Hybrid resonators for light trapping and emission control

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Chapter 5

Design and fabrication of hybrid antenna-cavity systems

We present the design and fabrication of hybrids consisting of microdisk cavities and aluminium nano-rod antennas. Using a two-step lithography process, we place the antennas on the disk edge to ensure coupling to the whispering-gallery modes in the disks, with high accuracy and excellent reproducibility. Taper-coupled spectroscopy is enabled by placing the hybrids on a diamond-sawed mesa. For fluorescence measurements, we develop a novel method to position colloidal quantum dots with nanometer accuracy at the antenna hotspot. We optimize the conditions to obtain near-100% success rate and virtually no quantum dots outside the intended areas. These results pave the way to experiments on hybrid systems. The quantum dot positioning method can also be applied for fabrication of e.g. single-photon sources based on other nanophotonic structures.
5.1 Introduction

When making a hybrid antenna-cavity system, the crucial question to ask is: how does one place an antenna near the cavity mode maximum? Various approaches have been used, with different degrees of control over antenna position. The most straightforward method, with no position control, is to use random distributed antennas in solution, either dropcasted onto the cavity or deposited in a flow-cell geometry [86, 90, 137, 138, 186, 187]. In some cases, this leads to an antenna with the right location and orientation. More control can be obtained by using a self-assembly technique where the cavities (polymer beads) are trapped within a template of gold nano-particles on posts [104, 188]. A truly deterministic methods that can place the antenna with approximately diffraction-limited resolution is direct laser printing [189]. Accuracies in the order of a few nm can be achieved if the antenna is grown directly on the cavity using ion-beam-assisted chemical vapour deposition [85], deposited in a multi-step lithography process [94, 97] or placed using an AFM tip [110]. An approach that offers both high positioning accuracy and in-situ tuning, is to use a near-field tip as the antenna, which can be moved through the cavity mode profile [142, 190]. Such tips may even be structured for e.g. magnetic response [191] or strong field enhancement [98, 192]. Recently, a similar and very promising approach used the reverse mechanism: a gold colloid is positioned on a flat mirror, and a Fabry-Perot-type cavity is formed between this flat mirror and a moveable cantilever containing a concave mirror [193].

Each approach has its advantages in terms of flexibility, scalability, fabrication time and precision. We have chosen to employ a two-step electron-beam lithography process. This technique allows great flexibility in the cavity and antenna geometries, and the relative alignment can, in principle, be done with extremely high precision (down to the e-beam resolution of a few nm). Its main disadvantages are a relatively laborious fabrication process and, since we use evaporation to deposit the antennas, lower antenna material quality than can be obtained with solution-processed techniques [4, 68]. It also somewhat restricts the choice of cavities. For example we cannot use a microtoroid cavity as it is not clear how to accurately place an antenna on it after the glass has been re-flown [47].

Once the hybrid systems are made, a second challenge arises: to benefit from the enhancement of local density of states (LDOS) that was predicted in Chapter 3, emitters need to be placed at LDOS ‘hotspots’ created by the antenna. These hotspots are typically just ~1-10 nm in size for plasmonic antennas [4, 76], putting extreme demands on the positioning accuracy. Although several methods have been proposed, emitter positioning remains one of the major bottlenecks in harnessing the potential of plasmonics for LDOS enhancement and field confinement [66]. For most emitters used in cavity quantum electrodynamics, such as epitaxially grown quantum dots [23], defect centers in diamond [194, 195] or organic molecules [196], little to no
position control is available and emitters are typically randomly distributed over a sample. A common strategy is then to first locate the emitter, and fabricate the cavity around it. An exception is the recent development of controlled color center generation in diamond using a focused ion beam [56, 197]. Several experiments in plasmonic systems have demonstrated some degree of control over emitter position. Linker molecules, with one functional group binding to the emitter and another to the metal, have been used to bind emitters specifically to plasmonic structures [4, 71, 198–200]. Additional positioning accuracy can be obtained by using the local curvature of nanoparticles to decrease screening by other molecules [4], or by screening parts of the sample by a lithographically patterned resist mask [71, 199, 200]. The latter method, however, has proven difficult to reproduce because the emitters may also diffuse through the mask [201]. An alternative approach has been to cover a sample with a homogeneous layer of emitters and to remove or extinguish the undesired emitters using reactive ion etching [185, 201, 202]. This, however, would not be suitable for our samples, since they contain overhanging structures and any emitters underneath them would be screened from the etch. Another interesting new method uses electro-hydrodynamic printing to deposit quantum dots with ~50 nm resolution [203, 204]. Yet, alignment to a photonic structure requires a transparent substrate. A clever alternative approach has been to use the high intensity plasmonic hotspots to do highly localized photo-chemistry. For example, multi-photon absorption in the hotspots can bind proteins [205] or polymerize photoresists locally [206, 207], and if emitters are functionalized for binding to the protein or dissolved into the resist [208], these become self-aligned to the antenna hotspot. Similarly, hot electron emission from plasmonic structures can also cause resist exposure [209] or drive a local chemical reaction [210] that enables covalent binding of an emitter.

We have chosen to use a combination of material-specific linker molecules and a nanopatterned resist mask for the positioning of our emitters, which are CdSeTe/ZnS colloidal quantum dots. This method provides excellent spatial resolution limited only by the e-beam resist. Under the right circumstances it can offer high success rate and very high selectivity, i.e. virtually no quantum dots present outside the intended areas. Moreover, it is a natural extension of the two-step lithography process used to create the hybrids: we can use the same alignment markers and mostly the same methods as used for positioning the antenna. A disadvantage is that the linker chemistry is specific to a certain combination of metal and emitter, and therefore not necessarily extendible to all other combinations.

In this chapter, we explain the design and fabrication of antenna-cavity hybrids. In Section 5.2, we focus on the cavities, after which we discuss the antennas in Section 5.3. Section 5.4 discusses how the hybrids can be accessed by a tapered fiber, through placement on an elevated mesa. We then move on to discuss the positioning of fluorescent emitters. Section 5.5 explains our
choice of fluorescent quantum dots as LDOS probes, and Section 5.6 describes how they are positioned with high accuracy in the antenna hotspots of our hybrid systems.

5.2 Microdisk cavities

As cavities, we use silicon nitride microdisks supporting whispering-gallery modes (WGM). While these do not possess the highest quality factors or lowest mode volumes known, they are in fact very suitable for hybrid systems. Most importantly, an antenna can be placed very near the mode maximum, which lies inside the disk at the disk edge [144]. This ensures we can attain high antenna-cavity coupling strengths or, in other words, low effective mode volumes. Moreover, both mode volume $V$ and quality factor $Q$ can be tuned through disk size [211], providing a convenient tuning mechanism. One can even study modes of different coupling strength within the same physical structure, because microdisks support several modes of different radial order $m_r$.

5.2.1 Design

To design microdisk cavities, we perform numerical simulations using the finite-element method (FEM) in COMSOL multiphysics v5.1. We use the axial symmetry of the system to perform two-dimensional simulations. The disks consist of Si$_3$N$_4$ ($n = 2$), surrounded by air, with a thickness of 200 nm and a varying diameter. We use the eigenmode solver to find the modes. Mode volumes are obtained by evaluating Eq. (2.23) for the mode profiles, $i.e.$ dividing the total integrated mode energy by the squared field at the mode maximum. To obtain effective mode volumes $V_{\text{eff}}$, which govern the antenna-cavity coupling strength, we divide this energy by the squared field in the radial direction (dominant direction for these modes) at the center of the antenna, which we choose as 300 nm from the edge. Fig. 5.1a and b show examples of eigenmode profiles of the fundamental ($m_r = 0$) and first order ($m_r = 1$) radial mode in a microdisk. The first order mode couples less strongly to the antenna, due to a lower mode amplitude at the antenna location compared to the $m_r = 0$ mode. Fig. 5.1c shows that, in theory, quality factor scales exponentially with diameter. This theoretical quality factor is only limited by bending losses, $i.e.$ light escaping due to the finite curvature of the disk. For all but the smallest disks, quality factors will in practice be limited by other losses such as absorption and scattering from edge roughness, which scale linearly with diameter [211]. Fig. 5.1d demonstrates the approximate linear scaling of mode volume with diameter. Also effective mode volume $V_{\text{eff}}$ scales linearly and lies between $123 \lambda^3$ to $21 \lambda^3$ for $m_r = 0$ modes in 15 to 4 µm diameter disks. The $m_r = 1$ modes always have $\sim$2.5 times higher $V_{\text{eff}}$ than the $m_r = 0$ modes.
5.2 Microdisk cavities

Figure 5.1: Whispering-gallery modes in silicon nitride microdisks. (a) Cross-cut of the radial field component $E_r$ for the fundamental ($m_r = 0$) radially polarized whispering-gallery mode in a disk with a 14.9 µm diameter and 200 nm thickness. We zoom in near the outer edge of the disk (edges indicated by white lines). The white patch on top of the disk indicates the location of the antenna (absent in this simulation). (b) Same as (a), for the $m_r = 1$ mode. (c) Exponential dependence of the fundamental mode quality factor $Q$ on disk diameter. (d) Approximately linear dependence of the dimensionless mode volume $V/\lambda^3$ of the fundamental mode. Results are obtained from FEM simulations. At diameters above 6 µm, $Q$ is limited by numerical errors.

at similar frequency. See Table 5.1 for $V_{eff}$ for modes in disks between 8 and 15 µm diameter. These results show that we can tune cavity losses and antenna-cavity coupling strength by changing the diameter. We can use this to choose a desired hybridized linewidth, as we will demonstrate in Chapter 6.

5.2.2 Fabrication

The microdisk fabrication process is sketched in Fig. 5.2a-c. We start with a 12x12 mm sample of 200 nm low-loss stoichiometric silicon nitride ($\text{Si}_3\text{N}_4$) on silicon. The $\text{Si}_3\text{N}_4$ was grown by Lionix international on silicon wafers by low-pressure chemical vapour deposition(LPCVD), which usually creates layers with lower optical losses and defect densities than plasma-enhanced chemical vapour deposition (PECVD) [212–214]. We spin coat a 450 nm layer of positive electron-beam (e-beam) resist (CSAR 6200, Allresist GmbH, nominal resolution $\sim$10 nm) on the sample*. We then use an e-beam lithography system (Raith Voyager, 50 kV) to write the disks as well as alignment markers that can be used for relative alignment of subsequent lithography steps.

*Although negative resist would decrease our writing time, the only known resist with similar resolution (hydrogen silsesquioxane) can, once exposed, only be removed by HF etching, which also etches the $\text{Si}_3\text{N}_4$. 89
Design and fabrication of hybrid antenna-cavity systems

Figure 5.2: Fabrication of the hybrid system, step-by-step. (a) A positive e-beam resist is spin coated on a 200 nm layer of silicon nitride on silicon. (b) In the first electron lithography step, we define the disks and alignment markers. After development, this pattern is transferred into the silicon nitride by reactive ion etching. (c) Remaining resist is cleaned from the sample and the sample is immediately transferred to a KOH bath for silicon wet etching, which creates an undercut below the disk. (d) For the antenna deposition, the sample is spin coated again, now with a MMA/PMMA resist bilayer. In a second lithography step, antennas are defined at the edges of the disks. (e) After development, metal (Al) is thermally evaporated onto the sample, creating the antennas. The sample is then transferred to an acetone bath to remove the resist and lift off the excess metal. (f) Finally, the sample is covered by a thick layer of resist and a mesa was created using a diamond wafer saw. Afterwards, the remaining resist was dissolved in acetone.

Details on the markers and how to perform the relative alignment are given in Section 5.A. The disks are written in 500 µm write fields, all positioned in a straight line which will eventually form the mesa. Disks are written with diameters between 20 and 4 µm. We use an electron dose of 160 µC/cm² at 50 kV acceleration potential, and a (curved) area step size of 10 (5) nm. Note that it is crucial that the disks are recognized in the pattern generator software as curved objects (i.e. not as polygons), such that they can be written with the beam moving in a circular path outward. If they are written line-by-line, this typically creates defects along the edges, which lower the quality factor. After exposure, the sample is developed by consecutive immersion in pentyl acetate (120 seconds), o-xylene (7 s), a 1:9 mixture of methyl isobutyl ketone (MIBK) and isopropanol (15 s) and pure isopropanol (15 s). This removes the exposed resist.

The pattern is transferred into the silicon nitride by inductively coupled plasma (ICP) reactive ion etching (RIE) in a commercial etching system (Oxford PlasmaPro100 Cobra). We use a mix of SF₆ and CHF₃ gasses at flow rates of 16 and 80 standard cubic centimetres per minute (sccm), respectively, with
5.2 Microdisk cavities

50 W RIE forward power and 500 W ICP power at a gas pressure of 9 mTorr and a temperature of 0 °C. The sample is etched for 100 seconds. This recipe creates smooth and relatively straight side walls, as shown in the scanning electron microscopy (SEM) image in Fig. 5.3a. We use perfluoropolyether oil between the sample and carrier wafer for thermal conduction.

Figure 5.3: Microdisk fabrication results. (a) Cross-cut of a disk, just after the Si$_3$N$_4$ etch. We see that the Si$_3$N$_4$ has been etched through, and it has straight side walls. The Pt is for imaging only. (b) Cross-cut of a disk, taken after Si under etching. We see a free-standing edge and an angled Si pillar, typical of KOH etching. The horizontal stripes are from the Pt used for imaging. (c) Top view of an under-cut disk with 8 µm diameter. When using a high acceleration voltage (20 kV), the electrons penetrate the disk and we image the pillar edges below it. (d) Four disks with different diameters in a row, after the Si under etching.

After the plasma etch, we clean the remaining resist and oil from the samples by a 10-minute bath in warm acetone (45 °C), followed by a ~15-minute base piranha etch. We then proceed to under-etch the silicon, creating free-standing disk edges. It is crucial that this etch is done within a few hours after the plasma etching, to avoid a native oxide layer forming on the bare silicon. Such a layer would make the under-etching process highly unpredictable, as
etch times depend strongly on the oxide layer thickness and the oxide screens some parts of the disk edges more than other parts, creating highly irregular etch patterns. The under etching is done by placing the samples in a 40 wt% potassium hydroxide (KOH) solution at 70 °C. KOH etches preferentially along the Si (100) crystal direction, which leads to angled pillars with irregular shapes, as shown in Fig. 5.3b-c. The etch rate, however, depends on disk size, as the larger curvature of smaller disks relaxes the directionality of the etch. For example, we found the etch rates in the in-plane direction (i.e. the rate at which the pillar radius decreases) to be 400, 500 and 950 nm/min for a 20, 15 and 8 µm diameter microdisk, respectively. We typically used etch times around 4 minutes, leading to a ~2 µm undercut at a 15 µm diameter disk. Our simulations show that a ~1.6 µm undercut is sufficient to avoid perturbation by the pillar of the fundamental \( m_r = 0 \) mode in a 15 µm disk. An example of a sample after all the microdisk fabrication steps is shown in Fig. 5.3d.

From the taper-coupled measurements presented in Chapter 6, we find quality factors of more than \( 10^5 \) for the cavity modes in 8, 12 and 15 µm disks. These are shown in Table 5.1. The highest observed \( Q \) was \( 8.5 \cdot 10^5 \), measured in a 15 µm disk. Furthermore, Table 5.1 shows that resonance frequencies in 8, 12 and 15 µm disks are equal (for nominally equal diameters) to within 0.037%, 0.015% and 0.015%, respectively, which amounts to a variability < 2% of the cavity free spectral range (frequency difference between modes of equal \( m_r \)) and can be translated to a reproducibility in disk diameter of 2-3 nm. These figures demonstrate the fidelity of the disk fabrication process. Results were measured on the antisymmetric WGMs in disks containing antennas (see Fig. 6.4), which were not significantly perturbed by the antenna.

<table>
<thead>
<tr>
<th>Disk diameter [µm]</th>
<th>( m_r )</th>
<th>( V_{\text{eff}}/\lambda^3 )</th>
<th>( Q )</th>
<th>( \omega_c/2\pi ) [THz]</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>0</td>
<td>52</td>
<td>1.2(2) \cdot 10^5</td>
<td>384.29(14)</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>135</td>
<td>0.9(2) \cdot 10^5</td>
<td>384.66(14)</td>
</tr>
<tr>
<td>12</td>
<td>0</td>
<td>89</td>
<td>2.1(5) \cdot 10^5</td>
<td>387.09(6)</td>
</tr>
<tr>
<td>12</td>
<td>1</td>
<td>238</td>
<td>3.3(9) \cdot 10^5</td>
<td>390.72(6)</td>
</tr>
<tr>
<td>15</td>
<td>0</td>
<td>123</td>
<td>2.6(9) \cdot 10^5</td>
<td>387.34(6)</td>
</tr>
<tr>
<td>15</td>
<td>1</td>
<td>301</td>
<td>4(1) \cdot 10^5</td>
<td>388.59(4)</td>
</tr>
</tbody>
</table>

Table 5.1: Cavity parameters. Dimensionless effective mode volume \( V_{\text{eff}}/\lambda^3 \) from simulations, quality factor \( Q \) and bare cavity resonance frequency \( \omega_c \) from the experiments discussed in Chapter 6, as function of microdisk diameter and radial order \( m_r \). Errors correspond to standard deviations.

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\(^\dagger\)Etch rate is extremely sensitive to temperature, so it is advised to place the beaker with the KOH solution in a large water bath to stabilize temperature.

\(^\ddagger\)The \( m_r = 1 \) modes in 8 µm disks were broadened due to overcoupling by the tapered fiber. Real quality factor is higher.
5.3 Aluminium nano-antennas

We use aluminium nano-rods as antennas. The main reason is that we want to study a wide range of cavity-antenna detunings, including in particular the range where the cavity is red-detuned from the antenna. Our results from Chapter 3 suggest that in this regime, hybrid systems should achieve optimal performance. The cavity modes we study will always be in the 765-781 nm range, set by the tuning range of our laser. Therefore we require antennas that are blue-detuned from these wavelengths. Due to the high plasma frequency of aluminium compared to e.g. gold, aluminium nano-rods can be tuned in resonance from the UV to the infra-red by changing particle aspect ratio [215]. Silver could also be used, however this is known to oxidise within days in ambient conditions, making experiments challenging. Aluminium rapidly forms an alumina (Al₂O₃) shell when exposed to oxygen in a self-terminating process that creates a stable shell of ~3 nm thickness [216, 217]. A disadvantage of aluminium is that it shows inter-band absorption at 780 nm [184].

5.3.1 Design

We perform FEM simulations of aluminium nano-rod antennas on an infinite Si₃N₄ substrate (COMSOL v5.1). Antenna width and thickness are taken as 58 nm and 40 nm, respectively, and we assume a tapered shape in the vertical direction with a taper angle of 60°, based on cross-cut images of other evaporated structures. The aluminium refractive index is taken from tabulated data [184], and we include a 3 nm alumina shell. We drive the antenna with a plane wave at normal incidence from the air side, polarized along the antenna long axes (x-axis), and calculate scattered and absorbed power as well as induced dipole moments (along all 3 axes) as a function of frequency. Division of the dipole moments by the incident field at the antenna location yields antenna polarizability tensor elements $\alpha_{xx}$, $\alpha_{xy}$ and $\alpha_{xz}$. Fig. 5.4 shows the resulting antenna scattering and absorption spectra, as well as polarizability $\alpha_{xx}$ along the antenna long axis, which dominates total polarizability $\vec{\alpha}$ throughout most of the spectrum. These results show that we can indeed tune antenna resonance frequency by changing antenna length, i.e. increasing antenna length causes a red-shift of the antenna resonance. For most of these lengths, the cavity modes in our laser tuning range will be red-detuned from antenna resonance, where hybrid systems should achieve optimal performance. Despite the interband absorptions that cause non-Lorentzian behaviour near 780 nm wavelength, the largest antennas can also access the blue-detuned regime, as evident from the sign change in $\text{Re}\{\alpha_{xx}\}$ for these antennas.
Design and fabrication of hybrid antenna-cavity systems

5.3.2 Fabrication

The antenna fabrication steps are schematized in Fig. 5.2d,e. First, we need to deposit a new layer of electron resist. At the location where we place the antennas, 300 nm from the disk edges, this resist needs to have an appropriate thickness for high-resolution lithography and easy lift-off. Using spin coating, we cover the under-etched samples with a layer of methyl methacrylate (MMA, Microchem MMA 8.5, dissolved in ethyl lactate), followed by a layer of polymethyl methacrylate (PMMA, Microchem 950 PMMA, dissolved in anisole). PMMA/MMA bilayers are frequently used for deposition processes, as the lift-off process is eased by the undercut that occurs naturally in such a bilayer [218]. The layer thickness, as measured on a scratch in the resist far away from the structures, is 780 nm (MMA) and 220 nm (PMMA). We use disk cross-cuts made by focused-ion-beam (FIB) milling on a test sample to determine the resist layer thickness on the disk. At 300 nm from the edge of a
5.3 Aluminium nano-antennas

5 µm disk, MMA and PMMA thickness are found as ~150 nm and ~60 nm, respectively. Given an antenna thickness of 40 nm, the bilayer is sufficiently thick for an easy lift-off, while the thin PMMA layer allows good resolution.

Next, we expose our sample in a second e-beam lithography step. The markers written in the first step are used for relative alignment of the antennas to the disks (see Section 5.A for further details). We write rectangular antennas of 50 nm thickness and different lengths between 60 and 180 nm. Antennas are positioned 300 nm from the disk edge, with antenna long axis always aligned in the radial direction, matching the electric field of the radially polarized whispering-gallery modes. Each disk contains one antenna. An electron dose of 500 µC/cm², a 50 kV acceleration potential and an area step size of 5 nm are used. Following exposure, the sample is developed in a 1:3 mixture of MIBK and isopropanol (80 s), followed by immersion in two beakers of isopropanol (15 s each).

We deposit a layer of aluminium, typically 30-40 nm thick using thermal evaporation at a rate of 0.05 nm/s and a chamber pressure at evaporation start of 5 · 10⁻⁷ mbar. As aluminium is easily contaminated by traces of oxygen [217], we ensure that no oxides (e.g. SiOₓ) were evaporated in the chamber shortly before. Also, before depositing on the sample, we evaporate a ~5 nm layer of aluminium into the chamber, which acts as a getter to bind gaseous oxygen. After evaporation, the sample is transferred to a warm acetone bath (50 °C) for ~30 minutes for the metal lift-off. This removes the MMA and PMMA resist, as well as the excess metal on top of it, leaving only the antennas. After a dip in isopropanol, the sample is dried in a nitrogen flow. Fig. 5.5b,c show SEM images of the resulting antennas on a microdisk cavity. We find that antennas are present on ~95% of the disks, and that length and width are on average ~8 nm larger than designed for, due to slight overexposure.

![Antenna fabrication results](image.png)

**Figure 5.5: Antenna fabrication results.** (a) FIB cross-cut of a 5 µm diameter disk, covered with a MMA/PMMA bilayer. Gold was added on top of the MMA and PMMA for imaging contrast. Platinum was deposited for FIB milling. At 300 nm from the disk edge, the MMA and PMMA thickness is 150 nm and 60 nm, respectively. (b) Aluminium antenna on 15 µm diameter disk, after lift-off. Dimensions are slightly larger than designed for, due to overexposure. (c) Image of a 4 µm diameter disk, viewed under a 52° tilt, with an antenna positioned at the lower edge.
5.4 Diamond-sawn mesas

To do cavity spectroscopy, we need to access the cavities using a tapered optical fiber [132]. As our samples are 12 mm wide and the cavities are only elevated above the substrate by a few micrometers, approaching the cavities to within less than a micrometer distance with a tapered fiber would be practically impossible, as the fiber would always touch the edge of the sample before reaching the cavity. One solution would be to use dimpled fibers [219]. However these are as difficult to make as they are easy to break. Instead, we chose to place our cavities on a thin mesa, elevated above the rest of the sample [144].

First, we spin-coat a several µm-thick layer of positive UV resist (MICROP-OSIT S1800) on the sample, to protect against dust and the cooling water used during the wafer sawing. A wafer saw (DISCO DAC-2SP/86 Automated Dicing Saw) is then aligned to the row of cavities using large Si$_3$N$_4$ triangles fabricated in the first lithography step at the top and bottom of the row (see Fig. 5.6a). First, we use a fine 40 µm saw to make cuts of 150 µm depth on either side of the mesa. The mesa width is chosen as 150 µm. Repeating this five times while moving the saw in steps of 30 µm outward, we clear a ~150 µm area on either side of the mesa. We then use a saw of 300 µm thickness to remove a 150 µm thick layer from the rest of the sample. After sawing, the resist is removed in a 45 °C acetone bath. Fig. 5.6 shows the resulting sample, with the 150 µm-wide mesa elevated above the rest of the sample.

![Figure 5.6](image)

**Figure 5.6**: The diamond-sawed mesa. (a) SEM image (sample tilted) of a field of disks on top of the diamond-sawed mesa. The triangular marker next to the field is used to align the wafer saw, together with an identical marker at other end of the mesa. (b) Optical microscopy image of the disks on the mesa.

5.5 Fluorescent quantum dots as LDOS probes

To study LDOS effects, we need fluorescent emitters on our sample. Many excellent works have compared properties of various emitters [65, 185, 195, 220, 221]. Single photon emitters used in quantum information processing can be subdivided into five categories: single atoms (usually suspended in vacuum)
Fluorescent quantum dots as LDOS probes

For our purpose, the emitter should fulfil the following criteria: (1) There should be emission in the 765-780 nm wavelength range of our laser, such that fluorescence studies can be compared to taper-coupled characterization experiments of the hybrid modes. (2) Emitters should be placeable at the antenna hotspot. (3) For practical purposes, emitters should be stable for several days in ambient conditions and photo-bleaching should be minimal. (4) Quenching by metals in close proximity to the emitter should be minimal. (5) Eventually, we would like to place a single emitter per antenna. The second criterion disqualifies single atoms, which need to be in vacuum, typically at distances much larger than a few nm from any interface. Most organic molecules suffer from rapid photo-bleaching or oxidation, whereas the few exceptions such as dibenzoterrylene (DBT) [232] require embedding inside a specific host crystal for good stability and optical properties, which makes positioning on a hybrid difficult. Defect centers in bulk diamond can have excellent properties, but our application would require a nanometer-sized probe. While nitrogen vacancy (NV) centers in diamond nanocrystals have shown high variability in quality [233], other defects such as germanium vacancy centers have shown great promise as bright and reproducible emitters [231, 234]. Rare-earth ions embedded in nanocrystals recently emerged as promising LDOS probes [235, 236]. How to obtain a single emitter per crystal, however, which is required for application as a single-photon source, is currently not clear. Semiconductor quantum dots (QDs) are either epitaxially grown, typically in a III-V semiconductor [46, 237, 238], or solution-processed to form colloidal nanocrystals [77, 141, 200, 239, 240]. The first option is not available in our structure. Colloidal quantum dots, however, can be very bright, efficient and extremely stable emitters, although they tend to suffer from blinking [65, 241, 242]. They are available at almost any emission wavelength, as this can be tuned by size.

We have chosen to use CdSeTe/ZnS core/shell quantum dots (Invitrogen Qdot 800 ITK Organic, Q21771MP), stabilized in decane using long alkyl ligands (trioctylphosphine oxide, TOPO), emitting near 800 nm wavelength with a typical room-temperature single QD linewidth of 50 nm (see Fig. 5.7a). Owing to the relatively large ZnS shell, these are known to be extremely stable. Individual quantum dots were shown to blink, with a high fluorescent quantum efficiency of 94% associated with the bright state [243]. Their small diameter of ∼10 nm (see e.g. Fig. 5.12) enables positioning at the antenna hotspot, yet the large shell thickness § may help keep the exciton in the core at sufficient distance from the metal (also helped by the 3 nm alumina shell on the antenna) to mitigate fluorescence quenching [152]. Importantly, as will

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§Exact core and shell thickness is not provided by the supplier, but typical cores sizes in CdSe quantum dots are 2-4 nm [244] and transmission electron microscopy images of Qdot 800 QDs suggest core sizes of 4-6 nm [245]
be explained in Section 5.6, functional chemical groups are available that bind specifically to the shell material, enabling covalent binding of the quantum dots to the antennas. Fig. 5.7b shows a typical fluorescence decay trace of one of the QDs, positioned on a glass substrate. We observe a bi-exponential decay trace with a fast and a slow lifetime, a common phenomenon in quantum dots which was suggested to originate from the bright and dark states [242, 246]. The slow decay is often associated to the bright state.

![Figure 5.7: Single Qdot 800 spectra and decay trace. (a) Emission spectra measured on three individual quantum dots. Size polydispersity causes small differences in emission frequency. (b) Fluorescence decay trace of a single quantum dot, fitted with a bi-exponential decay. Extracted lifetimes $\tau_1$ and $\tau_2$ are indicated. Average lifetimes from measurements on multiple QDs were $\tau_1 =2.8$ (0.7) ns and $\tau_2 =142.7$ (11) ns. The measurement setup is explained in Chapter 7.](image)

### 5.6 Positioning of quantum dots

Fig. 5.8 shows a step-by-step description of our quantum dot positioning method. This method is similar to that developed by Curto et al. [71, 199] for binding the same quantum dots to gold nano-antennas. The main difference is the linker chemistry: we use a functional group that can bind specifically to aluminium rather than to gold. Moreover, we use a thiol to bind directly to the QD, rather than binding to the QD ligands.

#### 5.6.1 Binding quantum dots using MDPA

First, we separately test the quantum dot binding, which is done using 12-mercaptododecylphosphonic acid (MDPA, purchased from Sigma-Aldrich) as a linker molecule. Alkyl phosphonic acids were demonstrated to form self-assembled monolayers on metal oxide surfaces, including aluminium and titanium oxide [247–249]. High selectivity was found for binding to the metal oxides over binding to siliceous materials such as SiO$_2$, owing to the instability of Si-O-P bond compared to e.g. Al-O-P bonds [249–252]. The thiol group on the other end of the MDPA molecule can form a covalent bond with the sul-
5.6 Positioning of quantum dots

Figure 5.8: Quantum dot positioning, step-by-step. (a) A positive e-beam resist is spin coated on the sample with hybrids. (b) We define holes at the antenna tips using a third lithography step, and develop the resist. (c) After a brief oxygen etch the sample is immersed in a MDPA solution for 24 hrs. The MDPA molecules form a monolayer on the substrate, binding preferentially to metal oxides. We then rinse and bake the sample. (d) The sample is transferred to a quantum dot solution. Quantum dots bind covalently to the thiol groups on the MDPA, but also disperse in the resist. (e) After quantum dot immersion, we rinse the sample and dissolve the resist.

phur atoms in the quantum dot shell, a property often used to cover quantum dots with thiolated ligands [253, 254].

Using UV lithography, reactive ion etching and thermal evaporation, we prepare samples containing large (>10 µm) patches of aluminium, silicon nitride and silicon. Note that the Si surface contains a few-nm layer of native oxide. Following a recipe by Attavar et al. [251], we prepare a monolayer of MDPA on our samples. After cleaning the samples in an oxygen plasma etch for 10 minutes, they are immersed in a 1mM solution of MDPA in methanol for 24 hours to form the monolayers. We use methanol because de-mineralized water slowly degrades aluminium [247]. Samples are then rinsed in pure methanol and annealed for 1 hour on a hotplate at 90°C, after which physisorbed phosphonic acid is removed by a triple methanol and water wash. At this point, the presence of the monolayer can already be observed, as the Al surfaces become strongly hydrophobic. We then proceed with the quantum dot binding. For this test, we used large (∼12 nm) PbS quantum dots stabilized in octane with oleic acid ligands. The samples are immersed for 24 hrs in the QD solution at a concentration of 4.8 mg/ml. Unbound quantum dots are then removed by a double octane rinse followed by an acetone and isopropanol dip. Fig. 5.9 and Table 5.2 compare results with and without the MDPA monolayer. A clear preference for quantum dot binding to Al over Si is observed on both samples. We find that QD density
Design and fabrication of hybrid antenna-cavity systems  

on Al increases by approximately a factor 3 when MDPA is used, indicating that it helps the binding. We would expect no quantum dots to be present on the sample without MDPA, as ligands should protect them from adsorption to the surface. These results suggest that this protection is imperfect, however for our purpose this is not a problem. We also find that QD density on the Si are not affected by the MDPA, which indicates that indeed the monolayer is only formed on the Al, and another mechanism is responsible for the QD attachment to Si. Densities on Si$_3$N$_4$ were roughly the same as for Si. When MDPA is used, selectivity of binding to Al over Si or Si$_3$N$_4$ is around 20-25.

![Figure 5.9: Selective QD binding using MDPA as a linker. SEM images of test samples after immersion for 24 hrs in a PbS quantum dot solution, without (a-b) and with (c-d) a preceding MDPA functionalization step. Quantum dots (size ~10 nm) are visible as small dots on both samples. We see a strong selectivity of quantum dot binding to aluminium (a,c) over silicon (b,d) in both cases. Quantum dot density on silicon is not affected by the MDPA, but density on aluminium increases with MDPA.](image)

5.6.2 PMMA masks for quantum dot screening

To make hybrids with quantum dots only present at antennas, higher selectivity is required than obtainable from just the chemical selectivity of the MDPA molecules. We therefore use a PMMA mask to screen parts of the sample from QDs. First tests are done on samples containing large patches of Si, Si$_3$N$_4$ and Al. We spincoat a 200-nm layer of PMMA (Microchem 950 PMMA, dissolved in anisole) on the samples and use e-beam lithography to define large crosses and circles of 0.5-4 μm diameter. Samples are developed and briefly exposed to an oxygen plasma etch for 20 seconds, which cleans the exposed sample yet does not etch through the PMMA. MDPA functionalization is performed
5.6 Positioning of quantum dots

<table>
<thead>
<tr>
<th>MDPA used</th>
<th>Substrate</th>
<th>QD density [µm⁻²]</th>
</tr>
</thead>
<tbody>
<tr>
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<td>80</td>
</tr>
<tr>
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<td>60</td>
</tr>
<tr>
<td>no</td>
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</tr>
<tr>
<td>yes</td>
<td>Al</td>
<td>1370</td>
</tr>
</tbody>
</table>

Table 5.2: Effect of MDPA on QD binding. Average quantum dot densities observed on Si and Al substrates, with and without MDPA functionalization. All samples were immersed in a quantum dot solution for 24 hours. Note that densities should be interpreted as a rough estimate, due to the limited sample size used. Densities were obtained by counting quantum dots in SEM images, where for each reported density approximately an area of 0.08-0.16 µm² was used for counting.

As described above, we decreased the annealing time from 1 hour to 15 minutes. After MDPA functionalization, samples are immersed in a 10 nM solution of Qdot 800 quantum dots in decane for 24 hours. They are then first rinsed in pure decane and subsequently kept in toluene for 5 hours, which both dissolves the PMMA and disperses the quantum dots that were dissolved in the PMMA. Fig. 5.10 shows SEM images of a sample. A clear difference between the parts covered and not covered by PMMA is visible, with high QD density inside the patterned areas and virtually none outside, both for the large cross and the small circles. This shows that PMMA masks are an excellent pathway to selective quantum dot positioning. We also find that the selectivity of Al vs. Si and Si₃N₄ has decreased, from 20-25 to ~2.5 times more QDs visible on Al than on the Si or Si₃N₄. It is possible that the Qdot 800 quantum dots are more likely to adsorb onto the substrate than the PbS quantum dots, which have different ligands. Fig. 5.11 shows fluorescence images of the same sample shown in Fig. 5.10, optically pumped with a 532-nm pulsed laser, which confirm the successful localization by the PMMA mask. However, we also see some fluorescence from the parts that were covered by PMMA. This suggests that QDs do diffuse through the PMMA mask, as was also suggested for Qdot 800 QDs with amino-functionalized ligands in aqueous solution [201].

5.6.3 Effect of immersion time

Having confirmed that we can accurately position quantum dots on aluminium structures, we now position them on our hybrids. To avoid

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Note that, while PMMA is not affected by immersion in the acidic MDPA solution (pH~5), we found that many other resists including Ma-N 2400 and CSAR 62, as well as the co-polymer MMA, became impossible to completely remove from the sample after MDPA immersion. It is likely that the acid causes cross-polymerization in the resist, making them insoluble in common solvents like acetone, anisole or n-methyl-2-pyrrolidone (NMP).
quantum dot diffusion through the PMMA, we use a thicker PMMA layer and shorter immersion time in the QD solution. The fabrication steps are shown in Fig. 5.8. The hybrids, consisting of 4-µm disk with 80-160-nm-long antennas, are covered with a 1100-nm layer of PMMA, which we measured to be 500 nm thick at the antenna location on the disks. At the disk edge, where the resist is most thin, thickness is still ≥270 nm. Following the procedure for alignment, exposure and development also used for the antennas, we define holes of 60 or 120 nm diameter, centered at the antenna apex pointing to the
Figure 5.11: Fluorescence imaging of quantum-dot patterned substrates. (a) Strong fluorescence contrast between inside and outside the cross. Bright spots correspond to quantum dot clusters. Image taken with a 10x, NA 0.25 objective. (b) Zoom-in of the same cross, just below the center, taken with 100x, NA=1.4 oil immersion objective. We still see strong contrast between inside and outside the cross (edges indicated by green dashed lines), as well as for the small circles below. We observe more fluorescence coming from the aluminium than from the silicon parts (edges indicated by white dashed lines). Images were taken on the same sample as in Fig. 5.10.

disk center. We use an electron dose of 500 $\mu$C/cm$^2$ and step size of 5 nm. After a 20-second oxygen plasma etch, MDPA functionalization and quantum dot deposition is done as for the test samples in Fig. 5.10. Fig. 5.12 shows SEM and fluorescence images of two samples, after 24 hours and after 5 minutes immersion time in the quantum dot solution. For long immersion time, we see quantum dots everywhere on the disk, both in SEM and in fluorescence. On the other hand, for short immersion time, quantum dots are only visible at the antenna tip and fluorescence is confined to the antenna. Fluorescence spectra, which are discussed in Chapter 7, confirm that the emission comes from the quantum dots. Note that most often, no quantum dots are visible at all in SEM images, although in fluorescence we observe a near-100% success rate of quantum dot positioning for the 120-nm holes (success rate is lower for the 60-nm holes). This suggests that quantum dots are in most cases not attached to the disk but only to the antenna, where they are difficult to discern from the antenna itself due to our low SEM imaging quality, caused by sample charging. These results show that we can accurately and with high success rate position quantum dots on our hybrids, with no quantum dots present outside the intended area.

5.7 Conclusions and outlook

We have, for the first time, successfully and reproducibly fabricated hybrid systems consisting of silicon nitride microdisks coupled to aluminium anten-
Design and fabrication of hybrid antenna-cavity systems

24 hr immersion  5 min immersion

Figure 5.12: Quantum dots on hybrids, effect of immersion time. (a-b) SEM images of hybrids, showing an area on the disk near the antenna. The samples were functionalized with quantum dots using immersion times of 24 hours (a) or 5 minutes (b) in the quantum dot solution. The inset in (a) shows a cartoon of the disk (blue) with antenna (red) and the hole in the PMMA (green, 120 nm diameter) where QDs are expected to be. (c-d) Fluorescence images of hybrids made with 24 hours (c) or 5 minutes (d) immersion times. For both samples, an area much larger than the disk size was illuminated by the pump laser. Dashed lines roughly indicate the disk edge.

These methods pave the way for experiments on hybrid systems, which
will be the topic of Chapters 6 and 7. The quantum dot positioning method presented here is applicable to placing various types of quantum dots in any nanophotonic system. Although our linker molecules are specifically chosen for binding to metal oxides such as alumina, these could easily be exchanged to facilitate binding to other materials such as gold, silver or silicon. In future work, the accuracy and specificity of our method could easily be further improved by more suitable choices of quantum dot ligands, for example. By changing the hole size in PMMA, immersion time or quantum dot concentration, we are confident that this method can also be employed to position a single quantum dot in a nanophotonic device, which would enable high-fidelity fabrication of single photon sources.
Appendices

5.A Marker alignment procedure

A crucial step in hybrid fabrication is the relative alignment of cavity and antenna. This requires the use of markers in the e-beam lithography, with which we align the coordinates system in which the antennas are written to that of the disks. The procedure is largely based on the work of Zhang [255].

![Figure 5.13: Marker alignment. Images of the sample design. (a) Full design, showing the 500-µm write fields containing the hybrids in a vertical row, as well as four 200-µm alignment crosses (yellow) at each corner, used for the coarse alignment. The top write field is a test field, on which we test alignment procedures. (b) Zoom-in of a write field, which contains 20 disks of 4 different diameters (8-20 µm). On the corners of the field, there are small alignment crosses for precise alignment. (c) Zoom-in of a small alignment cross, showing in green the area that is scanned in an automatic line scan during the precise alignment procedure. (d) Zoom-in of an 8 µm disk with an antenna at the bottom. The light blue rings, which define the disks, are separated from the big pads in dark blue, because the software recognizes them as circular elements. Therefore they are written in a concentric manner, which improves edge smoothness.](image)

Fig. 5.13 shows the sample design. In the first lithography step, we write the disks as well as the alignment markers. We write a large (200 µm) cross at each corner of exposed area with disks, and small (12 µm) crosses at the corners of each write field (500×500 µm). Additionally, we write an extra test field on which we test the alignment procedure in the second exposure step. During the second exposure step, we first find three of the large markers manually and use the 3-point sample-to-stage correction to adjust the coordinate system to that used in the first exposure step. We then do a test run on the test field, where we use automatic line scans to scan over the arms of the small crosses and find their center coordinates. This line scan measures
an intensity profile across the arm, and a threshold algorithm is used to find
the edges of the arms and from that the center coordinate. This threshold
algorithm, as well as the scan parameters, needs to be adjusted carefully to
give accurate position measurements. This is what we do on the test field. This
information is then automatically processed by the software (Raith Voyager),
and any shifts from the intended cross positions (e.g. due to imperfect stage
positioning) are corrected for in the sample-to-stage alignment. After this,
the write fields with the hybrids are written. It is important that new line
scans and sample-to-stage alignments are done at each write field, because the
sample moves between write fields and piezo drift or imprecision can cause
alignment errors.