Photolithography for the Investigation of Nanostructures

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Abstract

Developing a rapid, iterative, and limited-resource method of microfabrication with which devices with large localized electric fields can be generated will expand research capabilities for those interested in nanostructures. Photolithography is a common method of microfabrication, and it can be conducted within the confines of a small laboratory. The parameters for photolithographic methods, such as baking temperature, exposure, and development time, were optimized to yield interdigitated-finger devices with features on the order of 2μm capable of creating electric fields up to 10 kV/cm. One such device has been used to examine quantum dots (QDs) in toluene. QDs are semiconductor nanoparticles, with sizes in the range of 1-50 nm, which are often called "artificial atoms" due to their discrete energy levels arising from atomic-like quantum confinement. Many potentially useful properties of QDs depend on their behavior in external fields. Using devices created with photolithography, two trials have been conducted with QDs. In the first, QDs suspended in toluene were applied to conducting interdigitated fingers which had no bias applied; luminescence of the QDs showed that they did not preferentially align or cluster on the fingers. However, in a second trial, QDs in the presence of an applied electric bias clustered on fingers with lower potential. This indicates that the QDs are accumulating charge during handling, possibly from interaction with the toluene solution in which the QDs are stored. This could provide a method for preferential deposition and/or localization of QDs using electric fields. Future experiments will

work to isolate the charging mechanism and explore the potential for nanoscale manipulation of QDs using external fields.

Introduction and Background

Nanostructures intrigue scientists and engineers because of their unique properties and diverse applications. A nanostructure is an object or material with at least one dimension on the nanoscale. That is, it has features around the size of 1-100 nanometers. (1 nm is one billionth of a meter.) This small size contributes to nanostructures' properties and to their versatility. Manifestations of quantum physics are apparent at this scale, which differentiates them from macroscale materials. Nanostructures of common interest include nanotubes, nanowires, quantum heterostructures, and quantum dots.

The properties of nanostructures can be quantified, but investigating small materials requires small tools. Refining a method of on-site microfabrication gives a laboratory the ability to create such tools; photolithography is one such method, and is common enough that materials and processing recommendations are easily accessible. This thesis details the process of conducting photolithography and of optimizing some of its many steps, as well as the results of early attempts at experimenting on quantum dots with devices created on-site.

Chapter 1, "Device Fabrication and Applications," discusses the methods used in this research, including the manner in which different steps of processing were optimized. Photolithography was used to create simple devices used to perform experiments on quantum dots. The details of these preliminary experiments are included in this chapter.

Chapter 2, “Results,” presents the results of optimizing photolithography and preliminary experiments on quantum dots. These results are discussed in chapter 3, “Discussion,” and ideas for taking the project further are given in chapter 4, “Looking Forward.”

Photolithography

Photolithography rose to popularity in the 20th century as one of the most promising methods for fabricating integrated circuits[1] and other solid-state devices.[6] The drive for miniaturization in semiconductor technology over the past century has been largely satisfied by improving resist and exposure technology (two main components of photolithography).[7]

Photolithography draws parallels with (traditional) photography. Processing can be best understood if the similarities between the two are identified early on. The following figure illustrates the key similarities:

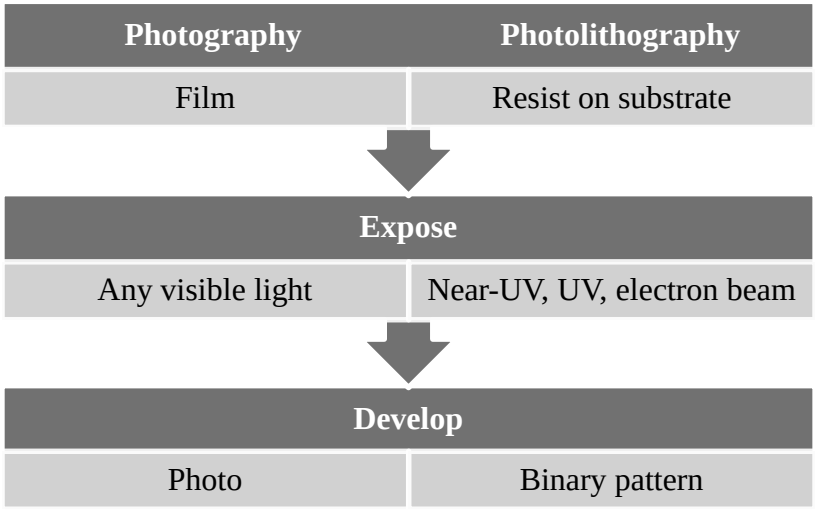

Figure 0.1 Similarities between photography and photolithography, detailed by processing steps.

Although Figure 0.1 greatly simplifies both processes, it provides the idea behind the analogy. With a goal of creating an image, a photosensitive material is exposed to light of the appropriate wavelengths. The material is then chemically developed, and the result is an image or pattern determined by the exposure.

In photolithography, a photoresist performs similar functions to photographic film. A photoresist, also simply called a resist, is a solution of photosensitive polymers. That is, it comprises a polymer and a solvent, and the polymer structure is altered by radiation.[1,6] The polymer's response to the exposing radiation allows a latent image to be created in the resist. Radiation, which can be used in photolithography includes x-rays, electron beams, ultraviolet, and ion beams; the optimal wavelength for exposure varies from one resist to another and is recommended by resist manufacturers. [6,7]

There are two primary photochemical mechanisms by which a latent image is established: crosslinking and chain scission.[1] The mechanism depends on the tone of the resist, which can be either negative or positive. Crosslinking is the establishment of new bonds between polymer chains within the resist, which strengthens the resist.[1] Crosslinking occurs in negative photoresists when the resist is exposed to radiation. The crosslinked regions adhere to the substrate and are less soluble than unaltered regions.[1,6] That is, crosslinked resist dissolves slower in a developer.

When a positive resist is exposed to radiation, polymer chains rupture or break apart, a process called chain scission.[1] As a result, exposed regions of resist become more soluble; these regions will dissolve more rapidly in a developer than unaltered

resist.[1,6] Thus, both crosslinking and chain scission create latent images in the resist, but the images will differ in tone once developed. The processing of resist is discussed thoroughly in section 1.1.1.

A number of resist properties contribute to the resolution and quality of the final product. Positive photoresists have inherently higher resolution, because negative resists tend to swell during the removal of uncrosslinked resist (developing).[6] This swelling makes negative resists unsuitable for creating devices with features smaller than 3.0 μm, whereas positive resists have been used to create patterns as small as 300 nm (an order of magnitude smaller).[6]

Another concern in producing optimal results with photolithography is the wall profile of patterns from a resist. The wall profile is the slope of the sidewalls of features, and is typically a relic of the resist chemistry and development. Wall profiles are illustrated in Figure 0.2.

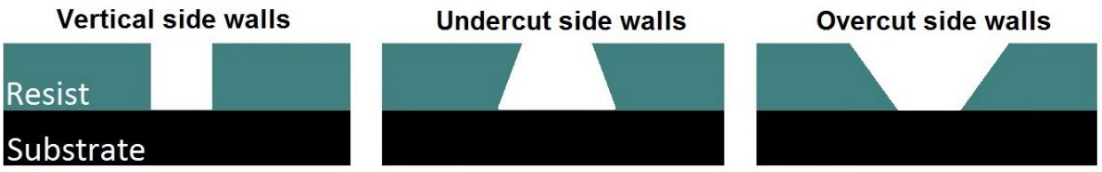

Figure 0.2: Wall profiles of resist patterns (after development but before post-processing).

Positive resists tend to have vertical or overcut wall profiles, and negative resists typically have undercut wall profiles.[1] In practice, vertical walls are the least likely, as it would require perfect processing and exposure. It follows that choosing to use positive or negative resist depends on the ultimate goal of the processing, and how it would be realized or hindered by undercut or overcut walls.

Quantum Dots

Quantum dots (QDs) are semiconductor nanoparticles with features on the order of 1-100 nm. QDs are sometimes called "artificial atoms," because electrons' confinement within QDs is similar to that seen in atoms.[2] Within a QD, the free motion of electrons is quantized; this is a result of QDs "quasi-zero-dimensional" structure.[2] Electrons are thus confined in all three spatial dimensions, behaving as they would in an atom.

QDs are particularly useful research materials because, unlike typical atoms, their shape and size can be controlled during fabrication.[3] The size of a QD is reflected in other properties, such as the wavelength of its luminescence. The color of a QD's luminescence is then "tunable," or can be customized.[3,4] This property makes QDs a versatile material.

Figure 0.3: Quantum dots luminescing at various wavelengths. Photo source: http://www.cnn.com/2015/04/02/tech/quantum-dots-mci/, courtesy of Nanoco.[4]

QDs have a wide range of applications, which makes them particularly rewarding research subjects. As a result, they are rapidly becoming a material of interest to the public, industry, and researchers. They have made the news as promising materials for digital screens and displays, such as televisions and cell phones; their tunable luminescence makes QDs well-suited to such technologies.[4,5] CNN describes QDs on their website as "tiny fluorescent semi-conductors that possess unique optical qualities," and notes their energy efficiency and vibrant color schemes.[4] Additionally, QDs are being explored in fields such as medical science, electronics and photovoltaics, and quantum computing.

1 Device Fabrication and Applications

As previously discussed, photolithography is a common method of microfabrication. The primary goal of this work was to create a suitable procedure for carrying out photolithography with on-hand resources, including optimizing all of the processing parameters. Once a working procedure was created, devices could be fabricated to allow a variety of experiments, including ones with quantum dots. The key device capability for the proposed QD experiments is the generation of localized electric fields. For example, observing energy shifts in QDs such as those resulting from the Stark Effect typically requires electric fields on the order of tens or hundreds of kV/cm.

1.1 Photolithography

The process for creating devices with photolithography varies greatly between laboratories depending on research goals and available equipment. The following procedure can be carried out by one researcher and requires a minimal amount of equipment.

1.1.1 Processing and Optimization

Photolithography begins with a substrate. The substrate is used as the foundation of the "film" on which a pattern will be created. Substrate choice depends on the ultimate operational goal of a given device. For example, SiO_2 (silicon dioxide) is a good choice if the substrate should be an insulator. Glass can be used if

transparency is desired. However, different substrates can require special attention, so processing must be optimized individually for each material.

Silicon is a prime candidate for substrates due to its availability and the ease with which it can be oxidized.[6] Silicon was used for the majority of work on optimization. Si and SiO_2 can be processed identically, so success with Si could be recreated with SiO_2 when devices with an insulating substrate were needed. Glass was more difficult to optimize, as problems with adhesion to the substrate were common.

Continuing the analogy to photography, the "film" of photolithography is a substrate coated with a resist. Recalling the chemistry of resist materials as discussed in the introduction, when a resist is exposed to proper wavelengths of light the chemical properties of the material will change. Notably, the solubility of the resist is altered.[1,6] The change in solubility depends on the tone of the resist; that is, it depends on whether the resist in use is a "positive" or "negative" resist. For a positive resist exposed regions become more soluble, and for a negative resist exposed regions become less soluble.[1,6,7] Solubility determines which regions will be washed away when the sample is treated with a chemical developer, so this mechanism is key to creating patterns with photolithography.

During the course of this research, a wide variety of resists were tested including ma-N 2410, PMMA (polymethyl-methacrylate), and AZ 5214 E. The properties of these resists are detailed in Table 1.

Resist	Resist manufacturer	Tone	Exposing radiation
ma-N 2410	micro resist technology	Negative	E-beam, Deep UV[8]
PMMA	MicroChem Corp	Positive	E-beam, X-ray, Deep UV[9]
AZ 5214 E	Clariant Corporation	Positive*	Broadband[10]

Table 1: Details of various resists

*AZ 5214E is an image-reversal resist; it is a positive resist, but adding a reversal bake and flood exposure to processing will result in a negative pattern.

It is recommended that the processing is carried out in a clean room. There is heavy emphasis on cleanliness in photolithography, which is motivated by the desire for uniformity and precision on small (micron-size) scales in the resulting devices. A clean room was not available for this research, but the fume hood under which any chemical processing was conducted provided some degree of protection from contamination. Additionally, samples were only handled using gloved hands, to prevent human contamination such as oils or sweat from reaching the sample (and to protect the handler from chemical hazards during processing).

The resist is applied to the substrate in a thin film, and this coating requires three steps. First, the substrate of choice must be thoroughly cleaned. Using laboratory-grade, low-lint wipes, acetone and methanol are used to vigorously scrub dust and contamination from the substrate. The sample is then transferred to a spin-coater, and acetone applied again. A puddle of acetone is created on the sample and allowed to sit for 20-30 seconds. The sample is then spun at approximately 3000 revolutions per minute (rpm) for 30 seconds to remove the acetone; during the spin, methanol is applied to the surface one final time to ensure the sample is clean of any

remaining contamination. Clean, dry, compressed air can then be used to ensure the sample is dry, and to discourage any dust particles from settling on the sample.

Once the substrate is clean, the resist is applied using the spin-coater. Due to the photosensitive nature of the resist, the remainder of the processing is carried out with the room lights off to minimize unwanted exposure. A few milliliters of resist are dropped onto the surface of the sample, and the sample is again spun at ~3000 rpm for 30 seconds. During the spin, the resist spreads out into a thin, uniform layer and subsequently dries.

Optimizing spin-coating was explored early on by testing with a negative resist, ma-N 2410. The goal of this optimization was to determine the best procedure for creating a ma-N 2410 coating. In order to identify the best conditions for coating, the results of three different schemes of spin-coating were qualitatively compared. In the first, the resist was not altered, and the spin-coating was conducted at 3000 rpm. In the second and third, a resist thinner was added to the solution, lowering the viscosity of the resist. The thinned resist was then spun at 1000 rpm in the second trial and 3000 rpm in the third trial. Microscopy was used to compare the appearance of each trial's coating. The results of this optimization are presented in section 2.1.

Once the resist has been applied, the sample is then subjected to what is called a "soft bake" or "prebake." Prebaking removes any residual solvents in the resist layer, and also strengthens the resist, relieving stress created by spin-coating and making the sample more robust for remaining processing.[6] This involves baking the sample on a hot plate at anywhere from 100°C to 180°C depending on which resist is in use.

At first, samples were baked directly on the hot plate, but there were concerns about consistent heating. These concerns included both even heating over the area of each individual sample (which would damage individual results), and even heating between different samples (which would damage reproducibility of results). Hot-plate baking was improved in two ways.

First, a small copper plate was placed directly on the hot plate. Samples were then placed on the copper plate to bake. The inclusion of the copper plate was motivated by its high thermal conductivity, which distributed heating more evenly over the area of the samples. That is, the copper plate improved the conductive heating of the sample. The second addition to the baking process was the inclusion of a lid, which was placed over the hot plate during baking. The lid added convective heating of samples, trapping heat over the hot plate and allowing the sample to be heated from more than just the bottom. Also, the lid prevented any drafts from the room from reaching the sample, which could have cooled the sample and interfered with even heating.

Once a sample has been coated and soft-baked, it must then be exposed to radiation. Keeping the photography analogy in mind, this step, called the image exposure, is "taking the photo." The image exposure creates the latent image in the resist, which will become visible upon developing the sample.[6] In order to create an image on the sample, the exposing radiation must be patterned, so various schemes were tested for patterning the radiation.

Early attempts at creating images involved using a laser to draw lines and features on the sample; however, this method was time-consuming, and useful results required more precision than could be achieved. The time and precision was limited by a set of motion stages on which the sample would rest during drawing, and controlling the motion stages with the desired precision (to obtain features on the order of a micron) proved to be a challenge. Each direction of motion (called x, y, and z) required its own stage, which made 3D movement and adjustment problematic. An illustration of this setup can be seen in Figure 1.1.

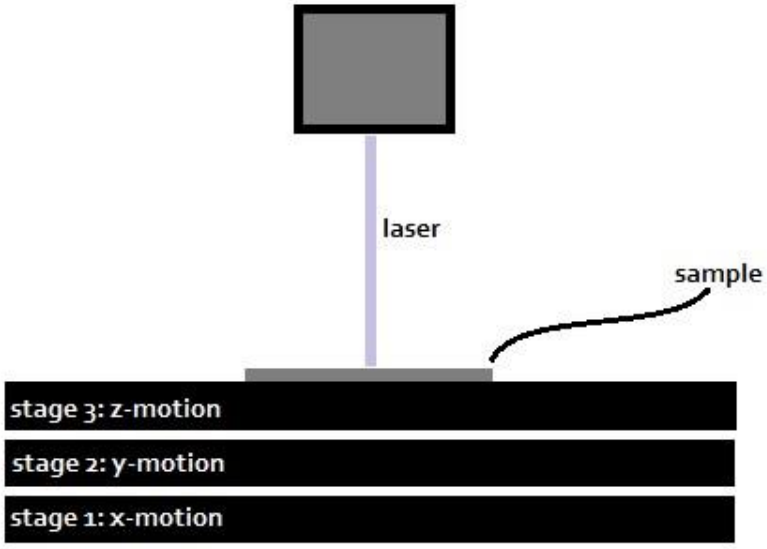

Figure 1.1: The laser-draw exposure method, which required three motion stages. 3D movement required motion from each stage.

A significant setback of this method was the difficulty of keeping the laser spot in focus on the sample. The laser would go out of focus after a few millimeters of lateral movement, as the stages weren't perfectly flat with respect to the laser source. Another problem was the power of the laser, which was initially high enough that it

burned the resist, rather than simply exposing it. Processing time and precision were both improved upon transitioning to the use of a photomask system for exposure.

A photomask is a stencil for exposure. The characteristics of a useful mask are: it is as flat as possible (in order to make optimal contact with the sample), the pattern is opaque to UV light, and the rest of the mask is transparent to UV light. Thus, a typical mask may be a flat glass or quartz plate with a pattern of chromium or titanium.[1]

The mask is brought into contact with the sample, gently enough not to damage the resist coating. The entire area of the sample is then illuminated, creating a pattern of exposed versus unexposed regions depending on the mask's design. This method is called contact printing, and is one of the oldest photolithographic methods.[6] Contact printing is useful because it adds reproducibility to processing, making it easier to recreate the same pattern many times; however, it must be conducted carefully, as the mask can damage the resist layer. Contact printing is illustrated in Figure 1.2.

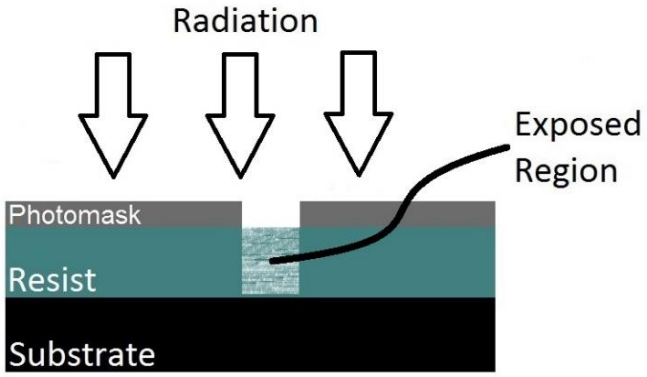

Figure 1.2: An illustration of contact printing. The photomask is brought into gentle contact with the surface of the sample, and the sample is flooded with radiation. The mask's patterns determine exposed and unexposed regions in the resist.

The first mask with which contact printing was attempted was created by adhering 3 mm mesh grids—typically used for transmission electron microscopy (TEM)—to a glass slide. This was immediately used to create another mask on a glass slide in the reverse of that image, which can be seen in Figure 1.3. The TEM-grid mask was small enough that it could be used by manually pressing it against the surface of the sample during the flood exposure. This mask could be used to create devices with features on the order of 50-100 µm.

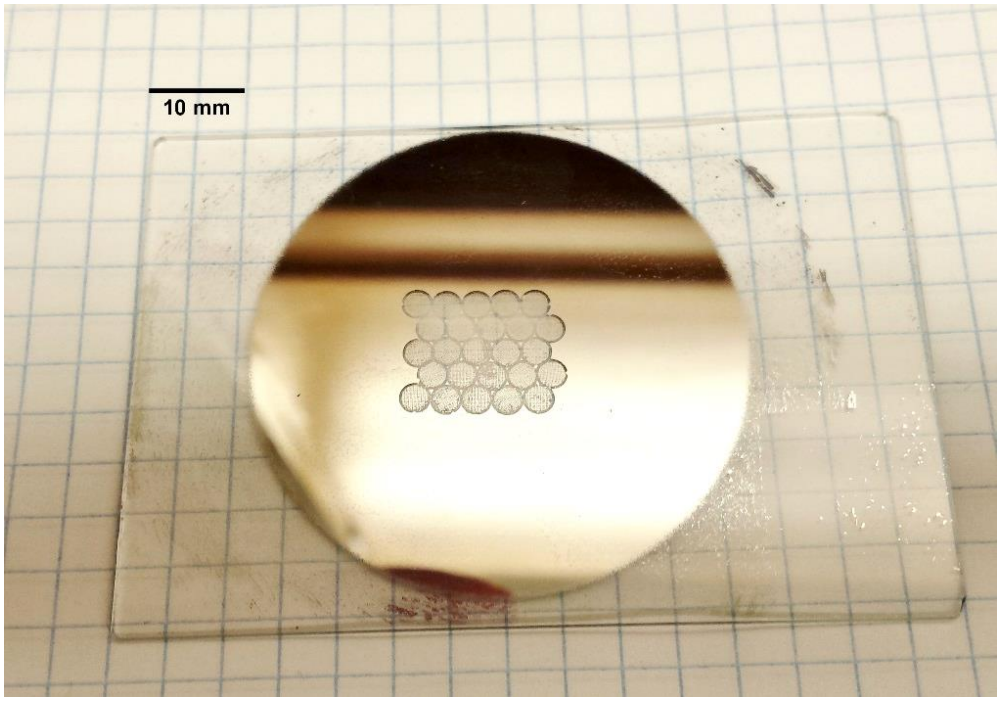

Figure 1.3: An early attempt at creating a photomask. This mask has features on the order of 50-100 µm.

After many attempts at using the mask shown in Figure 1.3, a new photomask was designed. The new photomask was printed professionally to ensure precision in the desired features. The mask is made up of a large region of interdigitated finger patterns, with the remainder of space taken up by alignment grids (grids of numbers that can be used for pinpointing location during microscopy). The alignment grids can

be used in a wide variety of projects which require microscopy, but the interdigitated fingers were designed for creating the electric fields needed for nanostructure study. This more precise mask could be used to create devices with features on the order of a few microns, and can be seen in Figure 1.4.

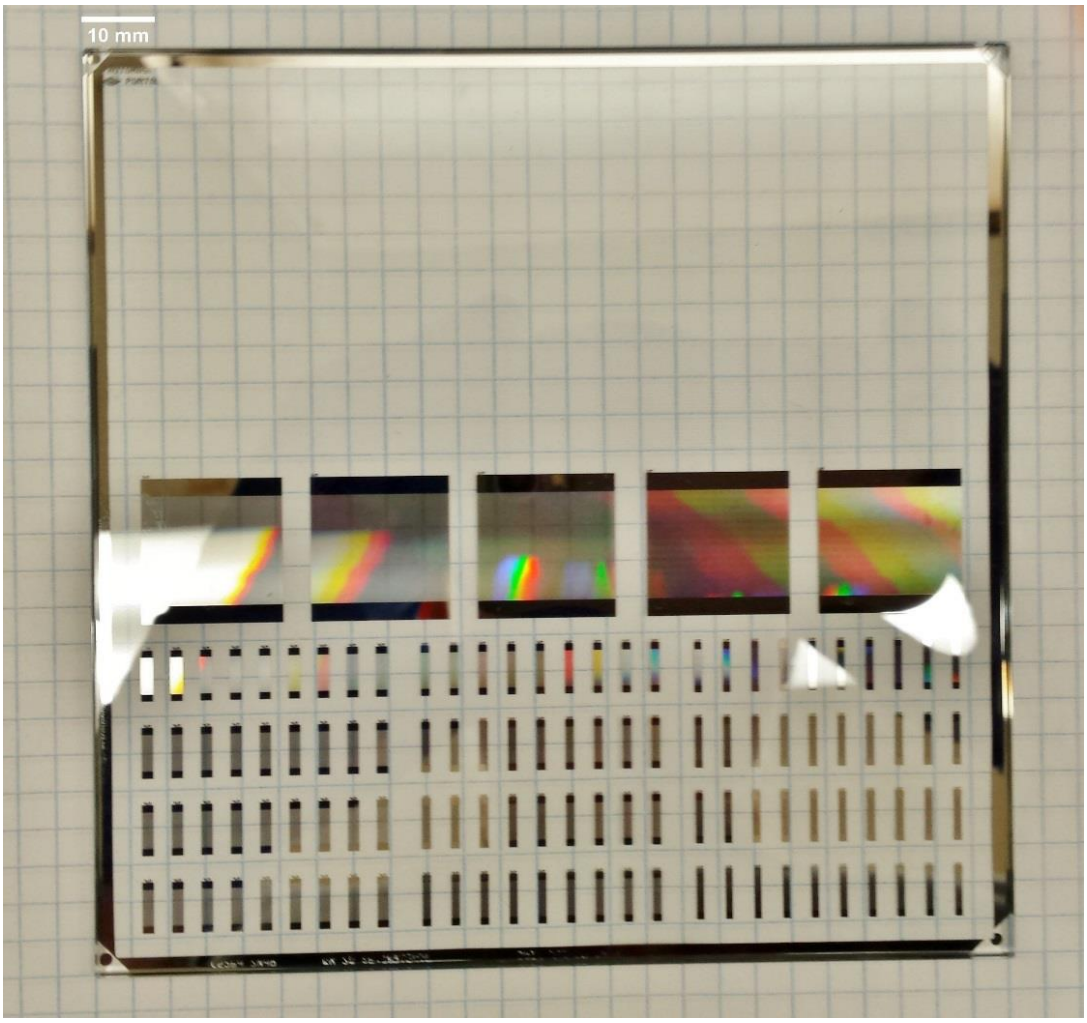

Figure 1.4: A professionally-printed photomask, with features on the order of 1-4 μm.

The interdigitated fingers on the mask are in the rows and columns on the lower portion of the mask. Features on the mask shown in Figure 1.4 vary in size from

1 µm to 4 µm. Figure 1.5 and Figure 1.6 show detail on one set of 1-µm interdigitated fingers.

Figure 1.5: One set of interdigitated 1-µm fingers. The fingers lie between two pads, effectively isolating the pads from each other and creating electrodes.

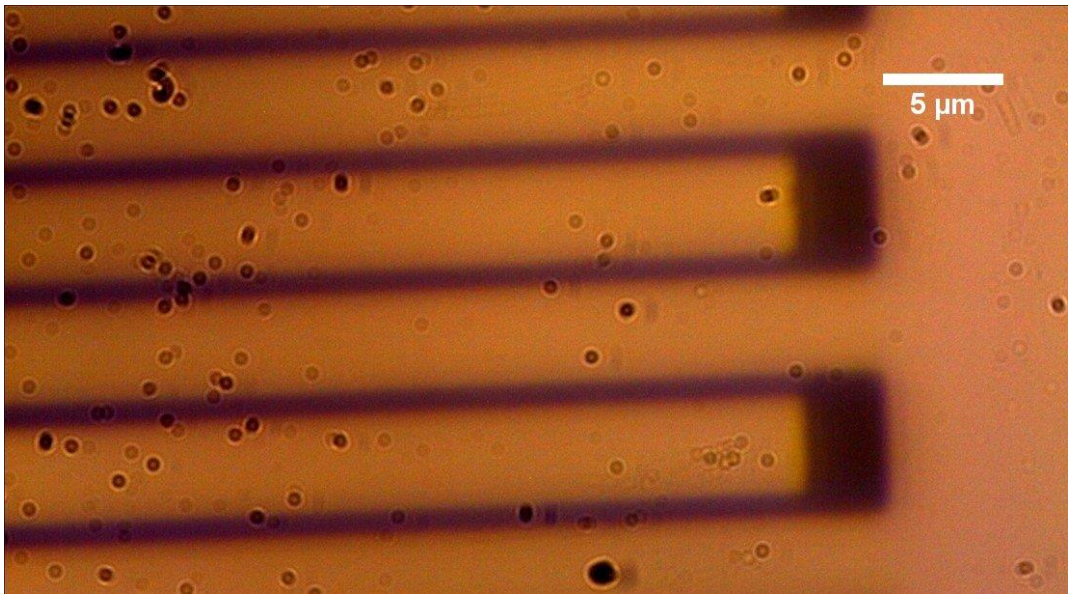

Figure 1.6: Detail on the interdigitated fingers. To the right of the fingers lies one pad, which the fingers isolate from another pad.

A custom rig was designed to securely hold this photomask in place during contact exposure. The mask holder was 3D-printed, and was held in place with optics table elements. Rig design and 3D printing are detailed in section 1.2. The exposing light source is mounted above the mask, allowing the area of the sample and mask to be flooded with radiation. During parameterization, light sources varied from diffuse 405-nm lasers to 365-nm LEDs, with LEDs found to be the easiest to use. LEDs provide the most consistent results, as they do not require as much precision as a diffuse laser, and don't require extra optics elements to be able to flood the full area of a sample. LEDs were easier to incorporate with other materials on hand to create a rig for exposure (see Section 1.2). Also, 365-nm LEDs were cheaper and safer than other options, and their light mimicked the 365-nm I-line emission of traditional mercury lamps (one of the first light sources used in photolithography).[6]

The final step of photolithography is developing, in which chemical developers wash away soluble regions of resist to produce the final product, a relief image of the mask. Depending on the tone of the resist, this image will be either a positive or negative relief, as can be seen in Figure 1.7. Developers to be used with each individual resist are recommended by the resist manufacturers; the developer must match the tone of the resist, or the latent image will not be developed.

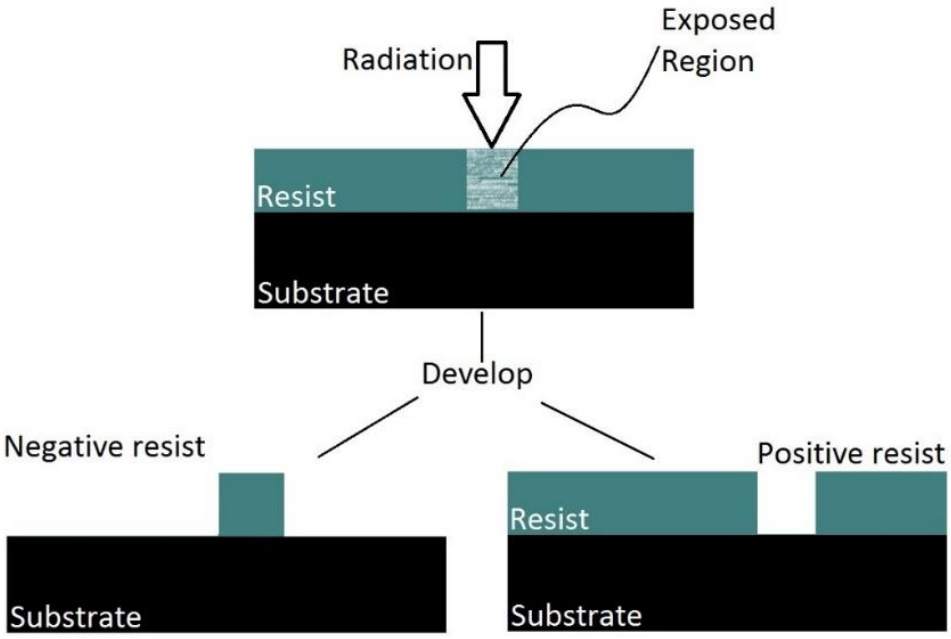

Figure 1.7: An illustration of exposing and developing photoresist on a substrate. The resulting image depends on the tone of the resist (negative or positive).

For a simple negative or positive resist, the processing is complete. However, AZ 5214 E, an image reversal (IR) resist, requires two extra steps of processing before development. This IR resist begins as a positive resist, but can effectively become a negative resist (that is, it will produce a negative-tone image) with two extra steps of processing.[10] Without these extra steps, the resist can be developed normally after the image expose to produce a positive image. If a negative image is desired, however, the sample is instead baked again after the image expose. This is called the "reversal bake," and is at a higher temperature than the prebake; the reversal bake is 111°C, while the prebake is only 100°C. During the reversal bake, crosslinking agents in exposed regions of resist are activated. Areas that crosslink adhere strongly to the

substrate, and are less soluble in the developer, as was discussed in the introduction to photolithography.

Refining the temperature for the reversal bake proved to be a challenge, as the crosslinking is a highly sensitive process. It requires great precision and accuracy in order to obtain consistent results; the bake is sensitive to 1°C, making it a significant challenge in processing optimization. Optimizing the reversal bake involved processing many samples with the IR resist over a range of reversal bake temperatures, and qualitatively comparing the resulting patterns. The pattern features were primarily studied by visually examining how sharp the desired features were, how uniform the remaining resist was, and how clean the regions without resist looked. Making these qualitative comparisons between many samples allowed the optimal reversal bake temperature to be identified; the results of this optimization are discussed in section 2.1.

Note that after the reversal bake, there are no soluble regions on the sample. Exposed regions have crosslinked, adhering them to the substrate. Unexposed regions have not crosslinked, but are still insoluble according to the positive tone of the resist. Thus, in order to be able to develop the image, the sample must be exposed again. The sample is subjected to a "flood expose," in which the entire surface of the sample is flooded with radiation (sans photomask). The regions which have not crosslinked, and are thus still normally-behaving positive resist, become more soluble. A negative-tone image results from developing. This process is illustrated in Figure 1.8.

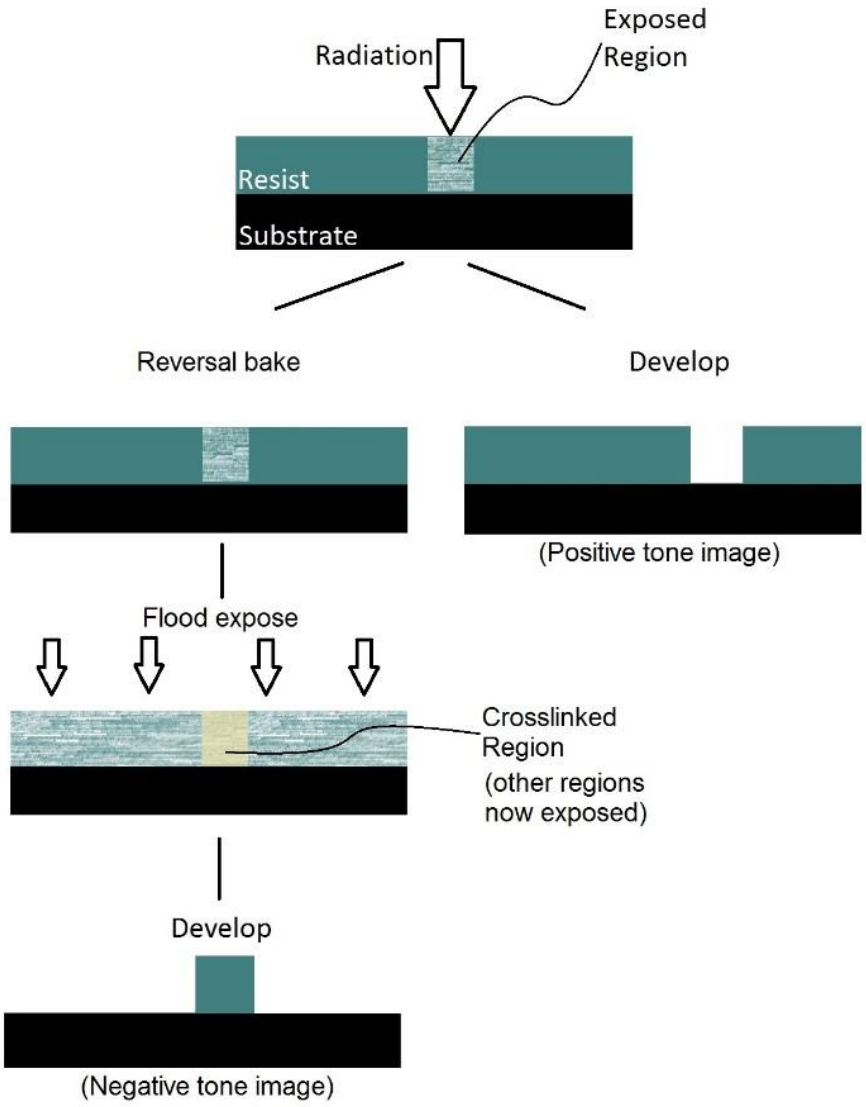

Figure 1.8: Extra processing steps for using an IR resist. The extra steps can be left out to yield a positive tone image, or can be included to yield a negative tone image.

Understanding single-tone resists versus IR resists follows from detailed understanding of the processing. Two final illustrations of photolithography step-by-step are below: single-tone resists are processed as in Figure 1.9, and IR resists are processed as in Figure 1.10.

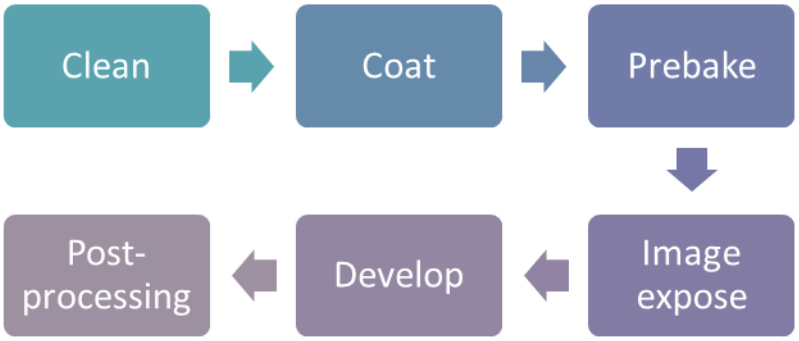

Figure 1.9: Flow chart detailing the processing steps for single-tone resists.

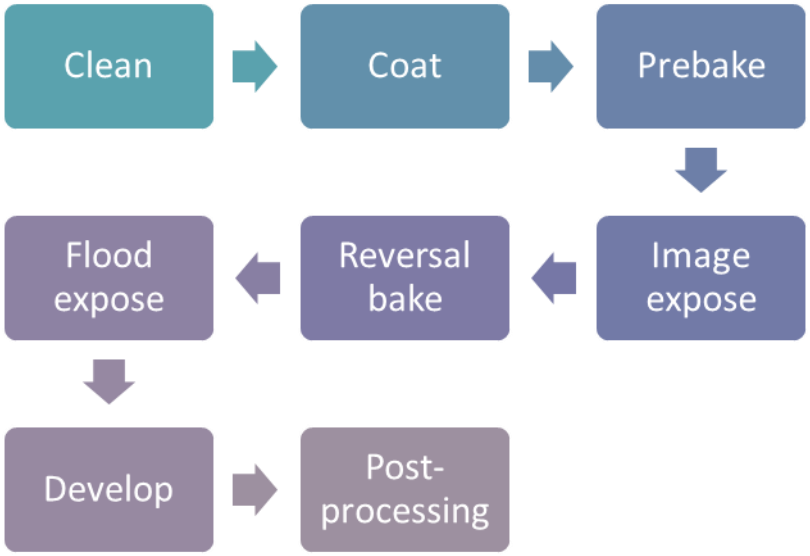

Figure 1.10: Flow chart detailing the processing steps for image-reversal (IR) resists.

1.1.2 Post-processing: Sputtering and Device Creation

Post-processing is the final step toward creating a working device. Once a pattern has been created and developed with the resist, sputtering is used to create the final pattern out of a metallic conductor. Sputtering is a method of thin-film material

deposition in which a target is bombarded with energetic particles and subsequently ejects atoms onto the surface of a sample.[11] This is as simple as creating an oxygen or argon plasma in the environment of the target, for which sputtering equipment is designed. The target is placed in a chamber filled with the desired gas and a voltage ionizes the gas, creating a plasma. When particles from the plasma strike the target, atoms of the target material are ejected "like the shower of sand when a golf ball lands in the bunker."[11] The shower of ejected particles then settle on the interior of the chamber, including any samples which were placed inside. A sputtering chamber can be seen in Figure 1.11.

Figure 1.11: A sputtering chamber filled with an oxygen plasma (the light purple glow is the plasma). This chamber is being used to plasma-clean a sample, but was originally designed to sputter.

Typical targets used are titanium, aluminum, chromium, and nickel. Sputtering can be used to create layers of these metals on the order of 100 nm thick.[11] Sputtering after conducting photolithography with a sample creates two distinct regions of metal on the sample: one which is adhered directly to the substrate (where no resist remained after developing) and one which sits on top of a layer of resist. Upon washing or cleaning, the metal which sat atop the resist layer would be removed. This technique, called lift off, leaves a pattern of only the metal which was directly adhered to the substrate.[1] A simple illustration of this method can be seen in Figure 1.12.

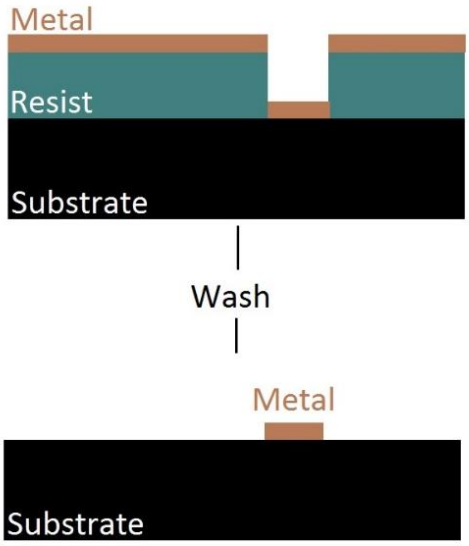

Figure 1.12: A simplified illustration of post-processing, in which a final pattern is created out of metal. This technique is called lift off.

Several methods were used to remove the unwanted regions of metal from the substrate. These methods are detailed in Table 2.

Cleaning method	Process	Notes
Acetone wash	Submerge sample in acetone and agitate	Often requires finishing with a laboratory wipe to remove excess metal
Mechanical exfoliation	Press scotch tape firmly onto sample and tear off in a swift motion	Imprecise and usually requires another cleaning method before or after
Plasma clean	Use a plasma-etching machine to clean the sample with an oxygen or argon plasma	Precise, uniform

Table 2: Methods of cleaning as part of post-processing.

AZ 5214E (the IR resist) was the first choice for samples which would receive this post-processing, as its negative wall profile was ideal for lifting off patterns.[10] Recalling from the introduction, negative resists tend to have an undercut wall profile. Conducting lift off with each type of wall profile is illustrated below in Figure 1.13.

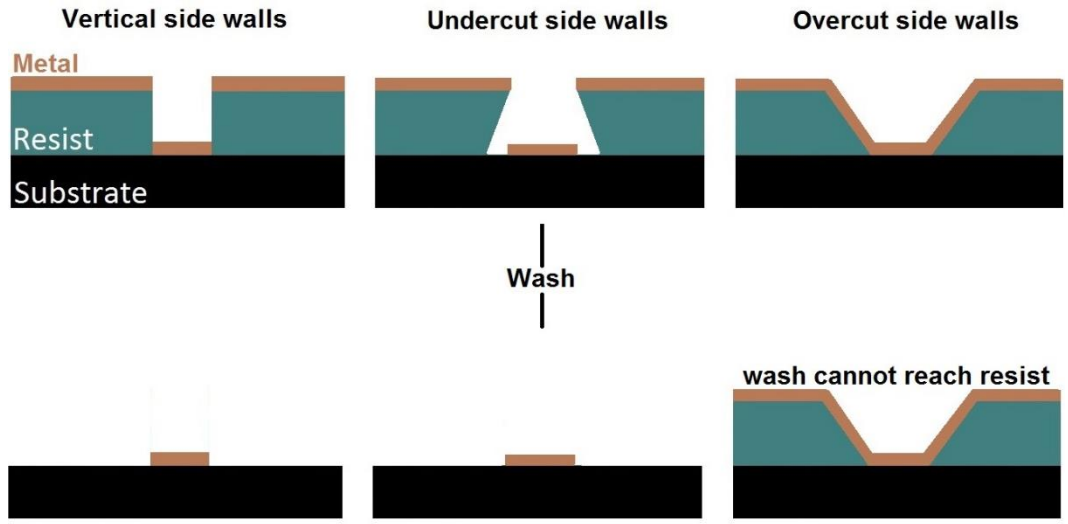

Figure 1.13: Results of lift-off with each type of wall profile

Keeping in mind that photolithography is more likely to yield overcut or undercut side walls than vertical side walls, the choice between the two for the lift-off method is clear. The cleaning method used to remove resist after sputtering is unlikely to reach any of the remaining resist through overcut side walls, but undercut side walls provide easy access to washing the resist away.

After lift off, a sample prober was used to measure the resistance of each set of fingers. A high resistance (on the order of 1 kΩ) indicated cleanly separated and uniform fingers; in theory, if the fingers were perfectly separated, then the resistance between the pads would be infinite. In practice, the finger systems have imperfections, but good-quality regions will yield higher resistances (and stronger electric fields). A finished sample in the sample prober can be seen in Figure 1.15 and Figure 1.14.

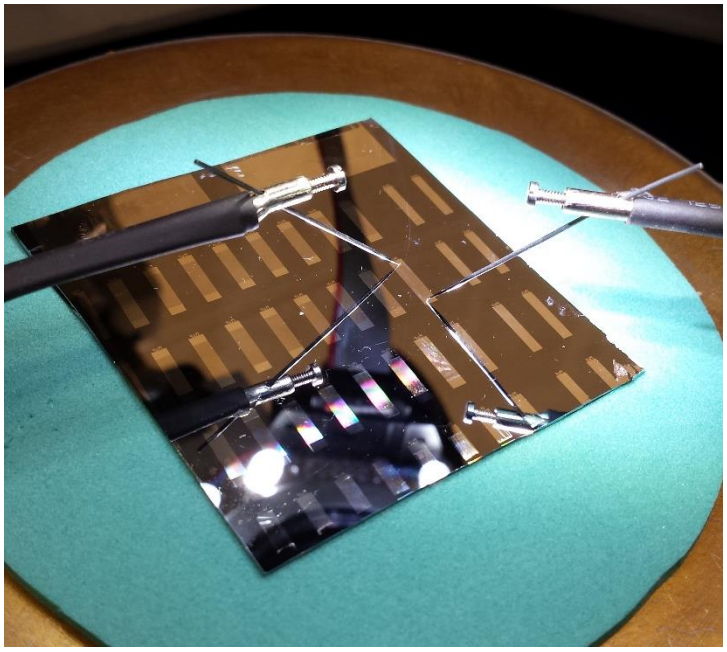

Figure 1.14: (left) A sample with multiple rows of 4 μm interdigitated fingers. A sample prober was used to measure the resistance of each set of fingers.

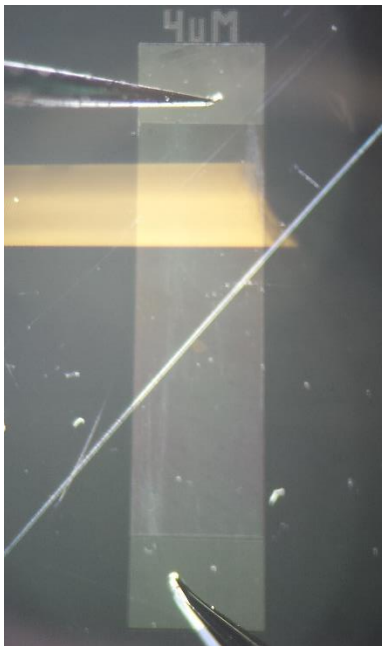

Figure 1.15: (right) One set of 4 μm interdigitated fingers, with the sample prober tips visible.

The next step to creating a usable device is creating leads to the metallic interdigitated fingers. Wires were attached to the pads which connect to the fingers using a conductive epoxy. Leads to the device enable application of an electric bias. A sample with leads attached can be seen in Figure 1.16.

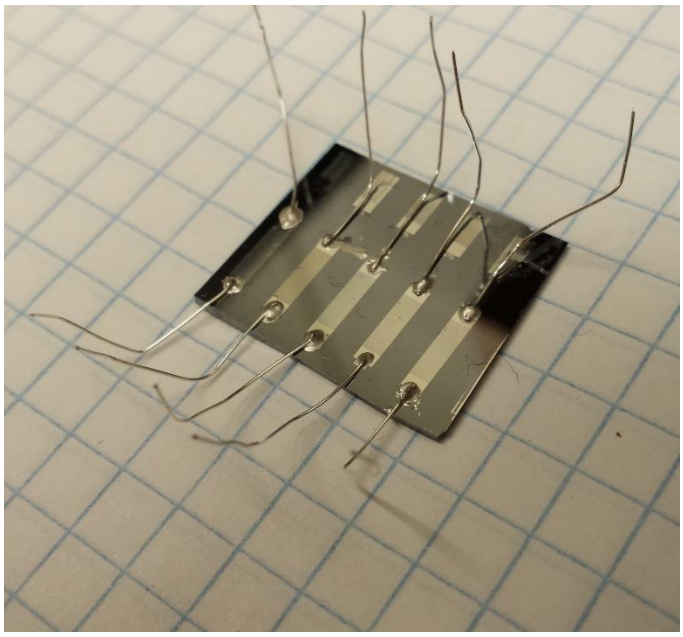

Figure 1.16: A sample of titanium interdigitated fingers with leads attached (wires are adhered to the sample with a conductive epoxy).

1.2 Rig Design and 3-D Printing

Contact printing requires great care in sample handling, as the contact between the mask and the sample can lead to damage to both the resist layer and the mask. For the professionally-printed mask (Figure 1.4), a custom rig was designed to carefully hold the mask in place during exposure. A sample could be inserted or removed below the mask without having to remove the mask, which limited handling of the mask and minimized the possibility of contamination. The rig consisted of a number of aluminum posts and clamps, simple motion stages, the mask holder, and LEDs, and can be seen in Figure 1.17: The contact-printing rig, which included a 3-D-printed mask holder.

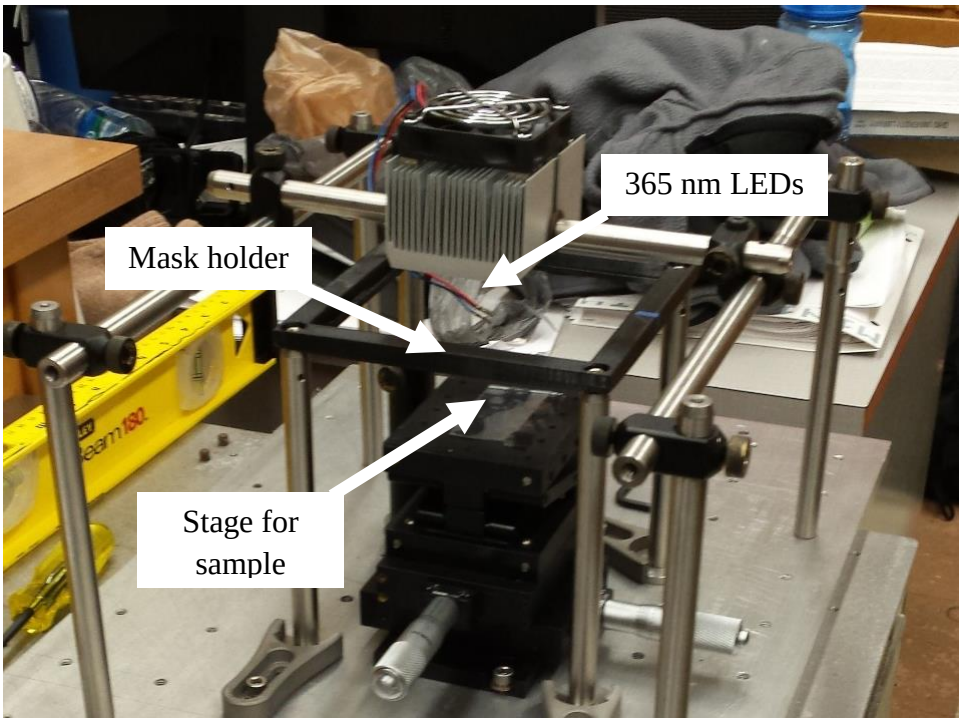

Figure 1.17: The contact-printing rig, which included a 3-D-printed mask holder.

Figure 1.18 is an image of the 3-D design of the mask holder used in the Figure 1.17 setup.

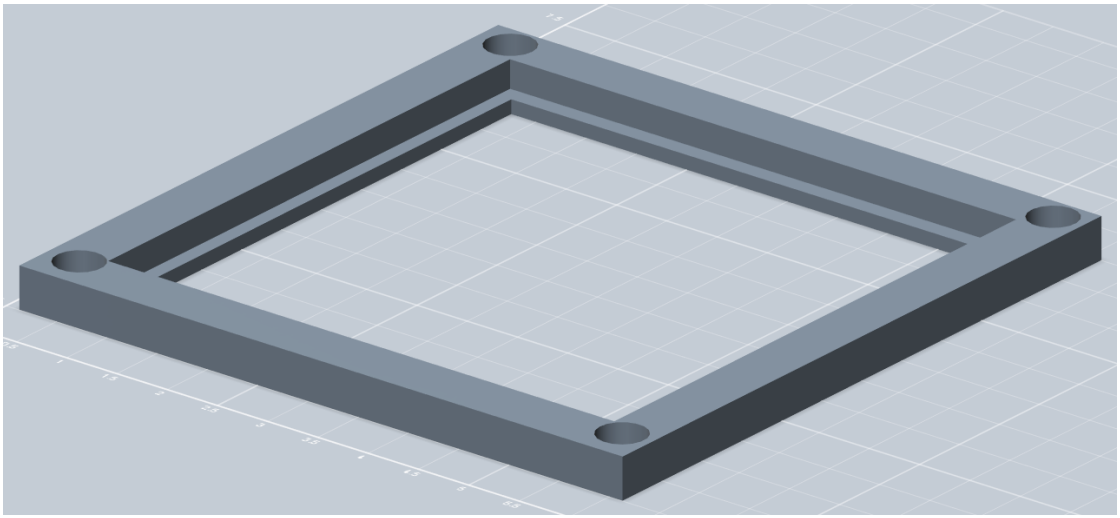

Figure 1.18: The 3D design file which was used to create the mask holder shown in the previous figure. Photo credit: Chris Wolfe.

The mask holder seen in Figure 1.17 and Figure 1.18 was printed using a MakerBot Replicator 2 3D printer. It was designed by Chris Wolfe, an undergraduate at Ohio University, using MakerWare, a free 3D design software which can create MakerBot-compatible 3D object files. Early attempts at printing objects using this software and the MakerBot were used to determine the limitations of the printer and of the polylactic acid (PLA), a biodegradable plastic which is the choice material for the 3D printer.

With the mask holder held in place on the aluminum posts, a sample could be brought into gentle contact with the photomask by placing it on the stage below and slowly raising the stage until the sample was flush with the photomask. A small piece of rubber was placed on the stage underneath the sample to prevent slipping, and to promote the best contact between the sample and the photomask.

Once the sample and photomask were flush, the sample was then exposed by turning on the LEDs. The LEDs were mounted on a heat sink with a small fan to prevent overheating, and leads from a power supply allowed the LEDs to be turned on and off quickly. With the IR resist, the flood expose was performed identically except for the photomask, which was left out of the mask holder so the entire surface of the sample could be exposed.

1.3 Experimenting with Quantum Dots

Finished devices can be used to investigate various nanostructures and their properties. Quantum dots (QDs) are readily accessible and were thusly used for the first attempts at experimenting with such devices.

1.3.1 Simple Quantum Dot Behavior

The earliest experiment conducted with quantum dots was a simple study on their behavior in an applied electric field. An interdigitated-finger device was used in this experiment, with titanium fingers and wire leads to the fingers, which were created as described in section 1.1.2.

Two trials were conducted to determine the behavior of unmodified/unexposed QDs under laser illumination. First, 1-2 mL of QDs suspended in toluene were dropped onto the surface of the fingers. This was done with no bias applied across the fingers, and the QDs were deposited in red light to prevent unwanted illumination. In the second trial, a 2.5 V bias was applied across the interdigitated fingers. The QDs were deposited with the bias applied, again in red light.

The toluene was allowed to dry in both trials; in the second trial (with the 2.5 V bias), the bias continued to be applied until the toluene had fully dried. Once the toluene dried, the QDs were fixed in place. The sample was then placed under a microscope, and a laser was shined on the fingers to excite the QDs. The QDs then fluoresced, becoming easily visible through the microscope. The results were determined qualitatively using this technique, and are presented in Section 2.2.

2 Results

2.1 Photolithography: Samples and Devices

One of the early parameters with which optimization was explored was the thickness of the resist film. Processing for spin-coating was tested with ma-N 2410 as described in section 1.1.1. The results of this optimization can be seen in the following figures. The unaltered resist (the resist which was not diluted with a thinner) was spun at 3000 rpm and provided results as in Figure 2.1

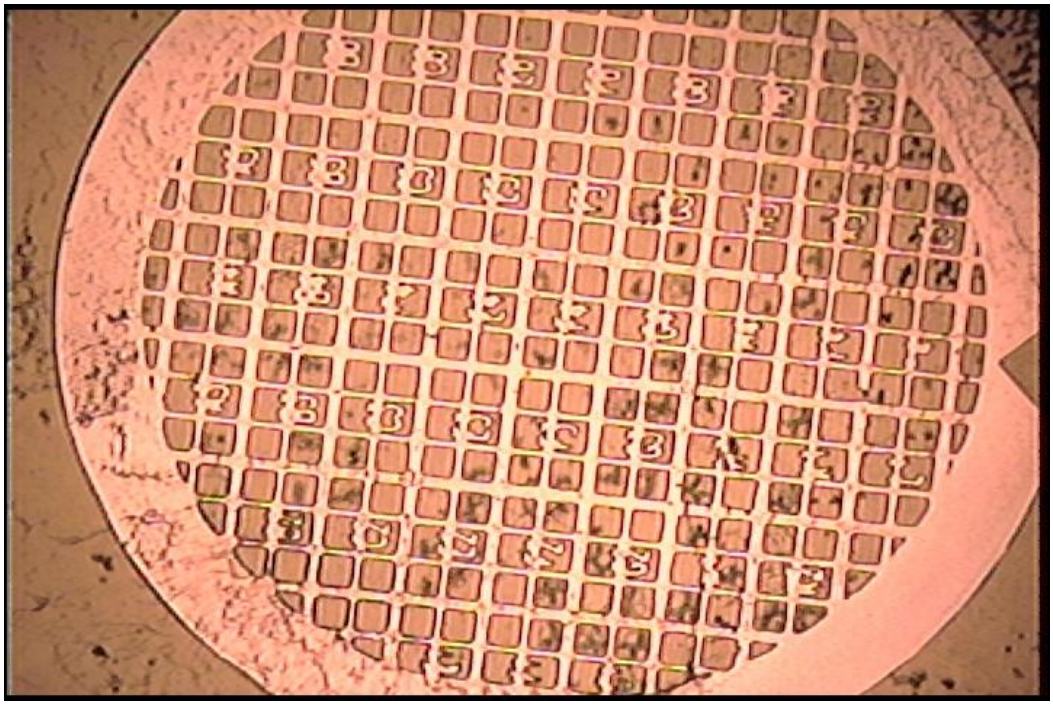

Figure 2.1: A sample produced with the TEM grid mask, an unaltered negative resist, and spin-coating at 3000 rpm.

The resist which was diluted with a resist thinner produced results as seen in Figure 2.2 when spun at 1000 rpm, and Figure 2.3 when spun at 3000 rpm. As can be seen in these figures, each result has imperfections, but the thinned resist was much more likely to overdevelop, which threatened its ability to create useful devices in the end.

The unaltered resist was much more resilient in the developer and thus provided more consistent results.

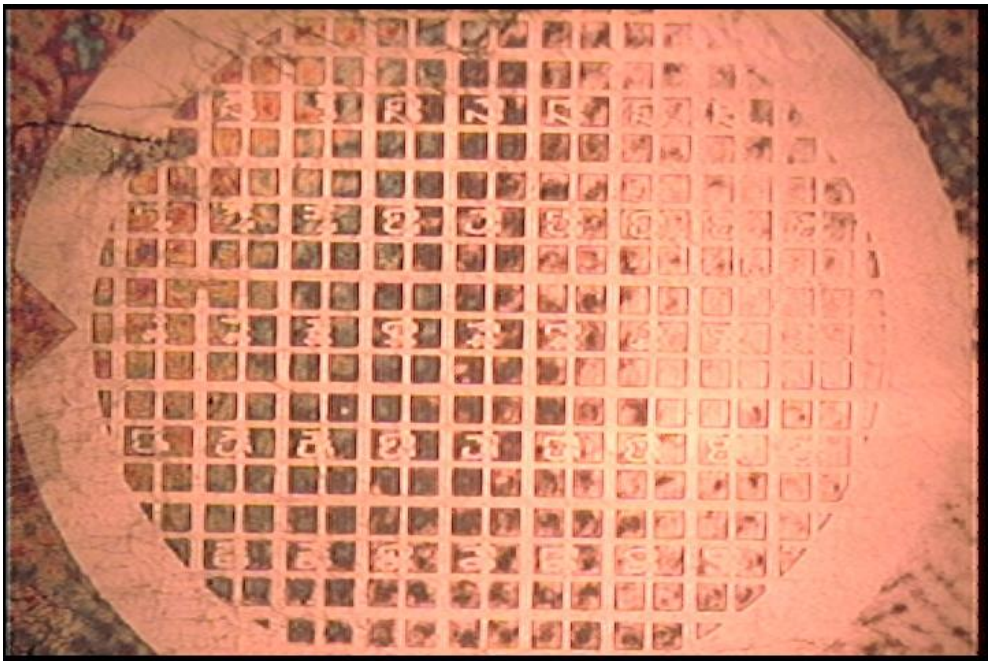

Figure 2.2: A sample produced with the TEM grid mask, a thinned negative resist, and spin-coating at 1000 rpm. The thinned resist's tendency to overdevelop is apparent on the right-hand side of this image.

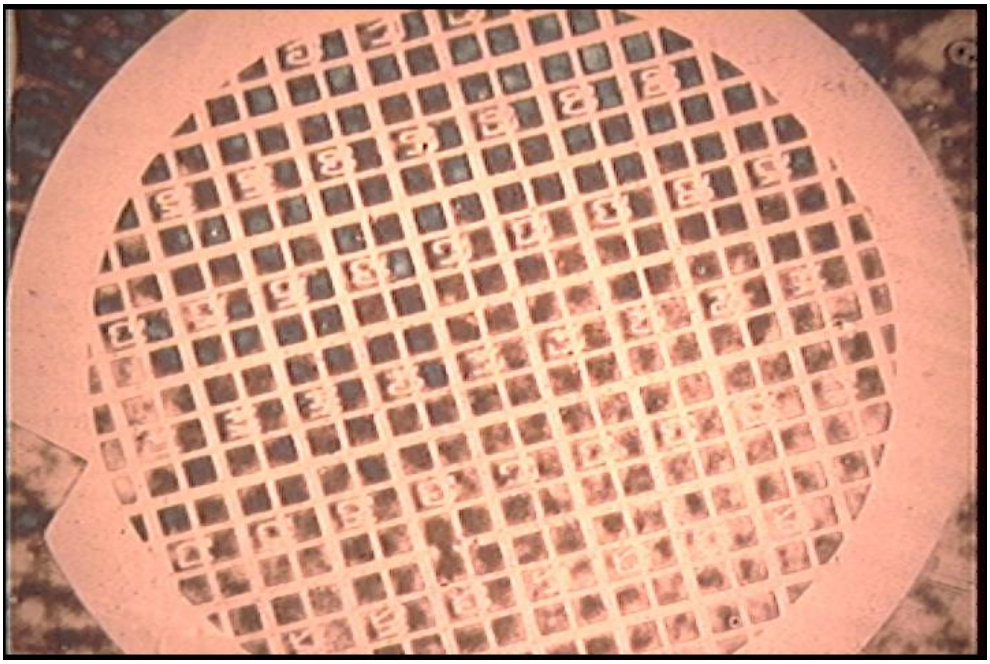

Figure 2.3 A sample produced with the TEM grid mask, a thinned negative resist, and spin-coating at 3000 rpm.

Early attempts at using the image-reversal (IR) resist AZ 5214E were wholly unsuccessful. It was determined that the key factor in processing was the temperature of the reversal bake (as described in section 1.1.1). The reversal bake was sensitive to 1 degree Celsius, and even small difference in temperature could lead to undesirable results. Comparing Figure 2.4 (for which the reversal bake was 110°C) and Figure 2.5 (for which the reversal bake was 111°C), it is clearly seen that the 111°C reversal bake yielded better features.

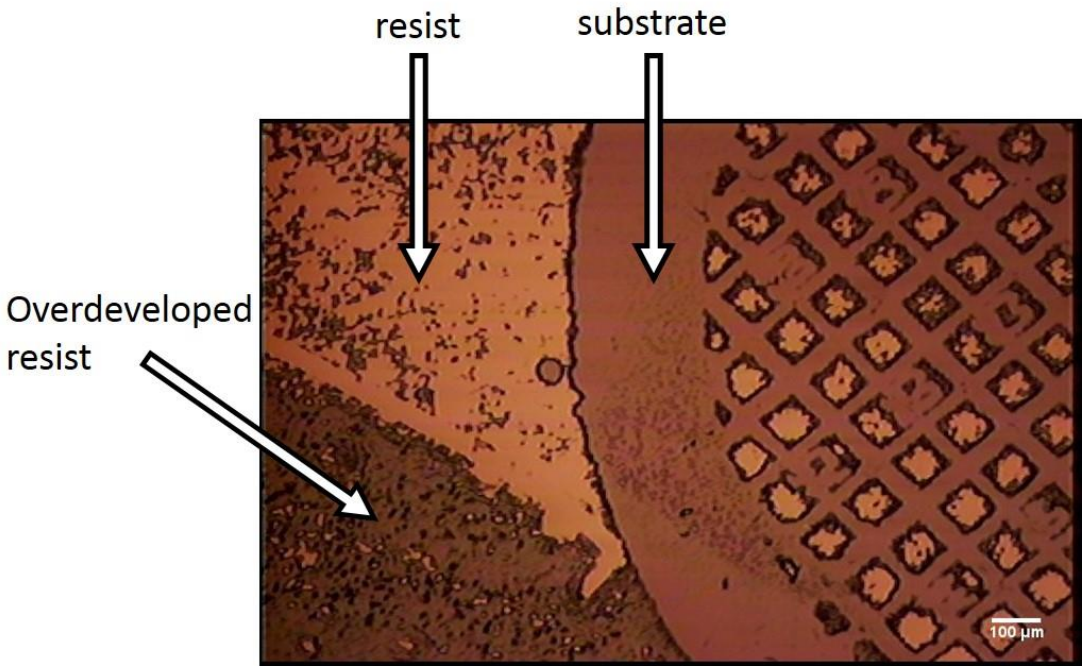

Figure 2.4: A sample created using the TEM grid mask (Figure 1.3) and IR resist. This is before processing parameters were well-optimized. Reversal bake temperature was 110°C.

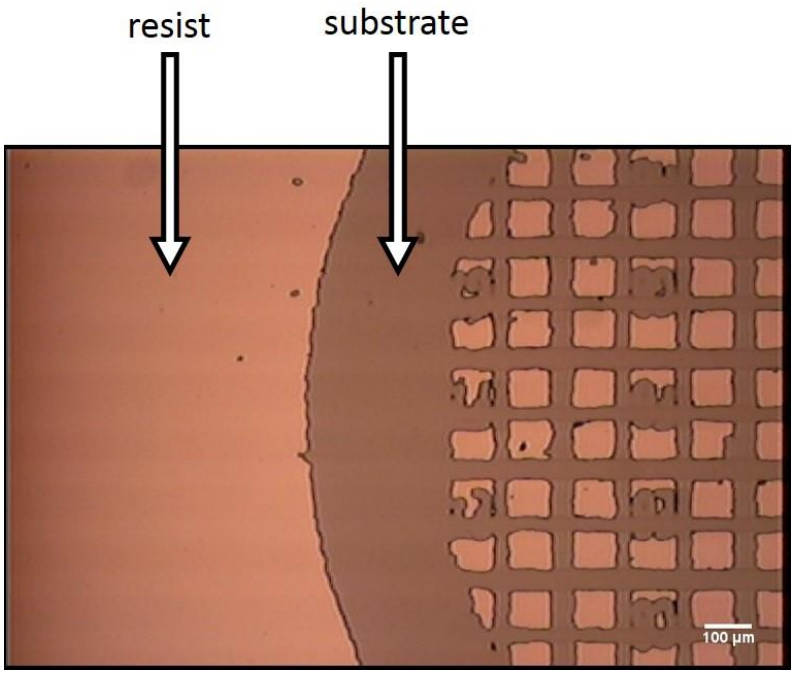

Figure 2.5: Another sample created using the TEM grid mask (Figure 1.3) and IR resist. This was after processing parameters were optimized. Reversal bake temperature was 111°C.

Once the reversal bake was optimized, the IR resist was then used with the professionally-printed photomask, and yielded results as in Figure 2.6.

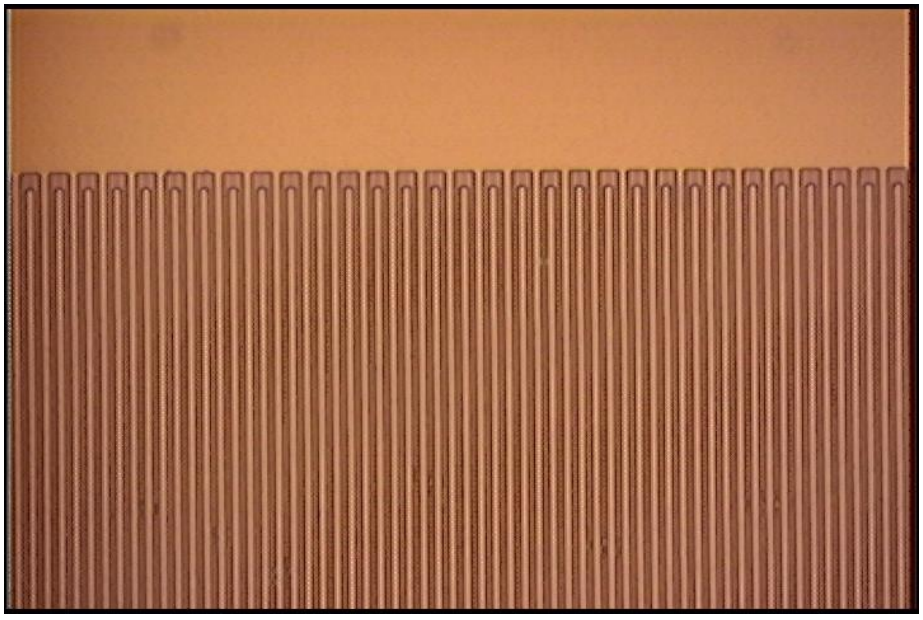

Figure 2.6: A region of interdigitated fingers created with the IR resist, after processing the IR resist was well-optimized.

The motivation for using photolithography as a microfabrication included its relative simplicity, and the possibility for group members with diverse needs to learn it quickly and create a wide variety of devices. As such, the refining of the procedure for photolithography included the creation of a document which could be displayed in the laboratory. This document is a step-by-step guide to conducting photolithography with the materials and equipment which are available within the laboratory, and is intended to be comprehensive enough that a researcher who has not previously created devices using photolithography can do so from start to finish with this resource. The document is included in Appendix A.

2.2 Quantum Dot Responses

Preliminary results of the experiment detailed in section 1.3.1 showed that with no bias applied during QD deposition, QDs did not preferentially arrange on the interdigitated fingers. With a bias applied, QDs clustered on the interdigitated fingers which were connected to the lower-voltage electrode. This effect can be seen from the striped pattern in Figure 2.7, which shows the QDs luminescing in laser light. This clustering effect is also apparent in Figure 2.8, which shows the QDs preferentially arranged in both laser light and white light.

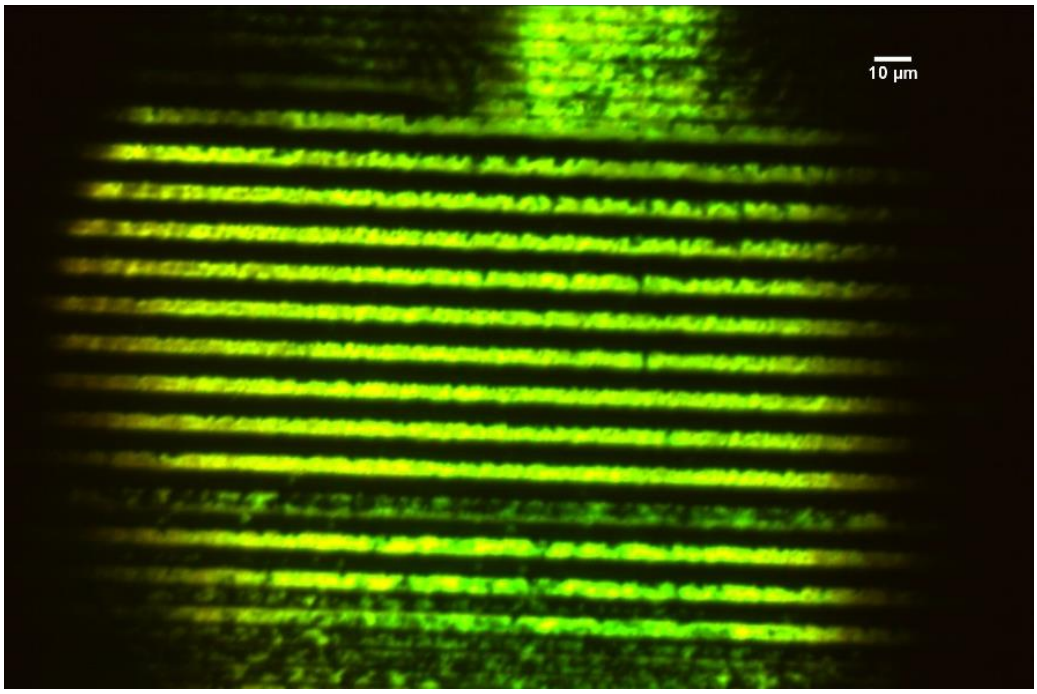

Figure 2.7: Results of the simple QD experiment, in which QDs clustered on the lower-voltage interdigitated fingers. This preferential clustering created the striped pattern as seen above. This picture was taken with only laser illumination on the sample.

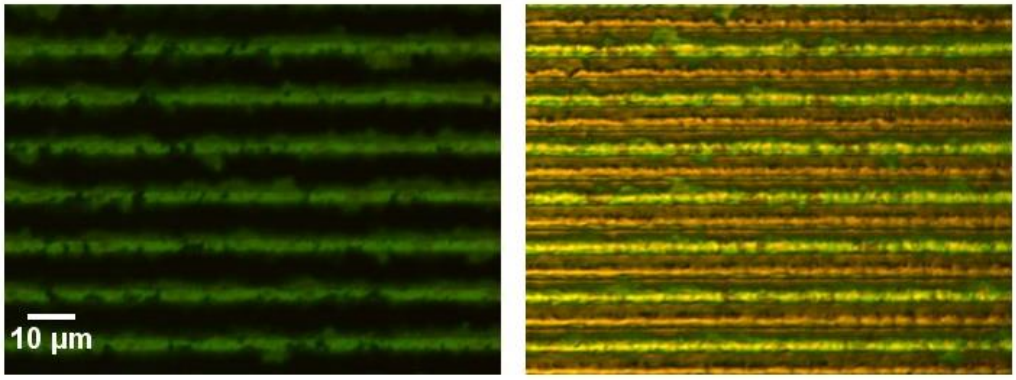

Figure 2.8: (left) Results of the simple QD experiment in only laser illumination, showing the luminescence of the QDs clustered on alternating fingers. (right) Results shown in white light and laser illumination, showing the fingers more clearly. (Photo credit: Eric Stinaff)

In Figure 2.7, it is notable that not all of the sample has the alternating pattern of clustered QDs, likely due to imperfections on the sample. For example, areas where the interdigitated fingers are not perfectly isolated from each other or are otherwise

damaged would not create clean patterned electric fields. Figure 2.9 shows the region in the top of Figure 2.7, where the striped pattern is not apparent.

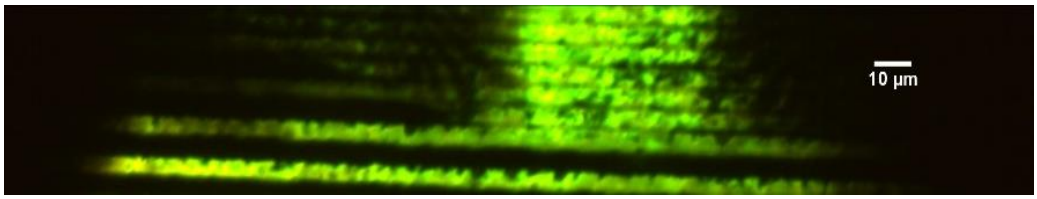

Figure 2.9: A portion of Figure 2.7; here, the QDs did not preferentially arrange on alternating fingers, likely due to imperfections on the sample.

In this region, the QDs are not preferentially arranged on the fingers, which makes the alternating pattern easier to recognize on the other fingers and indicates that the fingers in that area were probably damaged.

3 Discussion

The optimization of photolithography with the limited equipment which was available in this laboratory resulted in the ability to create microscale devices on-site, which was not possible before this research was conducted. This can affect the capabilities of diverse research groups, as a wide variety of patterns and devices can now be designed and fabricated using similar methods and equipment.

The inspiration for designing microscale device features was given by a simple identity of electricity and magnetism which gives the electric field between two parallel plates. If V is the voltage difference across the plates and d is the separation between the plates, the electric field E is given by:[12]

$$E = \frac{V}{d}$$

This relationship indicates that a large electric field can be obtained by using a large V or a small d. The devices created in this research provided a distance on the order of 1 μm (such as in the interdigitated-finger design), which meant a voltage of only 1 V could produce an electric field as large as 10 kV/cm. As stated in the introduction, this is large enough to observe the Stark Effect. This suggests the possibility of exploring a wide variety of energetic phenomena through novel device design.

The simple experiment described in section 1.3.1 was intended to be a stepping stone for approaching more complex investigation. Before conducting that experiment, it was assumed that the QDs as they came from the manufacturer were charge-neutral; observing the preferential clustering of the QDs proved that assumption to be incorrect. Though not an intended result of this research, the behavior of QDs within

the applied electric fields could provide a method of preferential deposition. Photolithography can continue to be used as a way of designing patterned electric fields, and this preferential deposition could be useful for a variety of applications including the design of microelectronics or new display technologies.

The behavior also provides an obstacle. In order to move forward with experimentation, charge-neutral quantum dots are required. Determining the manner in which the QDs are becoming charged is necessary. It is possible that the QDs are gaining or losing electrons to the toluene in which they are stored; this possibility can be explored by moving the QDs into other solutions and then looking for similar behavior.

4 Looking Forward

Many paths are present for continuing this research. Realistically, every step of photolithography can still be improved, either through designing new methods or by obtaining new equipment. For example, designing a rig with which sample alignment with the photomask could be conducted under a microscope would allow for the creation of more complex patterns and devices; with this capability, layered devices could be designed and fabricated. Obtaining access to a clean room could improve results by reducing potential sources of sample contamination.

More autonomous methods would likely improve the consistency of results. As is, much of the processing detailed in this thesis requires a so-called "magic touch," or an intuition for sample handling which can only be refined through practice. This is especially apparent in developing a sample; the time needed for developing appears to vary from sample to sample, and requires a keen eye and quick movement and reaction from the researcher. Under-developing a sample is easy to fix by simply replacing the sample in the developer, but over-developing is just as common and requires cleaning the sample and beginning the entire process anew.

The method for preferential deposition which was established through the experimentation described in this thesis is also yet to be rigorously tested. The experiment could be conducted with different sizes of QDs (only one size was used to obtain these results) to establish whether or not the QD behavior has any size dependence. Additionally, designing new devices which will produce different

patterns of electric fields will allow the consistency and versatility of the effect to be tested.

Once the charging mechanism for the QDs is isolated as suggested in chapter 3, experimentation can continue. Two early ideas have yet to be realized: observing the Stark Effect (as mentioned several times), and conducting an experiment on the torque of a QD. In order to observe the Stark Effect (a shift in energy levels caused by an electric field), the QDs will be deposited on a sample and fixed in place. If still in toluene, for example, the toluene will simply be allowed to dry, inhibiting further movement of the QDs. Once fixed, an electric field will be applied and spectroscopy will be used to identify any shifts in the energy levels.

In order to learn more about the mechanical motion of quantum dots, an experiment on torque will be conducted. The QDs will be deposited on a sample, but the evaporation of the solution in which they are suspended will be discouraged through careful design of the environment (for example, by depositing the QDs in a cold room). Then, before the solution dries, the QDs will be illuminated with a laser, inducing dipoles in the particles. Simultaneously, an electric field will be applied.

One possible result of this experiment is that the QDs will experience a torque which will tend to align each induced dipole with the electric field direction. This is one type of behavior that we could observe, and could be identified by looking for an increase in linearly polarized emission from the QD ensemble. Another effect that could be observed is physical ordering of the QDs as a result of the simultaneous

application of an electric field and incident light. The physical ordering could be identified by noting patterns in the luminescence of the QD ensemble.

Further experimentation with nanostructures can be carried out as different devices are designed and fabricated, and as new nanostructures are obtained.

Appendix: Photolithography and You: A Step-by-Step Guide

The following is a document which was created for display in the laboratory. It is meant to serve as a detailed guide to photolithography, to be used by anyone wishing to fabricate a device using the method.

Photolithography and You: A Step-by-Step Guide

1. Clean substrate
    a. Wipe with acetone and a Kimwipe
    b. Wipe with methanol and a Kimwipe
    c. Place sample on spin-coater and puddle acetone on surface for 30s
    d. Spin for 30s at 3000 rpm, squirt with methanol during spin
    e. *Glass substrate only: dry-bake at 180°C for 3 min (dries out the glass and improves resist adhesion)*
2. Coat substrate with resist
    a. *It is recommended that the remainder of processing be conducted with the lights off*
    b. With the sample on the spin-coater, create a puddle of a few mL of resist on the surface (cover most of the surface)
    c. Spin for 30s at 3000 rpm
3. Prebake / Soft bake
    a. Place sample on hot plate
    b. Bake for 1 min at 100°C
4. Image expose
    a. The mechanics of this step will vary based on current rig setup
    b. Bring sample into gentle contact with the mask

c. Expose entire area of sample for 5–7 seconds

5. **IR resist only: reversal bake**
    a. *The reversal bake is very sensitive—temperature is sensitive to 1°C*
    b. On hot plate, 111°C for 55s
6. **IR resist only: flood expose**
    a. Expose entire sample (do not use the mask) for 10 mins
    b. Rotate the sample 90° every 2.5 mins (prevents nonuniformities based on imperfect LEDs)
7. Develop
    a. Puddle or submerge:
    b. Puddle
        i. Place sample on spin-coater, drop a few mL of developer on (enough to completely cover the surface)
        ii. Wait 30s, then spin-dry (3000 rpm for 30s)
        iii. Repeat as needed until pattern is fully developed
        iv. Optional: rinse with DI water and dry (if developer sticks around on the sample)
    c. Submerge
        i. Place sample in petri dish with enough developer to completely cover the sample
        ii. Gently agitate the dish (hold it and make the developer “swish” around over the sample)
        iii. Developing can take anywhere from 30s-2 mins with this method: takes practice
        iv. If overdeveloping is a concern, do in 20-30 second chunks until sample is fully developed

Learn more about photolithography with these recommended references:

Thompson, L.F., Willson, C.G., & Bowden, M. J. (1994). *Introduction to Microlithography* (2nd ed.). Washington, D.C.: American Chemical Society.

- Great introduction, good resource if you're new to lithography
- Lots of detail on the physics & chemistry
- Dr. Kordesch has a copy

Madou, M.J. (2002). *Fundamentals of Microfabrication: The Science of Miniaturization* (2nd ed.). Boca Raton: CRC Press.

- Chapter 1 gives an exhaustive introduction to lithography
- Can be obtained through OhioLINK (library)

Nonogaki, S., Ueno, T., & Ito, T. (1998). *Microlithography Fundamentals in Semiconductor Devices and Fabrication Technology*. New York: Marcel Dekker. Retrieved November 25, 2014, from (permalink) http://www.library.ohiou.edu.proxy.library.ohiou.edu/ezpauth/redir/all_weak.php?http://search.ebscohost.com.proxy.library.ohiou.edu/login.aspx?direct=true&db=nlebk&AN=34973&site=ehost-live&scope=site

- Can read ebook through OHIO library website

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