscope (SEM) is a very powerful tool to perform CL measurements. The SEM electron optics is utilized to produce a focused e-beam for exciting small region of a sample. The e-beam diameter in the SEM is of the order of nanometers. The excited volume depends on the acceleration voltage of the electron beam. Electron energies ranging from 200 V to 50 keV (0.05-10nA) can be used in the SEM. The resulting probe volumes range from tens of nanometers to a few microns in diameter.

The light emitted from such region is captured by a light collecting optics, and an optical spectrum is obtained using a monochromator equipped with a high-efficiency light detector. By changing the energy of the electron beam it is possible to perform a depth profiling of the optical properties of the specimen. Scanning of the e-beam probe in frame mode produces images of the panchromatic light emission intensities or with specific wavelengths emitted. The lateral resolution of the technique depends mainly on the diffusion length of the excited carriers. It can be as small as the electron probe diameter in the case of very small diffusion lengths and low beam voltages.

There are several requirements concerning the specimens used. Electrically conducting samples are required in order to achieve high spatial and spectroscopic resolutions. The specimen should be stable under electron beam irradiation.

However, there are some limitations, because high magnification imaging requires high electron dose, so specimens need to be relatively beam insensitive. Specimens that degrade under the electron beam should be avoided, i.e. there should not occur any degradation or damage phenomena.

Suitable microscopes to performing SEM-CL are to be used, because the radius of the volume sampled by CL is much larger than the probe diameter. The CL sensitivity in the SEM for CL is primarily determined by the high electron brightness of its electron source. $LaB_6$ guns are preferred to field-emission guns. Cold stages (liquid N or He) are necessary in order to observe optical transitions without thermal broadening.
4.3 Experimental setup for SEM-CL

Two conventional scanning electron microscope apparatus (Jeol JSM6400, Tesla BS300) equipped with particular attachment have been used to conduct the SEM-CL experiments for studying the defects behaviour in the semiconductor crystals samples. To perform measurements at low temperature in the range 4.5K-300K for getting temperature dependences, both instruments are combined with the cooling stages (CF302) from Oxford Instruments Ltd. Controlled cooling down of the samples could be done by means of liquid helium or liquid nitrogen, respectively, flowing through a mini-cryostat integrated in the sample stage. The SEM-CL investigations were made utilising panchromatic and monochromatic mode.

The SEM-CL setup used is sketched in Figure 37.

![Figure 37. Scheme of SEM-CL setup with cooling stage (a). The device for the in-situ deformation (b).](image)

The operation principles of the setup are follow: electrons emitted from cathode (1) are focused by an electron optics (2) on the sample surface (3). The sample can be cooled from 300K down to 4.5K by means of the cooling stage (4). The CL radiation collected by light optics (see Figure 37 (b) for details) passes through a special monochromator (5) to different detectors to be measured in pan- and monochromatic mode. The digital image scanning system DISS 5 operates the electron beam during measurements and acquires the CL signal data quantitatively. It provides special capability of kinematical SEM operation.

For the first time the special micro-indentation setup was developed and installed for the purpose of local plastic deformation under in-situ conditions.

The tool attached for the in-situ deformation is shown in Figure 37 (b). It consists of indenting needle (9) integrated into the optical collection system made up by the spherical mirror segment and a flat 45°-mirror (7, 8). Indenting and scratching can be carried out with the needle (9) by mechanically touching the sample (10) during vertical movement of sample stage.
Plastic micro-deformation by means of in-situ scratching and indentation was used at temperature between 295K and 72K to introduce fresh glide dislocations in the crystalline samples examined. Sample treatment and correlated CL observation could be carried out simultaneously.

The thermal contact with the cryosystem (CF302, Oxford Instruments, UK) is achieved through the “dovetail”-holder (11).

The working parameters of the SEM-CL apparatus are:
1) resolution: 100 nm
2) image size: 512x512 pixels
3) contrast gradation: 8-bit grey scale resolution (255 levels)
4) spectral resolution: 1 nm
5) wavelengths range: form 200 to 1800 nm

4.3.1 Kinematical SEM-CL

Technique of kinematical SEM-CL has been developed as a special tool to reveal dislocations as extended mobile recombination centers in semi-conducting crystals [hoe01]. It may be applied to in-situ plastic deformation [hoe01a] resulting in generation and thermally activated propagation of glide dislocations, and is also applicable under specific conditions of the REDG effect [mae81]. Kinematical SEM-CL studies comprise the observation of dislocation dynamics on microscopic scale as well as an analysis of the CL contrast behaviour at both moving and resting dislocations. Such kind of experiments aims at disclosure of any correlation between dynamics and recombination behaviour at identical defect segments.

Kinematical mode of SEM-CL is realised by means of generating and storing image sequences with frame rates up to real-time imaging condition. The kinematical CL technique can document a complete history of dislocation movement and corresponding CL defect contrast behaviour over a long period. The kinematical SEM-CL is based on an advanced digital scanning and signal acquisition system available for the real-time imaging and fast data processing. Optimum frame rates being available depend on the pixel acquisition times which are limited by a given signal-to-noise ratio, and thus, result from frame sizes chosen as well. In order to save quantitative CL information over dynamic range of 8 bits, uncompressed AVI format must be exploited for movie storage. Sequential CL imaging based on panchromatic signal acquisition with frame rates up to 10 fps according to a minimum pixel acquisition time of 0.4 µs for frame size 500x500 is performed by utilizing the digital acquisition and processing system DISS 5 (point electronic GmbH).

4.4 Description of SEM-CL signal

Figure 38 contains schematically carrier and photonic processes occurring in the SEM-CL experiments. The carrier behavior is primarily represented by the electron-hole pair generation distribution \( g(r) \), the minority carrier diffusion length \( L = \sqrt{D\tau} \), and the radiative and non-radiative bulk lifetimes \( \tau_r \) and \( \tau_{nr} \) which determine corresponding recombination rates \( R_r \) and \( R_{nr} \).
Experimental methods

Figure 38. Scheme of SEM-CL experiments.

The continuity equation for the time-dependent excess minority carrier density \( q(r,t) \) is established as the balance of diffusion and drift currents, total recombination, and beam induced generation rates at each point \( r \) of the sample:

\[
- \frac{\partial}{\partial t} q(r,t) + \nabla \cdot [-D \nabla q(r,t) - \mu V(F(r,t)q(r,t))] - \frac{1}{\tau(r)} q(r,t) = -g(r,t) \tag{62}
\]

Here the total minority carrier lifetime \( \tau(r) = (\tau_{r,1} + \tau_{m,1})^{-1} \) is a defect-related function of the position \( r \) and \( D \) the diffusion coefficient, \( \mu \) the minority carrier mobility. The validity of zero requires a linear recombination model such as band-to-band recombination in the low-injection regime so that the majority carriers do not need to be considered. If electric fields \( F(r,t) \) zero, the stationary balance \( dF/dt = 0 \) is expressed by the steady-state continuity equation for diffusion:

\[
D \nabla^2 q(r) - \frac{1}{\tau(r)} q(r) = -g(r) \tag{63}
\]

Taking into account the actual sample geometry, boundary conditions are to be fulfilled as

\[
D \frac{\partial q}{\partial n} \bigg|_{r=r_s} = v_s q(r_s) \tag{64}
\]

for any surface or interface at \( r_s \) where a normal diffusion current is related to a non-radiative surface/interface recombination velocity \( v_s \). The carrier density must vanish (\( q(r) \to 0 \) for \( r \to \infty \)) in directions with practically infinite sample extensions.

Different models have been used in the literature [hil98] for the generation rate. To perform a correct quantitative analysis of experimental data, one has to use a realistic generation distribution \( g(r;U_0) = G_0 g_s(r,z) g_c(z) \) (\( G_0 \) is the total carrier generation rate). The basis for the CL contrast calculation are the equations (62) and (63), respectively.

The spectral CL signal defined as photon flux leaving the sample surface and collected by an ideal spectrometer [her84] is given by the integral of the radiative recombination rate over the
sample volume $\Omega_s$ corrected by losses due to spectral optical absorption $\alpha(h\nu)$ and total reflection at the sample surface for escape angles larger than the critical angle $\Theta_c$:

$$I^{CL}(U_B, h\nu) = \mathcal{Q}(h\nu, \varphi) \frac{\Theta}{\sin \Theta} \cdot \int_0^\infty \int_{\Omega_s} d^3x \cdot \frac{q(x)}{\tau_r} \cdot e^{(-\alpha(h\nu)z/\cos\Theta)}$$  \hspace{1cm} (65)

where $\mathcal{Q}(h)$ denotes the relative internal spectral distribution of the recombination radiation. In the case of panchromatic, spectrally integrated CL experiments, eq. (65) remains correct if "effective" parameters for quantum efficiency $\mathcal{Q}$ and $\alpha$ absorption are introduced. $I^{CL}(U_B, h\nu)$ is governed by the local carrier density $q(r)$ which can be deduced from eq. (62). It should be noticed that $q(r)$ directly depends on $\tau(r)$ that is affect by the presence of any recombination active defects.

### 4.4.1 CL contrast of extended defects

For comprehensive studies on the formation of the CL contrast from dislocations it is necessary to take into account the intrinsic nature of dislocation related recombination, as well as effects due to dislocation interaction with surrounding point defects. Moreover, there are additional geometrical contrast factors too. Generally, extended defects are supposed to change the local recombination properties of the sample. Dislocations in semiconductor crystals are known to be very efficient recombination centres. Hence, their electric activity resulting in a recombination contrast has to be considered with respect to bulk recombination rates. The knowledge of matrix signals and corresponding parameters is therefore a general requirement for quantitative analysis of the defect contrasts. The model case of a surface-parallel dislocation as applicable for many both misfit and glide dislocation geometries considered in [hil98] is shown in Figure 39. In Figure 39 (a) the situation for the carrier generation and recombination processes in the vicinity of a dislocation line is outlined. The Volume-Recombination-Model for the dislocation is utilized.

![Figure 39](image.png)

**Figure 39.** (a) Configuration of SEM-CL contrast measurement at a surface-parallel dislocation [hil98]. (b) Scheme for the carrier generation and recombination processes.

In the volume recombination model, the dislocation is characterized by a cylindrical region $r_D$ where the total lifetime $\tau'$ differs from the bulk value. A defect-induced recombination strength [don78] is defined as:

$$\gamma = \frac{\tau}{\tau'} - 1 = \frac{\tau}{\tau_D}$$  \hspace{1cm} (66)
The radius \( r_D \) of the dislocation cylinder may be preliminarily interpreted as a "capture cross section" but one can also try to infer this region from physical dislocation properties such the extension of the core region, strain field or the space charge region of a charged dislocation.

However, it can be shown that for \( r_D \ll L \), where \( L \) is minority carrier diffusion length, the shape of the contrast profile of the surface-parallel dislocation line is independent of \( r_D \). In this case, \( \gamma \) and \( r_D \) cannot be determined separately but form together a so-called defect strength \( \lambda \). On the other hand, impurity decoration or a gettering-induced denuded zone may cause a larger extension of the defect-related region as shown e. g. for GaAs in \([\text{bal76}]\). In such a situation or if specific defect bound emission occurs, the radiative recombination can be also affected. This is considered by introduction of a second defect cylinder \( \Omega_D \) of radius \( r_D \) with modified \( \tau_r \) and radiative recombination strength \( \gamma_r = \tau_r / \tau_r' - 1 \). In principle, this model is able to describe the complex structure of the well-known "dot-and-halo" contrasts.

As the e-beam probe approaches the dislocation site, the SEM-CL signal responds by decreasing as sketched in Figure 39 (b). A single line scan generates a CL intensity profile showing a local minimum at the defect position. The profile dip defines the defect-related CL contrast value \( c \) as part of the CL contrast profile:

\[
c(\xi) = \frac{I_{\text{CL}}(\xi) - I_{\text{CL}}}{I_{\text{CL}}^{\infty}}
\]  

where \( I_{\text{CL}}^{\infty} = I_{\text{CL}}(\xi \to \infty) \) is the matrix signal.

This relationship may be directly applied to SEM-CL experiment. On the other hand, the CL contrast profile may be described by:

\[
c_{\text{CL}}(\xi) = \lambda(r_D, \tau_D) \cdot c_{\xi}(\xi, \xi, U, \alpha, L, \tau)
\]  

This gives a rewritten form the CL defect contrast value as:

\[
c = \lambda \cdot c^*
\]  

where the defect strength \( \lambda \) appears as a parameter characterising the defect recombination activity. There is an access to simulation calculations for the profile function \( c^* \), thus, from quantitative CL contrast measurements the parameter \( \lambda \) may be determined. The \( \lambda \) value represents a “linear recombination velocity” specific for the extended line defect.