Electron-beam lithography towards the atomic scale
and applications to nano-optics

by

Vitor Riseti Manfrinato

B.S., University of São Paulo (2009)
S.M., Massachusetts Institute of Technology (2011)

Submitted to the Department of Electrical Engineering and Computer Science
in Partial Fulfillment of the Requirements for the Degree of

Doctor of Philosophy in Electrical Engineering and Computer Science

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

September 2015

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Abstract

Electron-beam lithography (EBL) is a high-resolution pattern generation technique widely used in research and development. However, EBL resolution has been limited to 4 nm isolated features and 16 nm periodic structures. Furthermore, the physical mechanisms that limit EBL resolution are not quantitatively clear. The fundamental understanding of the resolution limits of EBL is critically important to push nanotechnology toward the atomic scale.

In this thesis we show a comprehensive study of the resolution limiting factors of EBL. We demonstrated that low-energy (sub-5 keV) EBL is able to achieve sub-10 nm half-pitch structures. We investigated the resolution of EBL using an aberration-corrected scanning transmission electron microscope as the exposure tool at 200 keV. We achieved isolated features with critical dimensions of 2 nm and 5 nm half-pitch in hydrogen silsesquioxane resist. We analyzed the resolution limits of this technique by measuring the lithographic point-spread function (PSF). In addition, we measured the delocalized energy transfer in EBL exposure by using chromatic aberration-corrected energy-filtered transmission electron microscopy (EFTEM) at the sub-10 nm scale. We have defined the role of spot-size, electron scattering, secondary electrons, and volume plasmons in the lithographic PSF by performing EFTEM, momentum-resolved electron energy loss spectroscopy (EELS), sub-10 nm EBL, and Monte Carlo simulations.

Finally, we show two applications in nano-optics that demand sub-10 nm EBL. First, we performed lithographic placement of nanometer-sized photon sources, i.e., 5-nm-diameter colloidal quantum dots. Second, we fabricated sub-20 nm plasmonic antennas designed to engineer surface and volume plasmons in the ultraviolet region of the electromagnetic spectrum (3 to 30 eV).

Thesis Supervisor: Karl K. Berggren
Title: Professor of Electrical Engineering and Computer Science
Acknowledgements

First, I would like to gratefully thank my advisor, Prof. Karl Berggren, for the opportunity to work in his research group. I would like to further thank him for maintaining an exciting research environment, for providing an active and very important mentorship, for important career advice, for sharing his research philosophy, and for countless communication advice.

I would like to acknowledge the support from the Center for Excitonics, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0001088. Part of the work presented in this thesis was carried out at the Center for Functional Nanomaterials, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No DE-AC02-98CH10886. In addition, part of the work presented in this thesis was also carried out at the Electron Microscopy Center, Nanoscience and Technology Division of Argonne National Laboratory, a U.S. Department of Energy Office of Science Laboratory operated under Contract No. DE-AC02-06CH11357 by UChicago Argonne. Finally, I would like to also acknowledge support from the Gordon and Betty Moore Foundation.

There are many people that helped me in completing this thesis. I am very grateful to:

Dr. Eric Stach for providing an excellent research environment at Brookhaven National Laboratory and for advice and important discussions on material science and transmission electron microscopy;

Prof. Marc Baldo for keeping a great research environment in the Center for Excitonics;

Prof. Henry Smith for advice on the fundamentals of nanofabrication;

Prof. Moungi Bawendi for his collaboration and valuable lessons of fundamental science;
Prof. Terry Orlando and Prof. Leslie Kolodziejski for guidance on graduate student life;

Prof. James Fujimoto for mentorship and coursework guidance;

Dr. Charles Black for scientific advice and hospitality at Brookhaven National Laboratory;

Prof. Joel K.W. Yang for scientific discussions and advice;

Mark Mondol for fundamental advice on electron-beam lithography and nanofabrication;

Jim Daley for maintain a professional research environment and for clean-room mentorship;

Dr. Yong Zhang for important advice on transmission electron microscopy;

Carol Lynn Alpert and Karine Thate from Boston Museum of Science for valuable communication lessons;

Janet Fisher for help and advice in the EECS department;

Lihua Zhang for assistance with scanning transmission electron microscopy and spectroscopy, Yujia Yang for atomistic simulations and nanofabrication of Al nanostructures, Jinguo Wen for assistance with chromatic energy-filtered transmission electron microscopy, Nestor Zaluzec for assistance with momentum-resolved electron energy loss spectroscopy, Bowen Baker for assistance with Monte Carlo simulations, Richard Hobbs for fabrication of Al nanostructures and assistance with electron energy loss spectroscopy, Sarah Goodman for assistance with data analysis of electron energy loss spectroscopy, and Darcy Wanger, Hee-Sun Han, and David Strasfeld for preparation and optical characterization of colloidal quantum dots;

Akshay Agarwal, Jose Arrieta, Roman Caudillo, Bryan Cord, Jay-Byum Chang, Lin Lee Cheong, Huigao Duan, Katherine Harry, Chung-Soo Kim, Yong Ho Kim, Francesco Marsili, Dean Miller, Faraz Najafi, Sam Nicaise, Alejandro Perdomo-Ortiz, Javier Sanchez-Yamagishi,
Sebastian Strobel, Dong Su, and Donald Winston for their research collaboration and for teaching me many lessons about science and engineering;

Labmates from the Quantum Nanostructures and Nanofabrication (QNN) Group and NanoStructures Laboratory (NSL) at MIT for their friendship;

Community at the Center for Excitonics, Research Laboratory of Electronics (RLE), and Microsystems Technology Laboratories (MTL) for technical assistance and great research environment;

My parents, Wilson Manfrinato and Elza Maria Riseti Manfrinato, and my sisters, Fernanda Riseti Manfrinato and Vivian Riseti Manfrinato, my brothers-in-law Emerson Batistella and Carlos Henrique Ferro, niece Ana Beatriz Manfrinato Batistella, and nephew Gabriel Manfrinato Batistella, for believing in my work and for support.
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Chapter 1

Introduction

Lithography is the process of transferring information from a design to a substrate. In order to do that, we employ a form of radiation to be delivered at specific locations on the material, which is designed to be sensitive to that radiation. For example, a common modality of lithography is electron-beam lithography (EBL). In this case, one focused electron beam is shined onto an electron-beam sensitive material, called a resist. The resist usually coats a substrate. The electron beam is controlled by a pattern generator, and is scanned across the resist, exposing the desired pattern. The key concept in lithography is that the incoming radiation changes the resist in a specific way, breaking specific chemical bonds in the resist. After this radiation exposure, the resist (together with the substrate) is immersed in a developer solution. The developer is designed to dissolve only the exposed (unexposed) areas of the resist in the case of a positive (negative) tone process. Therefore, after a given amount of development time, the sample is dried leaving the designed pattern in the resist. There are many details in each step described above, and all of these steps have been the subject of intense research. (1-6)

Lithography is classified into two types based on the method of transferring the pattern to the resist. In direct-write lithography the designed pattern may be directly transferred to the resist. Some of the modalities include scanning EBL, scanning-optical-beam lithography, scanning-ion-beam lithography, scanning-probe lithography, among others. All of these techniques require a probe or a beam to be scanned across the sample, exposing the resist. Another classification of lithography consists of pattern-replication techniques, where a mask or a mold is used to transfer the pattern to the resist. Examples are optical-projection lithography and nanoimprint lithography.
In this thesis I will focus on EBL because this lithographic mode is widely available, and generally, EBL achieves higher resolution than the other direct-write techniques. Therefore, EBL is frequently used for prototyping in nanoscience and nanotechnology. EBL is also widely used in the semiconductor industry for writing masks for optical lithography.

One challenge existing since the invention of EBL is understanding the exposure mechanisms that limit the resolution of EBL. To overcome this challenge, we need to understand the spatial distribution of energy density deposited in the resist, that is, the point-spread function (PSF). Figure 1-1 shows the resolution limiting factors of EBL during the exposure process. Factors such as electron-beam spot size, electron scattering (dependent on electron-beam energy), phonon, photon, plasmon, and electron emission in the resist are combined during the exposure process, which complicates the analysis of the EBL PSF. Once an accurate model of the PSF is obtained it is possible to calculate, for a given design, the final deposited energy density in the resist. Then, the final energy density in the resist may be used to estimate if the resist is able to print such a designed pattern. Thereby, you can access the resolution limit and the feasibility of the EBL process.
The electron enters the resist with initial energy $\varepsilon_i$ (represented by a black arrow). The electron-beam spot size is depicted as the wider grey arrow. The electron-beam spot size may limit the minimum feature size achievable. The electron may experience an elastic or inelastic scattering event. In the case of an inelastic event, the energy loss $\varepsilon$ in this event, depicted as a red circle, may be transferred to a secondary particle or a quasi-particle (secondary electron, volume plasmon, photon, phonon, or exciton) that further deposits energy in the resist. The incident electron may be deflected and leaves the resist (represented by the black arrow leaving the resist). We have defined the direct (or forward-scattered) electron as the electron that passes through the resist. If the electron beam energy is reduced, the elastic cross section, inelastic cross section, and scattering angles would be increased. Therefore, the electron is more likely to leave the sample with a wider angular distribution (represented by the dashed arrow). The incident electron may also scatter by an angle large enough so the direct electron leaves from the top surface. These are the back-scattered electrons (represented by the dotted arrow). This process may be significant for samples thicker than the electron mean free path. The lithographic PSF is determined by the deposited energy density caused by all these electrons and secondary particles in the resist. The lithographic PSF is related to the maximum pattern density in a resist.

To investigate the effect of electron-beam energy on the resolution of EBL, we performed EBL at sub-5 keV. EBL at low energy may be advantageous due to lower proximity effect. (15, 21-23)
higher resist sensitivity (20, 23, 24) (more efficient energy transfer process), smaller energy deposition in the substrate, (23, 25) and lower cost and smaller footprint lithographic system. (25, 26) One major problem is that low-energy EBL has been regarded as low resolution (>25 nm half pitch) due to increased electron scattering and larger minimum spot size. (23, 27) However, recent technological advancements allowed us to achieve a 2 keV electron beam with sub-10 nm spot size. Furthermore, by anticipating the increased electron scattering at low energies, we developed a lithographic process with sub-20 nm thick resist. Therefore, we suppressed the direct electron beam scattering. (2) Chapter 2 shows the fabrication of 9 to 30 nm half-pitch nested L’s and 13 to 15 nm half-pitch dot arrays, using 2 keV EBL with hydrogen silsesquioxane (HSQ) as the resist. We obtained good agreement between experimental and Monte-Carlo-simulated PSFs at energies of 1.5, 2, and 3 keV. The long-range proximity effect was minimal, as indicated by simulated and patterned 30 nm holes in negative-tone resist.

The relatively large electron-beam spot size (>5 nm) in conventional EBL has always been a contributing factor in fabricating sub-10 nm structures. (2) To overcome this limitation, we performed EBL by using an aberration-corrected scanning transmission electron microscope (STEM) as the exposure system. This instrument delivers an electron beam full width at half maximum (FWHM) of only 1 Ångstrom, (28) which removes the effect of the incident electron beam spot size on the ultimate resolution. Furthermore, STEM exposures carried out at 200 keV would minimize electron scattering compared to EBL at typical energies of < 100 keV. (1, 8) Chapter 3 shows the fabrication of 2 nm isolated features and 5 nm half-pitch in HSQ, the highest resolution in conventional EBL resists. We also analyzed the resolution limits of this technique by measuring the PSF at 200 keV. Furthermore, we measured the energy loss in the resist using electron-energy-loss spectroscopy (EELS). We note that the necessary electron dose used in this
measurement was significantly higher than the electron dose required to expose the resist. Therefore, we assume that the exposed and unexposed resist behave similarly. Further assumptions and discussions will follow as needed.

For the last 40 years, secondary electrons (SEs) have been considered the major limiting factor on the resolution of EBL exposure.\((11, 13, 14, 18, 19, 29)\) However, the effect of SEs on EBL resolution has never been experimentally measured. In addition, volume plasmons (VPs - collective motion of charge density taking place in the bulk or volume of the medium) have been considered to play a role in SE emission,\((16, 30-33)\) and in EBL dose, but not previously in EBL resolution limits. In order to investigate the physical limiting factors in EBL, we designed several experiments to distinguish specific energy-loss events during EBL exposure, and we analyzed the spatial distribution of these processes. Specifically, we studied the effect of VPs and SEs in the resolution of EBL.

Chapter 4 shows for the first time the measurement of delocalized energy transfer in EBL exposure by using chromatic aberration-corrected energy-filtered transmission electron microscopy (EFTEM) at the sub-10-nm scale. We have defined the role of spot size, electron scattering, SEs, and VPs in the lithographic PSF by performing EFTEM, momentum-resolved EELS, sub-10-nm EBL, and Monte Carlo simulations. We expect that these results will enable alternative ways to improve the resolution limit of EBL. Furthermore, our approach to studying the resolution limits of EBL may be applied to other lithographic techniques where electrons also play a key role in resist exposure, such as ion-beam-,\((34-36)\) x-ray-, and extreme-ultraviolet lithography.\((37)\)

One example of an emerging scientific field that particularly benefits from nanolithography is nano-optics. Nano-optics consists of capturing, processing, and emitting light at the nanometer
scale—essentially it is engineering antennas for visible light.\textsuperscript{(38, 39)} A promising light source for nano-optics is a colloidal quantum dot (QD).\textsuperscript{(39)}

Semiconductor colloidal quantum dots (QDs) are important building blocks for nanoscience.\textsuperscript{(40, 41)} One distinct aspect of this system is the fine synthetic control of the electronic and optical properties of QDs at the sub-10 nm length scale.\textsuperscript{(42)} For convenience, QDs are usually studied in thin films\textsuperscript{(41)} (ensemble) deposited by dip coating. However, properties such as exciton lifetime and photoluminescence intermittency are obscured by ensemble measurements.\textsuperscript{(42)} A systematic investigation of single QDs and QD clusters is limited by complex or non-reproducible fabrication processes. In addition, single-QD patterning is one of the challenges in designing a system that takes advantage of the QD functionality and sub-10 nm dimension.\textsuperscript{(38)} Hence, placement of sub-10-nm QDs at desired positions is expected to be a powerful tool to quantitatively investigate QDs.

Previous reports have demonstrated template-directed placement of sub-20-nm-diameter clusters of gold colloidal QDs.\textsuperscript{(43-47)} Placement of sub-50-nm-diameter clusters of semiconductor colloidal QDs\textsuperscript{(48-53)} has been reported with electron-beam lithography, dip-pen lithography, scanning-probe lithography, and block-copolymer self assembly. However, for semiconductor QDs smaller than 10 nm in diameter, fabrication of sub-20-nm QD clusters has not previously been possible and is crucial to permit the investigation of few-QD clusters.

In Chapter 5 we demonstrated a technique to control the placement of 6-nm-diameter CdSe and 5-nm-diameter CdSe/CdZnS QDs through EBL. This QD-placement technique resulted in an average of three QDs in each cluster. Photoluminescence measurements of the fabricated QD clusters showed intermittent photoluminescence, which indicates that the QDs were optically
active after the fabrication process. This optimized EBL process is a step towards the integration of individual QDs in optoelectronic and nano-optical systems.

Furthermore, the field of plasmonics is also enabling many implementations of nano-optical devices.\(^{(54)}\) One interest in plasmonic nanostructures is the possibility to capture and manipulate visible light at sub-diffraction length scales,\(^{(38, 54, 55)}\) therefore achieving simultaneous advances in on-chip optics integration and optics scaling. One key application of sub-10-nm patterning in plasmonics is the engineering of nano-antennas.\(^{(56-60)}\) Antennas that have sub-10-nm gaps can provide factors of hundreds of electric-field enhancement from coupled surface plasmon (SP) excitation.\(^{(56, 58)}\) This technology is currently used for surface-enhanced Raman spectroscopy.\(^{(58)}\) In addition, sub-100 nm patterning enabled engineering SP resonances toward the ultraviolet (UV) region of the electromagnetic spectrum,\(^{(60-62)}\) therefore increasing the energy range of operation of plasmonic antennas.

In contrast to SPs, VPs have not been explored for nano-optical applications. The VP energy ranges from 3 to 30 eV, and the lifetime is usually at the sub-femtosecond time scale. The VP resonance has been reported to change as a function of dimension at the sub-20 nm length scale.\(^{(63-65)}\) Currently, there is an uncertainty on the phenomena that affect the VP at the nanoscale.\(^{(63, 65-67)}\) Previous reports have investigated VP resonances in thin films,\(^{(31, 68, 69)}\) chemically synthesized QDs,\(^{(63, 64, 70-72)}\) and nanowires.\(^{(66, 67)}\) However, a systematic process to control the VP resonance is needed, and a comprehensive understanding of the VP at nanoscale is lacking.\(^{(66)}\)

Chapter 6 presents the fabrication of sub-20 nm plasmonic antennas designed to engineer SPs and VPs, therefore enabling the engineering of plasmonic responses in the vacuum ultraviolet
(VUV) region of the electromagnetic spectrum (6 to 100 eV). Furthermore, we discuss the physical mechanisms behind SP and VP control and potential applications.
Chapter 2

Sub-5 keV Electron-Beam Lithography

Electron-beam lithography (EBL) at energies 30 keV and above is a well-established method of fabricating sub-20-nm-pitch structures (2, 9, 73). However, EBL at these high energies suffers from long-range proximity effects. Low-energy (sub-5 keV) EBL exhibits five key advantages over EBL at higher energies: (1) reduced dwell-time required for exposure (due to a higher resist sensitivity with only slightly reduced beam current); (23, 25, 74) (2) lower system cost and a smaller footprint; (25, 26) (3) significant reduction in long-range proximity effects; (20, 22, 23, 25) (4) lower probability of sample damage and substrate heating; and (5) more efficient delivery of energy into ultra-thin resists and self-assembled monolayers (75).

Previously, the finest pitch reported of adjacent lines fabricated at beam energies below 5 keV was 50 nm using calixarene, (24) 60 nm using ZEP-7000, (24) 50 nm using poly-methylmethacrylate (PMMA) (76) and 60 nm using hydrogen silsesquioxane (HSQ). (27) This range of resolution is not sufficient for applications that require high throughput and high pattern resolution, such as photomask fabrication and multiple-electron-beam lithography for integrated circuits. (25) The key challenges to achieving high resolution at low electron energies are the reduced electron range, the increased broadening of the incident beam (forward-scattering), and larger minimum spot size. To overcome these limitations, our experiments were conducted with ultra-thin (~ 15-nm-thick) HSQ in conjunction with high-contrast development (contrast value, $\gamma = 10$). (77) Monte-Carlo models of electron scattering at sub-5 keV (13, 16, 78, 79) have never been tested at sub-20 nm length scales. The validity of low-energy exposure models are thus an important question in the field.
Here we report fabricating 9 to 30-nm-half-pitch nested L’s structures, and 13 and 15-nm-half-pitch dot arrays at electron energy of 2 keV. The dots at the corners of the 4 µm × 4 µm arrays showed minimal deviation in diameter, indicating minimal long-range proximity effect. Monte-Carlo simulations of the point-spread function (PSF) at low electron energies are in agreement with experimental results. To demonstrate the expected reduced long-range proximity effect, we exposed a 2 µm × 2 µm area in HSQ, leaving a small central region unexposed. This type of structure would be extremely difficult to realize (even with proximity-effect correction) at higher energies.

2.2. Resolution Limit and Dose Requirements

The resolution of low-energy EBL is expected to be lower than that of high-energy EBL (e.g. 30 keV to 100 keV) due to increased electron scattering and generally larger spot size. In addition, the dose required to expose HSQ at low energies should also be much lower due to more efficient energy-transfer between the incoming electrons and the resist [6].

To experimentally determine the resolution limit of low-energy EBL, all samples were prepared by spin-coating HSQ (1% solids XR-1541, Dow Corning) on silicon wafers with native silicon dioxide at a spin-speed of 6.5 krpm. The resulting thickness was determined to be 15 nm using an ellipsometer. To avoid thermally-induced cross-linking of HSQ, which might lead to a loss in resolution, no pre-exposure bake was performed. (77) Unless stated otherwise, all exposures were carried out at an electron energy of 2 keV on a Raith 150 EBL system with a thermal-field-emitter source operating at 1800 K (~ 0.5 eV energy spread), a 20 µm aperture, 50 µm field size, a working distance of 6 mm and a beam current of 64 pA. After exposure, samples were immersed in salty developer (77) for 4 min at 24°C, rinsed under deionized water for 2 min, and blown dry
with nitrogen gas. The typical total processing period from spin coating to development was about 2-3 days. The fabricated structures were imaged by scanning-electron microscope (SEM) at 10 keV with ~ 6 mm working distance, and their dimensions were measured by image processing software (ImageJ).

Two designs of nested-L test structures, consisting of either five or seven single-pixel L-shaped-lines, were patterned in 15-nm-thick HSQ at half-pitches from 9 to 30 nm. Figure 2-1 shows nested L’s at half-pitches of 9, 10, 15, 20, and 30 nm (the 15-nm-half-pitch structure was fabricated in a separate experiment). Although the 9- and 10-nm-half-pitch structures could be resolved, residual HSQ was present between the lines, and the single isolated lines were washed away. On the other hand, structures patterned at 15, 20 and 30 nm half-pitches appeared to be fully developed.
Figure 2-1. Scanning-electron micrographs of nested L’s in 15-nm-thick HSQ exposed at 2 keV. (a) 9 nm half-pitch with a dose of 0.4 nC/cm (250 electrons/nm); (b) 10 nm half-pitch with a dose of 0.6 nC/cm (370 electrons/nm); (c) 15 nm half-pitch showing a clearly developed structure with a dose of 0.6 nC/cm (560 electrons/nm) (this experiment used cascading nested L’s); (d) 20 nm half-pitch with a dose of 0.9 nC/cm (560 electrons/nm); and (e) 30 nm half-pitch with a dose of 1 nC/cm (620 electrons/nm).

As previously suggested,(20) by using the ultra-thin resist we reduced the impact of forward scattered electrons, leading to higher resolution than seen previously.(27) In addition, the use of HSQ with high contrast development aided in achieving higher resolution. The minimum half-pitch observed (9 nm) coincided with the electron beam spot size (9 nm), which was measured previously in.(2)

To evaluate if we could maintain high resolution over large areas, we exposed 4 μm × 4 μm dot arrays on 15-nm-thick HSQ at 2 keV, with half-pitches of 15 nm and 13 nm (~ 1 Teradot/in.²)
or \( \sim 0.15 \text{ Teradot/cm}^2 \), as shown in Figures 2-2a and 2-2b, respectively. A small amount of residual HSQ was present between the 13-nm-half-pitch dots, and the dots had considerable variation in diameter. In contrast, the dots in the 15-nm-half-pitch array were uniform and without apparent residual HSQ between the dots. The dots at the corner of the array showed only minimal size deviation \((\sim 12\%)\), demonstrating that the long-range proximity effect was minimal, as expected.

**Figure 2-2.** Scanning-electron micrographs of a corner of a \(4 \mu m \times 4 \mu m\) dot array in 15-nm-thick HSQ, exposed at 2 keV. (a) 15 nm half-pitch with a dose of 2 fC/dot (12,000 electrons/dot) and (b) 13 nm half-pitch with a dose of 1.5 fC/dot (9,300 electrons/dot). The small deviation \((\sim 12\%)\) in dot diameter between the center and the corner of the array indicated minimal proximity effect.
Patterning the same structures as shown in Figure 2-1 at 30 keV required 6.4 (4,000 electrons/nm) to 16 nC/cm (9,900 electrons/nm), which is roughly 16 times higher than what was required at 2 keV. Similarly, the dot array with 26-nm-pitch in Figure 2-2b required 1.5 fC/dot (9,300 electrons/dot) at 2 keV and 18 fC/dot (110,000 electrons/dot) at 30 keV; about 12 times higher\(^1\). The increased resist sensitivity at low energies may pose problems for more sensitive resists such as PMMA by causing shot noise and increased line-edge roughness.(80)

2.3. Proximity Effect

In high-energy (e.g., 30 keV to 100 keV) EBL, a large background dose extends over several micrometers, due to back-scattered electrons. This long-range proximity effect is expected to be much less severe at low-energies due to the shorter electron range. However, this expectation has never been verified at length scales smaller than 50 nm, which is of ever-increasing importance in direct-write lithography.

We measured the point-spread function (PSF) at energies of 1.5, 2, and 3 keV. Isolated dots were patterned in 15-nm-thick HSQ with single-pixel exposures with doses ranging from 0.1 fC/dot (6×10\(^3\) electrons) to 10\(^5\) fC/dot (6×10\(^9\) electrons), followed by salty development.(77) The radii of the dots were measured from SEM micrographs using image processing software (ImageJ), as previously described.(14) The reciprocal dot dose was then plotted versus the dot radius, and each PSF was normalized. Figure 2-3a compares the experimental PSFs we obtained with the PSF at 30 keV, determined in 30-nm-thick HSQ.

\(^1\) The dose comparisons made here, at 2 and 30 keV, are regarding single-pixel lines and single-dot exposures. This type of single-pixel exposures would require more dose than aerial exposures, due to the concentrated electron distribution at the center of these structures.
Figure 2-3. The point spread function (PSF) was obtained by plotting reciprocal dot dose versus the dot radius, followed by normalization (the maximum of the PSF was set to unity). (a) PSF for 15-nm-thick HSQ at 1.5, 2, 3 keV and 30 keV for 30-nm-thick HSQ; (b) PSFs of (a) for sub-60-nm radius. The 1.5 keV PSF had widest beam spreading.
at sub-40-nm radius; (c) Experimental and Monte-Carlo-simulated PSFs at 2 keV, showing good agreement.

For PSF comparison in the long-range (radius bigger than 40 nm), we defined an “effective electron range”, which is as a point where the dose is $10^{-5}$ smaller than the incident dose. At this range, the deposited dose is considered negligible for all practical purposes. As shown in the Figure 2-3a, this “effective range” of the electrons at 1.5 and 2 keV is less than 200 nm. Figure 2-3b is a magnified view of the same PSFs at radii 60 nm and below. The PSFs at 2, 3 and 30 keV are approximately the same for the short range (radius smaller than 40 nm), presumably due to the use of thin resist. Only the 1.5 keV PSF has somewhat wider beam-spreading at this short range.

A Monte-Carlo simulation based on Refs (13, 78, 79) was conducted to determine if the measurements were in agreement with the modified Bethe energy dissipation law for low-energies. We assume that the high contrast of HSQ with salty development (contrast value, $\gamma = 10$) permits a direct comparison between the experimental and simulated PSFs. We also assume that the deposited energy density of the Monte-Carlo simulation represents a close approximation to the cross-linking distribution. The experimentally determined and simulated PSFs are in good agreement for energies 1.5, 2, and 3 keV. Figure 2-3c is a plot of the simulated and experimental PSFs at 2 keV.

There are several possible hypotheses that could explain the small observed mismatch between simulated and experimental PSFs, seen in Figure 2-3c. The high but finite contrast of the salty developer causes a broadening in the PSF, as observed at large radius. Mass-transport limitation during development(10) is a possible source of experimental deviation at the sub-20 nm scale. SEM metrology is also imperfect, particularly for dots with small radius, i.e. sub-20 nm dots are expected to have proportionally larger errors in the PSF measurement.
To demonstrate the reduced scattering range at low energies, we simulated the pattern in Figure 2-4a and exposed the pattern shown in Figure 2-5a. These patterns are illustrative of and sensitive to long-range proximity effects. If the background dose in the unexposed area is less than the threshold required for HSQ to cross-link, then a hole will be present. However, if the proximity effect is substantial, the hole will be exposed by the scattered electrons.
Figure 2-4. (a) Design of 2 μm × 2 μm patterned area with 40 nm × 40 nm unpatterned window at the center. (b) Normalized dose density (or aerial dose) calculated at the center of the unpatterned area, for low energy (2 keV) and high energy (30 keV). The exposure contrast at 2 keV is 5.5 times higher than at 30 keV. (c) Calculated process latitude (diameter variation versus hole diameter) of the pattern shown in (a), considering a 5% dose fluctuation. The process
latitude is higher and the diameter variation is lower for 2 keV than at 30 keV.

Figure 2-4b shows the normalized doses density (charge per unit area) calculated at the center of the pattern shown in Figure 2-4a for electron energies of 30 keV and 2 keV. The exposed area was divided into an address grid of 10 nm pitch (i.e., 200 × 200 address points) with 4 × 4 unexposed points at the center. For each point at position (x, y) in the structure, the distance \( d(x, y; n, m) \) to every exposed point at position \((n,m)\) in the array was calculated:

\[
d(x, y; n, m) = \sqrt{|x - n|^2 + |y - m|^2} \tag{2.1}
\]

For this calculation we considered radially symmetric PSFs:

\[
PSF(r, \theta) = PSF(r) \tag{2.2}
\]

In order to easily manipulate the PSFs for dose distribution calculations, a fitting function was obtained for each PSF. Typical double Gaussian are used as fitting functions. However, such fitting functions are not accurate for beam energies from 2 to 30 keV. For the 2 keV PSF, we used three Gaussian functions and achieve a close fit of the PSF in the measured range. For the 30 keV PSF, we used two Gaussians plus a hyperbolic function. The physical meaning of the fitted functions is not studied in this work. Because the hyperbolic function goes to infinity for radii close to zero and we do not have any data on the 30 keV PSF for distances less than 10 nm, the hyperbolic function is only applied at 10 nm and above and goes to zero below 10 nm. The PSF fitting functions and fitting parameters are provided below:

\[
PSF_{30 \text{ keV}}(r) = \frac{1}{\pi(1+\eta+2\tau \ln(\beta/\alpha))} \left[ \frac{1}{\alpha^2} \exp \left( -\frac{r^2}{\alpha^2} \right) + \frac{\eta}{\beta^2} \exp \left( -\frac{r^2}{\beta^2} \right) + \tau \frac{1}{r^2} \right] \tag{2.3}
\]

with fitting parameters: \( \alpha = 9.5 \text{ nm} ; \beta = 3100 \text{ nm} ; \eta = 4 ; \tau = 0.2 \) [20]. The hyperbolic term \( (\tau \frac{1}{r^2}) \) was set to zero for radii smaller than 10 nm.
\[ PSF_{2\text{keV}}(r) = \frac{1}{\pi(1+\eta+\tau)} \left[ \frac{1}{\alpha^2} \exp \left( -\frac{r^2}{\alpha^2} \right) + \frac{\eta}{\beta^2} \exp \left( -\frac{r^2}{\beta^2} \right) + \frac{\tau}{\gamma^2} \exp \left( -\frac{r^2}{\gamma^2} \right) \right] \] (2.4)

with fitting parameters \( \alpha = 10 \) nm; \( \beta = 40 \) nm; \( \gamma = 69 \) nm; \( \eta = 1.5 \); \( \tau = 0.3 \).

As previously described, (21) we used the abovementioned experimentally fitted PSFs to calculate the contribution to the dose density \( \delta(x, y) \) from every exposed point (with charge \( Q \)):

\[ \delta(x, y) = Q \sum_{n,m} PSF(d(x, y; n, m)) \] (2.5)

Exposure contrast \( K \) was used to quantify the proximity effects at the center of the pattern. \( K \) was defined as \( (Dose_{\text{max}} - Dose_{\text{min}})/(Dose_{\text{max}} + Dose_{\text{min}}) \), where \( Dose_{\text{max}} \) was the maximum dose in the entire pattern and \( Dose_{\text{min}} \) was the minimum dose in the unexposed central region of the pattern. As shown in Figure 2-4b, the background dose at 2 keV is much lower than that at 30 keV. \( K = 0.06 \) for 30 keV and \( 0.33 \) for 2 keV.

We also calculated the process latitude for this pattern at 2 and 30 keV, shown in Figure 2-4c. For holes from 0 to 40 nm diameter, a dose variation of 5% was considered. Such dose variation translates into a variation in hole diameter. Figure 2-4c shows a better process latitude for 2 keV exposures than at 30 keV exposures due to the reduced long-range proximity effect. For a hole with 30 nm diameter, the 2 keV exposure has \( \sim 10\% \) diameter variation while the 30 keV exposure has \( \sim 50\% \) diameter variation.

To experimentally confirm the dose simulation we exposed the pattern in Figure 2-5a. Exposures were performed using 15-nm-thick HSQ, at 2 keV and \( \sim 6 \) mm working distance with a 20 \( \mu \)m aperture. The samples were then developed using salty developer for 4 min at 24°C, rinsed with deionized water for 2 min, and blown dry with nitrogen gas. Figure 2-5b is a SEM micrograph of the fabricated pattern in the HSQ. The holes were 30 nm in diameter. A more complex pattern,
spelling the letters ‘EFRC’, was also fabricated (Figure 2-5c) with features at the 20 nm length scale.

![Figure 2-5. Holes and trenches patterned in 15-nm-thick HSQ at 2 keV. (a) Pattern consisting of 2 μm × 2 μm exposed area with 40 nm × 40 nm unexposed windows at the center. (b) Scanning-electron micrograph of close-packed 30-nm-diameter holes in HSQ, using 10 nm step size and 0.3 fC/dot (1,860 electrons/dot). (c) Scanning-electron micrograph of ‘EFRC’ letters with a minimum feature size of 15 nm and minimal edge roughness.](image)

A drawback of using low-energy EBL is the difficulty in patterning thick resists. The finite penetration depth of low-energy electrons limit the maximum resist thickness possible, and forward scattering reduces resolution as the resist thickness increases.(20) The use of bi-layer or tri-layer stacks becomes necessary. Transferring high resolution patterns from resist to an underlying material is a concern due to the thinness of the electron-beam resist. Fortunately, HSQ provides better etch resistance compared to organic resists, such as PMMA. We successfully etched 30-nm-pitch lines into 60-nm-thick XHRiC i-line anti-reflection coating polymer (Brewer Science), using 14-nm-thick HSQ as the etch mask fabricated at 2 keV.(81) The polymer XHRiC layer was patterned using reactive-ion etching in oxygen and helium for 50s and with a radio-
frequency power of 145W.

2.4. Conclusions

We have shown that low-energy EBL is capable of patterning with high resolution and a significantly reduced exposure dose. A resolution limit of 15-nm-half-pitch for nested L’s and large-area dot array in HSQ was achieved at 2 keV. We also fabricated 9-nm-half-pitch nested L’s and 13-nm-half-pitch large-area dot array, but resist residues were observed. The required dose at 2 keV was about one order of magnitude lower compared to that required at 30 keV. PSFs at low energies were experimentally determined and were in good agreement with Monte-Carlo simulations. From the experimental PSFs, the effective scattering range of electrons at energies 1.5 and 2 keV was less than 200 nm. The long-range proximity effects at sub-5-keV are much lower than at 30 keV, as demonstrated in the ‘hole-in-HSQ’ structures and the minimal dot diameter deviation at the corners of the large dot arrays.

The combined advantages of high resolution and reduced proximity effects make low-energy EBL an attractive alternative that may be useful for applications such as: bit-patterned media, nanoimprint molds, photomask manufacturing, and multiple-electron-beam lithography. With its more efficient energy transfer, low-energy EBL is also useful when patterning ultra-thin and surface-sensitive materials.
Chapter 3

Electron-beam lithography using an aberration-corrected STEM

Electron-beam lithography (EBL) is widely used to achieve high resolution patterns\(^2\) in nanotechnology research and development, but has been limited to 4 nm features\(^10\), 8 nm and 8 nm half-pitch\(^10\) (half of the periodicity of dense features) using conventional resists. A critical step to understand and thereby improve upon EBL resolution is quantifying the electron-beam deposited energy in the resist at the nanometer scale, i.e. the point-spread function (PSF). An accurate measurement of the PSF is fundamental to measuring the overlap of deposited energy in the resist that limits pattern density (half-pitch) and gives rise to proximity effect.\(^{15, 22}\) We measured the PSF at 200 keV from zero to 20 nm nm radii by combining an experimental method \(^{(14)}\) and a calculation based on a sub-4-nm test structure. We also performed electron energy loss spectroscopy (EELS) to identify the pathways of energy loss in the resist.

Phenomena that limit EBL resolution include:\(^2\): spot size, electron scattering, secondary-electron range, resist development, and mechanical stability of the resist. Many approaches have been used to investigate EBL resolution limits, addressing: electron-resist interactions,\(^{(8, 11, 13, 14, 22)}\) resist processing,\(^{(20, 85, 86)}\) and development.\(^{(43, 77, 87)}\) In order to improve the resolution, scanning transmission electron microscope (STEM) exposures at 100-350 kV acceleration voltages have been done to reduce resist-interaction volume (including the reduction of spot size).\(^{(1, 82, 88)}\) STEM lithography has also been done with conventional resists, such as poly(methyl methacrylate) (PMMA) \(^{(1)}\) and calixarene \(^{(88)}\), and in low-molecular-weight resists that are sublimated by electron-beam irradiation, such as NaCl.\(^{(82)}\) The results on PMMA and
calixarene showed 6 nm features and a 15 nm half-pitch. The results on NaCl showed ~2 nm features and 2 nm half-pitch, but with excessive exposure dose (~500 times higher than conventional resists). Electron-beam-induced deposition (EBID) is also capable of 2 nm feature size and 2 nm half-pitch,\textsuperscript{(89)} but this technique is also 100 to 1000 times slower than EBL. Thus, a technique is needed that can achieve sub-5-nm-length-scale resolution at the dose level of conventional resists.

Here we show, with an aberration-corrected STEM, the fabrication of 2 nm isolated features and a 5-nm-half-pitch dot array using hydrogen silsesquioxane (HSQ) resist: to our knowledge, these are the highest resolution patterns of EBL achieved in conventional resists. We anticipate that this EBL technique would enable the fabrication of novel plasmonic nanostructures,\textsuperscript{(56, 57)} molecular devices,\textsuperscript{(90, 91)} and bio-inspired functional materials.\textsuperscript{(92)} We compared this technique with a 30 keV EBL system by measuring for the first time the PSF at 200 keV from zero to 20 nm radius, and calculating the resist energy-density contrast.

### 3.2. STEM Lithography

We investigated the resolution limits of EBL with a dedicated aberration-corrected STEM for a minimum spot size limitation (0.15 nm) and we used a 10-nm-thick SiN\textsubscript{x} membrane as substrate for transmission electron microscopy (TEM) metrology. Thus, the EBL resolution was limited by the minimal forward scattering cross-section of 200 keV electrons, secondary-electron range, and resist development limitations at nanoscale.\textsuperscript{(10)} The resist used was HSQ because it provides the highest resolution available.\textsuperscript{(9, 10)} We used this system to determine the minimum realizable half-pitch and isolated lines with the smallest line width. These results gave us the practical resolution limits of the STEM as an EBL tool. Then, we measured the PSF to evaluate the fundamental
resolution limit of the system. We used the measured PSF to calculate the energy-density contrast at 200 keV and compared with a 30 keV exposure.

3.2.1. Sample processing

The samples were prepared by spin-coating HSQ (1% solids XR-1541, Dow Corning) on 10- or 50-nm-thick Si₃N₄ membranes (purchased at Ted Pella or TEMwindows.com) at a spin-speed of 8 krpm. The resulting thickness was 10-15 nm, measured by fallen over structures on TEM. To avoid thermally-induced cross-linking of HSQ, which might lead to a loss in resolution, no pre-exposure bake was performed (77). After exposure, samples were immersed in a beaker containing salty developer (1% weight NaOH + 4% weight NaCl) for 4 min at 24°C, rinsed under deionized water for 2 min, rinsed in isopropyl alcohol for 15 s, and gently blown dry with nitrogen gas for 1 minute. The typical total processing period from spin coating to development was about 4-5 days.

3.2.2. STEM exposures

The electron-beam exposures were carried out on a Hitachi HD 2700C dedicated aberration-corrected STEM with a cold-field-emitter source (~ 0.4 eV energy spread), 0.15 nm spot size (28), and a beam current of 70-100 pA.

We loaded our samples overnight, ~15h before exposure, to remove contaminants from the chamber. We avoid using any artificial structures (e.g., colloidal particles) for focusing the electron beam in the sample, thus reducing electron-beam-induced contamination.

We used the Ronchigram method to focus the electron beam in the sample (93). Briefly, this method consists of adjusting the focus, stigmation, and aberration corrections by monitoring the electron beam diffraction, as shown in Figure 3-1. For example, Figure 3-1A presents the electron
beam in focus but stigmatic. Figure 3-1B shows the electron beam in focus and not stigmatic, presenting a smooth plateau in the back focal plane, indicating a focused electron beam. Typically, we focused the electron beam 5 to 10 µm away from the exposure area.

![Ronchigram images](image)

**Figure 3-1.** Ronchigram image (from the diffraction camera) while adjusting focus, stigmation, and aberration correction. (A) Shows a focused and stigmatic electron beam while (B) shows a focused and non-stigmatic electron beam, ready for exposure.

We did our exposures by imaging the resist with a Digiscan Control Unit, embedded within the Digital Micrograph Suite (Gatan, Inc.) choosing: (1) the desired dwell time; (2) microscope magnification; (3) number of pixels; and (4) beam current. These parameters define the area and pitch of interest. No pattern generator was used. We investigated the minimum fabricated pitch (or highest pattern density) by exposing dot arrays with varying pitch at 4 µm × 4 µm area. To investigate the minimum feature size, we used a different design because features smaller than 4 nm usually collapsed, thus resulting in small contrast when imaged in the TEM. We decided to expose square-like gratings or network structures that would give robust mechanical support for linear structures, increasing resist adhesion and avoiding feature collapse during development. The exposures were carried out without a pattern generator, so the pattern geometries were limited. Therefore, we used a design depicted in Figure 3-2 that roughly approximates a square-like grating.
Figure 3-2. TEM micrograph of square-like grid or network structure exposed to give support for small width lines. Wider lines (coming from the rightmost circle) gave mechanical support for finer lines. This pattern also inhibits feature collapse during the solvent drying of the development step.

3.2.3. TEM Metrology

We chose to do TEM instead of SEM metrology because TEM enables higher spatial resolution and TEM metrology enables visualization of sub-5-nm resist residues between fabricated structures, which is important to define the minimum pitch, as demonstrated in Reference (10).

The TEM metrology was done on JEOL JEM 2010F transmission electron microscope at 200 keV. The images were taken slightly defocused in order to provide a slight Fresnel fringe to enhance edge contrast. This has a small to negligible effect on the measured resolution.

3.2.4. Image processing

The feature size variation was calculated using TEM micrographs and imaging processing with ImageJ. Specifically for post diameter deviation, we transformed the TEM micrographs in black and white, for a given pixel threshold that would not dramatically change the post size. Then, we
used “analyze particles” on ImageJ to calculate the area of all posts. We calculated the diameter of each post based on its area, considering that the posts are circular. Then, the standard deviation of all diameters was obtained. For feature size analysis of isolated lines, we converted the TEM micrograph in black and white, for a given pixel threshold that would keep the same full width at half maximum (FWHM). Then, we used “find edges” on ImageJ to obtain the contour of the feature size. We obtained the standard deviation of all measured line widths, sampled with 0.3 nm spacing and 250 nm long.

3.2.5. Results and Discussions

Figure 3-3 shows the patterning capabilities of the STEM lithography technique. Figure 3-3a shows the schematics of the fabrication and metrology processes as previously described. After development, no apparent resist residues between the dots were found in the fabricated structures, as shown in Figure 3-3B and 3-3C. The 5-nm-half-pitch structure in Figure 3-3C represents a significant improvement over previous reports at 30 keV.(10) Challenges associated in fabricating these small features include resist collapse (94) and adhesion problems. Figure 3-3D shows an HSQ isolated line with the smallest width that did not collapse during development, which had average line width of 4 nm. To avoid resist collapse, we fabricated network-like structures. As shown in Figure 3-3E and 3-3F, 2 nm features were realized. We were also able to fabricate down to 1 nm features, but with poor uniformity (Figure 3-4).
Figure 3-3. (A) Schematics of the STEM exposure, development, and TEM metrology. HSQ was spin-coated to be \(~10\) nm on a 10-nm-thick SiN\textsubscript{x} membrane substrate, except on (C) where the SiN\textsubscript{x} membrane was 50 nm thick. The exposure was at 200 keV with 0.5-2 nm step size. (B) 10-nm-half-pitch HSQ dot array with 5.1 \(\pm\) 0.8 nm average feature diameter. (C) 5-nm-half-pitch HSQ dot array with 5.6 \(\pm\) 1.2 nm average feature diameter. The dose was (B) 18 and (C) 6 fC/dot (108,000 and 36,000 electrons/dot). (D) shows an isolated feature with average line width of 4 \(\pm\) 0.8 nm. The linear dose was 21 nC/cm (14,000 electrons/nm). The diameter and line width variation represent one standard deviation. (E) and (F) show the minimum feature size obtained by this method, with features as small as 2 nm with a linear dose of 8 nC/cm (5,300 electrons/nm).

We measured the dose for the patterns above (which is inversely proportional to pattern speed), in order to compare with other patterning methods. For instance, the dose to expose the 2 nm features (8 nC/cm) was 250 times smaller than used to expose NaCl resists,(82) and \(~1000\) times smaller than used for electron-beam-induced deposition.(89)

Here we show a structure that had poor uniformity but with even smaller feature size. We fabricated a dot array with 15 nm pitch, but slightly overdosed. Figure 3-4 shows the resultant array with HSQ structures down to 1 nm. This result gave the smallest resist structure ever written.
by EBL in conventional resists. This pattern had poor uniformity and due to limited control of the electron beam in the STEM we could not fabricate a network pattern to support these 1-nm features without affecting resolution. Nevertheless, this shows that HSQ could achieve 1 nm feature size, but with poor reproducibility to date.

**Figure 3-4.** Bright field transmission electron micrograph of HSQ structures exposed by the STEM at 200 keV. The HSQ thickness was 20 nm and it was on top of a 50-nm-thick Si$_3$N$_4$ membrane. The lines had a pitch of 15 nm, with feature size variation from 1 to 6 nm. The feature variation was due to different dwell times (electron dose) between dot and inter-dot exposures of the scanning beam (a beam blanker was not available). The HSQ structures appear to be fully developed, with some fallen-over posts indicated by slightly darker areas than the background.

These minimum features were only achieved by the combined use of sub-nanometer spot size, proper STEM stability, high-contrast development (contrast value, $\gamma = 10$), high-resolution (and
sub-nanometer line-width roughness) capabilities of HSQ resist, and sub-nanometer metrology obtained with TEM. In addition, the ultrathin SiNx membrane should not affect the resolution compared to bulk substrates. The reason for this robustness is that the buildup of background energy density caused by backscattered electrons from a bulk substrate would only be significant for dense patterns with area on the order of the backscattered electron range (~10 µm), which is not the case in Figure 3-3.

Aberration-corrected STEM lithography has also a throughput advantage due to reduced spot size and increased beam current. The STEM system has 0.15 nm spot size at 100 pA. In principle, one could design an aberration-corrected EBL system with 2 nm spot size and beam current of 18 nA, i.e. with ~4× higher beam current than state of the art EBL tools.

3.3. Point-Spread Function

Understanding the PSF is key for evaluating the resolution capabilities of EBL. To compare the resolution limit of this technique with others, we measured the PSF and used it to calculate the energy-density contrast ($K$) for a given pitch ($p$).

3.3.1. Lithographic PSF: dot-exposure method

Isolated posts were patterned with single-pixel exposures with doses ranging from 1 to $10^3$ fC/dot, followed by salty development(77). The reciprocal dot dose was then plotted versus the dot radius, as described in Reference (14), given the functional form of the PSF. We normalized the PSFs at 30 and 200 keV by setting the same intensity of each PSF at 2 nm radius:

$$normalized \text{ PSF}(r_i) = \frac{1}{Dose(r_i)} * Dose(r = 2nm)$$  \hspace{1cm} (3.1)
This normalization was used to compare the PSFs without the effect of different resist sensitivities at these beam energies. We should note that the differences in PSF curvature are the important factors to calculate energy density contrast and compare resolution capabilities.

Figure 3-5 shows clearly that the PSF at 200 keV is sharper than that at 30 keV, indicating that 200 keV electrons have a significantly smaller short-range proximity effect (collaborative exposure from surrounding areas).

![Normalized Point Spread Function](image)

**Figure 3-5.** The point-spread function (PSF) for ~10-nm-thick HSQ at 30 and 200 keV on SiN<sub>x</sub> membrane substrate, showing that 200 keV electrons have a much narrower PSF compared to 30 keV. The PSF was measured by using single-pixel exposures(14).

### 3.3.2. Calculated PSF

In the PSF measurement in Figure 3-5, we were not able to achieve the fabrication of isolated posts with radius smaller than 2 nm. Then, we calculated a PSF fitting function that would simulate the “H”-shaped feature shown in the leftmost inset of Figure 3-6 to obtain the PSF for sub-2 nm radius.
Figure 3-6. 200 keV PSF (red diamonds) and the fitting function (red curve). We iteratively calculated a PSF, named here as “calculated PSF”, necessary to simulate the “H”-shaped test structure shown in the leftmost inset (see Methods). The rightmost inset shows the resultant energy density contours using this calculated PSF. Specifically, the red contour in this inset defines the simulated structure using the calculated PSF. The calculated PSF (black curve) had an extra bell-shaped function with a knee at 1 nm radius.

In order to calculate the PSF for sub-2 nm radius, which is not experimentally possible to date, we used an “H”-shaped test structure with 2-nm minimum feature size. The “H”-shaped structure is shown at the leftmost inset of Figure 3-6. The measured 200 keV PSF was fitted with two functions with the form \( \frac{a}{1 + \frac{r_c}{b}} \) (one analytical approximation for electron beam current density), forming the fitted PSF. However, representing the PSF with two of these fitting functions was not sufficient to generate the energy density contour (rightmost inset of Figure 3-6) that approximates the H-shaped structure. So, we added another function with the form \( \frac{a}{1 + \frac{r_c}{b}} \) for the sub-2nm radius. We chose to set the function power, \( c \), as 4.2 for keeping the same drop off from the experimental PSF data. So, we optimized \( a \) and \( b \) (for \( c = 4.2 \)) to obtain an energy-density contour that matches
the “H”-shaped structure, therefore generating the calculated PSF. The fitted PSF and the calculated PSF are shown in Figure 3-6 and given below:

\[
\text{fitted PSF}(r) = \frac{0.81}{1+\frac{r}{3}} + \frac{0.19}{1+\frac{r}{5.8}}
\]

\[
\text{calculated PSF}(r) = \frac{0.75}{1+\frac{r}{1}} + \frac{0.2}{1+\frac{r}{3}} + \frac{0.05}{1+\frac{r}{5.8}}
\]

These PSFs were normalized to have intensity equal to unity for radius equal to zero.

One remaining issue to compare energy density contours to a fabricated structure is to consider the resist contrast (development effects). The resist contrast translates dose density to resist thickness, i.e., translates deposited energy density into topographical shape in the resist. The resist contrast for sub-10-nm isolated lines is significantly larger than 10, as shown in Figure 3-7. So, we can assume that the energy density contour in the resist closely matches the edges of a fabricated structure.

Figure 3-7. Contrast measurement for isolated HSQ lines. Left: bright-view TEM images of isolated lines exposed at different doses, from which we were able to obtain the thickness remaining of HSQ lines at different exposure doses. Due to high aspect ratio, all isolated HSQ lines collapsed, translating the thickness measurement to be width measurement. The original thickness of HSQ spin-coated for EBL was 100 nm, and the exposure was done at 100 keV. The development was done in 1% NaOH + 4% NaCl for 4 min at 24°C. Right: the contrast curve (thickness
remaining vs. dose) of the isolated HSQ lines, showing an almost ideal development contrast, i.e. there was no gradual thickness transition when changing the dose.

### 3.3.3. Energy density contrast calculation

Quantifying the resolution limit translates into calculating the energy density (eV/nm$^3$) deposited in the resist for dense patterns. We usually assume a uniform energy distribution through resist depth once the thickness (10 nm) is much smaller than the mean free path (272 nm), which is the case here. Then, PSF gives the areal energy density (eV/nm$^2$). To evaluate how close we could expose and develop two adjacent structures with distance $d$, we need to calculate the energy density contrast:

$$K(d) = \frac{E_{\text{max}} - E_{\text{min}}}{E_{\text{max}} + E_{\text{min}}}$$

where $E_{\text{max}}$ is the maximum energy density and $E_{\text{min}}$ is the minimum energy density (eV/nm$^2$) in the resist, for a given pattern. Calculating $K$ as a function of distance $d$ is a method to quantify the ability to resolve a pattern given a measured PSF. Assuming the contrast curve measured for 30 keV electrons and extrapolated for HSQ thickness of 10 nm (with same development as done here) (9) we conclude that $K \geq 0.25$ for a resolvable pattern.

Figure 3-8 shows the consequence of having a narrow PSF on pattern density. The confined deposition of energy density translates into reduction of the short-range proximity effect, which was critical for achieving a higher resolution at 200 keV than at 30 keV. Figure 3-8 also shows the importance of the PSF at sub-5-nm scale for estimating the resolution limit of an EBL system. For $K$ of 0.5, we predict a resolution limit of 5 nm pitch for the 200 keV STEM system and 16 nm pitch for 30 keV EBL system in Reference (10).
Calculated energy density contrast, $K(p) = \frac{E_{\text{max}} - E_{\text{min}}}{E_{\text{max}} + E_{\text{min}}}$, for the fabrication of two adjacent posts at 30 and 200 keV. The blue and red curves were calculated using the fitted PSF for 30 and 200 keV, respectively. The black curve was calculated using the calculated PSF, predicting higher resolution than using the fitted PSF at 200 keV.

Some challenges still remain to reaching sub-2-nm features and sub-5-nm half-pitch, such as feature collapse due to high-aspect-ratio features and capillary force during development, poor adhesion of the resist to the substrate, and mass-transport limitation during development.\(^{10}\) Thus, a resist/development system that allowed patterns to be resolved with smaller $K$, should result in even higher resolution than 5 nm half-pitch being realized. In addition, we did not observe isolated features smaller than 4 nm. One hypothesis is that HSQ may have a minimum stable volume after development. Therefore, linear structure may be more stable than isolated (or post) structures due to larger volume and smaller surface-to-volume ratio. However, further experiments need to be done to confirm this hypothesis.

### 3.4. Electron Energy Loss Spectroscopy of HSQ

The complexity of resist exposure, containing many energy-loss processes, makes the direct measurement of the PSF a major challenge in beam-based lithography. For this reason, understanding the effects of secondary electrons in exposures have been limited to analytical\(^{18}\)
and Monte-Carlo models \((11, 13, 16, 95)\). To quantify the energy loss pathways in EBL, we directly measured the energy loss in HSQ using electron energy loss spectroscopy (EELS).

### 3.4.1. EELS acquisition

Electron energy loss spectroscopy (EELS) was done on Hitachi 2700C dedicated aberration-corrected STEM with a cold-field-emitter source \((\sim 0.4 \text{ eV energy spread})\) at 200 keV. The beam current was \(\sim 20 \text{ pA, 0.3eV/channel dispersion.} \) The electron beam convergence semi-angle was 28 mrad. The spectrum was taken with 0.06s dwell time with 12s of integration time, over an area of 100 × 100 nm.

### 3.4.2. Calculation of Volume Plasmon Energy in HSQ

To calculate the volume plasmon energy in the EELS spectrum, we used the free-electron gas model\((31)\):

\[
E_{\text{bulk plasmon}} = \hbar \sqrt{\frac{n e^2}{m_0 \varepsilon_0}}
\]  

(3.5)

where \(n\) is the electron density, \(e\) is the elementary charge, \(m_0\) is the rest electron mass, \(\varepsilon_0\) is the vacuum permittivity, and \(\hbar\) is the reduced Plank’s constant.

The HSQ electron density may vary during exposure. So, considering the HSQ with mass density of 2.654 g/cm\(^3\),\((96)\) the calculated bulk plasmon peak is 24 eV. However, considering the HSQ with mass density of 1.4 g/cm\(^3\) (value sometimes used in the literature) the calculated bulk plasmon peak is 17.5 eV. The measured bulk plasmon was 22.5 eV, which is between 17.5 and 24 eV, as calculated above.
3.4.3. Results and Discussions

Figure 3-9 compares the low-loss EELS spectra in (red circles) 20-nm-thick HSQ on top of a 10-nm-thick SiNₓ membrane and in (blue diamonds) a sample consisting only of a 10-nm-thick SiNₓ membrane. We observed in Figure 3-9 the volume plasmon loss peak at 22.5 eV. This volume plasmon peak is the largest energy loss component in HSQ. Generation of secondary electrons from plasmon decay (16, 30, 33, 97) in the resist could be a significant route to resist exposure and may limit the resolution. However, further investigation would be necessary to validate this hypothesis.

Figure 3-9. Electron energy loss spectra of 10-nm-thick SiNₓ membrane (blue) and 20-nm-thick HSQ on top of 10-nm-thick SiNₓ (red). The spectra were normalized by dividing the electron counts by its maximum value. The difference between these two spectra represents the energy loss in HSQ and is shown at the top (green – multiplied by ten for clarity). The bulk plasmon loss is the peak with highest intensity, at 22.5 eV. The inset shows a magnified view of the bulk plasmon loss peak.

To calculate the percentage of deposited energy only in HSQ and only in the SiNₓ membrane we considered a sample of 20-nm-thick HSQ on top of a 10-nm-thick SiNₓ membrane and a
reference sample consisting only of 10-nm-thick SiN$_x$. Figure 3-10 shows the experimental procedure to compare these two samples and the results.

![EELS analysis of deposited energy in HSQ and SiN$_x$.](image)

**Figure 3-10.** EELS analysis of deposited energy in HSQ and SiN$_x$. EELS spectrum for the following samples (all spectra were divided by its maximum value): (black) 20 nm HSQ on top of 10 nm SiN$_x$; (orange) Pure 10 nm SiN$_x$; (green) Normalized 10 nm SiN$_x$, obtained by a convolution between the pure 10 nm SiN$_x$ and a blurring function $e^{-\frac{(x-4)^2}{0.92}}$ to match the zero loss peak of the 20 nm HSQ on top of 10 nm SiN$_x$ sample. This normalization technique was used for a realistic comparison between the two samples (20 nm HSQ/10nm SiN$_x$ and 10 nm SiN$_x$) because these samples have different zero loss peak FWHM; (blue) Subtraction of the electron counts between the 20 nm HSQ on top of 10 nm SiN$_x$ sample and the normalized 10 nm SiN$_x$ sample; (red) Deconvolution of the electron counts between the 20 nm HSQ on top of 10 nm SiN$_x$ sample and the normalized 10 nm SiN$_x$ sample. For the deconvolution we used a 3-eV-FWHM Gaussian reconvolution function to avoid the deconvolution noise. (98) By considering the subtraction method without normalization of the SiN$_x$ sample, 62% of the deposited energy was only in HSQ. By considering the...
subtraction method with normalization of the SiN\textsubscript{x} sample, 39\% of the deposited energy was only in HSQ. By considering the deconvolution method to obtain the signal from HSQ, 49\% of the energy was deposited only in HSQ, which is the most accurate method.

The ratio of the deposited energy only in HSQ is given by:

\[
\frac{\text{deposited energy}_{\text{HSQ}}}{\text{deposited energy}_{\text{HSQ} + \text{SiN}_x}} = \frac{\sum_{\epsilon=0}^{\epsilon_{\text{threshold}}} \epsilon I_{\text{loss, HSQ}(\epsilon)} \epsilon}{\sum_{\epsilon=0}^{\epsilon_{\text{threshold}}} \epsilon I_{\text{loss, HSQ} + \text{SiN}_x(\epsilon)} \epsilon}
\]

(3.6)

where \( \epsilon \) is the energy loss, \( I_{\text{loss, HSQ}(\epsilon)} \) is the electron counts as a function of energy loss \( \epsilon \) for the deconvoluted 20-nm-thick HSQ as described in Figure 3-10, \( I_{\text{loss, HSQ} + \text{SiN}_x(\epsilon)} \) is the electron counts as a function of energy loss \( \epsilon \) for the 20-nm-thick HSQ on top of a 10 nm-thick SiN\textsubscript{x} sample, and \( E \) is the threshold energy where we consider the inelastic spectrum to begin, set to 5 eV. We estimated deposited energy of 49\% only in HSQ and 51\% only in SiN\textsubscript{x} for the 20-nm-thick HSQ on top of a 10-nm-thick SiN\textsubscript{x} sample.

3.5. Conclusions

In summary, we showed that 200 keV EBL with an aberration-corrected STEM is capable of patterning 2 nm isolated features and 5 nm half-pitch structures in HSQ, with significantly smaller dose than competing techniques such as electron beam induced deposition. We showed that 200 keV EBL exposures lead to higher contrast than 30 keV exposures. In addition, we determined the electron energy loss in HSQ at 200 keV, observing the volume plasmon loss in HSQ.
Chapter 4

Direct measurement of the point-spread function

Electron-beam lithography (EBL) is the main top-down pattern-generation technique in nanotechnology and industry because it provides arbitrary patterning capabilities at the sub-5-nm scale.\(\text{(9, 10, 99)}\) EBL at this scale is increasingly important in templated self assembly of block-copolymers,\(\text{(100-103)}\) colloidal quantum dots,\(\text{(39, 45)}\) nanowires,\(\text{(104)}\) and DNA origami.\(\text{(105)}\) Furthermore, the fabrication of novel plasmonic,\(\text{(56)}\) magnetic,\(\text{(106)}\) and nanoelectronic devices\(\text{(107)}\) would benefit from a complete understanding of the EBL exposure process. Since the invention of EBL 50 years ago,\(\text{(7)}\) the resolution-limiting factors of EBL have not been precisely quantified.\(\text{(1, 2, 8-10)}\) To understand the resolution limits, we need to study each component of the EBL point-spread function (PSF),\(\text{(10, 13, 14, 18)}\) which is a significant experimental challenge. The processes of electron scattering, phonon, photon, plasmon, and electron emission in the resist are combined, which complicates the understanding of the EBL PSF. Here, we disentangle the most important components involved in the EBL PSF at the sub-10-nm scale. We show direct evidence of the effect of electron scattering and delocalized processes on the EBL PSF by using recently developed chromatic-aberration-corrected energy-filtered transmission electron microscopy (EFTEM).\(\text{(108)}\) We further quantify the influence of volume plasmons (VPs) and secondary electrons (SEs) in EBL resolution by using momentum-resolved electron energy loss spectroscopy (EELS), sub-10-nm EBL, and numerical and Monte Carlo simulations. Understanding the factors contributing to the EBL PSF is critical to advance nanotechnology research and development. This understanding will help improve proximity effect correction algorithms\(\text{(21, 29, 109)}\) and push the resolution of EBL toward the sub-5-nm scale. The
limiting factors in EBL may also limit other lithographic techniques, such as ion-beam and extreme-ultraviolet lithography.\(^{(37)}\) In addition, the measurement of the EBL PSF at the Angstrom scale gives a unique measure of the interaction-volume of an electron beam with a sample, which is important for studying the resolution limits of scanning electron microscopy.\(^{(28, 78)}\)

The PSF consists of the spatial distribution of energy density deposited in the resist and contains all physical phenomena that contribute to the resolution limit during the resist exposure. The measurement of the PSF enables the calculation of maximum pattern density or minimum pitch \(\text{\(^{(10, 36)}\)}\) and the estimation of the process latitude for a given resolution.\(^{(20)}\) We note that there are resolution-limiting factors that do not depend directly on the PSF, such as resist development,\(^{(9)}\) feature collapse,\(^{(10)}\) resist molecular structure, chemical diffusion (i.e., crosslinking redistribution), and chemical amplification processes. Previously, the PSF could be measured only lithographically by exposing single pixels (or other test structures) for a large dose range, followed by resist development.\(^{(14)}\) One problem with this method is that the lithographic PSF contains many processes combined, leading to a challenging analysis. A direct measurement of each component of the PSF would be ideal to analyze and improve the resolution limits of EBL. During EBL, the electron beam can excite SEs, surface plasmons, VPs, phonons, and photons that may further deposit energy (or break bonds) in the resist. In Figure 4-1, we illustrate the two processes with the largest cross-sections, the generation of SEs and VPs. SEs have historically been considered to be the largest contributor to the EBL PSF.\(^{(13, 14, 18)}\) The role of SEs on the PSF has been extensively modeled, \(\text{\(^{(11, 13, 16, 18, 19)}\)}\) but it has not been directly measured to date. Previous results were limited by comparing the lithographic PSF to numerical models. \(\text{\(^{(10, 19)}\)}\) Furthermore, the role of VPs on SE emission has been studied \(\text{\(^{(30, 110, 111)}\)}\), but the VP effect on the PSF has not been experimentally investigated.
Figure 4-1. Illustration of electron scattering mechanisms in a resist during electron-beam lithography. (a) The electron travels through the resist and may exit the resist without a scattering event or it may experience an elastic scattering event, also without energy loss. We have defined the direct electron beam as the electron that passes through the sample. The elastic scattering event is depicted as a blue circle. (b) The electron beam may alternatively experience an inelastic scattering event. The energy loss in this event, depicted as a red circle, is transferred to a secondary electron that further deposits energy in the resist. (c) The electron may also suffer an inelastic scattering event and excite a VP. VPs are longitudinal oscillations of valence electrons taking place in the bulk of the resist. These VPs propagate and may directly expose the resist or decay as SEs, which further deposit energy in the resist. This VP decay process is depicted as a green circle. The hypothesis for the resist exposure is that a portion of the deposited energy density leads to molecular crosslinking or bond scission in the resist. The lithographic PSF is determined by a combination of all these energy-loss processes.
In order to study the mechanisms that limit EBL resolution, we divided the lithographic PSF into three main components: (1) the direct-beam PSF; (2) the VP PSF; and (3) the SE PSF. The direct-beam PSF is the spatial distribution of local-energy-density deposited directly by the electron beam. We refer to energy deposition caused by SEs and VPs in the resist as delocalized exposure mechanisms. We consider these mechanisms as delocalized because these particles originate at an inelastic scattering position of the direct beam (to a good approximation), and then deposit energy away from the direct-beam PSF. Each PSF will have a characteristic broadening, which limits the resolution of EBL. We employed chromatic-aberration-corrected EFTEM to measure the direct-beam PSF. Furthermore, we observed that the excitation of VPs was the dominant (largest cross-section) energy loss mechanism. We performed EELS and Kramers-Kronig analysis(31) to obtain the VP PSF. The effect of SEs was simulated by numerical and Monte Carlo methods. We compared the direct-beam PSF, VP PSF, and simulated SE PSF to the lithographic PSF, determining the role of electron scattering, SEs, and VPs in the EBL PSF at the sub-10-nm scale.

4.2. Methods
Here we describe the experimental and simulation methods used in this chapter. This section describes the measurement of the direct-beam PSF, VP PSF, and lithographic PSF. In addition, this section includes the simulation of the SE PSF.

4.2.1. Spherical- and chromatic-aberration corrected energy-filtered TEM
We performed EFTEM on the sample consisting of a 20-nm-thick HSQ film on top of a 10-nm-thick SiNx membrane.
EFTEM analysis operating at 200 keV with a FEI-TITAN, equipped with CEOS spherical- and chromatic-aberration correction (ACAT) was completed at Argonne National Laboratory. The chromatic aberration coefficient was 1 µm and the spherical aberration coefficient was 2.5 µm. We used a 50 µm diameter condenser aperture and focused the electron beam to a 0.8 nm fill width at half maximum (FWHM) spot, with a beam current of 230 pA. The sample was determined to be in focus by observing the phase-contrast and the Fast Fourier Transform of the image. In order to measure the electron-beam energy loss and maintain the incoming beam energy at 200 keV (as done in conventional EBL), we used the drift tube energy shift to set the spectrometer to a given energy and used a 5 eV energy slit for energy filtering. Due to the use of the drift tube, we considered data with energy loss less than 120 eV. Energy losses of more than 200 eV from the drift tube may affect the alignment of electron-optics. The spectrometer collection aperture used was 2 mm in diameter. We used a chromatic-aberration-corrected EFTEM to avoid chromatic aberrations in the objective lens. Therefore, the change of the transmitted electron spatial distribution as a function of energy loss was due to scattering in the sample, not due to the inability of the objective lens to properly focus these electrons on the conjugate image plane. The focal length of the incoming electron beam was not changed during the experiment, again to maintain the standard condition of EBL. The dwell time for image acquisition was varied from 0.1 to 1s to maximize the signal-to-noise ratio. The final EFTEM images were obtained by integrating over 40 frames and were aligned to each other using the built-in beam-drift alignment from Digital Microgaph (Gatan, Inc).

We imaged the transmitted electrons with EFTEM, i.e. the spatial distribution of electrons as a function of energy-loss. The measured transmitted electrons lost energy in the range from zero to 120 eV (±2.5 eV). Figure 4-2 shows the raw images of transmitted electrons as a function of
energy-loss. Each image was taken in a nearby and fresh location of the sample. We observed negligible broadening of the electron-beam for energy-loss less than 90 eV. However, at 95 eV or higher energy-loss, a broader electron-beam was observed due to excitation of Si-L2,3 edges (core electrons).
Figure 4-2. Energy-filtered images of transmitted electrons at 200 keV. The energy-loss ranges from 0 to 300 eV, with a 5 eV width. The dwell time was set to maximize the signal at each micrograph. The sample consists of 20-nm-thick HSQ on top of 10-nm-thick SiN. We observe a small spatial broadening of the transmitted electron distribution.
at 100 eV. For energies higher than 200 eV, we observe an asymmetric electron distribution, possibly due to high energy shift in the spectrometer.

To verify the physical integrity of the sample throughout the EFTEM measurements, we acquired EELS spectra as a function of time. If the electron beam induced sputtering of the sample, we would observe an attenuation of the VP peak with respect to the zero loss peak. Figure 4-3 shows that there was no significant variation in the VP peak intensity for up to 2.5 min of exposure, which is less than the dwell time used for each EFTEM image. We note that each EFTEM image was taken in a nearby and fresh location of the sample. We can observe a minimal decrease in the plasmon peak for exposures longer than 5 min. Consequently, electron-beam induced sputtering is not a critical issue for the image acquisition times used in this experiment.

Figure 4-3. Low-loss electron energy-loss spectra for the HSQ/SiN$_x$ sample at different acquisition times, using a 0.8 nm FWHM spot size at 200 keV. For acquisitions longer than or equal to 5 min we observe a small decrease of the VP peak at 22.5 eV. This indicates minimal electron sputtering of the material.
4.2.2. Assumptions and calculation of the direct-beam point-spread function (PSF)

We have two main assumptions for measuring the direct-beam PSF:

(1) We consider that all energy lost by the direct-beam between 5 and 120 eV contributes to resist exposure.

(2) The position of the detected electron beam is approximately the position of the energy lost in the resist. For this consideration, we achieved single scattering regime and calculated that the delocalization of inelastic scattering is not significant compared to the direct-beam PSF.

To verify the appropriate range of energy loss to be taken into account in the direct-beam PSF measurement, we acquired an EELS spectrum from 0 to 700 eV on 20nm/10nm HSQ/SiNx. We extrapolated the spectrum with a fitting curve up to 1 keV, as shown in Figure 4-4 below. We considered 1 keV as a threshold energy because single inelastic scattering events with energies higher than 1 keV are likely to come from inner-shell ionization and generation of high-energy secondary electrons (SEs), which should not contribute significantly to the sub-10-nm direct-beam PSF. SEs with energies higher than 1 keV will not contribute significantly to the PSF at sub-10-nm radius because these SEs propagate hundreds of nanometers away from the point exposure, creating a uniform background of deposited energy at sub-10-nm radius.
Figure 4-4. Plot of percentage of accumulated absorbed energy vs energy-loss in the range 10 to a given energy loss. We consider an energy threshold of 1 keV (which is equivalent to 100%). 53% of the accumulated energy lost was in the 10 to 120 eV range. Single inelastic scattering events with energies higher than 1 keV are most likely to come from inner-shell ionization and generation of high-energy SEs, which should not contribute significantly to the sub-10-nm direct-beam PSF.

If we consider that all energy lost to the sample is due to electrons that lose 10 eV to 1 keV of energy, the 10 to 120 eV energy-loss range contains 53% of total absorbed energy. Therefore, the energy range from 10 to 120 eV captures the majority of the energy-loss of interest. In addition, VP resonance occurs between 10 and 50 eV, which contains 35% of the total absorbed energy. However, we note that the integrated tail of the VP peak extends up to ~100 eV. For example, a portion of the energy loss at 100 eV may be due to VP excitation.

Furthermore, we measured the energy-density threshold for HSQ exposure. We measured an average energy-loss per electron of 4.2 eV for a sample consisting of 20-nm-thick HSQ on top of 10-nm-thick SiN$_x$. We have estimated that HSQ absorbs 62% of the total energy-loss, and we
considered a threshold dose for large area exposure of 230 electrons/nm². Therefore, we have estimated that the threshold energy density for HSQ exposure is \( \sim 30 \) eV/nm³.

To evaluate our hypothesis of a single scattering regime in our HSQ+SiNₓ sample, we measured the log-ratio relation (112):

\[
\frac{t}{\lambda} = \log \frac{I_{\text{total}}}{I_{\text{zero}}} \quad (4.1)
\]

where \( t \) is the sample thickness (HSQ+SiNₓ), \( \lambda \) is the inelastic mean free path, \( I_{\text{total}} \) is the integrated EELS or summed EFTEM over all the spectrum, and \( I_{\text{zero}} \) is the integrated zero-loss peak of the EELS or the EFTEM zero loss peak. Single scattering regime requires \( t/\lambda < 1 \). The \( t/\lambda \) measured was 0.26 using EFTEM and 0.24 using EELS (and 0.12 for SiNₓ only). Therefore, we may assume that the sample was in the single-scattering-event regime.

To evaluate whether inelastic scattering delocalization is critical to our analysis, we calculated the delocalization PSF based on an analytical formulation previously reported (31). Figure 4-5 shows that the delocalization PSF decays by more than 4 orders of magnitude from 0.1 to 12 nm radius. The direct-beam PSF does not account for delocalization, but such effects would introduce a negligible broadening to the direct-beam PSF. Delocalization of inelastic scattering for energy loss larger than 25 eV is also negligible compared to the SE (as previously reported in electron-beam-induced deposition (113)) and VP PSFs.
Figure 4-5. Radial distribution of the probability of energy loss (for 5, 25, 50, 75, 100, and 120 eV), that is, the inelastic or delocalization PSF. (31) The incident electron energy was 200 keV.

We have calculated the energy deposited by the electron beam, named ‘direct-beam PSF’, by weight averaging of the intensity of transmitted electrons from 2.5 to 122.5 eV energy-loss:

\[
PSF_{\text{direct-beam}}(r) = \sum_{\varepsilon_f=5 \text{ eV}}^{120 \text{ eV}} \varepsilon_f \rho_{\text{EFTEM}}(r; \varepsilon_f)
\]  

(4.2)

where \(\varepsilon_f\) is the filtered electron energy loss (using a 5 eV slit), \(\rho_{\text{EFTEM}}(r; \varepsilon_f)\) is the electron counts per second as a function of radial distance \(r\) at a given energy loss \(\varepsilon_f\).

4.2.3. EELS

Electron energy-loss spectroscopy (EELS) was performed on a Hitachi 2700C dedicated aberration-corrected STEM with a cold-field-emitter source (~ 0.4 eV energy spread) at 200 keV. A beam current of ~20 pA, 0.05 - 0.3 eV/channel dispersion (depending on the desired energy range) and 2 mm collection aperture were used. The electron beam convergence semi-angle was
28 mrad, and the collection semi-angle was 14 mrad. The spectrum was taken with 0.04s dwell time with 10-50 frames.

The angle/momentum-resolved EELS was done on a FEI Tecnai F20ST TEM/STEM with a field-emitter-source (~1eV energy spread). An acceleration voltage of 200 kV, beam current of 60 pA, illuminated area 1.3 μm in diameter, 0.6 mm collection aperture, 970 mm camera focal length, 0.2eV/channel dispersion, were used. The dwell-time (0.1 to 100 s) and number of frames (1-100) were adjusted to maximize the signal-to-noise ratio without saturating the detector.

The relationship between the angle (θ) of an inelastic-scattered electron and the magnitude of the transferred scattering vector (q) and momentum (ℏq) is(31):

\[ q^2 \approx k_0^2 (\theta^2 + \theta_E^2) \]  \hspace{1cm} (4.3)

where \( k_0 \) is 2505 nm\(^{-1} \) for 200 keV incident electrons, and \( \theta_E \) is 0.065 mrad for 22.5 eV energy loss also with 200 keV incident electrons.

We calibrated the angular scale with a <111> oriented single-crystal silicon film. In the diffraction plane shown in Figure 4-6, we first aligned the [000] beam (non-diffracted) with the collection aperture. Then, we calibrated the beam tilt necessary to translate the [220] diffracted beam to the position of the [000] beam. The beam tilt was calibrated using an in-house computer script. Therefore, the tilt from [000] to [220] on Si corresponded to two times the Bragg scattering angle for the <220> direction, e.g. 13 mrad. EELS spectra were recorded only for specific values of scattering angle, from zero to 19.5 mrad with varying angular step size. The electron beam incident outside of the collection aperture was therefore blocked. The angular resolution was given by the collection angle or collection aperture size, corresponding to 0.32 mrad and 0.6 mm respectively. The convergence angle was also set to 0.32 mrad. The calibrated EELS system was then used to measure angle-resolved EELS for SiNx and HSQ.
Figure 4-6. Electron diffraction of single-crystal Si oriented in the <111> direction. The <111> direction is into the plane of the page and is represented by the central spot, which was covered to enhance image-contrast. The six hexagonally arranged spots represent diffraction from the family of crystal planes (114) as shown.

The angle-resolved EELS spectrum of ~25 nm thick HSQ on top of 10-nm-thick SiNx is shown in Figure 4-7 below. We observed from Figure 4-7 that the VP dispersion is subtle, shifting by 1.3 eV for a change in scattering angle of 0.0 to 4.5 mrad.
Figure 4-7. Momentum- or angle-resolved EELS. Electron count contours plotted as a function of electron energy-loss and scattering angle. The electron counts are shown in natural logarithmic scale. We observed the VP peak at 22.5 eV. We also observed a ‘shoulder’ that increases in intensity with increasing energy and line-width, which we call the dispersive VP component.

The VP peak usually presents a dispersive (leads to shift in energy) and a non-dispersive component. The non-dispersive component is due to a double scattering process, being an elastic scattering event with exchange of momentum plus a VP scattering event without exchange of momentum. In Figure 4-8 we plotted the ratio of volume-plasmon intensity to the zero-loss peak intensity from the angle-resolved EELS spectra. We observed that, above 5 mrad, the VP peak intensity correlated well with the zero-loss peak intensity. This suggests that the energy-loss spectrum above 5 mrad was dominated by the non-dispersive VP. The dispersive VP peak was observed for angles smaller than 5 mrad.
Figure 4-8. Ratio of the volume-plasmon intensity to the elastic (or zero loss) intensity as a function of scattering angle. We observed that the VP peak intensity correlated well with the elastic peak intensity for scattering angles larger than 5 mrad. This correlation suggests that the energy-loss spectrum is dominated by non-dispersive VPs for scattering angles larger than 5 mrad.

There are two factors to take into account in the EELS spectra shown in Figure 4-7: (1) the effect of SiNₓ membrane; and (2) the effect of electron-beam damage.

We measured the $t/\lambda$ ratio as discussed in the previous session to quantify the amount of energy-loss in 10-nm-thick SiNₓ and ~25-nm-thick HSQ. For these experiments the collection aperture was 3 mm. We would like to perform measurements in a HSQ film that is thick enough to have the majority of the EELS signal from HSQ and not from SiNₓ. We would also like to be in the single-scattering-event regime ($t/\lambda < 1$). The log-ratio for 10-nm-thick SiNₓ was $t/\lambda_{\text{SiN_x}} = 0.18$. While the log-ratio for ~25-nm-thick HSQ on top of 10-nm-thick SiNₓ was $t/\lambda_{\text{HSQ-SiN_x}} = 0.40$. We estimated that 60% of energy-loss from the HSQ/SiNₓ sample occurred in HSQ and that both samples were sufficiently thin to remain in the single-scattering-event regime.

To evaluate beam-damage, we noticed that the longest EELS acquisition time was 500 s (60 pA beam current), over a 1.3 µm diameter area, for 30 different scattering angles at the same
position in the sample. We imaged the exposed area and monitored the VP peak before and after all acquisitions. We did not observe signs of sample damage (e.g. reduction of VP intensity).

4.2.4. Atomistic Simulation of HSQ Interband Transitions

Atomistic simulation of HSQ was performed with the *Abinit*\(^{(114, 116)}\) package using projector augmented wave (PAW) density functional theory (DFT) under the local density approximation (LDA). To simulate a single HSQ cage molecule (H\(_8\)Si\(_8\)O\(_{12}\)) containing 28 atoms, the molecule was placed in a large vacuum box with dimension of 20 × 20 × 20 Bohr\(^3\). Different box sizes were tested and convergence was achieved for the chosen box size. The maximal plane-wave kinetic energy cutoff in the simulation was set to 50 Hartree. Convergence was also confirmed for this parameter value. Since the molecule-in-box model represents an isolated system, only one \(k\) point was included in the \(k\)-grid for the calculation.

We first optimized the structure of the HSQ cage using Broyden-Fletcher-Goldfarb-Shanno minimization. The HSQ cage structures before and after optimization are illustrated in Figure 4-9. Simulated structural parameters are compared to experimental values obtained from XRD\(^{(117)}\) in Table 1, confirming that the simulation generates correct HSQ cage structure.
Figure 4-9. Cage structures of a single molecule of HSQ before and after structural optimization. We note that HSQ is an amorphous material that contains cage and network structures.

<table>
<thead>
<tr>
<th></th>
<th>Experiment(117)</th>
<th>Simulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>bond length RSi-O</td>
<td>162 pm</td>
<td>173 pm</td>
</tr>
<tr>
<td>bond angle A_{Si-O-Si}</td>
<td>147.5°</td>
<td>144.5°</td>
</tr>
<tr>
<td>bond angle A_{O-Si-O}</td>
<td>109.6°</td>
<td>108.5°</td>
</tr>
</tbody>
</table>

Table 4-1. Comparison of structural parameters obtained from experiment(117) and simulation.

We then calculated the electronic structure of a HSQ cage using DFT. Goedecker-Teter-Hutter LDA pseudopotentials(118) were used for H, Si, and O atoms. Only the valence electrons were considered under the frozen-core approximation. Figure 4-10 illustrates the calculated density of states (DOS) for a HSQ cage.
Figure 4-10. Simulated density-of-states (DOS) for a HSQ cage. The δ function representing each molecular orbital is smeared by an energy of 0.01 Hartree. The Fermi level is indicated by the red dashed line.

Simulation of HSQ optical properties is based on the simulation result of its electronic structure. Random phase approximation (RPA) was used to calculate the dielectric function $\epsilon$ of HSQ. The energy-loss function was thus calculated from $Im(-1/\epsilon)$. The energy-loss function is shown in Figure 4-11. By comparing the simulated energy-loss function with experimentally obtained EELS data, we conclude that the VP resonance is either not resolved or strongly underestimated by the simple DFT-LDA calculation of an isolated HSQ cage molecule. However, interband transitions are resolved and lead to peaks in the simulated energy-loss function. In the experiment, the energy-loss is dominated by VP resonance. So, to better compare the simulation
with the experiment and determine the contribution from interband transitions, we performed a second-derivative on the EELS spectrum to find the interband transitions. Table 2 shows the comparison between EELS interband transitions with the simulated interband transitions. For proper comparison, we shifted the simulated peaks by +2.46 eV. It can be seen that simulation and experiment achieve a reasonable agreement. It was necessary to shift the simulated peaks because the DFT-LDA method is known to underestimate the band-gap, or energy intervals between molecular orbitals.

![Energy loss function graph]

**Figure 4-11.** Simulated energy-loss function of an isolated HSQ cage molecule.

<table>
<thead>
<tr>
<th>measured peaks (eV)</th>
<th>6.3</th>
<th>7</th>
<th>8.5</th>
<th>10.5</th>
<th>12.1</th>
<th>12.9</th>
<th>14.4</th>
<th>-</th>
<th>-</th>
<th>17.3</th>
<th>18.5</th>
<th>19.8</th>
<th>21</th>
<th>22.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>simulated peaks (eV)</td>
<td>-</td>
<td>7.8</td>
<td>-</td>
<td>10.5</td>
<td>12.2</td>
<td>13</td>
<td>14.4</td>
<td>15.1</td>
<td>16.4</td>
<td>17.6</td>
<td>-</td>
<td>19.3</td>
<td>-</td>
<td>22</td>
</tr>
</tbody>
</table>

**Table 4-2.** Comparison between measured peaks in the low-loss EELS spectrum with atomistic simulation of interband transitions of HSQ-cage structure.
4.2.5. Lithographic point-spread function

Here we present the experimental methods to measure the lithographic PSF.

Sample processing

Samples were prepared by spin-coating HSQ (1% solids XR-1541, Dow Corning) on 10-nm-thick SiNx membranes (TEMwindows.com) at a spin-speed of 8 krpm. The resulting HSQ thickness was 10-15 nm. To avoid thermally-induced cross-linking of HSQ, which might lead to a loss in resolution, no pre-exposure bake was performed(77). After exposure, samples were immersed in a salty developer (1% weight NaOH + 4% weight NaCl) for 4 min at 24°C, rinsed under deionized water for 2 min, rinsed in isopropyl alcohol for 10 s, and gently blown dry with nitrogen gas for 1 minute. The typical total processing period from spin coating to development was about 4-5 days.

STEM lithography

Exposures were performed on a Hitachi HD 2700C dedicated aberration-corrected scanning transmission electron microscope (STEM) with a cold-field-emitter source (~ 0.4 eV energy spread), 0.15 nm spot size, and a beam current of 70-100 pA.

We did our exposures by imaging the resist with a Digiscan Control Unit, embedded within the Digital Micrograph Suite (Gatan, Inc.) choosing: (1) the desired dwell time; (2) microscope magnification; (3) number of pixels; and (4) beam current. These parameters define the area and pitch of interest. No pattern generator was used.

TEM metrology
The TEM metrology was done on a JEOL JEM 2010F transmission electron microscope at 200 keV. A standard <011> Si sample was used to calibrate the magnification for the TEM camera. The images were taken slightly defocused in order to provide a slight Fresnel fringe to enhance edge contrast. This has a small to negligible effect on the measured resolution.

**Lithographic PSF: dot-exposure method**

Isolated posts were patterned with single-pixel exposures with doses ranging from 1 to $10^3 \, \text{fC/dot}$, followed by salty development(77). The reciprocal dot dose was then plotted versus the dot radius, as described in Reference (14), given the functional form of the PSF. We minimized the effect of resist development in the PSF measurement by choosing a developer (salty development(77)) with high contrast ($\gamma = 10$), which reduces the uncertainty of the dot-radius measurement. The standard deviation for the radii of the PSF data sets was 0.3 nm.

### 4.3. Results and Discussions

Here we present the direct-beam PSF, the VP PSF, simulations of the SE PSF, and an analysis connecting these results to the resolution limits of EBL at the sub-10 nm length scale.

#### 4.3.1. Direct-beam PSF

We first measured the direct-beam PSF at 200 keV. The spherical- and chromatic-aberration-corrected EFTEM (Argonne chromatic aberration-corrected TEM – ACAT – $C_C=1\, \mu\text{m}, C_S=2.5\, \mu\text{m}$) is the ideal instrument for this measurement because the correction of chromatic aberration permits electrons with different energies to be imaged at the same focal plane. Figure 4-12 shows the direct-beam PSF measurement (see Methods for details). We measured the number of electrons ($\rho_{\text{EFTEM}}$) that were transmitted through the resist as a function of radial position ($\vec{r}$) and energy loss ($\epsilon_l$), as depicted in Figure 4-12a and shown in Figure 4-12c. In Figure 4-12d we show the direct-
beam PSF, which was calculated using $\rho_{\text{EFTEM}}(|\vec{r}|; \xi_f)$ for $\xi_f$ varying from 5 to 120 eV. The exit position of each electron is considered approximately equal to the position where this electron lost its energy. This approximation is reasonable because we achieved the single-inelastic-scattering regime and the effect of delocalization of inelastic scattering is small compared to the direct-beam PSF (see details in Methods). The entire energy loss could be deposited locally (at $\vec{r}$) or a portion of this energy could be delocalized through the sample due to SE and VP propagation. The latter delocalization effects may lead to a broadening of the lithographic PSF relative to the direct-beam PSF and need to be analyzed.

**Figure 4-12.** Measurement of the direct-beam PSF using chromatic-aberration-corrected energy-filtered TEM. (A) Schematic of the experiment. The focused incident electron beam had initial energy $\xi_i$ of 200 keV and 0.8 nm full-
width at half maximum. The electron beam is transmitted through the sample and may experience a radial deflection $\vec{r}$ and energy loss $\varepsilon$ due to scattering events. The electrons may be counted in EELS mode ($\rho_{\text{EELS}}$) or in EFTEM mode ($\rho_{\text{EFTEM}}$). Electrons were counted as a function of energy loss $\varepsilon_i$, $\rho_{\text{EELS}}(\varepsilon_i)$. Electrons were also counted as a function of radial distance $r = |\vec{r}|$ from the center of the beam for a filtered energy loss $\varepsilon_f$, $\rho_{\text{EFTEM}}(r; \varepsilon_f)$. We used a 5 eV energy filter slit to select the energy loss $\varepsilon_f$ (see details in Supporting Information). (B) (squares) Total electron counts ($\rho_{\text{EFTEM}}$ integrated over area $A$ of 200 nm$^2$) as a function of energy loss $\varepsilon_f$ from 0 to 120 eV. The VP peak was observed at 22.5 eV. The integrated $\rho_{\text{EFTEM}}$ (squares) correlates well with $\rho_{\text{EELS}}$ (line). (C) $\rho_{\text{EFTEM}}(r; \varepsilon_f)$ with $\varepsilon_f$ from 5 to 120 eV. The shape of $\rho_{\text{EFTEM}}(r; \varepsilon_f)$ did not change significantly until the Si-L2,3 edges (core electrons) are excited at 99 eV. The inset shows a bright field EFTEM image used to compute $\rho_{\text{EFTEM}}(r; 20\text{eV})$ (we considered $\rho$ to be radially symmetric). (D) (dotted line) $\rho_{\text{EFTEM}}$ in vacuum (no sample), $\rho_{\text{EFTEM}}^{\text{vacuum}}(r; 0\text{eV})$; (dashed line) $\rho_{\text{EFTEM}}(r; 0\text{eV})$; and (continuum line) radial distribution of deposited energy density, defined as ‘direct-beam PSF’ $\text{PSF}_{\text{direct-beam}} = \sum_{5\text{eV}}^{120\text{eV}} \varepsilon_f \rho_{\text{EFTEM}}(r; \varepsilon_f)$ – see details in Supporting Information). The direct-beam PSF represents the energy density locally deposited by the direct (or forward-scattered) electrons.

4.3.2. Volume-Plasmon point-spread function

The role of VPs on SE emission has been extensively investigated (30, 32, 97, 110, 111) in electron microscopy, but the effect of VPs on EBL resolution has not been established. VPs may decay via interband or intraband transitions, releasing a SE (16, 30, 111) In the context of the free electron approximation, VPs with high momentum may decay and generate single electrons (31, 119) We determined the dielectric function of our resist, hydrogen silsesquioxane (HSQ), to obtain the VP PSF. VPs may directly expose the resist or decay into SEs that expose the resist.

The Kramers-Kronig analysis (KKA) is discussed in details by Egerton in Reference (31). This method permits calculation of the dielectric function as a function of energy-loss. First we obtain the energy-loss function from the electron energy-loss spectrum in the single scattering regime:

$$J^1(E) \approx S(E) = \frac{\hbar E}{\pi \alpha_0 m_0 v^2} \text{Im} \left[ \frac{1}{E(E)} \right] \ln \left[ 1 + \left( \frac{\beta}{\varepsilon E} \right)^2 \right]$$  (4.4)
where $J'(E)$ is the electron energy-loss spectrum; $S(E)$ is the electron energy-loss spectrum in the single scattering regime; $I_0$ is the intensity of the zero loss peak; $t$ is the sample thickness; $a_0$ is the Bohr radius; $m_0$ is the electron rest mass; $v$ is the incident electron velocity; $\varepsilon(E)$ is the dielectric function; $\beta$ is the collection semi-angle; $\theta_E$ is the characteristic scattering angle; and $E$ is the energy loss.

The energy loss function, $Im\left[\frac{-1}{\varepsilon(E)}\right]$, is related to the dielectric function $\varepsilon(E)$. By using the KKA sum rule and KKA transformation, $\varepsilon(E)$ is obtained. The complex index of refraction is then obtained by:

$$n = n + ik = \sqrt{\varepsilon(E)} = \sqrt{\varepsilon_1(E) + i\varepsilon_2(E)}$$

(4.5)

where $n$ and $k$ are the real and imaginary part to the complex index of refraction, respectively. In addition, $\varepsilon_1(E)$ and $\varepsilon_2(E)$ are the real and imaginary part of the dielectric constant as a function of energy $E$, respectively.

We assumed that the VP decay length is the same as the decay length of an electromagnetic wave at the same frequency. A detailed discussion on the validity of this assumption can be found in References (120-124). The decay length $L$ is the length scale where the intensity of the VP decays to $1/e$ of its original value:

$$L = \frac{\lambda_0(E=22.5 \text{ eV})}{4\pi k(E=22.5 \text{ eV})}$$

(4.6)

where $\lambda_0$ is the VP wavelength in vacuum, and $k$ is the extinction coefficient or imaginary part of the complex index of refraction, both at the VP frequency.

Finally, the VP PSF is calculated using the relation:
\[ PSF^{\text{volume-plasmon}}(r) = \frac{e^{-r/\lambda}}{2\pi r} \left[ \frac{1}{\text{nm}^2} \right] \] (4.7)

The factor \(1/r\) is due to the cylindrical symmetry of the VP generation and propagation from a linear source perpendicular to the resist surface (the electron beam). This PSF form is similar to those used previously.\((17, 120, 125)\) We did not consider VP scattering in this analytical form of the VP PSF.

In Figure 4-13a-d, we show the low-loss EELS spectrum and the results of the KKA previously described to determine the dielectric function of HSQ and the VP PSF. The VP PSF will be compared to the other PSFs in section 4.3.5 of this Chapter.
Figure 4-13. Measurement of the VP PSF and analysis of VPs. (a) (dashed line) EELS spectrum of 40-nm-thick HSQ on top of 10-nm-thick SiNx at 200 keV. Kramers-Kronig analysis (KKA) provides a relationship between the EELS spectrum and the (continuum line) energy-loss function (proportional to the imaginary part of the reciprocal of the dielectric function - see details in Supporting Information). (b) Dielectric constant $\varepsilon(E) = \varepsilon_1 + \varepsilon_2$ and complex index of refraction $n = n + ik$ from KKA. (c) Decay length $L = \frac{\lambda_0}{4\pi k}$ for an electromagnetic wave as a function of energy. (d) We calculated the VP PSF from the decay length at the VP energy, 22.5 eV. (e) VP energy as a function of scattering angle or momentum of the direct electron beam squared. We observed that VPs have a quadratic dispersion, as expected from the Lindhard model. (f) EELS spectra with varying scattering angle. The increase of the VP-peak width for increasing scattering angle confirms the non-localized nature of the VPs.
To further investigate the VP peak, we performed EELS as a function of scattering angle or momentum (see Methods for details on angle-resolved EELS). In summary, the incident electron beam was tilted and the EELS spectrum was collected at specific angles (with 0.32 mrad angular resolution) defined by the collector aperture. In Figure 4-13e and 4-13f we show the evolution of the VP peak as a function of scattering angle. The VP dispersion in HSQ agreed with the expected behavior from the Lindhard model. This result suggests that the energy loss peak at 22.5 eV in the EELS spectrum is indeed a VP resonance.

Furthermore, we performed atomistic simulation of the HSQ-cage structure (a significant portion of the exposed HSQ film still contains the HSQ-cage structure) to understand the small energy loss peaks or ‘shoulders’ at energies from 5 to 20 eV, as shown in Figure 4-13a. The electronic transitions from the simulation agree with the measured energy loss spectrum (see Methods for details). The atomistic simulation result suggests that these peaks are vertical interband transitions, which are important decay pathways for VPs, which may produce SEs that subsequently expose the resist.

4.3.3. Simulated SE PSF

In order to compare the effect of SEs to the lithographic PSF, we performed numerical simulation of the SE PSF and Monte Carlo simulations of the lithographic PSF. The numerical SE PSF model presented here is sourced from References (18) and (19). This model is based on the classical inelastic scattering cross section for SE generation, modified-Bethe stopping power, and random walk approximation for SE propagation. This SE PSF model is simplified, but useful in giving an intuition of the role of SEs in EBL. The Monte Carlo modelling was carried out to achieve higher accuracy than the numerical method. The Monte-Carlo simulation is based on the Mott elastic cross section, the classical inelastic cross sections, the modified-Bethe
stopping power\(^{(78)}\). The simulation results will be compared to the other PSFs in section 4.3.5 of this Chapter.

The SE PSF model presented here is inspired by works of Hartley\(^{(19)}\) and Neureuther\(^{(18)}\) and is illustrated in Figure 4-14. The model presented here is simplified but effective in giving an intuition of the role of SEs in EBL.

**Figure 4-14.** Illustration of the secondary-electron (SE) PSF model. Number of SEs \(N_{SE}\) versus SE energy \(E'\) versus radial distance \(r\). The number of SEs as function of energy is given by the differential cross-section \(\frac{d\sigma_{SE}}{dE}\). From the position \(r=0\), the SEs travel away from the center losing energy continuously. The colored lines represent the energy of SEs at different initial energies at \(r=0\). High-energy SEs propagate longer distances but are in smaller number. The rate of energy loss is given by the modified Bethe stopping power. To estimate the electron penetration depth from the maximum penetration depth, we use the random-walk approximation \(r_{average} = \frac{r_{max}}{\sqrt{N}}\), where \(N\) is the number of inelastic collisions. The \(PSF_{SE}\) is obtained by the summation of the energy loss density of all electrons at a given radius.

**SE Generation:** The number of secondary electrons generated at radial distance \(r=0\) with energy \(E'_{(r=0)}\) is given by:
\[ N_{SE}\left(E_{(r=0)}^j\right) = \frac{\partial \sigma_{SE}}{\partial E} n_E N_{pe} l \left[ \text{e}^{-}\text{erg} \right] \]  

(E_{(r)})^j \text{ is the SE energy as a function of radial distance } r, \text{ starting with energy } j \text{ at } r = 0. \frac{\partial \sigma_{SE}}{\partial E} \text{ is the classical differential electron inelastic cross section (probability of SE emission per unit energy) for core and valence electrons, } n_E \text{ is the electron density, } N_{pe} \text{ is the number of incident primary electrons, and } l \text{ is the resist thickness.} 

SE propagation: The maximum propagation and random-walk (based on spherical cross section) estimation of SE propagation is given by:

\[ r_{max} \approx \frac{E_{(r=0)}^j}{S(E_{(r=0)}^j)} \]  

(4.9)

\[ r_{average}^j = \frac{r_{max}}{\sqrt{N}} \]  

(4.10)

where \(|S(E_{(r-\Delta r)}^j)|\) is the stopping power for low-energy electrons, and \(N\) is number of inelastic collisions.

SE energy deposition: The linear-density of deposited energy along the averaged (random walk) secondary-electron path is given by:

\[ \frac{\Delta E_{(r)}}{\Delta r_{average}} = \frac{E_{(r=0)}^j}{r_{average}^j} \left[ \text{erg} \right] \left[ \text{nm} \right] \]  

(4.11)

SE point-spread function (SE PSF): The final calculated SE PSF is given by:

\[ PSF^{SE}(r) = \sum_{j=10 \text{ ev}}^{E_{\text{primary/2}}} = \frac{N_{SE}(E_{(r=0)}^j)\Delta E_j}{2\pi r} \frac{E_{(r=0)}^j}{r_{average}^j} \delta_j \left| S(E_{(r=0)}^j) \right| r_{average}^j \left[ \text{erg} \right] \left[ \text{nm}^2 \right] \]  

(4.12)
The term $\delta_j > |s(E_{r=0})| r_{average}^j (=1$ if the inequality is satisfied) removes electrons that will not reach a distance $r_{average}^j$ from the sum. The term $\Delta E_j$ is the energy increment of the sum (1 eV in the simulation in this work).

4.3.4. Monte Carlo simulation of the lithographic point-spread function

Our goal is to have a trustworthy Monte-Carlo model to simulate the lithographic PSF and compare it with experimental results. The physics of our Monte Carlo code, mainly based on references (13, 79), is summarized below.

**Stopping power:** We used Joy’s Bethe-modified stopping power (78), which is accurate with respect to experimental data from 50 eV to 30 keV, and is a reasonable approximation from 10 eV to 30 keV (128). We used the relativistic Bethe stopping power for electrons with energies higher than 30 keV.

**Elastic cross section:** We used the Mott elastic cross-section, which is known to be more accurate than Rutherford at lower energies (<10 keV). (129)
Figure 4-15. Elastic electron cross-section as a function of incident electron energy. The Mott cross section provides higher accuracy for lower primary electron energies than does the screened Rutherford cross-section.

**Inelastic cross section:** In Figure 4-16 we compared the following inelastic cross sections: (1) Classic; (2) Moller (as used in *Casino*(129)); (3) Moller for valence electrons and Gryzinski*(16)* for core electrons; and (4) Moller for valence electrons and Vriens for core electrons,(18, 19) named “Moller+Vriens”. The lower bound cut off energy for inelastic scattered electrons was 10 eV.
Figure 4-16. Inelastic electron cross-section as a function of incident electron energy. The Moller model gives the smallest cross-section while Grysinski model gives the largest cross-section for large energies.

We chose to simulate the SEs with the classical inelastic cross section as a reference model because this model fits well with the lithographic PSF from ~10 to ~1000 nm. We also tested the Moller+Vriens model, which provides a higher inelastic cross-section causing the SEs to have a larger effect on the PSF. As shown in Figure 4-17, the PSF using the Moller+Vriens model is wider than the PSF with the classic model.
Figure 4-17. Monte-Carlo-simulated PSFs with different inelastic electron cross-sections. Red circle is the PSF using the classical inelastic cross section, green circle is the PSF with the Moller+Vriens inelastic cross section.

In addition, we compared the Monte Carlo PSF with the numerical SE PSF (both simulations do not include VPs). Figure 4-18 below shows only a similar trend between these two PSFs from 10 to 100 nm radius. The numerical SE PSF is simplified and it does not take into account the complex scattering by the direct-beam and SEs. Therefore, we rely on the Monte Carlo simulation for analyzing the role of SEs in the lithographic PSF.
Both PSFs were calculated using the classical inelastic scattering cross section and the modified Bethe stopping power for electron energies smaller than 30 keV.

We note that the PSF simulations and measurements obtained here were determined using a 10-nm-thick SiN$_x$ membrane supporting the resist, and not a usual bulk substrate. Therefore, our experiments do not contain the contribution from backscattered electrons. In addition, our experiments were performed with electron beam energy of 200 keV, which is higher energy than in conventional EBL ($\leq$ 125 keV). We simulated the lithographic PSF at 200 keV (including SEs but excluding VPs) considering a 20-nm-thick HSQ resist on top of 10-nm-thick SiN$_x$ membrane and also on top of 300-µm-thick Si substrate, as shown in Figure 4-19. The shape of the PSFs differ only for radii larger than 50 nm. There is also a similar experimental report confirming this trend for lower energies.\textsuperscript{(14)} Therefore, the PSF measurements presented here are accurate for sub-50-nm radius. For further information on the effect of backscattered electrons in the PSF, we refer to References. \textsuperscript{(29, 109, 130)}
Figure 4.19. Monte-Carlo simulated PSFs with different supporting substrates. These simulations include SE generation but do not include VP generation. (green circle) Monte-Carlo PSF of 20-nm-thick HSQ on top of 10-nm-thick SiN membrane. (red diamond) Monte-Carlo PSF of 20-nm-thick HSQ on top of 300-µm-thick Si substrate. We used the classical inelastic scattering model for both PSFs. The other models used were previously described in this section. We observed a deviation between the PSFs for radius larger than 50 nm.

4.3.5.Lithographic point-spread function and its components

Figure 4-20a describes the measurement of the lithographic PSF by the dot-exposure method (see Methods for details), (14) which takes into account all physical phenomena relevant to EBL exposure.
Figure 4-20. Components of the Lithographic PSF. (a) Schematics of the dot-exposure method for measuring the lithographic PSF. (left) A single-pixel exposure generates an energy density profile in a given plane of the resist (z=0), which is the lithographic PSF. The feature radius is defined when the deposited energy density is equal to the threshold energy density. We assumed constant threshold energy density and no chemical diffusion or crosslinking-redistribution effects. (right) Energy density contours at the threshold energy density and TEM micrographs of a developed feature, presented in top-view and side-view. We have repeated this process for many doses (units of Coulombs/pixel) and the lithographic PSF is constructed by plotting the reciprocal dose versus feature radius. (b)
Components of the lithographic PSF (maximum value of all PSFs was set to unity): (blue) direct-beam PSF, (green) VP PSF, (purple) SE PSF by numerical method, (black circles) lithographic PSF by Monte-Carlo simulation including SEs, (gray) fitted lithographic PSF (from previous Chapter), and (red squares - dataset 1 - and red triangles - dataset 2) lithographic PSF from dot-exposure method. From the direct-beam PSF to the lithographic PSF we have the total effect of delocalized energy transfer in EBL. The numerical SE PSF and Monte-Carlo lithographic PSF differ due to the simplified treatment of electron scattering in the numerical SE PSF model. (c) (blue) deposited energy density due to SEs, calculated from Monte-Carlo lithographic PSF including SEs and the instrument spot size; (black) deposited energy density due to VPs, calculated from VP PSF and direct-beam PSF for energies smaller than 50 eV; and (green) total deposited energy density (see calculation details in Supporting Information). The lithographic PSF was overlaid with the total deposited energy density. The VPs were necessary to match the total deposited energy density to the lithographic PSF.

Figure 4-20b shows a comparison of the measured direct-beam PSF and VP PSF, and the two simulated SE PSFs, to the lithographic PSF. The largest contributor to the lithographic PSF at the sub-1-nm radius range was the direct-beam. This shows that despite SE emission and VP excitation, the spot size and electron scattering are the absolute limiting factors for fabrication of small, isolated features by EBL. The difference between the lithographic PSF and the direct-beam PSF is due to the sum of all delocalized processes in EBL exposure, including SEs and VPs. This result suggests that if a new resist could be developed to attenuate SE and VP emission, then the resulting lithographic PSF will be closer to the direct-beam PSF, therefore increasing the resolution.

The classical formulation of the lithographic PSF is a convolution of the direct-beam PSF and the SE PSF\((11, 13, 14, 18)\)

\[
PSF^{\text{litho}}(r) = PSF^{\text{direct-beam}}(r) \ast PSF^{\text{SE}}(r)
\]  

\(4.13\)
This formulation was conceived assuming that high-energy SEs are the particles responsible for delocalization of deposited energy in the resist.

Here we assumed that delocalization of deposited energy in the resist was caused by SEs, created by direct ionization of valence and core electrons ($PSF_{\text{direct-SE}}(r)$), and by VPs, which may also decay into SEs. The total effect from VPs and SEs originated from VPs is $PSF_{\text{VP-SE}}(r)$:

$$PSF_{\text{VP-SE}}(r) = PSF_{\text{VP}}(r) \ast PSF_{\text{VP-SE decay}}(r)$$ (4.14)

where $PSF_{\text{VP}}(r)$ is given in Figure 4-13d and provides the energy-density deposited by VPs. $PSF_{\text{VP-SE decay}}(r)$ provides the energy deposition caused by SEs that originated from VPs. The $PSF_{\text{VP-SE decay}}(r)$ may not be necessary because we have not defined whether VPs directly expose the resist or whether SEs emitted from VPs expose the resist. Either way, this $PSF_{\text{VP-SE decay}}(r)$ has negligible spatial effect because these SEs have small energies (<50 eV), and therefore have a small maximum range (<1nm). For simplicity, we excluded the $PSF_{\text{VP-SE decay}}(r)$.

We assumed that an energy-loss event from 10 to 50 eV is due to VP excitation, and an energy-loss event from 50 to 1000 eV is due to SE generation. This division is a good approximation due to the relative cross sections of VPs and SEs in these respective energy ranges. We acknowledge that there are cascading possibilities following these primary excitations, such as excited VPs generating SEs. In addition, the excited SEs may generate VPs and other SEs. Therefore, this is a first order approximation of the effect of SEs relative to VPs. Furthermore, we note that this approximation defines an upper limit of energy loss due to SEs and VPs because a small fraction of energy loss events at 200 keV may not directly generate a SE or VP.\(^{(17, 131)}\)

According to the energy division above, the lithographic PSF may be written as:
\[ PSF_{litho}(r) \approx a \times PSF_{direct\text{-}beam \, E>50\, eV}(r) + PSF_{direct\text{-}SE}(r) \]

\[ + b \times PSF_{direct\text{-}beam \, E<50\, eV}(r) \times PSF_{VP}(r) \] \hspace{1cm} (4.15)

According to the nomenclature in Figure 4-20c, we can write formula (4.15) as:

\[ PSF_{litho}(r) \approx total - energy - density(r) \approx a \times energy - density^{SEs}(r) + \]

\[ b \times energy - density^{VPs}(r) \] \hspace{1cm} (4.16)

where \(a=65\%\) and \(b=35\\%\), which are the percentages of measured energy loss for SEs (50<\(E<1000\) eV) and VPs (10<\(E<50\) eV) respectively (see Figure 4-4). Formula (4.16) was normalized by setting the spatial integration of \(PSF_{litho}(r)\) to unity. \(energy - density^{SEs}(r)\) was simulated by the Monte Carlo model described in section 4.3.4 and it was convolved with the instrument spot size. An alternative calculation would be to convolve the direct-beam PSF for energies higher than 50 eV to the SE PSF. We chose not to do this alternative calculation because the direct-beam PSF was not measured up to 1000 eV. \(energy - density^{VPs}(r)\) was calculated by a convolution between the direct-beam PSF for energies smaller than 50 eV and the VP PSF.

Figure 4-20c shows the contribution of SEs and VPs to the lithographic PSF. The total deposited energy density obtained shows a satisfactory agreement with the lithographic PSF. The VPs were more important than SEs for a radius larger than 2 nm, limiting the fabrication of dense structures at the sub-10-nm scale (sub-10-nm pitch). We limit the comparison between the energy density deposited due to VPs and SEs for radii smaller than the decay length of VP, that is, 12 nm. For radial distances larger than 12 nm, the VP PSF will further decrease by VP scattering, and the SE PSF will become the largest PSF component. This argument is consistent with previous comparisons of the lithographic PSF to simulations including SEs.(10, 19, 99)
To evaluate whether SEs originated from direct atomic ionization (valence and core electrons) and not VPs (and not SEs generated from VPs) could be responsible for the lithographic PSF, we compared the lithographic PSF to two different Monte-Carlo simulated PSFs. Here, we included the effect of the instrument spot size. Figure 4-21 shows that the classical and the Moller+Vriens inelastic scattering models did not generate PSFs that match the shape of the lithographic PSF. This result suggests that SEs are not sufficient to simulate the lithographic PSF at the sub-12-nm scale. As previously discussed, the total deposited energy density including SEs and VPs shown in Figure 4-20 better represents the lithographic PSF.

Figure 4-21. Comparison between the lithographic PSF and Monte-Carlo simulated PSFs convolved with the instrument spot size (maximum value of all PSFs was set to unity): (red squares represent dataset 1 and red triangles represent dataset 2) lithographic PSF from dot-exposure method; (dotted line) fitted lithographic PSF (from previous Chapter) which is accurate down to 1 nm radius because this fitted PSF was obtained using 2-nm-wide feature as test structure; (continuum line) Monte-Carlo simulated PSF including SE generation using the classical inelastic cross...
section model; (dashed line) Monte-Carlo simulated PSF including SE generation using the ‘Moller+Vriens’ inelastic cross section model.

4.4. Conclusions

We have shown for the first time the measurement of delocalized energy transfer in EBL exposure at the sub-10-nm scale by using chromatic aberration-corrected EFTEM. The measurements here focused at the EBL PSF at 200 keV and at the sub-10-nm length scale, without considering the effect of backscattered electrons. We have defined the role of spot size, electron scattering, SEs, and VPs in the lithographic PSF by performing electron microscopy and spectroscopy, sub-10-nm EBL, and numerical simulations. We expect that these results will enable novel ways to improve the resolution limit of EBL.

VPs can be excited by electrons and high-energy photons, such as extreme ultra violet (EUV). (69) EUV lithography is of increasing interest because it is considered the next generation lithographic technology for high volume manufacturing of semiconductors. (37, 132) Therefore, we note that the VP and SE PSFs may be important factors in the resolution limit analysis of EUV lithography. Furthermore, the experimental knowledge of the lithographic PSF at the sub-10-nm scale gives a unique way to measure electron-sample interaction volume, which is important to test theoretical models for scanning electron microscopy. (16, 28, 30, 95, 111)
Chapter 5

Controlled Placement of Colloidal Quantum Dots in Sub-15-nm Clusters

Semiconductor colloidal quantum dots (QDs) are important building blocks for nanoscience. One key aspect of this system is the fine synthetic control of its electronic and optical properties. For convenience, many optical and electronic studies use a thin film of QDs deposited by spin casting, dip coating or drop casting. This ensemble configuration is extensively used to investigate the fundamental properties of QDs, such as band-gap engineering, energy transfer, and multi-exciton generation, which are relevant to the future applications of QDs in solar cells and light-emitting diodes. However, properties such as exciton lifetime and photoluminescence intermittency are obscured by ensemble measurements and can be better understood at the single-QD or few-QD-cluster level. Most single-dot and cluster studies are performed on films spun from very dilute solutions, which results in a random distribution of quantum dots on a substrate. Some of these measurements would benefit immensely from accurate position control of sub-10-nm QDs, which has not previously been possible. Single-QD patterning is one of the challenges in designing a system that takes advantage of the single-dot properties of QDs. In addition, systematic investigation of single QDs, dimers (clusters of two QDs), and trimers (clusters of three QDs) is limited by complex, or non-reproducible fabrication processes. Hence, placement of sub-10-nm QDs at desired positions is expected to be a powerful tool to quantitatively investigate this system.
Previous reports have demonstrated template-directed self assembly of colloids at the 100-nm scale.\((48, 139-143)\) In the sub-100-nm scale, there are reports of template-directed placement of sub-20-nm-diameter clusters of gold colloidal QDs,\((43-47)\) and sub-50-nm-diameter clusters of semiconductor colloidal QDs\((48-53)\) using electron-beam lithography, dip-pen lithography, scanning-probe lithography, and block-copolymer self assembly. However, for semiconductor QDs smaller than 10 nm in diameter, sub-20-nm patterning has not previously been possible and is crucial to permit placement of single QDs and small QD clusters.

This thesis presents a simple and effective patterning technique to control the position of individual QDs by using sub-10-nm electron-beam lithography (EBL). We show that the placed QDs are luminescent and present intermittent photoluminescence (PL), known as blinking, which indicates the presence of single QDs.\((133-135)\) Applications that may emerge through the use of this technique are the fabrication of single-photon emitters,\((38, 39)\) excitonic circuits,\((144-146)\) and a large variety of nano-optical devices.\((55, 147)\)

5.2. Methods

Here we describe the experimental methods used in this chapter, consisting of QD synthesis, EBL parameters, electron microscopy, and optical characterization.

5.2.1. Synthesis of CdSe(Zn\textsubscript{x}Cd\textsubscript{1-x}S) core(shell) QDs

CdSe cores were synthesized according to previously reported procedures.\((148, 149)\) Overcoating with an alloyed shell was carried out via modifications to previously reported procedures.\((150)\) Briefly, CdSe cores precipitated from the growth solution by the addition of methanol were re-dispersed in hexane and injected into a degassed solution of 6 g of 99\% trioctylphosphine oxide (TOPO) and 0.4 g \textit{n}-hexylphosphonic acid. After removing the hexane under reduced pressure at
50°C, the flask was back-filled with dry N\(_2\) and the temperature increased to 170°C before adding 0.25 mL of decylamine and stirring for 30 min. Precursor solutions of diethylzinc (ZnEt\(_2\)), dimethylcadmium (CdMe\(_2\)), and hexamethylidisilathiane [(TMS)\(_2\)S] were prepared by dissolving the appropriate amounts of each in 4 mL of TOP and loading them into two separate syringes for metal and sulfur under an inert atmosphere. The molar quantity of ZnEt\(_2\) required to achieve the desired shell thickness (typically 5 monolayers) was calculated according to the methods of Leatherdale.\(^{151}\) For an alloyed shell, an appropriate mole fraction ZnEt\(_2\) was replaced by CdMe\(_2\). A 1.5-fold molar excess of (TMS)\(_2\)S was used. The precursor solutions were injected simultaneously into the 170°C bath at a rate of 4 mL/h. The QDs were stored in the growth solution under ambient conditions and centrifuged once more before use.

5.2.2. Electron-beam Lithography (EBL)

EBL was carried out at an electron energy of 30 keV on a Raith 150 EBL system with a thermal-field-emitter source operating at 1800 K (~ 0.5 eV energy spread), a 20 \(\mu\)m aperture, 50 \(\mu\)m field size, a working distance of 6 mm and a beam current of 150 pA.

5.2.3. Scanning electron microscopy

The colloidal quantum dots were placed on Si and 300-nm-thick SiO\(_2\) on Si substrates (using the described fabrication method), and imaged in a thermal-field-emitter source Zeiss scanning electron microscope (the same used for lithography) at 10 keV, using in-lens secondary-electron detector, with electron-beam current of ~ 250 pA, and 6 mm working distance. No contrast enhancement techniques (such as metal deposition) were used.
5.2.4. Transmission electron microscopy

The TEM sample was prepared by dropping a dilute hexane solution of QDs onto a TEM grid (Ted Pella, Ultrathin Carbon Type-A, 400 mesh, Copper) resting on filter paper. TEM imaging was performed on a JEOL 200CX in bright field mode, with an accelerating voltage of 120 kV onto a 1.3Mpix AMT digital camera. Only standard condenser and objective apertures were used.

5.2.5. Optical characterization

The samples were observed with wide-field and confocal scanning microscopy using an air microscope objective (100×, 0.7 NA) and a 514-nm CW argon ion laser for excitation. The collected emission was detected by an avalanche-photodiode-based single-photon detector. The background from the laser was removed using a 514-nm filter.

5.3. Fabrication Process and Discussions

The fabrication process for QD placement is illustrated in Figure 5-1. A poly(methylmethacrylate) (PMMA) resist was spin coated on a silicon substrate to a thickness of 40 nm, and baked at 200°C for 2 minutes on a hotplate. Then, a design with single-pixel exposures (doses from 10 to 200 fC/dot) and 10- to 20-nm-diameter areal exposures (doses from 400 to 4,000 µC/cm²) were exposed on PMMA by EBL. This exposure was used to obtain an array of templates, PMMA holes, with varying diameters. EBL was carried out at an electron energy of 30 keV on a Raith 150 EBL system (see details in Methods). The QD deposition was carried out at a relative humidity lower than 38%. In particular, working in a nitrogen glove box improved QD assembly uniformity(52). The QD solution (6-nm-diameter CdSe or 5-nm-diameter CdSe/CdZnS) was spin cast or drop cast on top of the PMMA templates, and the remaining resist was removed by dissolution in acetone for 3 min. This process resulted in QD clusters attached to the substrate. Figure 5-1b shows the
patterned PMMA with templates from 8 to 21 nm in diameter. The placed QDs were analyzed in a Zeiss scanning electron microscope (SEM), as shown in Figure 5-1c (see metrology details in Methods).

Figure 5-1. Overview of the fabrication process for placing QDs. (a) Schematics of the fabrication process: PMMA was spin-coated to a thickness of 40 nm on Si, followed by EBL; Then, 6-nm-diameter CdSe QDs were spin-coated or drop cast; Finally the PMMA lift off was done with acetone, leaving clusters of CdSe QDs. (b) Top: scanning-electron micrographs of PMMA templates with 8 nm (minimum feature size used) and 21 nm diameters. Bottom: SEM image cross-section across the PMMA templates. (c) Left: SEM of a patterned CdSe QD cluster (dimer). Right: SEM cross-section over one CdSe QD, with full-width at half maximum of 6 nm.

In order to minimize the number of QDs in each cluster and increase the patterning yield, defined here as the percentage of the templated sites that were occupied by at least one QD, the QD solution concentration, the QD solution purification(42), the resist thickness, the feature size, and the lift off process were systematically optimized.

The concentration of ligands on the CdSe and CdSe/CdSnS surfaces and in solution was varied to investigate their effects on the placement process. As synthesized, the majority of the ligands
on the QD surface are phosphonic acids(152). Quantifying the exact composition of ligands on a QD surface is still a challenge in the field, so its concentration is a qualitative rather than a quantitative measure. Nevertheless, the ligand concentration was decreased by performing multiple purification processes on the QD solution, thereby decreasing the phosphonic acid concentration. The purification process was done by adding 750 µL of 4:1:8 hexane:butanol:methanol to a 100 µL aliquot of QD solution (stored in the growth solution). The resulting solution was centrifuged at 4,000 rpm for 3 min. The QDs then precipitated in the vial, allowing us to remove the solvent and to re-dilute the precipitated QDs in 100 µL of hexane. This process corresponded to one purification process. Figure 5-2 shows an experiment to verify the CdSe/CdZnS attachment on the 300 nm SiO₂ on top of Si. Figure 5-2a and 5-2b show a sample with QDs that received one purification(149). Figure 5-2c and 5-2d present a sample with QDs that received three purification steps and therefore had a lower concentration of the phosphonic acid ligand. The sample that received three purifications had no QD attachment problem after the acetone lift-off process, as shown in Figure 5-2d. Presumably, the reduced concentration of ligands promoted QD adhesion, which enables high pattern uniformity for placing CdSe/CdZnS QDs. In addition, working in an environment with a relative humidity lower than 38% or in a glove box improved the uniformity of QDs assembly(52).
Figure 5-2. Scanning electron micrographs of 5-nm-diameter CdSe/CdZnS spun on SiO$_2$ substrates. (a) shows QDs purified one time without further processing. (b) shows QDs as prepared in (a) followed by acetone dipping for 3 min to reproduce the lift-off conditions of the QD-patterning process. The large majority of the QDs were washed away. The inset of (b) is a higher magnification image of a small-area agglomeration of QDs. (c) consists of QDs purified three times without further processing. (d) consists of QDs as prepared in (c) followed by acetone dipping for 3 min. The large majority of the QDs remain attached on the substrate. The insets of all figures show higher magnification of the darker areas, which are QD agglomerations. The QD attachment after acetone processing is clearly improved with three purification steps, which indicate the smaller concentration of ligands on QD surface and in solution favors its adhesion on the substrate.

To achieve the smallest QD clusters, the EBL development process was optimized to decrease the size of the templates. One technique to improve the resist contrast and decrease the minimum feature size for PMMA is by carrying out the development at low temperature.(43, 153) The
samples were developed in IPA:MIBK (3:1) for 30 s and blown dry with nitrogen. The development temperature was varied from 0°C to 15°C, as shown in Figure 5-3a-c. The minimum feature size achieved at 0 and 7°C was 8 nm and at 15°C was 10 nm. Therefore, the temperature of 7°C was chosen to provide minimum template size for the QD placement process.

![Image](https://via.placeholder.com/150)

**Figure 5-3.** Optimization of the template size, QD solution concentration, and resist thickness for the QD-placement process. All scanning-electron micrographs show templated 6-nm-diameter CdSe QDs. The PMMA mask used was 40 nm thick for (a) through (e) and 12 nm for (f). (a)-(c) show micrographs of sub-12-nm holes in PMMA exposed by
EBL, and developed for 30 s in 3:1 IPA:MIBK from 0°C to 15°C. (a) was developed at 0°C and shows 8-9 nm holes. (b) was developed at 7°C and has the same minimum resolution as (a), and (c) was developed at 15°C and shows larger features, i.e., 10-12 nm holes. (d) shows QD patterns generated by a solution with a low (0.5 µM) concentration of QDs, and (e) with high (2 µM) concentration of QDs. The sample depicted in (d) had 75% of patterned sites without QD clusters, while in (e) only 20% of the sites had no QDs. It should be noted that the high concentration solution (e) led to larger QD clusters. (f) consists of a patterning with templates developed at 7°C, a 2-µM solution of QDs, and a 12-nm thick resist instead of 40 nm, in order to reduce clustering of QDs in each site. The sample had only 20% of sites with missing QDs and with significantly smaller QD clusters than (e).

The concentration of colloidal QDs in solution was varied to investigate its effect on the patterning resolution and pattern yield. Figure 5-3d-e shows QD patterning using 0.5- and 2-µM QD solutions. The solution with the lower concentration produced smaller clusters (less than 10 QDs), but the pattern yield was only 25%. The solution with the higher concentration provided an 80% pattern yield, but with larger QD clusters than the ones obtained with the diluted solution. Therefore, the 2-µM solution was chosen for the best yield performance and other parameters were optimized to decrease the number of QDs in each cluster.

After the optimization of the solution purification, solution concentration, and resist development, the resist thickness was varied to obtain the smallest QD clusters. Figure 5-3e shows patterning using 40-nm-thick PMMA as a mask. The relatively thick resist creates a template with a higher volume that accommodates and attracts more QDs per template. In order to reduce the number of QDs in each cluster, a 12-nm-thick PMMA was used instead. Figure 5-3f shows the results of the optimized process, using 12-nm-thick PMMA as the mask, a development temperature of 7°C, and a 2-µM QD solution. The QD clusters were successfully patterned at the desired position. The leftmost columns of QDs in Figure 5-3f show the smallest QD clusters, where single QD, dimers and trimers were placed.
Finally, we tested the effect of resist thickness on the quality of the QD lift off described in Figure 5-1. A poly(methylmethacrylate) (PMMA) resist was spin cast on two silicon substrates to a thickness of 14 and 49 nm, and baked at 200 °C for 2 minutes on a hotplate. The QD deposition was carried out at a relative humidity lower than 38%. The 2-µM QD solution (5-nm-diameter CdSe/CdZnS) was dip coated on top of the PMMA resist, forming 1-2 layers of QDs. Then, the sample (QD/PMMA/Si) was immersed in acetone for 3 min. The result is show in Figure 5-4. The sample with 49-nm-thick PMMA had no apparent QDs re-deposited during lift off, however the 14-nm-thick PMMA sample had a few QDs distributed over the sample, as indicated by the bright spots. The dark regions on both samples, corresponding to low secondary yield compared to SiO2, are presumably PMMA residues from the lift off process. From this we conclude that thicker PMMA films were more effective in lifting off the QDs from the sample. However, thin PMMA (sub-20 nm) decreased the number of QDs in each cluster, so a compromise between resist thickness and QD concentration has to be chosen depending on the application.
Figure 5-4. Scanning electron micrographs of two samples submitted to a lift-off test with different resist thicknesses. The top sample had a QD thin film on top of 49-nm-thick PMMA. The bottom sample had QD thin film on top of 14-nm-thick PMMA. After immersion of both samples in acetone for 3 minutes, the top sample was free of QDs but the bottom sample had some re-deposited QDs.

Figure 5-5 shows the results of the optimized process, achieved by using 12-nm-thick PMMA as the mask, a development temperature of 7°C, and a 2-µM QD concentration. We achieved placement of a few QDs in each cluster for the smallest templates, as shown in Figure 5-5b. We also observed a few QDs present outside the patterned area; we suspect that these QDs were re-deposited during the lift-off process.
The fabrication was optimized to minimize the number of QDs in each cluster. (a) QD clusters were fabricated using templates with 15-20 nm diameter. (b) QD clusters were fabricated using templates with 8-15 nm diameter; these were the smallest clusters fabricated. (c) Histogram of the number of QDs in each cluster versus the number of clusters, using the smallest fabricated templates. We analyzed 54 sites designed for QD clusters. The QDs were counted from...
the SEM micrographs. Representative SEM images were added to the histogram. The top of (d) and (e) shows the designed templates with ~12 nm diameters for placing QDs in close proximity to one another, with gaps of ~36 nm in (d) and ~12 nm in (e). The bottom of (d) and (e) shows SEM micrograph of clusters of QDs composed of 5-nm-diameter CdSe/CdZnS (core/shell).

In order to quantify the statistical distribution of this process, a histogram of the fabricated structures in Figure 5-5b is shown in Figure 5-5c. The QDs in each cluster were counted from SEM micrographs. The pattern yield (percentage of the templated sites occupied by at least one QD) was 87%. An average of three QDs in each site was observed. For this average value, only clusters with an identifiable number of QDs (64% of total) were considered. QD clusters with undetermined number of QDs were 36%. From these undetermined clusters, 24% (8% of total) had area smaller than 12×12 nm (2×2 dots), so they were expected to have less than 5 QDs in each cluster. 76% of the undetermined clusters (27% of total) had area larger than 12×12 nm, so they were expected to have more than 5 QDs in each cluster. The difficulty in counting QDs is due to the SEM resolution limits, residues of PMMA and solvents (i.e., acetone, hexane) from the fabrication process, and possible QD vertical stacking.

This technique allows QDs to be placed with the accuracy and resolution of EBL. Figure 5-5d shows placement of pairs of QD clusters with ~36 nm separation. We also defined the dimer placement yield, which is the percentage of two adjacent templated sites occupied by at least one QD in each site. The dimer placement had 55% yield (the placement yield of each QD cluster was 78%). Figure 5-5e shows placement of pairs of QD clusters with ~12 nm separation. The dimer placement here had a 36% yield (the placement yield of each QD cluster was 66%). We hypothesize that the placement yield was significantly smaller for 12-nm gaps due to two factors: (1) reduced template uniformity; and (2) the template size was close to the hydrodynamic radius of the QDs (~10 nm).
We hypothesize that the variation in the number of QDs placed in each site came in part by a non-chemical-equilibrium deposition of the hydrophobic QDs on the hydrophilic SiO$_2$ substrate. Because of this non-equilibrium, during solvent drying the QDs were forced to being deposited on the SiO$_2$ surface. Nevertheless, this process presented high resolution and simplicity, not requiring a pre-treatment of the substrate.

5.4. Optical Characterization

For the application of patterned QDs in excitonic or nano-optical devices, optical characterization is required. We investigated the resilience of the photoluminescence (PL) following the patterning process. By generating small QD clusters, we expected to be able to observe intermittent PL, i.e., “blinking”.(154)

The CdSe QDs (or core QDs) are not ideal for spectroscopic techniques that require high quantum yield because numerous non-radiative pathways are available in these QDs. For this reason, we used core/shell dots (CdSe/CdZnS) to maximize the PL signal. We generated samples using CdSe/CdZnS core/shell (5-nm diameter) QDs deposited on 300-nm-thick SiO$_2$ on a silicon substrate. The sample fabrication follows the same procedure previously described. We stored the samples in a nitrogen glove box before the PL measurements to prevent any QD oxidation.

The samples were observed with wide-field and confocal scanning microscopy, as shown in Figure 5-6. Figure 5-6a shows a TEM micrograph of the 5-nm CdSe/CdZnS QDs used for optical characterization. In Figure 5-6b, the QD clusters were placed in a rectangular grid with 2 μm × 5 μm spacing to easily resolve their position in the PL microscope. We obtained significant PL signal of the QD patterns, with ~10 to 200-nm dimensions. We also observed a few QDs present outside the patterned area. These QDs may have moved and re-deposited during the lift-off process. The top row in Figure 5-6b had 200-nm-QD clusters with constant PL. The PL signal was also constant.
for micrometer size clusters. The two lower rows of QDs in Figure 5-6b are made of QD clusters from ~10 to 20 nm. We chose one QD cluster at the bottom row (~15 nm diameter) and measured the PL time trace for 160 s, as shown in Figure 5-6d1. We notice significant PL intermittency. This behavior was also observed for sub-40-nm QD clusters. Figure 5-6d2 is the histogram of the PL counts. This PL intermittency shows that we generated small enough QD clusters so that we can resolve PL fluctuation caused by QD blinking; thus, the placed QD clusters may be used for further experiments and applications.

**Figure 5-6.** (a) Transmission electron micrograph of CdSe/CdZnS core/shell QDs randomly deposited on a carbon membrane, with average diameter of 5 nm used for optical characterization. (b) Wide-field photoluminescence image of CdSe/CdZnS QD clusters placed in a rectangular array of 2 µm x 5 µm. The peak of emission wavelength was 576 nm.
nm. (c) SEM of QD clusters that are ~10 nm to 42 nm in diameter (the top bright clusters in (b) are 200-nm markers of QDs). (d1) Photoluminescence time trace of one QD cluster. The time trace shows intermittent luminescence (blinking). (d2) PL intensity versus frequency. The PL intensity presented a bi modal distribution, indicating blinking.

5.5. Conclusions

In summary, we demonstrated a technique to control the placement of few-QD clusters through EBL. This QD placement allows QD clusters of one to five QDs to be fabricated. The process was developed by optimizing QD solution, resist thickness, and template size. One figure of merit in this process is the pattern yield, defined here as the percentage of templated sites occupied by at least one QD. A pattern yield of 87% was achieved with an average of three QDs in each cluster. We performed PL of the fabricated QD clusters, showing that the QDs are optically active after the fabrication process, presenting blinking in the photoluminescence. This optimized top-down lithographic process is a step towards the integration of individual QDs in optoelectronic systems.
Chapter 6

Lithographic engineering of surface and volume plasmons

Plasmonic resonances in nanostructures have promising applications in nano-optics, photovoltaics, sensing, and targeted drug delivery. For example, surface plasmon (SP) resonances can be applied to increase photon absorption while reducing the thickness of the absorbing layer for photovoltaic devices. Investigation of the effect of nanostructure size on SPs is critical for engineering plasmonic resonances for applications in sensing and nano-optics.

Volume plasmons (VPs) are the bulk analogues of surface plasmons and may be defined as collective longitudinal charge-density waves in the bulk of a material. VP resonances lie in the 3-30 eV energy range and have not yet – to our knowledge – been precisely controlled. VPs interact weakly with classical light but may be excited by vacuum ultra violet (VUV) light in thin films and by x-rays and electrons, including photoelectrons generated by VUV radiation. Therefore, the engineering of VPs may permit the control of the optical properties of materials in the 3-30 eV range, enabling new nano-optical devices in the VUV.

Previously, Scholl et al. have reported the diameter-dependent scaling of the SP resonance energy for Ag nanoparticles grown by self-assembly. Ag nanoparticles exhibit SP resonances in the UV-visible region of the spectrum at 3-4 eV. Scholl et al. observed the SP of Ag to shift from 3.2 eV to 3.8 eV as the nanoparticle diameter was reduced from 20 nm to 2 nm. Previous efforts were also successful in controlling the SP energy by lithographic methods. However, these methods usually considered features larger than 20 nm, limiting the
maximum achieved energy of SPs. The minimum SP energy and the spectral control (that is, the range from the minimum to the maximum SP energy as a function of feature size) will also depend on the chosen material and the dielectric environment. Aluminum is a material of interest due to its greater relative abundance and lower cost compared to gold and silver, as well as its wide spectral control of SP energy.\footnote{62} Recently, Bisio \textit{et al.}\footnote{160} have measured a broad, high-energy SP resonance from 6-9 eV in Al nanostructures prepared by molecular-beam epitaxy (MBE) on patterned LiF substrates. The structures prepared by Bisio \textit{et al.} consisted of particles with sub-10-nm dimensions formed by self-assembly. However, the particles had a large distribution of diameters and may interact strongly with one another due to the sub-nanometer gaps between the particles. Therefore, there is a need for nanofabrication at the sub-20 nm length scale for improving the control of the SP energy.

The engineering of VPs is a significant challenge because VPs typically decay on the sub-femtosecond time scale and on the sub-20-nm length scale. Previous results show that control of VP energy is limited to small (<1 eV) VP energy shifts in chemically synthesized nanostructures, such as colloidal particles\footnote{63, 64, 70-72}, nanowires,\footnote{65, 66} and thin films.\footnote{68} Therefore, there is a need to develop a systematic top-down process to fabricate nanostructures that could control VP resonances and take advantage of this newly developed control.

We fabricated sub-100 nm plasmonic nanostructures by high-resolution electron-beam lithography (EBL), which exhibit plasmonic resonances in the UV (3 - 14 eV) and VUV (6.2-124 eV) regions of the electromagnetic spectrum. We investigated the SP and VP modes in Al nanodisks with diameters in the sub-10 nm regime by high spatial- and energy-resolution electron energy loss spectroscopy (EELS). A full investigation of SP and VP modes in sub-10 nm Al nanostructures is key to the future implementation of nano-optical devices in the VUV and the
production of low-cost plasmonic devices fabricated in Al.

6.2. Methods

Here we present the fabrication methods, EELS experimental conditions, and EELS post processing to analyze SPs and VPs in nanodisks and nanoprisms.

6.2.1. Fabrication

Figure 6-1 illustrates the overall fabrication process. Many trial samples were used to optimize the electron-beam dose and lift off parameters. The experimental results presented in this Chapter came from two distinct samples (TE42 and TE60).

The samples were prepared by spin-coating PMMA (poly(methyl methacrylate)) on 5- or 10-nm-thick SiNₓ membranes (TEMwindows.com) at a spin-speed of 5 krpm. We baked the TEM grid (PMMA on top of SiNₓ membrane on a silicon frame) directly on a hot plate at 180°C for 2 min. The resulting PMMA film thickness was 50 nm. This resist thickness was estimated by a previous calibration, which consists of spinning PMMA on a Si substrate, baking PMMA at 180°C for 2 min on a hot plate, and measuring the resist thickness by ellipsometry.

After preparing the sample consisting of PMMA-coated SiNₓ, EBL was performed using 125 keV electrons in an Elionix F-125 system with a 100 pA beam current. We exposed circular holes in the PMMA with varying diameter for the fabrication of nanodisks and triangular windows in the PMMA for the fabrication of nanoprisms. The PMMA holes were exposed as single pixels for holes with diameters smaller than 20 nm, and we designed areal exposures for holes with diameter larger than 20 nm (with 0.1 nm step size). Areal exposures were also used for the nanoprism fabrication. The diameter of holes smaller than 20 nm was controlled by the delivered
dose density, which was varied from 0.2 to 50 fC/dot. The diameter for holes larger than 20 nm was controlled by the designed diameter and dose density delivered, which was varied from 13 to 32000 mC/cm². We note that single-pixel and areal exposures may overlap in final deposited dose and final feature size.

Figure 6-1. Schematics of the fabrication process and the final sample. (a) Steps of the fabrication process: (1) Electron-beam lithography on a sample consisting of PMMA on top of a SiNₓ membrane, followed by PMMA development. (2) Electron-beam evaporation of Al to a thickness of 15-20 nm. (3) PMMA lift-off in NMP. We also fabricated nanoprisms in this sample, with the process described above. (b) Schematics of the Al nanodisks fabricated to investigate SPs and VPs in nanostructures (for simplicity, we did not show the top surface of Al oxide in the nanodisk). The Al nanodisks had diameters varying from 6 to 120 nm. The Al had a native oxide layer of 2.6 nm on average. The Al oxide varied from 2 to 4 nm in thickness.

For resist development, samples were immersed in 3:1 IPA:MIBK (3:1 isopropyl alcohol:methyl isobutyl ketone) for 30s at 0°C and gently blown dry with nitrogen gas for 1 minute.
The 0°C temperature was achieved and maintained using a chiller, which uses a thermometer connected to the chiller control unit.

We then deposited Al to a thickness of 15-20 nm on the patterned sample using an electron-beam evaporator system. We chose an electron-beam evaporator because it presents a smaller effective source size of Al than a thermal evaporator system. A small source size at the Al target yields directional Al deposition. Directional Al deposition translates to reduced deposition on the sidewall of the resist, which facilitates the lift-off process.

Finally, the PMMA lift-off was done in NMP (N-Methyl-2-pyrrolidone) at 55°C for 90 minutes. To achieve a precise temperature control of the NMP solvent (which is flammable with a flash point of 92°C), we suggest placing the beaker with NMP into a secondary water bath. The water bath should then be heated by a hot plate. This water bath control is appropriate to control the temperature and to avoid having NMP reach its flash point, but care should still be taken.

6.2.2. EELS acquisition

Electron energy loss spectroscopy (EELS) was performed using a Hitachi 2700C aberration-corrected STEM with a cold-field-emitter source (~0.4 eV energy spread) at 200 keV at Brookhaven National Laboratory. The beam current was ≈20 pA, with a dispersion of 0.05 eV/channel. The electron-beam convergence semi-angle was 28 mrad, and the collection semi-angle was 14.5 mrad (2 mm collection aperture). We performed spectral imaging as implemented in the Digital Micrograph software (Gatan, Inc.). Spectral imaging consisted of point by point EELS acquisition, with a predetermined step size of 0.5-10 nm, along a selected array of points, for a given acquisition time for each spectrum. We also performed a summation of 10 to 30 spectra at each point to improve the signal to noise ratio while avoiding detector saturation. To
evaluate whether we lost spectral resolution after performing the summation of multiple spectra, we compared the full width at half maximum (FWHM) of the zero loss peak for one spectrum and for multiple spectra. We did not observe a significant increase in the FWHM for multiple spectra acquisition, which was 0.4-0.5 eV. For the EELS measurements of peak energy, full width at half maximum (FWHM), and electron counts (intensity) in this Chapter we used one EELS spectrum at each spatial pixel. Averaging of multiple spectra between different pixels was not performed.

Finally, the measurements shown here were obtained from two samples, TE42 and TE60, over three EELS sessions (each session was in a different date). Sample TE42 provided most of the SP data from one EELS session. Sample TE60 provided all VP data, which was acquired in two different EELS sessions using the same sample and same acquisition parameters described above.

6.2.3. EELS post-processing

Post-processing of EELS data was carried out in the Digital Micrograph (DM) software (Gatan, Inc.). The first step for post-processing is to align the zero loss peak (quasi-elastic peak) of all spectra at each position. DM has a specific routine to implement this function. After this step, the zero loss peak in each pixel is aligned with an accuracy of about 1 pixel or 1 channel (0.05 eV).

To obtain an energy measurement from the EELS spectrum with accuracy better than 0.05 eV, we fitted the peak of interest with a Gaussian fitting function. The precision of this procedure depends on the nature of the peak that is being fitted, the signal-to-noise ratio of the spectrum, and the numerical method. Nevertheless, fitting an EELS peak may enable sub-pixel accuracy, and usually an accuracy of 0.02-0.05 eV for our system.

In order to obtain the peak-energy, FWHM, and intensity of the VP peak, we performed a background subtraction. First, we selected the signal of interest in the EELS spectrum, which was
13-17 eV in our experiment (the VP peak is at 15 eV). Then, we selected two regions in the spectrum that would be fitted to generate a fitting function for background subtraction. The areas defined as background were in the energy window from 10 to 13 eV and from 17 to 20 eV. These two windows contain mostly the low-energy part of the VP signal from the SiN₅ (22 eV) and Al₂O₃ (21 eV). After obtaining the background function, we subtracted the background from the signal of interest, resulting in the VP signal of pure Al. This procedure is repeated for each pixel of the spectral image. The fitting function was a second order polynomial. We evaluated that this fitting function was sufficient to fit the spectrum at the energy of interest by analyzing the fitting residuals of areas of only SiN₅ and areas of SiN₅ and Al₂O₃. After a successful background subtraction, we measured the VP peak energy, FWHM, and intensity by Gaussian fitting in DM and in Matlab (to obtain the uncertainty), as shown in Figure 6-2c. The final VP peak energy and VP FWHM accuracy was 0.1 eV.

![Figure 6-2](image.png)

**Figure 6-2.** Post processing of EEL spectra. (a) STEM-EELS image. An EELS spectrum was acquired at each 1 nm².
pixel in the image of the Al nanodisk shown. (b) An example of a raw EELS spectrum acquired from an Al nanodisk in this work. The ZLP (zero loss peak), SP peak of Al, and VP peak of Al are visible here. (c) Method of isolating the VP peak in the EELS spectrum. In the raw spectrum, the intervals 10-13 eV and 17-20 eV were fit to a second order polynomial. This function was subtracted from the raw spectrum to isolate the VP peak in the interval 10-13 eV, which was then fit to a Gaussian. (d) Method of isolating an SP peak in the EELS spectrum. The ZLP was fit to a log function over the interval 0.9-2.45 eV, and this function was subtracted from the raw spectrum. The isolated SP peak was fit to a Gaussian. The three spectra are offset for clarity.

The SP energies were acquired and processed as described in Figure 6-2d. We performed the zero loss peak modeling by fitting a log function in the positive tail of the zero loss peak. Then, we removed the fitting function from the raw data. Finally, we did a Gaussian fitting of the SP peak of interest in a specific energy range of the spectra. Due to the lower intensity of the SP peaks compared to VP and zero loss peaks, the SP energy accuracy was equal or smaller than 0.6 eV.

6.3. Results and Discussions

Here we present the physical characterization of SP and VP resonances in Al nanostructures by using EELS. We show the control of SP resonances (multiple modes) over a wide spectral range (3 to 8 eV) in Al nanostructures and we show the control of VP resonances at sub-20 nm Al nanodisks. Furthermore, we discuss the connection between SPs and VPs, and potential applications.

6.3.1. Surface Plasmons

In order to investigate and control the behavior of SPs at the smallest length scales, we fabricated Al nanodisks from 6 to 120 nm diameter.

In Figure 6-3a we show a high angle annular dark field (HAADF) STEM image of a typical
nanodisk used in our experiments. Figure 6-3b shows the HAADF signal acquired during EELS, which corresponds to a cross section of the STEM image in Figure 6-3a. In figure 6-3c we show a typical EELS spectrum at the Al-Al₂O₃ interface. We observed four distinct SP modes in this spectrum, but five distinct modes over all the sample. We used the measured SP energies for larger diameters (110 and 120nm) as a reference to name the modes from SP1 to SP5. Then, we follow the evolution of these peaks for decreasing diameter. Figure 6-3d shows the SP modes as a function of the core Al diameter of the disks. We did not observe all SP modes in all Al nanodisks due to low signal-to-noise ratio of the SP peaks and due to limited resolution of the EELS system. The behavior of SP1 matched with literature measurements obtained by optical scattering measurements.(61, 62, 160) However, we have fabricated significantly smaller structures than those previously reported for Al,(60-62, 159, 161) and we measured the SPs from 1 to 8 eV by using EELS. Therefore, we demonstrated wider spectral control of the SPs in Al nanodisks than previously reported.
Figure 6-3. (a) Scanning transmission electron micrograph of an array of Al nanodisks, 20-nm-thick, on top of 10-nm-thick SiNx. We performed EELS along the yellow line. (b) HAADF signal collected during EELS acquisition along the yellow line in (a). The red arrow indicates the EELS spectrum shown in (c) at the Al-Al2O3 interface (determined by analyzing the VP peaks of Al at 15 eV and Al2O3 at 21 eV). (c) EELS spectrum indicated in (b) showing the energy spread of the electron gun below 2eV and four SP peaks at 2.8 (SP1), 3.7 (SP2), 4.8 (SP3), and 7.3 eV (SP5). (d) SP1-SP5 energies as a function of the disk core diameter (excluding the native Al oxide). The experimental error for measuring the SP energies was equal or smaller than 0.6 eV (as discussed in Methods section).
We observed an increase in SP energy for decreasing diameter for SP1, SP2, and SP3. SP5 energy decreased for decreasing diameter. We also observed smaller number of SP modes for smaller disks.

The lowest energy SP mode in Figure 6-3d, SP1, has been investigated in the literature and is a localized SP mode of dipole character.\(^{(61, 62)}\) The SP2, SP3, SP4, and SP5 modes should be higher order modes. However, further simulation of the EELS spectrum and surface charge distribution in the nanodisk should be performed to correctly assign these SP modes.\(^{(162)}\)

We decided to investigate SP modes in a nanostructure with different geometry than the nanodisk, which may present different SP modes. For this purpose, we designed an Al nanoprisn shown in Figure 6-4a1 (same fabrication process as before - sample TE42 - , using triangular areal EBL exposures instead of circular areal exposures – see Methods section). Figure 6-4a2 shows the HAADF signal acquired during EELS. We acquired one EELS spectrum at each pixel in Figure 6-4a2 (pixel area of 10×10 nm\(^2\)). Figure 6-4b1 and 6-4b2 show the EELS spectra acquired in the marked pixels (1-5) in Figure 6-4a2. Figure 6-4b1 clearly shows the position dependent excitation of SP modes due to geometric constraint from the nanoprisn. We observed excited SP modes from 1 to 5 eV. Figure 6-4b2 shows the VP at 15 eV in 1 (center of the nanoprisn) and attenuated VPs in 2 and 3 (at the edges). In the next section we will discuss the position dependent excitation of VPs, known as the boundary effect\(^{(31)}\) (begrenzung effect).
6.3.2. Volume Plasmons

Previous reports that investigated VP energy as a function of feature size show modification of VP energy for features smaller than 20 nm. We fabricated Al nanodisks from 6 to 18 nm in diameter and investigated the VP energy, FWHM, and intensity as a function of diameter.
In Figure 6-5a1 we show a typical nanodisk used in our experiments. Figure 6-5a2 shows the HAADF signal acquired during EELS. We acquired one EELS spectrum at each pixel (1×1 nm²) position in Figure 6-5a2. Figure 6-5a3 shows the integrated VP signal from Al between 13 and 17 eV (with background subtracted) obtained by EELS post-processing (see methods). This result allow us to measure the Al core diameters. Figure 6-5b shows a small increase of VP energy by decreasing the nanodisk diameter. In contrast, Figure 6-5c shows a significant decrease of VP intensity by decreasing the nanodisk diameter. By fitting this data with a linear function, we extrapolated that the VP intensity should be zero for 1 nm diameter nanodisk. In addition, Figure 6-5d shows a significant increase of VP FWHM by decreasing the nanodisk diameter. We modeled the variation of the VP FWHM as a function of diameter using the formula in the inset of Figure 6-5d, which uses an effective mean free path relationship to the nanodisk geometry.(163) This formula originated from a proposed dielectric constant for sub-10 nm structures that has been verified for plasmonic metallic clusters.(63, 164) This model agrees reasonably well with the data.
Figure 6-5. Volume plasmons. We measured the dependence of VP peak energy, intensity, FWHM, and relaxation time on nanodisk diameter. (a1) Scanning transmission electron micrograph of an Al nanodisk, 15-nm-thick, on top of 5-nm-thick SiN. (a2) High angle annular dark field signal collected during EELS acquisition across the entire nanodisk in (a1). Each pixel in (a2) contains one EELS spectrum. (a3) Shows the integrated EELS signal from 13 to 17 eV after EELS post processing described in the methods section. The gray scale level in (a3) is proportional to the integral of the VP of pure Al. Dark pixel means there is no VP integrated signal from Al. White pixel indicates a large VP integrated signal from Al. For (b)-(e) we analyzed the EELS spectrum at the central region of each nanodisk that contained the highest VP intensity, which is approximately equal the geometrical center of each nanodisk. (b) VP
peak energy at the center of the nanodisks as a function of the core diameter of the nanodisks. The core diameter is the diameter of pure Al, not including the native AlO$_x$. We observed a small increase in the VP energy for smaller nanodisks (modeling and discussions are toward the end of this section) (e) Ratio of the VP intensity (electron counts from 13 to 17 eV, with background subtracted) and the total intensity (-3 to 50 eV) at the center of the nanodisks as a function of core diameter. The fitting curve of experimental data suggests that the VP intensity tends to zero for ~1 nm diameter nanodisks. (d) VP full width at half maximum (FWHM) as a function of the core diameter of the nanodisks. We observed a significant increase in the VP FWHM for smaller nanodisks. The dashed line represents a model of VP FWHM as a function of diameter considering the effective mean free path of electrons in a nanodisk. The model agrees with experiments. (e) Calculated VP dephasing time (time for the VP amplitude to decay of $1/e$) as a function of core diameter of the nanodisks. The calculation was performed using the formula in the inset, which used the FWHM data from (d). We performed a linear fitting of the VP dephasing time. The slope of the fitting was 19.4 as/nm, which indicates control of VPs in the attosecond time scale using high-resolution EBL.

Figure 6-5e shows the calculated VP dephasing time as a function of VP FWHM. The relationship used in this calculation is in the inset. This relationship between the dephasing time and the VP FWHM is based on the Heisenberg’s uncertainty principle. We note that the slope of the linear fitting to the data was only 19.4 as/nm. Assuming that the calculated dephasing time is valid and considering the 2 nm feature size accuracy achieved in this study, we are able to control the VP dephasing time with 39 as accuracy. Therefore, VPs in nanostructures may be an interesting system for attosecond nanoscience. Nevertheless, direct experimental evidence of our 39 attosecond accuracy is still to be determined.

There are many physical phenomena that may influence the VP energy, FWHM, and intensity as a function of size. Previous studies have considered the following phenomena: VP dispersion,(63, 65, 66, 70-72) quantum confinement of VPs,(65-67, 70, 71) quantum confinement of the band gap and interband transitions,(67, 71, 72) the boundary effect,(67) and strain.(65, 67)

Figure 6-6 describes the measured boundary effect (begrenzung effect). Considering a
nanostructure and a normal electron-beam excitation, the probability of energy loss by VP excitation is maximal at the center of the nanostructure, and decreases when the electron beam approaches an edge. This decreasing probability of VP excitation at the edge translates to an equal increase in the probability of SP excitation at the same edge. This is the boundary effect. However, we observed that it was not only the VP signal intensity that decreases towards the edge. The VP energy and FWHM were also modified near an edge, similar to a previously reported result. Consider the nanodisk shown in Figure 6-6a and the marked trajectory. Figure 6-6d shows that at (or close to) the nanodisk edge the VP intensity is zero and the SP intensity is maximum. The VP intensity is maximum at the center of the nanodisk. Figure 6-6e and 6-6f show that at the nanodisk edge the VP energy is slightly higher than at the center. Figure 6-6f shows that at the nanodisk edge the VP FWHM is significantly higher than at the center. The boundary effect shown in Figure 6-6e and 6-6f is similar to the measurements shown in Figure 6-5. Therefore, we believe that the increased VP energy and VP FWHM for decreasing diameter is partially due to increased proximity of the bulk to the surface or increased surface-to-volume ratio. An increased surface-to-volume ratio would increase VP damping at the surface of the nanodisk, as indicated by the increased VP FWHM.
Figure 6-6. The boundary-effect. (a) HAADF scanning transmission electron micrograph of a 12 nm diameter Al nanodisk. The blue dashed line represents the electron beam path in (d) and (e). The scale bar applies to each of the images (a-c). (b) EEL map acquired at the VP energy (13-17 eV) after background subtraction. The gray-scale level is proportional to the integral of the area under the VP peak of Al. (c) EEL map acquired at the SP1 energy (2.85-5.3 eV) for the same nanodisk. The gray-scale level is proportional to the integral of the area under the SP peak of Al. (d) Normalized SP1 and VP intensities plotted as a function of the position of the electron-beam on a 12 nm diameter nanodisk. The VP intensity decays exponentially near the Al-AlO$_3$ boundary. The VP intensity is nominally constant at the center of nanodisks greater than 20 nm in diameter. The exponential decay of the VP intensity begins at a threshold distance from the boundary, described classically in terms of Bohr’s delocalization distance $b_{\text{max}} = v/\omega_p$, where $v$ is the velocity of the incident electron and $\omega_p$ is the volume plasmon frequency. Bohr’s delocalization distance represents the maximum distance at which inelastic scattering can occur from an electrostatic scattering source e.g. an atomic nucleus or a free-electron, measured in terms of the impact parameter $b$. A 200 keV electron has a velocity of $2.086 \times 10^8$ ms$^{-1}$, and the VP energy of Al is $\approx$15 eV, resulting in a value of $b_{\text{max}} = 9.2$ nm. (e) VP and SP1 energy as a function of electron-beam position on the same nanodisk analyzed in (d). The VP energy was observed to increase
as the beam approached the edge of the nanodisk from the center of the nanodisk. (f) VP energy and FWHM at the center of the particle as a function of beam position. Both VP energy and FWHM increase as the beam approaches the edge of the particle. While the decrease in VP intensity at the particle edge may be an artifact of decreasing thickness at the edge, the increase in VP energy and FWHM is a result of the boundary effect.

We should note that the results shown in Figure 6-5 may include strain contributions to the VP energy. The VP energy ($E_p$) in the Drude model is given by:

$$E_p = \hbar \sqrt{\frac{e^2 n}{m \varepsilon_0}}$$  \hspace{1cm} (6.1)

where $\hbar$ is the reduced Plank’s constant; $e$ is the elementary charge; $n$ is the volumetric electron density; $m$ is the electron mass at rest, and $\varepsilon_0$ is the dielectric constant in vacuum. Strain would introduce a variation in the electron density, $\Delta n/n$, which would change the VP energy. Given that we did not measure the strain across the nanodisks, the boundary effect and variation in strain could not be disentangled from Figures 6-5 and 6-6.

Another possible explanation for the observed VP energy increase is the dispersion of VPs. The VP energy is related to the VP scattering vector $q$ and momentum $\hbar q$ by:

$$E_p(q) = E_p(0) + \frac{\hbar^2 a q^2}{m_o}$$  \hspace{1cm} (6.2)

where $E_p(q)$ is the VP energy at scattering vector $q$; $E_p(0)$ is the VP energy at zero scattering vector; $\hbar$ is the reduced Plank’s constant; $m_o$ is the electron mass at rest; and $\alpha$ is the proportionality constant for dispersion (measured as 0.38 for Al(115)). During EELS acquisition, the electrons are collected for a range of angles ($\theta$ - electrons propagating in the optical axis have 0°) allowed by the collection aperture, which correspond to a range of scattering vectors ($q$). Thus, the measured VP energy in EELS is integrated over the collected VP scattering vectors.
Nevertheless, given that the VP intensity is proportional to $\theta^2$ and $q^2,(31)$ smaller scattering angles and smaller scattering vectors have larger contribution to the final recorded VP energy.

We estimated the effect of the VP dispersion discussed above by using the dispersion coefficient measured by Batson et al.\textit{(115)} Here we make the assumption that the VPs form standing waves across the diameter of the nanodisk. Therefore, the VP wave vector $q$ (considered equal to the scattering vector) is quantized along the diameter of the nanodisk, with minimum wave vector of $\pi$/diameter. We assumed a simple model of 2D confinement in the x and y axis, with wave vectors $q_x=q_y$ and $q_z=0$. We note that in these conditions the VP wave vector $q$ may take values of $n\pi$/diameter, with integer $n$. Here we assume $n=1, 2, and 3$. The allowed VP wave vectors would be integers of $\pi$/diameter, with maximum values of $0.9 \text{ Å}^{-1}$(cut off wave vector for Al). We calculated the VP energy as a function of modes $n$ and diameter. Figure 6–7 shows the calculated VP energy a function of nanodisk diameter along with experimental data. The increase in VP energy by the calculation suggests excitation of low-order (combination of $n=1, 2, 3$) VP modes. Nevertheless, a precise confirmation of this result would require momentum-resolved EELS in these Al nanodisks.
Figure 6-7. Plot of the increment of VP energy from $E_p(0)$ as a function of nanodisk diameter, that is, $E_{p(0)} = E_{p(0)} + \alpha h^2 n^2 \pi^2 / (\text{diameter}^2 m_0)$. The result suggests that the measurements contain low-order confined VP modes.

Then, we improved our modeling of VPs. We still considered the VPs as standing waves but we employed the hydrodynamic formalism. Based on the linearized hydrodynamic equations Reference (165) describes a method to obtain longitudinal current density solutions in a metal. Their approach resulted in the following expression for the approximate longitudinal resonance frequencies $\omega_v$ of the current density, which is the Newman BC (boundary condition) Helmholtz equation:

$$\omega_v (\omega_v + i\eta) = \omega_p^2 + \kappa_v^2 \beta_F^2$$

(6.3)

where $\omega_v$ also represents the VP frequency for the mode $v$; $\eta$ is the damping coefficient for the VP in the Drude model; $\omega_p$ is the VP frequency in the Drude model; $\kappa_v$ is the eigenvalue of the Helmholtz equation; $\beta_F$ is the hydrodynamic velocity of plasma pressure waves in metal. The eigenvalue $\kappa_v$ is found by solving the Helmholtz equation:
(6.4)

where \( \psi_v \) is the scalar velocity potential defined as a function of the current density \( J \equiv \nabla \psi_v \).

Considering that the VP damping is negligible, \( \eta = 0 \), the aluminum VP frequency \( \omega_p = 15 \text{ eV}/\hbar \), and \( \beta_F^2 = \left( \frac{3}{5} \right) v_F^2 = 2.4 \times 10^{30} \left( \frac{\text{nm}}{s} \right)^2 \), we need to determine \( \kappa_v \) before solving for \( \omega_v \).

Given the solution for the Helmholtz equation, \( \psi, \kappa_v \) can be found applying the boundary condition \( \mathbf{n} \cdot \mathbf{J}(r = R) = \nabla \psi_v (r = R) = 0 \), which means that the current density normal to the metal/vacuum interface at radius \( R \) is zero, as described in Reference (165).

The solution for the Helmholtz equation in spherical coordinates is:

\[
\psi_{lm}(r, \theta, \varphi) = j_{l}(kr)Y_{l}^{m}(\theta, \varphi)
\]

(6.5)

where \( j_l \) is the spherical Bessel function of the first kind and \( Y_{l}^{m} \) is the spherical harmonics. We note that there are other common solutions for the Helmholtz equation.(166) The radial solution of the Helmholtz equation may also be the spherical Bessel function of the second kind and spherical Hankel functions of the first and second kind (and a linear combination of them). However, we excluded the spherical Bessel function of the second kind because of the singularity at the origin. So, we want to avoid solutions that provide infinite velocity potential and infinite current density. We also excluded the spherical Hankel function solutions because for large arguments they are appropriate solutions for traveling waves instead of standing waves, which is the assumed case for VPs.

The solution for the Helmholtz equation in cylindrical coordinates is:

\[
\psi_{lm}(r, \theta, z) = j_{l}(r\sqrt{k^2 - m^2})\cos(l\theta)\cos(mz)
\]

(6.6)
where \( J_l \) is the Bessel function of the first kind. Similarly to the spherical solutions, we avoided solutions in the form of Bessel functions of the second kind and Hankel functions (first and second kind) for the same reasons discussed above.

For spherical coordinates and \( l=1, m=0 \):

\[
\psi_{10}(r, \theta, \varphi) = \left( \frac{\sin(kr)}{kr} - \frac{\cos(kr)}{kr} \right) \left( \frac{1}{2} \sqrt{\frac{3}{\pi}} \cos(\theta) \right)
\]

(6.7)

For cylindrical coordinates and \( l=1, m=0 \):

\[
\psi_{10}(r, \theta, z) = J_1(kr)\cos(\theta)
\]

(6.8)

Applying the boundary condition for spherical coordinates at \( r=R \) and for cylindrical coordinates at \( r=R \) we obtain the equation to determine \( k_v \):

\[
\vec{n} \cdot \vec{J} = \vec{n} \cdot \nabla \psi_v = \vec{r} \cdot \nabla \psi_v = \left( \frac{\partial \psi_v}{\partial r} \right)_{r=R} = 0
\]

(6.9)

For spherical coordinates:

\[
\left( \frac{\partial j_l(kr)}{\partial r} \right)_{r=R} = 0
\]

(6.10)

The solution for this equation is \( w_n = k_n R \).

For \( l=1 \): \( w_n = 2.081; \ 5.940, ... \)

For \( l=1 \): \( k_1 = 2.081/R, \ k_2 = 5.94/R, \) etc.

For cylindrical coordinates:

\[
\left( \frac{\partial j_l(r \sqrt{k^2 - m^2})}{\partial r} \right)_{r=R} = 0
\]

(6.11)
For $l=1$ and $m=0$: $w_n=1.841, 5.331, \ldots$

For $l=1$ and $m=0$: $k_1=1.841/R$, $k_2=5.331/R$, etc.

As intuitively expected, the solutions $w_n$ for spheres are slightly larger than for disks because spheres have larger surface-to-volume ratio.

The final frequency $\omega_{1n}$ ($n>0$) and energy $E_{p1}^{1n}$ are computed by the relations:

$$\omega_{1n} = \sqrt{\omega_p^2 + \frac{w_n^2}{R^2} \beta_F^2}$$  \hspace{1cm} (6.12)

$$E_{p1}^{1n} = \sqrt{E_p^2 + \frac{w_n^2}{R^2} h^2 \beta_F^2}$$  \hspace{1cm} (6.13)

Figure 6-8 shows the modeling results compared to experimental data. The agreement between the data and low-order VP energy suggests that only low-order VP modes are being excited inside the Al nanodisks. Nevertheless, a precise confirmation of this result would require high-precision momentum-resolved EELS and a comprehensive simulation of all possible VP modes combined.

![Figure 6-8](image)

**Figure 6-8.** The circular markers are the measured VP peak energy (as shown in Figure 6-5). The dashed lines represent the analytical model (165) described above $(m=0)$, composed of standing waves of VPs confined in the nanodisk. Red dashed line is the $l=1$ mode with lowest wavevector; blue dashed line is the $l=1$ mode with second
lowest wavevector, and the green dashed line is the $l=2$ mode with lowest wavevector. This model suggests excitation of low-order standing wave VPs.

We also considered the quantum confinement of VP energy. An analytical model of quantum confinement of VPs suggest VP energy scaling as $1/(\mu \text{diameter}^2)$ (where $\mu$ is the exciton effective mass). (70) It was not possible to match this scaling trend with our results to date due to lack of precision in determining energy shifts at sub-10 meV energy scale.

Therefore, we suggest that the observable increase in VP energy and FWHM is due to the boundary effect, with possible strain contributions, and due to standing waves of low-order VP modes. Nevertheless, we note the need for developing a comprehensive theoretical framework to model the VP energy and FWHM at the sub-10 nm length scale.

6.4. Conclusions

We demonstrated a wide spectral control of SPs in Al by using sub-20-nm EBL. We pushed SP energies towards 7 eV by patterning nanodisks at the sub-20 nm length scale. Furthermore, we lithographically controlled for the first time the VP energy, FWHM, and intensity. We proposed that the increased energy and FWHM was due to the boundary effect and standing waves of low-order VP modes. However, factors such as strain and quantum confinement were not fully considered and may also contribute to the observed results.

Furthermore, we expect that applying our experimental process to semiconductor materials, instead of a metal, should yield wider spectral control of VPs. We expect this based on previous experimental results on Si, (72) Bi, (71) Ge, (66, 70) and GaN. (67) The reason is that patterning these semiconductor materials at sub-10 nm length scale would result in a modification of their electronic structure that would affect the VP energy, usually causing a blue shift in the VP energy.
Chapter 7

Summary and Future Directions

Here we present a summary of this Thesis in its entirety and we discuss future directions of research.

We have shown that low-energy (sub-5 keV) electron-beam lithography (EBL) is capable of patterning with high resolution and a significantly reduced exposure dose. A resolution limit of 15-nm-half-pitch for nested L’s and large-area dot array in HSQ was achieved at 2 keV. We also fabricated 9-nm-half-pitch nested L’s and 13-nm-half-pitch large-area dot array, but resist residues were observed. The required dose at 2 keV was about one order of magnitude lower compared to that required at 30 keV. Point-spread functions (PSFs) at low energies were experimentally determined and were in good agreement with Monte-Carlo simulations. From the experimental PSFs, the effective scattering range of electrons at energies 1.5 and 2 keV was less than 200 nm. The long-range proximity effects at sub-5-keV are much lower than at 30 keV, as demonstrated in the ‘hole-in-HSQ’ structures and the minimal dot diameter deviation at the corners of the large dot arrays.

One immediate question following this study is the ultimate resolution limit of low-energy EBL without electron-beam spot size limitation. The previously described minimum feature size of 9 nm (isolated pattern) coincided with the 9 nm spot size of the instrument. The minimum achieved half-pitch was also 9 nm, but there many other factors than spot size for fabrication of dense structures. So, performing the same experiment using sub-2 nm spot size, currently available in commercial tools,(167) might improve the resolution limit of sub-5 keV EBL, while maintaining the reduced dose and reduced long-range proximity effect.
A comprehensive investigation of shot noise at the sub-10-nm length scale is of critical importance today for the semiconductor industry and magnetic storage industry.\(^{(168)}\) The main reason is that shot noise significantly affects the line-edge roughness for sensitive resists.\(^{(80)}\) We have shown that low-energy EBL can reach the sub-10-nm length scale with high sensitivity. So, low-energy EBL is an ideal system to investigate shot noise at the sub-10 nm length scale.

We showed that 200 keV EBL with an aberration-corrected STEM is capable of patterning 2 nm isolated features and 5 nm half-pitch structures in hydrogen silsesquioxane (HSQ), with significantly smaller dose than competing techniques such as electron-beam-induced deposition. We showed that 200 keV EBL exposures lead to higher contrast than 30 keV exposures. In addition, we determined the electron energy loss in HSQ at 200 keV, observing the volume plasmon loss in HSQ.

This EBL capability of patterning 2 nm features, and possible extension to 1 nm features, shows a promising path for extending EBL to the molecular scale. Further development of this technique, specifically in patterning yield, feature size uniformity, and resist stability should be the next steps for enabling top-down nanofabrication at the sub-nanometer scale. Applications that immediately benefit from such EBL technology are the fabrication of sensitive plasmonic sensors,\(^{(57, 58)}\) further miniaturization of electronic devices, and fabrication of single molecule circuits.\(^{(91)}\)

We have shown for the first time the measurement of delocalized energy transfer in EBL exposure at the sub-10-nm scale by using chromatic aberration-corrected energy-filtered transmission electron microscopy (EFTEM). The measurements here focused at the EBL PSF at 200 keV and at the sub-10-nm length scale, without considering the effect of backscattered electrons. We have defined the role of spot size, electron scattering, secondary electrons (SEs),
and volume plasmons (VPs) in the lithographic PSF by performing electron microscopy and spectroscopy, sub-10-nm EBL, and numerical simulations. We expect that these results will enable novel ways to improve the resolution limit of EBL.

One remaining challenge for the direct measurement of the lithographic PSF is to directly measure the SE PSF, that is, deposited energy density by SEs. For this, we suggest an analogous experiment performed here but instead of probing transmitted electrons, one may probe emitted SEs. This measurement may be accomplished in a low-energy electron microscope (LEEM) system. However, the detected SEs would be only the SEs that escaped from the resist, originated from the bulk and the surface of the resist. The goal here is to detect how SEs propagate and lose energy inside the resist. So, we envision that SE imaging and spectroscopy would provide the location and energy of the emitted SEs across the top surface of the resist. Then, by using the position and energy of SEs on top of the resist and by performing Monte Carlo simulation of the SE emission process, one may be able to back-calculate the SE PSF in the bulk of the resist. One alternative simplification may be using thin resists and assuming that the energy density deposited by SEs is uniform throughout the resist thickness.

Another important challenge in lithography is to directly image the resist cross-linking or bond scission. Recent advancements of near-field Raman(169) and near-field infrared spectroscopy(170) provide chemical information of materials at the sub-20 nm length scale, with minimum damage to the material analyzed. So, performing near-field chemical mapping of exposed resists may be an interesting approach to directly image the lithographic PSF.

Furthermore, VPs can be excited by electrons and high-energy photons, such as extreme ultraviolet (EUV).(69) EUV lithography is of increasing interest because it is considered the next generation lithographic technology for high volume manufacturing of semiconductors.(37, 132)
Therefore, we note that the VP and SE PSFs may be important factors in the resolution limit analysis of EUV lithography.

We demonstrated a technique to control the placement of colloidal quantum dots (QDs) through EBL. This QD placement allows QD clusters of one to five QDs to be fabricated. The process was developed by optimizing QD solution, resist thickness, and template size. One figure of merit in this process is the pattern yield, defined here as the percentage of templated sites occupied by at least one QD. A pattern yield of 87% was achieved with an average of three QDs in each cluster. We performed photoluminescence measurements of the fabricated QD clusters, showing that the QDs are optically active after the fabrication process, presenting blinking in the photoluminescence. This optimized top-down lithographic process is a step towards the integration of individual QDs in photonic systems.

The process described above may be directly applied for placing colloidal QDs in nano-optical systems (39) and for fabricating nitrogen vacancy centers into photonic chips (171). Our QD-placement technique may be also useful in studying QDs and nitrogen vacancy center photophysics without inhomogeneous broadening.

In addition, we demonstrated a wide spectral control of surface plasmons (SPs) in Al by using sub-20-nm EBL. We pushed SP energies towards 7 eV by patterning nanodisks at the sub-20 nm length scale. Furthermore, we controlled for the first time the VP energy and full width at half maximum (FWHM) by using sub-10 nm EBL. We proposed that the increased energy and FWHM was due to the boundary effect and VP dispersion. However, factors such as strain and quantum confinement were not fully considered and may also have contributed to the observed results.

We expect that applying our experimental process above to semiconductor materials, instead of a metal, should yield wider spectral control of VPs. We expect this based on previous
experimental results on Si, Bi, Ge, and GaN. The reason is that patterning these semiconductor materials at sub-10 nm length scale would result in a modification of their electronic structure that would affect the VP energy, usually causing a blue shift in the VP energy.

Engineering the VP energy and FWHM results in engineering the dielectric constant of materials at VUV (vacuum ultraviolet) and EUV (extreme ultraviolet) regions of the electromagnetic spectrum. Therefore, the patterned VP resonators described above may allow new optical devices at VUV and EUV.

The lifetime of VPs is usually at the sub-femtosecond time scale. So, by engineering the VP FWHM we are engineering the VP lifetime at the attosecond time scale. Once EUV(172) electron,(173) and X-rays(174) attosecond sources become more available there will be an opportunity to probe the lithographic engineered VP lifetime.

Finally, once we fully understand the behavior of VPs in nanostructures, we plan to design a resonator for maximizing the VP lifetime and propagation length. This may allow VPs to be used in signal processing at the sub-100 nm length scale. This application would be an analogue of SP nano-optics,(55) but using VPs as the signal. Demonstrating such application would be the first step towards volume-plasmonics.
References


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