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INTRODUCTION

1.1. ELECTRON MICROSCOPY

Electron microscopy enables the study of matter down to the sub-nanometer scale. The emergence of electron microscopes has resulted in major breakthroughs in different fields of science and technology, including biology, materials science and electronics. Abbe's law, stating that the minimum distance between two points that can be resolved is directly proportional to the wavelength of the source, sets a limit for the spatial resolution of conventional optical microscopes ($\sim 200\,\text{nm}$) [2]. A broad range of optical techniques have been successfully demonstrated to overcome this limit, based on both far and near-field excitation and detection, such as stimulated emission depletion and near-field scanning optical microscopies [2–4]. Additionally, other imaging methods can be used to resolve features down to the nanoscale, including atomic force and scanning tunneling microscopy [5]. In electron microscopy, the small wavelength of the electron wavefunction ($\sim 7\,\text{pm}$ for a 30 keV electron) compared to that of light ($300-800\,\text{nm}$) results in a much larger spatial resolution than that of optical microscopes. In practice, the resolution of current electron microscopes is mainly limited by aberrations of the electromagnetic lenses and the interaction volume inside the sample, and not by the Abbe limit [6].

The first electron microscope was demonstrated in the early 1930s by E. Ruska and M. Knoll, and achieved a magnification of 17.4 [7, 8]. The first prototypes of transmission electron microscopes (TEMs) relied on the formation of an image with 50 keV electrons transmitted through a very thin specimen. Further developments by E. Ruska, M. Knoll and others resulted in higher spatial resolution, soon exceeding that of optical microscopes [8]. Figure 1.1a shows one of the first TEM images of a bacteriophage, obtained by H. Ruska in 1940 [9, 10]. However, the use of TEMs was limited to very thin samples. In order to overcome this limitation, the scanning electron microscope (SEM) was developed in the late 1930s and early

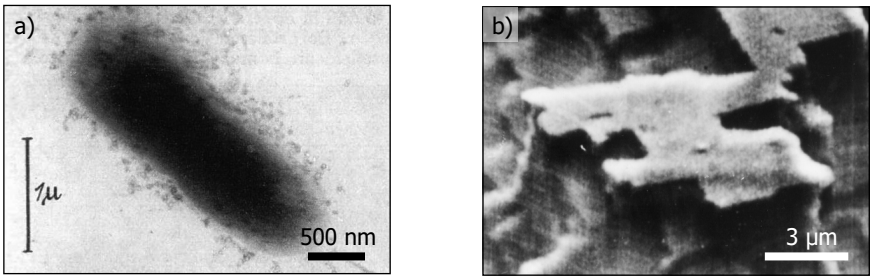

Figure 1.1: Early electron microscope images. (a) One of the first TEM images of a bacteriophage obtained by H. Ruska in 1940 [9]. Adapted from Ref. [10]. (b) SEM image of etched aluminum acquired by D. McMullan in 1952-1953 using the first commercial SEM from Cambridge Scientific Instrument (16 keV, 150 pA, 25° angle of incidence). Adapted from Ref. [11].

1940s, with initial works from M. Knoll, who first achieved a resolution of ~ 100 µm, followed by M. von Ardenne and V. Zworykin [11]. The latter reached a resolution of 50 nm [12]. Posterior improvements in the electron optics and secondary electron analysis resulted in the first commercial SEM being developed 1965 by Cambridge Scientific Instruments [12]. One of the first images obtained with such an SEM is shown in Fig. 1.1b, corresponding to etched aluminum [11]. SEMs rely on the raster scanning of a focused electron beam on a specimen and the collection of the generated secondary electrons, instead of the transmitted electrons as in TEMs. The development of SEMs enabled the study of the surface of bulk samples, thus setting a new milestone in the development of electron microscopy.

1.2. ANALYTICAL ELECTRON MICROSCOPY

Electron microscopes were initially developed to resolve features with a high spatial resolution, thus giving structural information about the sample. However, the interaction of electrons with a specimen results in a plethora of processes, which can be investigated to give direct access to other properties of the material.

One of the main electron-based spectroscopy techniques is electron energy loss spectroscopy (EELS), based on the quantification of the amount of energy lost by the electron when going through a (thin) sample. EELS gives information about the different inelastic scattering events that the electron undergoes in the sample, including the excitation of bulk plasmons, inner-shell electrons and vibrational modes [13]. The recent advances in monochromated EELS have enabled the study of low energy (< 10 meV) processes, including phonon spectra [14, 15]. Another analytical technique that is commonly used in electron microscopes is energy-dispersive X-ray spectroscopy (EDS), which relies on the analysis of X-ray emission. The latter originates upon excitation by the primary electron of core electrons to higher energy states, and their subsequent decay [8]. EDS is widely used for the study of chemical composition of samples with high spatial resolution.

Other analytical techniques used in combination with TEMs, including scan-

Technique	Signal	Main applications	(S)TEM/SEM
EELS	Transmitted electrons	Multiple (see text)	(S)TEM
EDS	X-ray	Chemical composition	(S)TEM/SEM
CL	Emitted light	Optical properties	(S)TEM/SEM
EBSD	Back-scattered electrons	Crystal structure	SEM
EBIC	Induced electron current	Electrical properties	SEM

Table 1.1: Overview of some common analytical electron microscopy techniques in both (S)TEM and SEMs.

ning transmission electron microscopes (STEMs), and SEMs are electron back-scattered detection (EBSD), electron-beam induced current (EBIC) and cathodoluminescence (CL). The latter will be further discussed below. Table 1.1 offers an overview of some common analytical techniques in electron microscopy, together with their most typical applications.

1.3. CATHODOLUMINESCENCE

Cathodoluminescence (CL) refers to the light emitted after excitation of a material with a high-energy electron beam. CL was initially observed in the 19th century, prior to the discovery of electrons, as a glow in vacuum tubes from cathode rays [16]. During the 20th century, CL found its technological application in cathode-ray tubes, which were widely developed as display screens. In parallel, the commercialization of electron microscopes also triggered interest in CL for the study of minerals [17] and semiconductors [18], among others [19]. Additionally, the small size of the electron probe makes CL an attractive tool to study localized excitation of plasmonic and dielectric resonances [20–24].

We can classify CL emission into two types, coherent and incoherent CL, depending on the mechanism of electron excitation and light emission [25]. When exciting a sample with high-energy electrons both types of CL emission can be present, but one typically dominates over the other, depending on the characteristics of the material [26].

1.3.1. INCOHERENT CATHODOLUMINESCENCE

Incoherent cathodoluminescence refers to the spontaneous emission of light after excitation of a sample with an electron beam [25]. The term 'incoherent' accounts for the fact that the emitted CL light does not exhibit a phase relation with the excitation source, that is, the time-varying electromagnetic field created by the incoming electron. Hence, incoherent CL can be considered as a similar form of light emission as photoluminescence, but using electrons instead of photons as the initial excitation source. In this case, the electron acts as a localized source of energy. Moreover, given the high energy of electrons compared to optical transitions, electron excitation enables the excitation of transitions with higher energy than in PL, with the latter typically limited by the energy of the incoming photon.

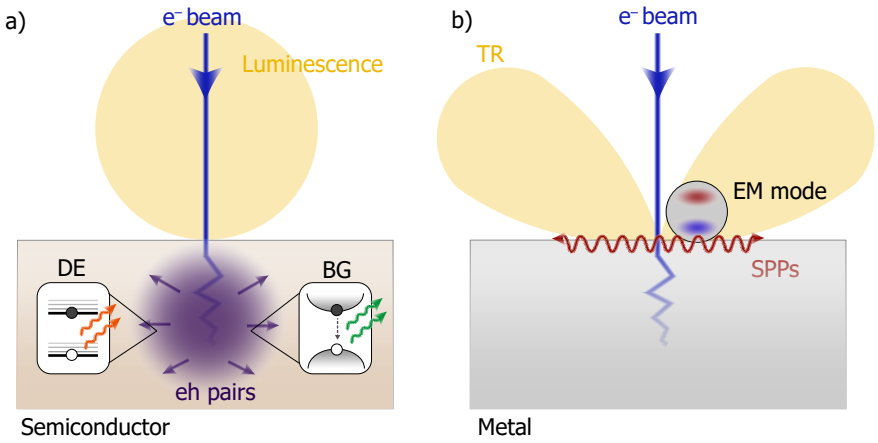

Figure 1.2: Schematic of the different mechanisms of CL emission. (a) Incoherent CL emission: in a semiconductor, the primary electron loses energy through inelastic collisions with the sample, which can result in the creation of charge carriers (eh pairs). The latter can either recombine radiatively through band-edge emission (BG) or excite an interband defect, which can decay by emitting a photon (DE). (b) Coherent CL emission: in a metal, the electron can induce transition radiation (TR), resulting from the polarization of the metal-vacuum interface, and excite surface plasmon polaritons (SPPs), among others. The electron can also excite an electromagnetic (EM) mode of a nanoparticle, for example, a plasmonic resonance.

A schematic of the mechanism of emission of incoherent CL is shown in Figure 1.2a. An electron travelling through a material undergoes multiple inelastic scattering events. One of the main forms of electron energy loss is through the excitation of bulk (or volume) plasmons. Bulk plasmons are collective excitations of valence electrons in a material, and typically have energies in the tens of eV range [13]. The deexcitation of these plasmons (on a fs timescale) results in the generation of one or more energetic charge carriers. In semiconductors, these typically thermalize to the lower energy states of the conduction band within a timescale of several hundreds of fs to ps [27–29]. The thermalized charge carriers can recombine by emitting a photon (band edge emission) or through intermediate energy states in the band gap [19]. Incoherent CL is the dominant form of CL emission in semiconductor and wide-bandgap materials. In this thesis we further explore the mechanisms resulting in the emission of incoherent CL.

1.3.2. COHERENT CATHODOLUMINESCENCE

In coherent CL, the emitted light maintains a phase relation with respect to the electromagnetic field of the electron [19]. Coherent CL results from the polarization of matter by the electromagnetic evanescent field of the electron, and the subsequent decay through emission of light. Fig. 1.2b shows a schematic of different processes that lead to the emission of coherent CL. One of the predominant forms of coherent CL is transition radiation (TR), which originates when an electron transits the in-

terface between two different media. This results in a polarization of the interface, and the subsequent decay through far field emission, which resembles that of a vertical point dipole [25]. Another type of coherent CL is Cherenkov radiation, which arises when an electron travels inside a material at a speed larger than the speed of light in that medium, thus allowing the transformation into far field radiation of the electron evanescent field [25]. Electrons travelling along a periodic array can also result in far field coherent radiation, a phenomenon known as the Smith-Purcell effect.

One of the major applications of coherent CL is the study of plasmonic and dielectric resonances in nanoparticles [20–24]. The evanescent field of the electron can couple to electromagnetic modes in metals and dielectric structures, and the subsequent decay is emitted in the form of coherent CL. Hence, the electron beam can be used to locally probe different resonances, thus taking advantage of the high spatial resolution given by the electrons [30] compared to optical excitation, in addition to its large spectral excitation bandwidth [31].

1.3.3. CL DETECTION MODALITIES

The most common method to analyze CL emission is by studying its spectrum. In this case, CL light is typically directed towards a spectrometer, thus enabling the analysis of its spectral components. CL spectroscopy is both used in incoherent CL, in which it can give valuable information about band edge recombination, the presence of defects in materials and composition of minerals, and in coherent CL, to distinguish between different resonant modes, for example. In recent years, CL analysis has developed beyond spectroscopic studies to offer more detailed information about the process of light emission.

The angular emission pattern of CL light can be studied using angle-resolved CL (ARCL). In this case, the CL beam is directly projected on a 2D detector, such that each point on the camera corresponds to a specific angle of emission [32, 33]. An optical filter is usually placed along the CL beam path to select the desired spectral range. More recently, angle-resolved CL has been extended to provide full energy-momentum (wavelength-angle) information by combining angle-resolved acquisition with spectroscopy [34, 35]. CL polarimetry has also been developed, offering information about the full polarization state of the emitted light. The technique is based on the use of a quarter-wave plate and a linear polarizer along the CL beam path, and the detection of the transmitted light using a 2D detector [36]. More recently, phase-resolved experiments have been performed. In this case, transition radiation was used as a reference field for interferometric investigation, thus enabling the extraction of the phase information of scattered surface-plasmon polaritons [37, 38].

An important feature of light emission is the temporal emission statistics, which give information about excitation and emission dynamics of emitters. Time-resolved CL (TR-CL) measurements usually require the excitation of a sample with a pulsed electron beam. Pulsed electron beams can be obtained by either blanking the electron beam or using a laser-driven electron source, as will be discussed below. In

both cases, the CL emission is guided to a sensitive detector (usually a single-photon detector) and a histogram of the decay statistics is recorded using a time correlator. The time resolution of this method is determined by the detection system, typically corresponding to tens of ps. Hence, this technique is usually suitable for the study of carrier dynamics and lifetime of emitters (for example, quantum dots or quantum wells). Additionally, the temporal information of the emitted light can be extracted by measuring the second-order autocorrelation function ($g^{(2)}(\tau)$) [39], in which two photon-counting detectors are used to record a histogram of the time delay between CL photons. In this case, the emitter lifetime can be obtained without the need of a pulsed electron beam. Moreover, $g^{(2)}(\tau)$ measurements in CL can be used to characterize bunching ($g^{(2)}(0) > 1$) and antibunching ($g^{(2)}(0) < 1$) of optical emitters [39, 40]. Photon bunching in CL occurs due to the fact that one electron can generate more than one photon, and can be used to extract the interaction probability of electrons with optical emitters [41, 42], as will be further explored in this thesis (Chapter 5).

Finally, in this thesis we introduce a new CL technique: pump-probe CL (PP-CL) microscopy, based on the combined excitation of electron and laser pulses on the sample, similar to optical pump-probe measurements. In this case, the sample is excited using either electron or laser pulses, and the resulting state is probed with laser or electron pulses, respectively. The precise control of the time delay between pump and probe beams ensures a high temporal resolution, in principle only limited by the electron pulse width (~ ps or less). Moreover, PP-CL microscopy enables fundamental studies of the dynamics of electron-matter interaction. The development of PP-CL microscopy emerges together with new developments in ultrafast electron microscopy aimed to further explore electron and matter interaction, as will be described below.

1.4. ULTRAFAST ELECTRON MICROSCOPY

Conventional electron microscopes allow us to image materials and nanostructures down to the nanometer scale. However, they typically offer a stationary image, without information about the dynamics of the system. Yet, many key processes that determine material properties occur at very short timescales (fs-ns regime), including charge carrier transport, chemical bond formation and molecular vibrations. Over the years, several instruments have been developed to bring the time dimension to electron microscopy, leading to the emergence of the field of ultrafast electron microscopy (UEM).

We can distinguish two different modalities to obtain time-resolved information in an UEM [43, 44]. The first, and most common one, is the stroboscopic mode [45]. It relies on the repeated excitation of a sample with electron pulses, and the collection of the signal over many ($> 10^7$) experimental cycles to achieve high enough statistics. This method can only be used to study reversible processes, given that the specimen should decay into a stationary state before the arrival of each pulse. The integration over many cycles facilitates the use of pulses containing a very low number of electrons per pulse (usually less than 1), which results in a

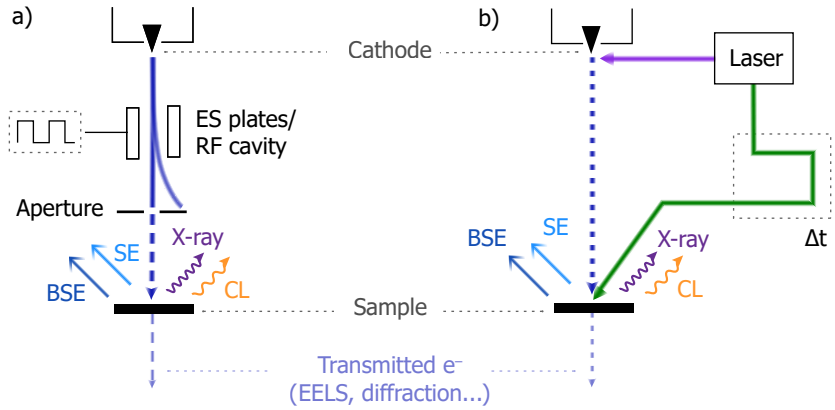

Figure 1.3: Schematic of the two main techniques to obtain a pulsed electron beam in an UEM. (a) Electron beam-blanker: the electron beam is swept over an aperture with a fixed frequency, thus resulting in a pulsed electron beam on the sample. The deflection of the beam is typically achieved by driving electrostatic (ES) plates or using a radio-frequency (RF) cavity. (c) Laser-driven electron cathode: a pulsed laser (usually with fs pulse width) is focused on the electron cathode to induce the photoemission of electron pulses. The same laser beam can be split to synchronously excite the sample at a tunable delay Δt with respect to the electron beam, in a pump-probe fashion. In both techniques (a and b) the transmitted, secondary (SE) and back-scattered (BSE) electrons can be further analyzed, together with X-ray and cathodoluminescence (CL) emission.

high spatial and temporal resolution. In contrast, the second modality of UEM, the single-shot mode, is based on the acquisition of signal after a single electron pulse. The pulses usually contain a large number of electrons ($> 10^5$) to ensure that the collected signal is high enough. Single-shot mode can be used to study irreversible processes, but the use of dense electron pulses typically results in low spatial and temporal resolution.

There are currently two main techniques to obtain a pulsed electron beam in an UEM: electron beam blanking and the use of a laser-driven electron source [44]. Both of them can use either single-shot or stroboscopic modes, and can be applied to SEM and TEMs.

1.4.1. UEM WITH BEAM-BLANKING

The method of beam blanking consists in the sweeping of the electron beam across a small aperture, such that the beam is effectively cut. Figure 1.3a shows a schematic of this technique. The first realizations of beam blanking relied on the deflection of the electron beam by applying a pulsed voltage to a set of electrostatic plates, leading to temporal resolutions in the ns range [45–47]. Further developments of this technique have resulted in even higher temporal resolution, reaching electron pulse widths of a few tens of picoseconds [48, 49], mainly limited by the jitter in the electronics and rise time of the electric pulse [44]. Recently, a design has been proposed in which the plates are driven by a photoconductive switch upon laser

excitation, leading to an electron pulse width of 100 fs [50]. Alternatively, the electron beam can also be deflected using an RF cavity, resulting in a higher temporal resolution, down to 100 fs, at a fixed frequency [51, 52]. Ultrafast electron microscopes using beam blankers can achieve high spatial resolution, close to that for the continuous mode. The main loss in spatial resolution comes from the positioning of the crossover in conjugate mode and deflection of the beam across the electrostatic plates or microcavity [44, 48, 49, 53].

1.4.2. UEM WITH LASER-DRIVEN ELECTRON CATHODE

A key technique to obtain ultrashort electron pulses is by directly changing the way in which electrons are emitted from the electron source. To do so, a pulsed laser (usually with fs pulses) is focused on the electron cathode, resulting in the photoemission of electrons upon photon absorption. Over the years, different configurations have been proposed, using a variety of electron sources, ranging from flat cathodes to sharp nanotips, as used in conventional electron microscopes.

In order to overcome the initial ns temporal resolution of the first beam-blanker techniques, several works in the 1980s and 1990s developed laser-driven cathodes in SEM, TEMs and electron-diffraction systems [43, 54–56]. In the late 1990s, Bostanjoglo and co-workers performed several studies using single-shot UTEM, focusing on the investigation of irreversible processes such as laser-induced melting [57, 58]. In this case, two ns Nd:YAG lasers were used to excite the electron cathode in a conventional thermionic source, and the sample, respectively, achieving 200 nm spatial resolution and ~ 10 ns electron pulses. Subsequent work by LaGrange *et al.* resulted in a higher spatial resolution (~ 20 nm) for 30 ns pulses containing ~ 10^7 electrons [59, 60].

The first UTEMs with atomic spatial resolution and femtosecond electron pulse widths were achieved by the group of Zewail in the 2000s [61, 62]. In this case, the electron cathode of the TEM, a LaB_6 microtip, was irradiated with fs laser pulses, and the same laser was used to synchronously excite the sample. Working in the single-electron regime, with pulses containing one or a few electrons on average, reduces Coulomb interaction between electrons, which is one of the main sources of temporal and spatial broadening of pulsed electron beams [63, 64]. In these experiments, the acquisition of signal was usually performed using the stroboscopic mode, such that many cycles of the experiment were recorded to ensure good statistics. The brightness of UTEMs was further improved by using a Schottky field emission gun (FEG) as the electron source, achieving Å spatial resolution with 200 fs electron pulse width [65]. A UTEM using a cold-FEG has also been demonstrated [66], thus enabling the development of ultrafast electron holography. These new improvements resulted in a rapid growth of applications of UTEMs over the past years [67–71] .

In parallel to the emergence of UTEMs, ultrafast SEMs (USEMS) were also developed. Following some earlier work in the 1980s [54], Merano *et al.* demonstrated an USEM to perform time-resolved CL measurements on GaAs nanostructures [72, 73]. In this case, a flat gold cathode was used, achieving temporal and

spatial resolutions of 10 ps and 50 nm, respectively. USEM with a Schottky FEG was demonstrated by Zewail and co-workers, yielding an improvement of both spatial and temporal resolution (~ 10 nm and ~ 300 fs) [74, 75]. Since then, different groups have performed time-resolved SEM studying both changes in secondary electron yield [76] and cathodoluminescence [77–81], including two commercial systems for time-resolved CL developed by Attolight and Delmic.

1.5. NEW DEVELOPMENTS IN UEM: PUMP-PROBE INSIDE THE ELECTRON MICROSCOPE

The fast development of ultrafast electron microscopy has opened new possibilities to perform novel experiments inside an electron microscope. As can be observed from the first works on UEM, time-resolved measurements are tightly linked to pump-probe experiments: usually a laser beam is used to bring the sample out of equilibrium, and the electron is used to probe the state at different delays with respect to the arrival of the laser pump, in a stroboscopic fashion. Combining the time resolution from UEM with the spectroscopic methods for electron microscopy presented in Table 1.1 in a pump-probe configuration brings a variety of novel techniques to study electron-matter interaction.

Some examples of applications of pump-probe UTEM include the study of the dynamics of structural changes using real and Fourier-space imaging [62, 82], chemical bond formation at the atomic scale [83], laser-induced magnetization dynamics [84] and phase transitions [85, 86]. One of the most prominent new applications of UTEM is photon-induced near-field electron microscopy (PINEM), in which the laser-induced optical fields in nanostructures are probed through the analysis of the electron energy spectrum [87–89]. In this case, the electron exhibits quantized energy gain or loss due to strong interaction between electrons and optical near fields. In USEMs, several pump-probe works have been performed to study photoinduced carrier dynamics in semiconductors [90]. In these cases, the change in secondary electron emission is investigated as a function of delay between optical pump and electron probe.

In addition to the study of material properties, the development of UEM have also attracted more interest into the study of the electron itself. Several works have demonstrated tailoring of the electron wavefunction, resulting in attosecond electron pulses [89, 91, 92], electron acceleration [93] and vortex beam formation [94, 95], among others.

1.6. MOTIVATION AND OUTLINE OF THE THESIS

The developments in UEM allow us to access new domains in the study material dynamics at the nanoscale. However, the interaction of electrons with matter involves many different processes, including both elastic and inelastic scattering, and coherent and incoherent excitation of the specimen. These processes occur at different timescales, ranging from fs, typical for bulk plasmon decay, up to μs, in the

case of thermal effects, for example [29, 43]. This broad range of interactions can result in complex analysis of (time-resolved) electron microscopy experiments. To take advantage of the full capabilities of the new EM developments, it is important to have an in-depth understanding of the dynamics of electron-matter interaction. In this thesis we investigate fundamental properties of the interaction between electrons and matter through the analysis of light emission (CL). We introduce pump-probe cathodoluminescence microscopy as a novel technique to study the interaction of fast electrons with matter through the absorption and emission of light. Similar to the works discussed above, in PP-CL we use electrons and light to excite the sample. In contrast to previous works, we study the light emitted by the sample, either PL or CL, thus enabling for the first time the opportunity to use the electrons as a pump, which gives new insights into electron-matter interaction.

In **Chapter 2**, we describe the design, technical implementation and full characterization of our ultrafast SEM, based on a laser-driven Schotky FEG, including the analysis of the energy, spatial and temporal resolution of the new microscope.

In **Chapter 3** we introduce the technique of pump-probe cathodoluminescence microscopy. We show the technical development of the setup, characterization and alignment procedure. We also discuss the main considerations to account for in PP-CL experiments, including a comparison between CL and PL measurements in semiconductors, and introduce the first results of PP-CL experiments on Cu_2ZnSnS_4.

Chapter 4 presents the first results of PP-CL using electrons as a pump. We investigate the charge-state conversion of NV centers induced upon electron excitation, together with the back-transfer in the ms timescale, and model the state transfer dynamics using a rate equation model, from which all the characteristic timescales are derived.

Finally, in **Chapter 5** we further investigate how electrons interact with matter through the analysis of second-order autocorrelation ($g^{(2)}(\tau)$) measurements. We present a fully analytical model and experimental data of the photon emission statistics of InGaN/GaN quantum wells under different conditions. We describe the amplitude of bunching ($g^{(2)}(0)$) as a function of electron fluence, excitation probability, emitter lifetime and electron pulse width when using continuous, ns-pulsed and ultrashort pulsed electron beams.

Overall, this thesis provides new insights into electron-matter interaction through the study of cathodoluminescence, and presents a new technique to further explore electron excitation and photon emission dynamics at the nanoscale.