Angle-resolved cathodoluminescence nanoscopy

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In this Chapter we present a cathodoluminescence spectroscopy technique which combines deep subwavelength excitation resolution with angle-resolved detection capabilities. The cathodoluminescence emission is collected by a paraboloid mirror and is projected onto a 2D CCD array. The azimuthal and polar emission pattern is directly deduced from the image. As proof of principle, we use the technique to measure the angular distribution of transition radiation from a single crystalline gold surface under 30 keV electron irradiation. We find that the experiment matches very well with theory, illustrating the potential of this technique for the characterization of nanophotonic structures.

3.1 Introduction

In nanophotonics, the research field concerned with the manipulation of light at the nanoscale, basic building blocks like waveguides [15], nanoantennas [29], and nanocavities [111], often have subwavelength geometrical features. Optical phenomena in these structures cannot be resolved with far-field optical microscopy due to Abbe's law of diffraction that provides a limit to the smallest distance over which individual objects can be distinguished. Several spatially resolved spectroscopy techniques have been developed to reach a resolution
below that limit, including scanning near-field optical microscopy (SNOM) \cite{103}, stimulated emission depletion (STED) microscopy \cite{3}, photoactivatable localization microscopy (PALM) \cite{5}, and stochastic optical reconstruction microscopy (STORM) \cite{6}.

Alternatively, cathodoluminescence (CL) imaging spectroscopy is a technique that has a high spatial resolution as well, as it uses an electron beam as an excitation source. In CL spectroscopy, a focused electron beam is raster scanned over a sample. The electron beam effectively acts as a supercontinuum light source that excites the sample according to the local density of optical states (LDOS) \cite{63,112}. Previous work has shown that CL imaging spectroscopy is a powerful technique for probing (nano)photonic environments. In particular, in the field of plasmonics, where large spatial variations in the LDOS can occur on deep subwavelength length scales, CL spectroscopy has proven to be an important characterization technique \cite{69,111,113}.

So far, the CL technique was limited to measuring spectral response as a function of excitation position, and no information about the total angular distribution of the CL emission could be collected. Yamamoto and coworkers developed a technique by which the angular distribution of CL was measured by translating a pinhole in front of a CCD camera, thus collecting point-by-point angular data \cite{106,107}. In this Chapter, we present a further advanced experimental technique to resolve the angular distribution of the CL emission. We demonstrate the technique by measuring transition radiation (TR) for a single crystal gold substrate.

### 3.2 Fourier microscopy with a paraboloid mirror

In our CL system we measure the angular profile by projecting the beam emanating from the paraboloid mirror onto a 2D CCD camera (see Fig. 2.4 for setup configuration). Figures 3.1(a) and (b) show how each pixel in the 2D CCD image is mapped onto angles $\theta$ and $\phi$, calculated using the known geometrical properties of the paraboloid and the experimental settings:

\[
d_{\text{eff}} = d_{\text{pix}} n_{\text{mag}} b \\
y = y_{\text{pix}} d_{\text{eff}} \\
z = z_{\text{pix}} d_{\text{eff}} + d_{\text{foc}} \\
r = \sqrt{y^2 + z^2} \\
x = ar^2 - \frac{1}{4a} \\
\theta = \cos^{-1}\left(\frac{z}{\sqrt{x^2 + r^2}}\right) \\
\phi = \tan^{-1}\left(\frac{y}{x}\right)
\]
3.2 Fourier microscopy with a paraboloid mirror

where \( d_{\text{eff}} \) is the effective pixel size which can be calculated from the hardware binning setting in the CCD array \( b \), the individual CCD pixel size \( d_{\text{pix}} \) (13 \( \mu \)m), and the demagnification factor of the image by the achromatic lens \( n_{\text{mag}} \) which corresponds to 2.01 in this case. \( y_{\text{pix}} \) and \( z_{\text{pix}} \) are the CCD pixel numbers in the \( y \) and \( z \) direction respectively, from which the \( x \) and \( z \) distance from the virtual paraboloid apex can be calculated. Note that one needs to add the focal length of the off-axis paraboloid \( d_{\text{foc}} \) (0.5 mm) to get the correct \( z \)-distance from the apex. Using \( y \) and \( z \) we can find \( x \), where \( a \) is the parabola coefficient (1/10). The solid angle covered per pixel (\( \Omega \)) which is used to correct the data to photon flux per unit of solid angle is given by

\[
\Omega = \frac{d_{\text{eff}}^2}{2a} \frac{2ar^2-x}{(x^2+r^2)^{3/2}}
\]  

Here we take the assumption that the pixels are small enough that we can locally regard the mirror surface flat so that we neglect the curvature of the mirror within the projected area of one CCD pixel [107]. Figure 3.1(c) shows \( \Omega \) for our mirror geometry. Integrating over all pixels that fall within the beam gives a total acceptance angle of 1.46\( \pi \) sr, equivalent to a NA = 0.96 for a microscope objective. Taking only the half space on the closed side of the mirror (see Fig. 2.4(c-e)), the collected solid angle is 0.96\( \pi \) sr, i.e., 96% of the radiation; the remaining 4% leaves through the small opening between mirror and sample. Since we have the ability to rotate the sample by 180°, we can almost entirely reconstruct the emission pattern for the upper hemisphere, corresponding to an effective NA of 0.999.

Figure 3.1: Maps relating pixel position in the CCD image to (a) polar angle \( \theta \), (b) azimuthal angle \( \phi \), and (c) the solid angle per pixel, allowing conversion to an absolute radiation pattern. (d) CCD image showing the measured transition radiation from a single-crystalline gold sample. The white dashed line indicates the mirror contour, and the white circle indicates the position of the hole in the mirror. The scale bar is 2 mm which corresponds to 154 CCD pixels.
3.3 Angular pattern of transition radiation

When an electron passes through an interface between two dielectric environments, it induces a dipole moment on the surface which radiates into the far field which is known as (TR). The TR angular pattern is very similar to that of a vertical point dipole on a surface \[112\]. To test the angle-resolving capabilities of the setup, we measured the TR emission from a polished single-crystalline Au \(<111>\) surface irradiated with 30 keV electrons over the full spectral band of the CCD. A CCD image is recorded with a collection time of only 10 s. For each measurement, we collected an additional image with the electron beam blanked as a reference. Subsequently, this signal was subtracted from the TR-measurement to remove dark counts from the CCD and signal originating from other sources than the sample.

Figure 3.1(d) shows a CCD image obtained using the method described above. The semicircular shape of the paraboloid end face can clearly be recognized. The dark concentric rings in the image are caused by radial imperfections in the mirror which are inherent to the diamond turning fabrication process of the mirror. Also, the hole in the mirror is visible close to the center of the beam. The area around the hole corresponds to emission angles that are almost normal to the surface. This area is relatively dark, while other parts corresponding to more grazing angles appear to be brighter (see Fig. 3.1(a)). This particular pattern in the CCD image points towards a toroidally shaped emission pattern as predicted for transition radiation.

![Figure 3.2](image)

**Figure 3.2:** TR emission probability per incoming 30 keV electron per nm bandwidth as a function of wavelength for the entire upper hemisphere calculated for a gold substrate.

Figure 3.2 shows the probability of exciting a TR photon on a gold surface integrated over the entire upper hemisphere, which was calculated using the theory described in Ref. \[63\] and tabulated optical constants \[114\]. Broadband emission is expected in the 350 – 950 nm spectral band, with a dip around 500 nm which is related to the plasmon resonance frequency in gold. Integrating the probability
of TR emission from 350 to 950 nm, we find a generation rate of $10^{-4}$ photons per incident electron. In this experiment, a current of 12 nA was used which should then generate $8 \times 10^6$ photons s$^{-1}$. Taking into account the acceptance angle of the mirror, known reflection losses in the optics, and the quantum efficiency of the CCD camera, we expect $\sim 4 \times 10^6$ photons s$^{-1}$ to be detected by the CCD camera. Integrating over all pixels in Fig. 3.1(d), we find a collection rate of $3.9 \times 10^6$ photons s$^{-1}$; similar to the calculated value. This indicates that the angle-resolved CL technique provides an accurate absolute measurement of the emitted radiation intensity.

![Figure 3.3: Angle-resolved cathodoluminescence emission patterns of the transition radiation for single-crystalline Au (30 keV e$^-$. (a) Normalized measured emission pattern collected without color filter showing the total emission intensity as a function of emission angles $\theta$ and $\phi$. (b) Normalized calculated emission pattern for the same spectral range as in (a). (c) Emission pattern integrated over $\phi$ for transition radiation at $\lambda_0 = 400$ and 900 nm (solid lines) and theory (dashed lines).](image)

To investigate the angular emission pattern in more detail, the CCD image in Fig. 3.1(d) was converted into a radiation pattern using the conversion maps shown in Figs. 3.1(a-c). The data were interpolated to yield points that are equally spaced in $\theta$ and $\phi$. Figure 3.3(a) shows the angular distribution of TR emission mapped onto a polar grid where the radius represents polar angle $\theta$, and the polar plot angle represents azimuthal angle $\phi$. Fig. 3.3(b) shows the calculated angular distribution for 30 keV electron beam excitation integrated over the spectral sensitivity band of the CCD camera (350 – 950 nm). Data for angles that are not collected by the mirror
are set to zero (black). CL emission close to the surface normal (around $\theta = 0^\circ$) is not collected because of the hole in the mirror. Radiation emitted almost grazing to the surface ($\theta > 85^\circ$) is also not collected because of the small space between mirror and sample (0.5 mm). The largest loss in acceptance angle, clearly visible in the upper part of Figs. 3.3(a) and (b), corresponds to the open part of the paraboloid (see Fig. 2.4(b)). The experiment clearly shows a toroidal emission pattern, in good agreement with calculation. Indeed, the radiation pattern is very similar to that of a vertically oriented point dipole located close to a reflective surface \[103\].

Next, we investigate the wavelength dependence of the angular radiation pattern. Band pass filters (40 nm) were placed in the beam path with center wavelengths $\lambda_0$ ranging from 400 nm to 900 nm in steps of 50 nm, and emission patterns were measured at each wavelength. For these measurements, an integration time of 120 s was used to enable accurate measurements at 900 nm where the sensitivity of the CCD detector is lowest. To accurately compare experiment and theory, the emission patterns were integrated over azimuthal angle $\phi$. Data in the range $\phi = 150^\circ - 210^\circ$ were not taken into account as this corresponds to the section where the aberrations in the mirror are largest (see Fig. 3.3(a)). Figure 3.3(c) shows the normalized CL intensity as function of $\theta$ for $\lambda_0 = 400$ nm and 900 nm together with theoretically predicted emission patterns. We find excellent agreement between experiment and theory. The overall shape of the lobes is well reproduced, and the small difference in lobe orientation between these wavelengths (peak emission around $\theta = 60^\circ$ for 400 nm and around $\theta = 70^\circ$ for 900 nm) is clearly observed.

### 3.4 Conclusions

In conclusion, we have presented an experimental technique for angle-resolved cathodoluminescence spectroscopy. We determined the angular distribution of transition radiation from a single crystal gold substrate and found that the experimental results agree very well with theory. A photon count rate in the order of $10^6$ photons s$^{-1}$ is observed, corresponding closely to the calculated value. The mirror collection geometry corresponds to an effective NA = 0.96. Combining the angle-resolved capabilities with the high spatial excitation resolution of electron microscopy makes this cathodoluminescence technique an interesting tool for studying a wealth of optical phenomena in a wide variety of photonic nanostructures.