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A Maskless Photolithography Apparatus for the Microfabrication of Electrical Leads

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A MASKLESS PHOTOLITHOGRAPHY APPARATUS FOR THE MICROFABRICATION OF ELECTRICAL LEADS

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Abstract

Graphene is a new and exciting, two-dimensional material. Particularly interesting are the electrical features of graphene. The small size of graphene used in this experiment (on the scale of microns) presents the need for small electrical leads. Photolithography can be used to make appropriately sized leads by depositing metal onto substrates in specific patterns. The technique uses light to transfer geometric patterns onto a light sensitive photoresist on the surface of a substrate. We have built a low cost, maskless photolithography apparatus assembled from a computer, a consumer grade projector, and a microscope. With multiple exposures, we can make features ranging from approximately 1 μm to 785 μm. The 1 μm feature size is near the theoretical minimum for the wavelength of blue light used, and will be more than sufficient for contacting the flakes of graphene, which average 50 μm in size.

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1. INTRODUCTION

Lithography is a useful technique for making small structures or patterns, on the scale of microns. Photolithography makes use of a light sensitive material, photoresist, to make the patterns. Depositing metal onto the patterned photoresist makes the structures permanent. In this experiment, the technique of photolithography is used to make electrical leads to study graphene, the first truly two-dimensional material ever created.

1.1 Maskless Photolithography

In photolithography, masks can be used to make shadows and thus define a pattern in the photoresist. Another option is to project a pattern directly from a light source. The latter is known as maskless photolithography. The technique is mainly used in microfabrication, the design of miniature structures. Traditional methods for building macroscopic structures do not work on such a small scale. Photolithography is also used as part of the process for making integrated circuits.

A downside to using photolithography in an academic setting is the cost. A state of the art photolithography apparatus costs up to 30 million dollars [1]. The technique of spin coating the photoresist onto the sample adds to the cost of photolithography. A spin coat machine costs a few thousand dollars [2].

In this experiment, we built a maskless photolithography apparatus for a total cost of a few thousand dollars. This price does not include the microscope and computer, as most research labs have them at their disposal. A common food processor and a projector contributed to the cost. The food processor, with a few modifications, replaced the spin coat machine, and the projector worked with the microscope and computer to replace the photolithography apparatus. The photolithography apparatus in this experiment is maskless because the computer makes the patterns of light.

This experiment aims to show that a maskless photolithography apparatus built with relatively inexpensive parts can still make small patterns. This experiment achieved a smallest feature size of ~1 μm, which is near the theoretical minimum. The results of the experiment also show that this maskless photolithography apparatus can make complex patterns that vary in size.

The complex patterns in this experiment were made to be electrical leads to test electrical properties of a sample of graphene. These leads must attach to a sample that is ~50 μm across. The small leads can connect to macroscopic leads, which can be connected to an external electrical circuit.

1.2 Graphene

Graphene is a material composed of a single layer of carbon atoms. This means that graphene is, for all intents and purposes, a two-dimensional material [3]. Prior to the discovery of graphene, scientists studied carbon in three dimensions (graphite), one dimension (nanotubes), and zero dimensions (buckyballs), but never as a two-dimensional material. Buckyballs are considered zero dimensional because they do not extend in any planar direction. While graphene's two-dimensional nature is in itself exciting, scientists think another feature of graphene, its resistance, can potentially lay the foundation for new technology [4].

The resistance of bulk materials is typically modeled as

$$R = \rho \frac{L}{A} \tag{1}$$

where ρ is the resistivity of graphene, L is the length of the sample, and A is the cross sectional area (Figure 1.1). Since graphene is two-dimensional, $A \approx 0$. Equation 1 suggests that resistance should approach infinity for graphene, but experimental tests show otherwise [3]. A thin material that still has electrical conductivity is desirable for small circuits, and others are still thinking of great applications for graphene. These applications include use in solar cells, single-molecule gas detection, distillation, and transistors [3, 5, 6].

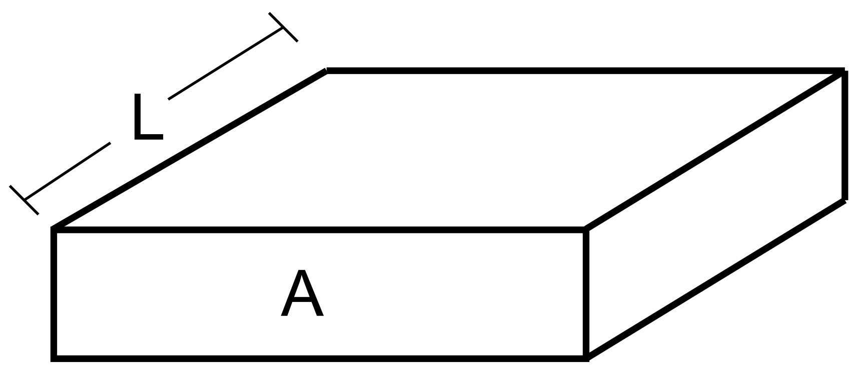

Figure 1.1: A schematic of a conducting material of length, L, and cross sectional area, A. When a current passes through the cross sectional area, then the resistance of the material is given by Equation 1. A sample of graphene has $A \approx 0$, which should make the resistance infinite. Studies have shown that R does not approach infinity for graphene, which makes it interesting to study.

2. THEORY

2.1 Feature Size

There are limitations to the size of features that can be made using photolithography. These limitations depend on many different factors of the experiment. The wavelength of light, λ, affects the feature size. A spectrum of blue light (Figure 2.1a) exposes the photoresist in this experiment. The color of light is described by PowerPoint's Red/Green/Blue scale. Standard blue is 0/0/255. Darker shades of blue used in the experiment range from 0/0/130 to 0/0/200 and have a lower intensity than the standard blue (Figure 2.1c). As shown in Figure 2.1, the maximum intensity of blue light coincides with the wavelength of sensitivity for the photoresist.

Another factor that limits the feature size is the numerical aperture (NA) of the microscope. The numerical aperture describes the resolving power of the microscope. It depends on the angle at which light leaves the microscope. In most cases, the NA is less than 1. A technique called immersion can increase the NA to values greater than 1, but that technique is not explored here. Each magnification on the microscope has its NA printed on the outside of the lens. For the 50x magnification used in this experiment, the $\mathrm{NA} = 0.80$. The NA is unitless.

The third factor of the feature size is a dimensionless scaling factor, k_1. This is related to the pitch limit, which refers to the angle at which light leaves the microscope. k_1 also depends on the computer being used, which affects the distance between pixels. In this experiment, $k_1 = 0.61$. These three variables: λ, NA, and k_1, determine the minimum line width, W_{min} that can be printed using photolithography. The relationship is

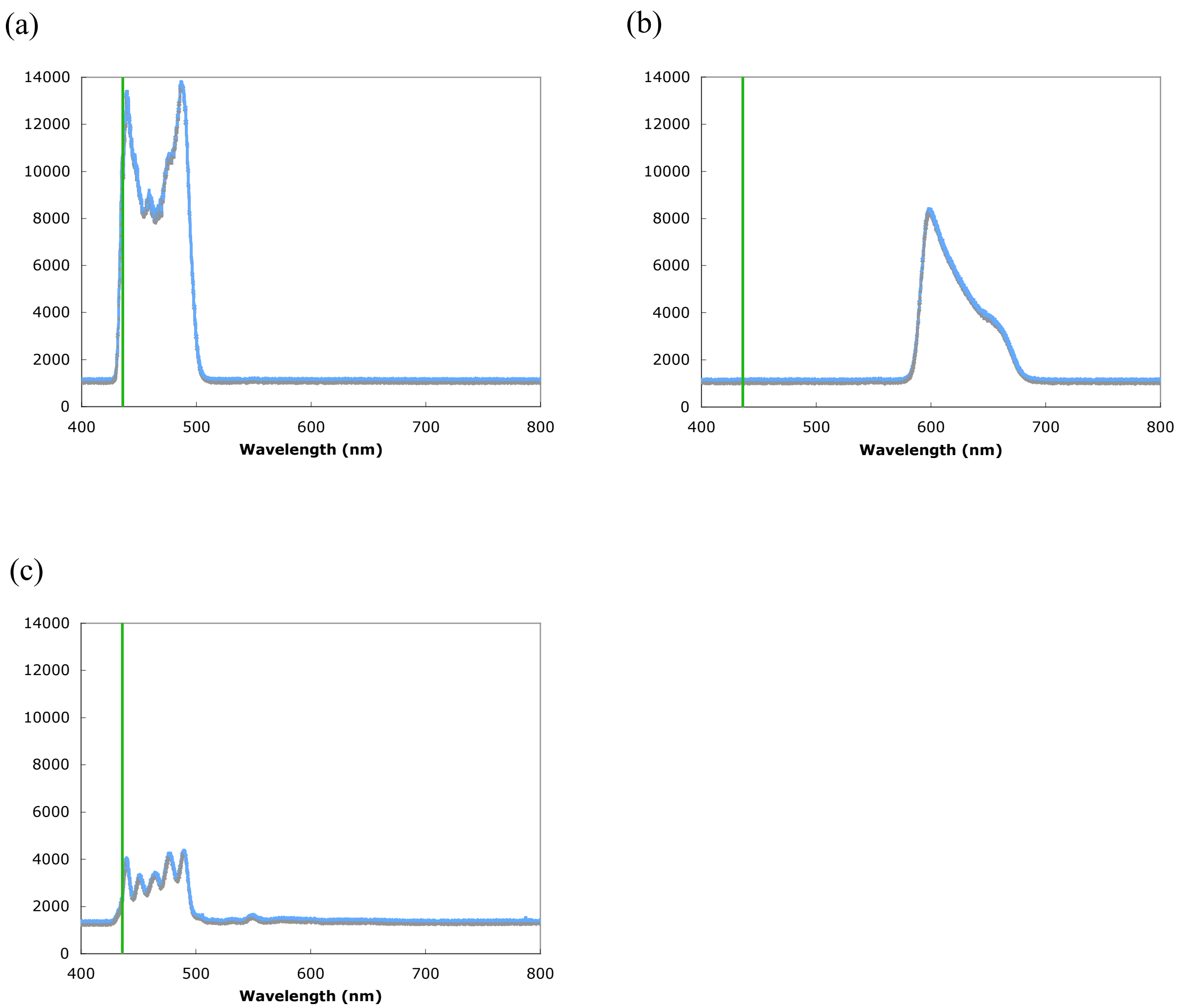

Figure 2.1: Spectra of (a) standard blue (0/0/255), (b) red, and (c) dark blue (0/0/130) lights used in this experiment. The green line (436 nm) represents peak sensitivity of the photoresist. This wavelength coincides with a maximum of intensity for both blue lights and is far from the maximum of red light. The intensity of the dark blue light is much lower than standard blue and can help control overexposure.

given by [7]

$$W_{\min} = k_1\left(\frac{\lambda}{NA}\right). \qquad (1)$$

For the blue light used in this experiment, we assume the average wavelength of $\lambda = 460$ nm. Using Equation 1 and the values above, the theoretical minimum line width for this maskless photolithography apparatus is $W_{\min} \approx 350$ nm. Currently, the record for the smallest feature size is ~50 nm. Brueck, *et al.* used a 193 nm ArF laser and a technique called immersion to achieve this feature size [8]. That technique involves more complex systems than the ones used in this experiment.

2.2 Exposing the Photoresist

As shown in Figure 2.1, the photoresist is sensitive to light with a 436 nm wavelength. The light affects the chemistry of the photoresist and leads to cross linking of the polymer. This makes the photoresist more soluble, which causes it to rinse away in the developer [9].

Although the photoresist is most sensitive to blue light, the white light from common fluorescent lights can still expose the photoresist. Unintentionally exposing the photoresist often has a negative effect. This may result in a pattern with less definition around the edges. At worst, the pattern will be overexposed, which causes the pattern to develop in unwanted places. Using red light can help avoid this problem since it will not expose the photoresist (Figure 2.1b).

Intentionally exposing the photoresist with blue light can also lead to overexposure. When exposing complex patterns, large features and small features tend to develop at different rates. Using darker shades of blue can help guard against overexposure because of the lowered intensity (Figure 2.1c). Larger features usually take a shorter amount of time to expose because they contain more pixels than the lines of the pattern. The pixels can overlap when they reach the photoresist, which may be caused by spherical aberrations of the lens (Figure 2.2). A spherical aberration occurs when the lens focal length varies slightly with respect to distance from the lens center. Light farther from the center of the lens focuses at a point closer to the lens than light passing near the lens center. Each pixel overlaps slightly with its neighbor, increasing the total intensity at each point on large features. Therefore, large areas, with two dimensions of overlap, develop quicker than the lines in the pattern. Since a darker shade of blue lowers the total intensity, we can make large features darker than the small features and expose both for the same amount of time without fear of overexposure.

The design of the pattern can also control overexposure. As the lines of the pattern get closer together, they start to have an effect on each other. The lines in the

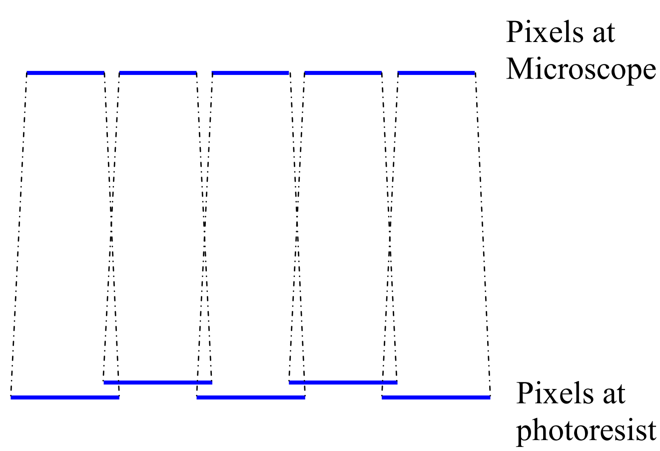

Figure 2.2: As an image exits the microscope, spherical aberrations cause it to be slightly out of focus. This means that pixels will overlap slightly with their neighbors. The places that overlap will have a higher total intensity, which can lead to overexposure. The pixels at photoresist shown here are offset to illustrate the effect more clearly.

center of the pattern are so close that they add intensity to each other. In Figure 2.3a, the pattern leads to overexposure (Figure 2.3c). The pattern in Figure 2.3b also has added intensity near the center. The gap in the center of the pattern counteracts the added intensity and results in the desired cross pattern with small amounts of overexposure (Figure 2.3d). All of these factors influenced the design of the experiment.

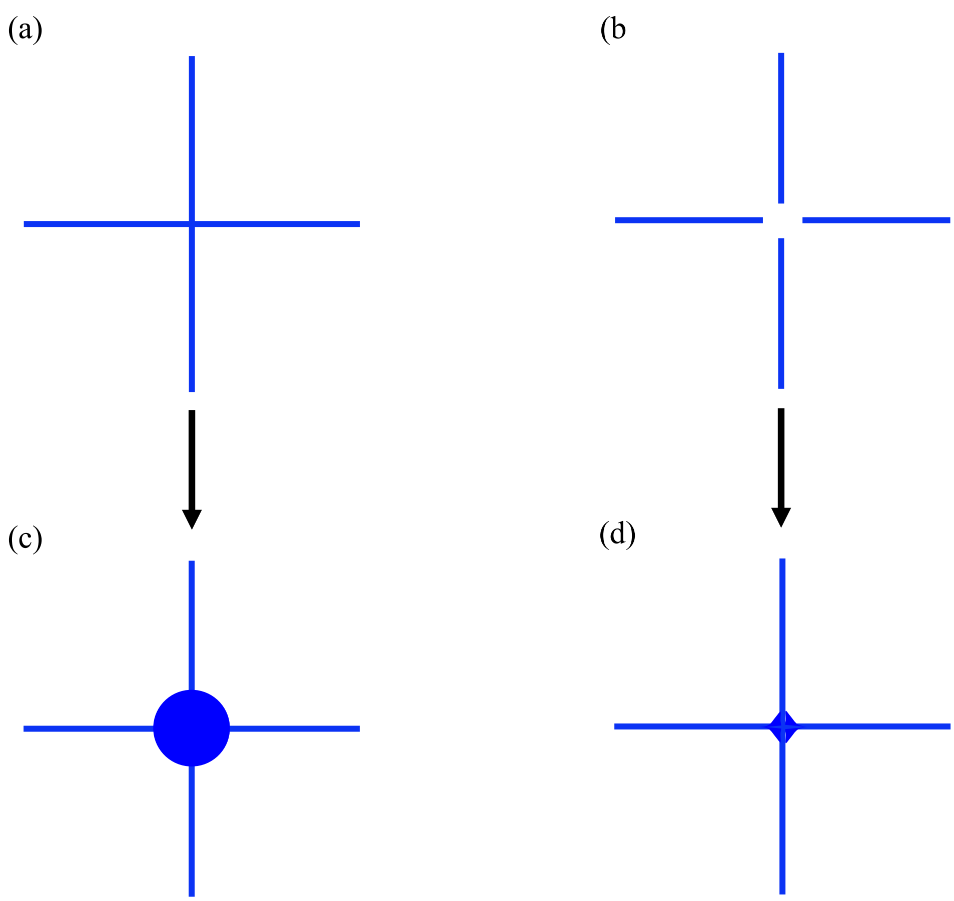

Figure 2.3: A pattern with lines that cross (a) leads to overexposure in the center (c). When a gap is left in the center of the pattern (c), minimal overexposure occurs (d).

3. EXPERIMENT

The multiple components of this experiment went through several test runs to make the final process a success. These include the building of a maskless photolithography apparatus, the exposure of the photoresist, the metal deposition, and the mechanical exfoliation of graphene. The maskless photolithography apparatus was built and calibrated to complete the photolithography technique. This technique ultimately determines the pattern of metal that is deposited onto a sample. The goal is to make electrical leads connect to a piece of graphene on the sample.

3.1 Maskless Photolithography Apparatus

The maskless photolithography apparatus starts with the formation of a pattern. An easy way to make this pattern is to use a drawing program on a computer. In this experiment, the patterns were drawn in Microsoft PowerPoint.

The computer is connected to an LCD Projector [10] in order to transfer the pattern to the sample. The lens of the projector is reversed to change the focal point from a few feet to a few inches. This is more practical and keeps the size of the machine relatively small. Brass rods were machined to hold the lens in place since the original screws were not long enough once the lens was reversed. The projector sits on a steel plate that has four adjustable legs. These legs are attached to a larger steel plate that also has adjustable legs. The two plates work together to keep all parts of the machine as level as possible. Also, the larger plate provides more sturdiness for the small plate and allows the small plate to hang over the base of the microscope as seen in Figure 3.1a. To

(a) (b)

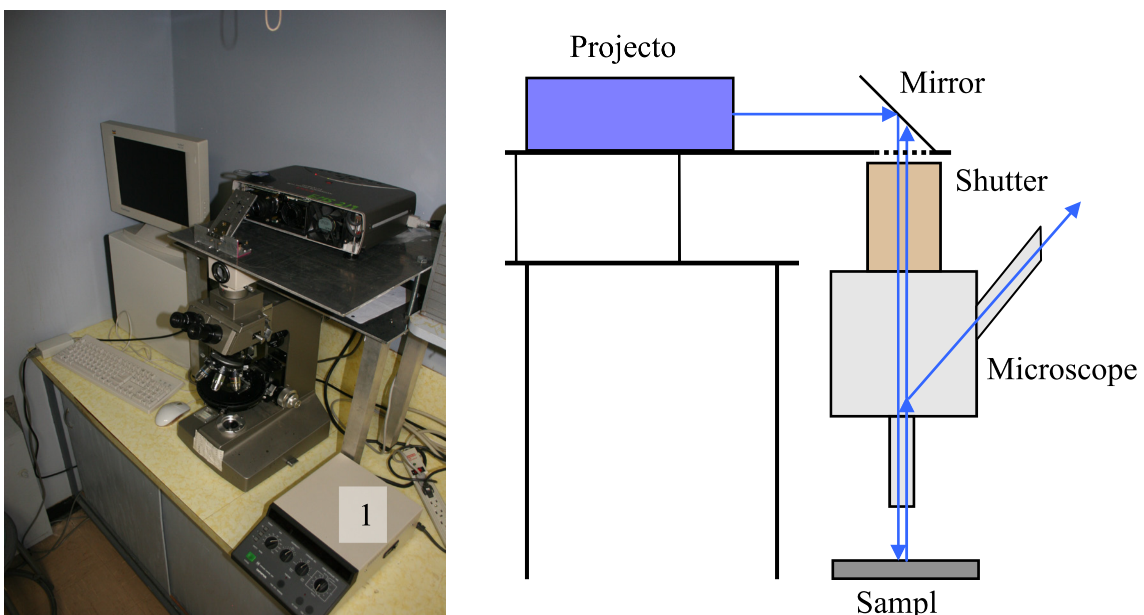

Figure 3.1: (a) Photograph of computer, projector, mirror, microscope and automatic exposure control unit (1). (b) Schematic of the light traveling through the maskless photolithography apparatus. Light starts at the projector and is redirected by the mirror. It then passes through the shutter of the automatic exposure control unit and then the microscope. After reflecting off the sample, the image can be observed through the viewing lens.

increase stability, the small plate is also screwed to the shutter of the automatic exposure control unit, which is connected to the microscope (Figure 3.1b).

A 1” by 1” silver mirror is also attached to the small plate on a custom mirror mount. The mirror redirects the light from the projector so that it shines directly into the shutter and the microscope. The mirror is mounted on a piece of sheet metal that is on a hinge (Figure 3.2). The mount is designed so that the mirror angle and position can be adjusted to the desired position, and then secured. The mount rests on the head of a long screw with a high thread count. This screw controls the angle of the mirror. The base of the mount is connected to the small plate. There are slots in the small plate so that the mount can slide towards or away from the projector. The mounting screws are tightened once the mirror is accurately positioned.

The controls for the automatic exposure control unit (Figure 3.1a) are separate from the shutter (Figure 3.1b). The automatic exposure control unit can keep the shutter open or closed for a set amount of time. After selecting a time, the start button is pressed. This will keep the shutter open for the selected time. The exposure time ranges from a couple seconds to 50 minutes. This capability is very useful for exposing the photoresist, which is further discussed below. There is also a camera port on the shutter for microscopic pictures.

After the light travels through the shutter, it enters the microscope. An Olympus microscope was used in this experiment. It has four levels of magnification: 5x, 10x, 20x and 50x. The 5x and 50x magnifications were predominantly used. All of the samples were placed on a glass slide under the microscope.

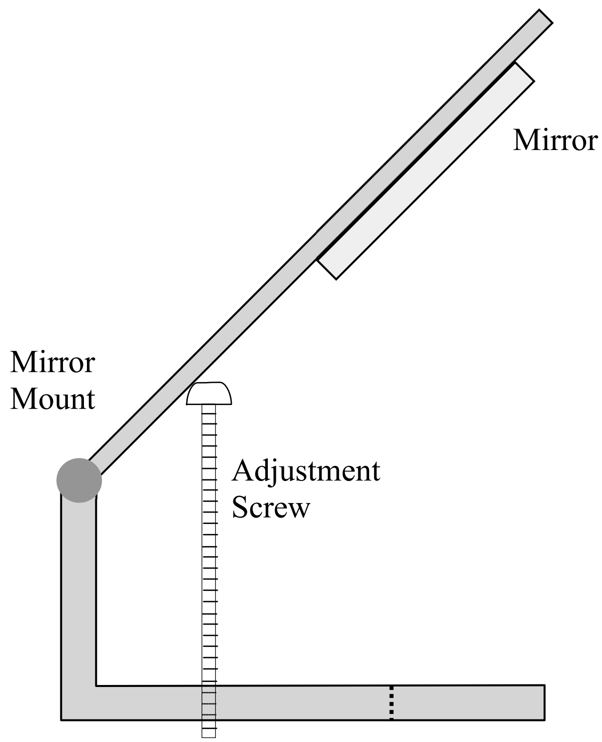

Figure 3.2: The mirror is attached to the mirror mount with four screws and washers. The adjustment screw controls the angle of the mirror. The whole mount is also able to slide from left to right.

3.2 Photolithography Technique

Photolithography is the technique of removing parts from a film or substrate. In this experiment the film or substrate is on a silicon chip that has a layer of silicon dioxide. The layer of silicon dioxide is an insulator, which is important for future use in an electrical circuit. A diamond scribe is used to cut 1 cm by 1 cm chips from a large wafer. A scribe is a pen shaped tool with a sharp point of diamond.

After the chips are made, the next step is to put graphene on them. This process will be explained in Section 3.4. Once the graphene is in place, photoresist is applied. The type of photoresist used in this experiment is the commonly available Microposit S1813 Positive Photoresist [11]. The photoresist is applied using a technique called spin coating. This technique involves spinning the sample at a high speed with the photoresist on it. Centripetal force causes the photoresist to spread out evenly over the sample. A modified food processor is a relatively simple and inexpensive way to spin coat. For this experiment, the blade of the food processor was replaced with a small platform made of aluminum. The chip is attached to the platform with candle wax, which is first melted with a heat gun. The candle wax hardens after approximately 5 minutes.

Before photoresist is applied to the chip, it is important to ensure only red lights are used in the room. This experiment was done in a photography dark room. This keeps the photoresist from overexposing since it is not sensitive to red light, as shown previously in Figure 2.1. A few drops of photoresist are placed on top of the chip and the food processor is turned on for 60 seconds. After spin coating, the chip is baked on a hot plate for three minutes at 100° C. This dries the photoresist, which causes it to harden and stick to the chip better. The chip is now ready to be exposed.

The sample is exposed using the maskless photolithography apparatus. First the graphene is located on the chip using the microscope. There is a filter on the microscope so that its light does not expose the photoresist. After finding a desirable piece of graphene, the pattern on the computer is loaded. Then the automatic exposure control unit opens the shutter and makes the pattern visible on the sample. The initial pattern on PowerPoint is always in red so that the sample can be positioned to the correct location without exposing the photoresist. Once the pattern is focused, the shutter closes while the next slide in the PowerPoint file is advanced. This slide is exactly the same as the previous slide, except every red feature is replaced by blue. The automatic exposure control unit is then set for a certain time period. When the expose button is pressed it will open the shutter for the set amount of time.

In this experiment, a technique was developed to make complex patterns. The small parts of the pattern are exposed at 50x magnification as described by the technique above. Without moving the sample, the microscope is switched to the 5x magnification. Larger parts of the pattern are then exposed. After the second exposure, the chip is partially developed.

The chip is rinsed in a developer for 45 to 60 seconds. This washes away all of the photoresist that was exposed to blue light and leaves the rest on the chip (Figure 3.3). After the chip is rinsed in distilled water and blown dry, it can be exposed again. This second round of exposure allows us to add larger features to the pattern. The four large rectangles in Figure 3.6a were made using this technique. These large pads are made for future use in an electrical circuit. After the second round of exposing and developing the sample, the chip is prepared for metal deposition.

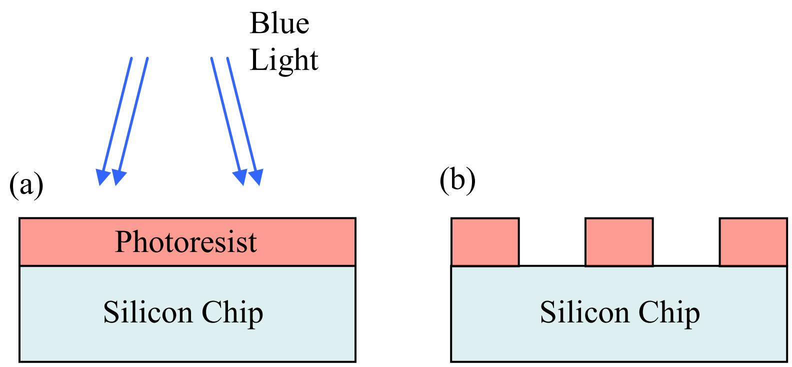

Figure 3.3: (a) Blue light exposes the photoresist in a pattern. (b) After putting the chip in developer, the exposed parts of the photoresist washed away.

3.3 Metal Deposition

Metal is thermally evaporated onto the chip. Thermal evaporation occurs inside a vacuum chamber to reduce the chance of contamination. Otherwise, the metal may mix with particles in the air as it evaporates and condenses on the chip. To further decrease the level of contaminants, the whole apparatus must be cleaned regularly with acetone. A schematic of the inside of the vacuum chamber is shown in Figure 3.4.

A chip is placed on the mount, which has four small clips to hold multiple chips. It is important that the clip does not cover any part of the pattern. Once the chip is secure, the mount is placed inside the chamber. It hangs upside down from a metal rod in the center of the chamber as shown in Figure 3.4.

A piece of the metal that will be evaporated is placed in a tungsten boat; for this experiment it was either nickel or gold. The boat is held by two rods that connect to a variable transformer. The variable transformer gives the user control over how much current is used. There is also a transformer connected in series with the variable transformer. The transformer decreases the alternating voltage from the variable transformer and increases the alternating current to a suitable level for the circuit. This also gives the experimenter more precision when controlling the current with the variable transformer. The alternating current heats up the metal, hence the name thermal evaporation. It is also important to have the cover in front of the mount. An arm outside the chamber moves the cover back and forth into position. This prevents metal or other material from touching the sample before desired. Once the vacuum chamber is setup, it must be pumped down before thermal evaporation can begin. The process starts with roughing, which uses a mechanical pump to remove the air. When the pressure drops to 30-60 millitorr (atmosphere is 760 torr) then the diffusion pump can be used. The diffusion pump in this experiment can bring the pressure down to ~10^{-6} torr. At this

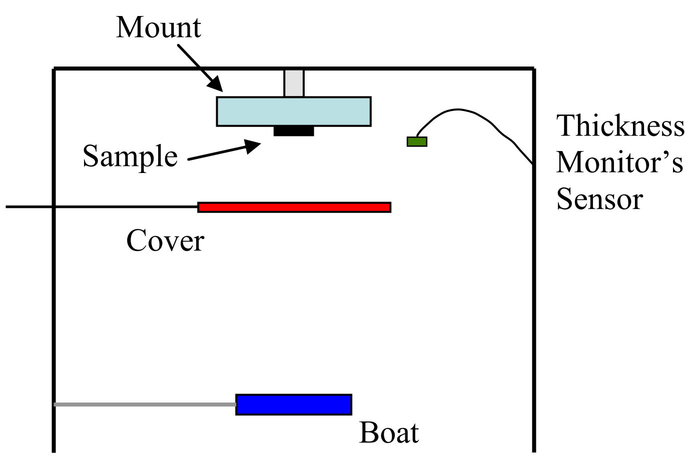

Figure 3.4: Schematic of the inside of the vacuum chamber. The supporting rods hold the mount upside down. The sample is attached to the mount with clips. The cover prevents metal from sticking to the sample until desired. The boat holds the metal and is heated by the variable transformer. The thickness monitor can determine the rate of evaporation of the specific metal being used.

pressure, few particles are in the air. This is important since some metals react with these particles, especially at high temperatures.

The variable transformer is then turned on to heat the metal in the boat. It must be increased slowly; otherwise the sudden increase of heat may break the boat. A thickness monitor determines the evaporation rate of the metal. The sensor of the thickness monitor is positioned near the mount for a good reading (Figure 3.4). The thickness monitor calculates the evaporation rate using the density and acoustic impedance of the specific metal. Values used in this experiment are shown in Table 1 [12].

Table 1: Density and acoustic impedance of metals evaporated in this experiment.

Material Name	**Density**	**Acoustic Impedance**
	g/cm^3	$x10^5$ $g/(cm^2$ sec)
Gold	19.300	23.180
Nickel	8.910	26.680

Once the evaporation rate reaches the desired level, the cover is moved so that the metal reaches the sample. For this experiment, the desired evaporation rate was ~2 Å per second. At higher rates the metal tends to make a less even surface. Lower rates may allow contaminants to land on the sample. The cover is moved back into place after the desired thickness is reached. In this experiment the thickness was ~100 nm, which usually took 8-10 minutes to reach. The variable transformer is then used to reduce the heat slowly. The chamber and sample must cool for a couple hours to prevent air particles from reacting with the hot metal.

The next step removes the excess metal from the chip. A technique called lift off removes the photoresist and leaves the desired pattern of metal on the chip. This technique starts with acetone, heated in a beaker to ~60° C. The chip is placed in the beaker and swirled around. As the acetone works its way through the excess photoresist, pieces of metal will start to float away. The metal that stuck directly to the chip, i.e. the metal of the pattern, stays in place. This process is shown in Figure 3.5 and some samples of the results of lift off are shown in Figure 3.6.

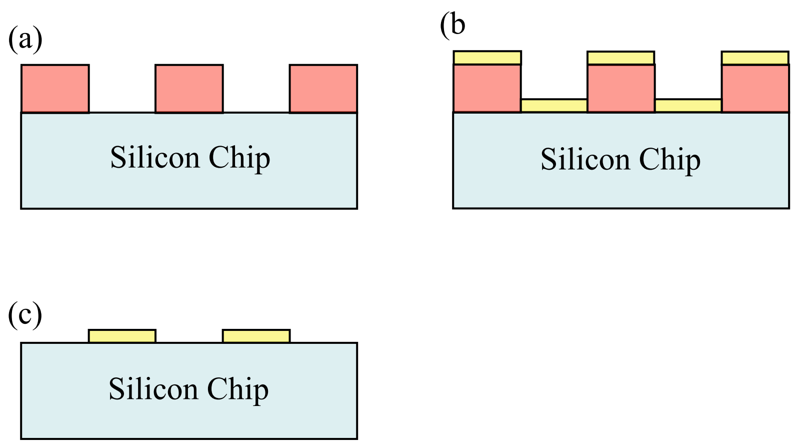

Figure 3.5: (a) A chip with the pattern in the photoresist (red). (b) The chip now has metal deposited on it and in (c) it has been rinsed in acetone, leaving only the metal (yellow) in the desired pattern.

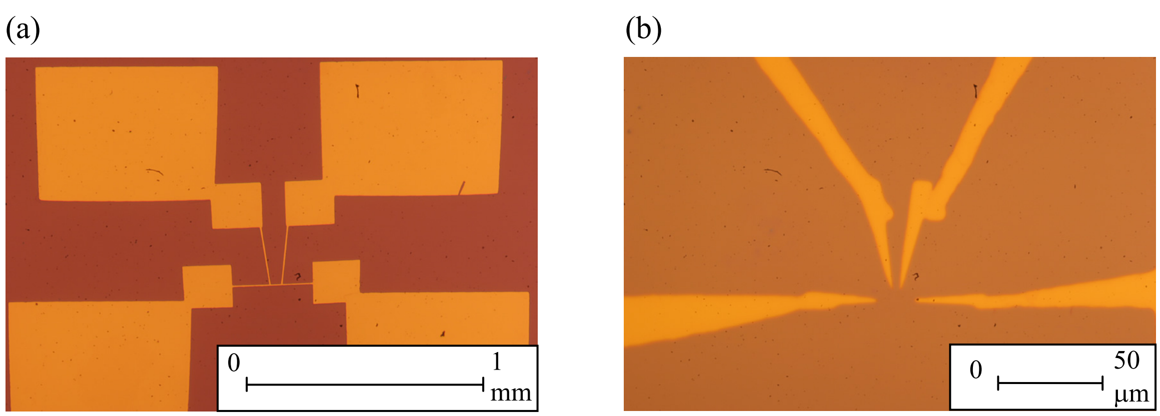

Figure 3.6: Two different gold patterns on a silicon chip at 5x (a) and 50x (b) magnification. The large rectangles in (a) were made by doing a second round of exposure and are ~785 µm in width. The smallest features in (b) are ~1 µm.

3.4 Mechanical Exfoliation of Graphene

The previous sections described the process of making electrical leads on a sample. This experiment aimed to attach these leads to a piece of graphene. The graphene comes from a flake of graphite. The flakes in this experiment were 2-5 mm thick. Mechanical exfoliation, or the “Scotch tape method” makes pieces of graphene from the graphite flakes [3]. First, a flake of graphite is placed onto a piece of tape. The tape is folded over the flake and then slowly pulled apart. Next, a new piece of tape is stuck to the first piece with the graphite in between them. The two pieces are also slowly pulled apart. A third piece is then stuck to the second one, and the process is repeated. After approximately 10 repetitions, parts of the graphite flake will have a milky gray look when held up to the light. This is where the graphene is located. To make this process easier, the tape is folded onto itself at the ends. This prevents the two pieces from completely sticking together, and provides non-sticky places to grip the tape.

After locating the graphene, it is deposited onto a silicon chip. The setup for deposition is shown in Figure 3.7. Sticky side up tape holds the chip still. Two more pieces of tape hold down the first piece (Figure 3.7). The tape containing graphene is placed on the chip, with the graphene near the center. The tape is then rubbed lightly with a finger for ~30 seconds and then 5 more minutes with the backside of a pair of tweezers. This deposits the graphene onto the chip. The tape must be removed slowly to avoid pulling the graphene off. This takes about 5 minutes and feels like the tape is not moving at all. Pulling tape off of the chip is easier than pulling tape off of tape. This noticeable effect may cause the experimenter to pull the tape too fast. To reduce this effect, the chip is placed at an angle as shown in Figure 3.7.

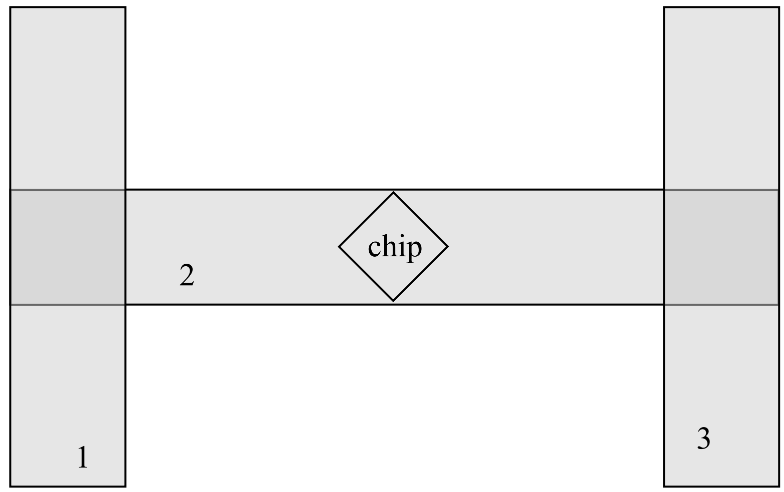

Figure 3.7: Schematic of the setup for depositing graphene onto the silicon chip. The chip is on tape that has its sticky side up (2). Two other pieces of tape (1 & 3) hold it on the table with their sticky sides down. The chip is placed at an angle to make the deposition of graphene easier.

It is necessary to search for suitable pieces of graphene with the microscope. These pieces are nearly transparent, as shown in Figure 3.8. An ideal piece is ~50 μm away from other material, such as thicker pieces of graphite or tape residue (Figure 3.8). Otherwise, the material may interfere with the metal deposited in that space.

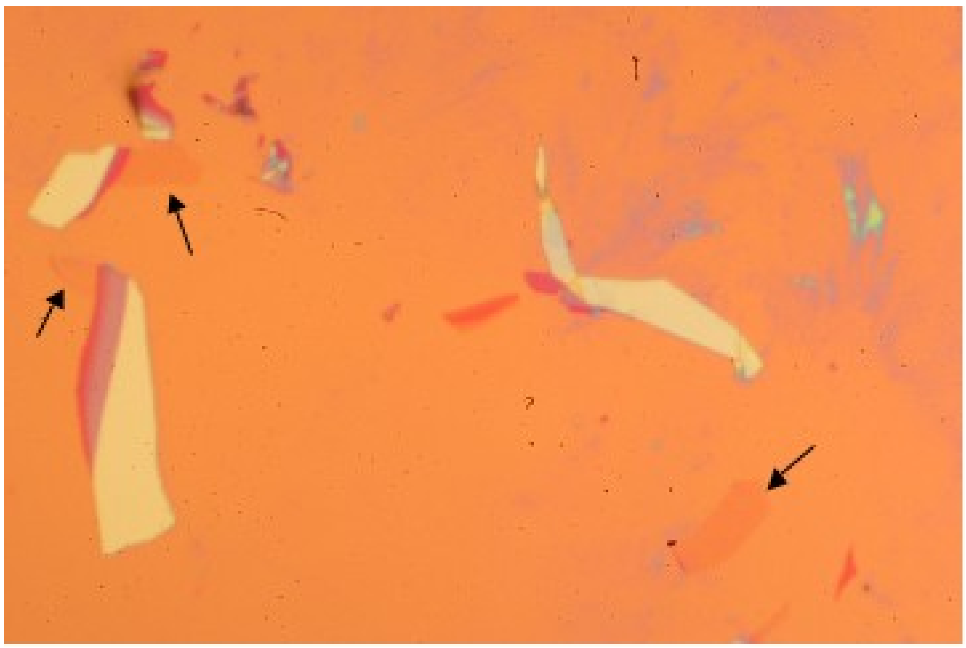

Figure 3.8: Picture of sample at 20x magnification. The arrows show possible pieces of graphene, which are practically transparent. The piece in the lower right corner is further from other material, which makes it a good choice. The darker colors and yellow pieces are graphite, and the colorful marks in the top right corner are tape residue.

4. RESULTS AND ANALYSIS

This experiment achieved a line width of ~1 μm. This result was only possible with a careful choice of experimental parameters, as will be discussed here. Important factors included the shade of blue light, careful alignment of patterns, and pattern design.

The first issue to resolve was the effect of two lines being close together. Exposing two close lines can overexpose the gap between the lines. If this happens, then the pattern will have one large line instead of two separate lines, which ruins the pattern. Decreasing exposure time protects the gap from overexposure, but leads to underexposed lines. A two-part approach solved the problem. First, the lines were designed to angle away from each other (Figure 4.1a). This increased the distance between the lines at the top. Since the bottom part of the lines remained close together, another technique was necessary. This solution used darker shades of blue to expose the photoresist. The darker blue does not expose the area between the lines because the intensity of the light is much lower (as shown previously in Figure 2.1c).

These different shades of blue fixed another issue as well. Test exposures revealed a concentrated intensity near the top of the PowerPoint slide. The bottom of the slide did not expose as well as the top. Parts of the pattern near the bottom were made a brighter shade of blue to counteract this.

Shading also fixed an issue with overexposure of larger features. These features (e.g. the rectangles in Figure 4.1b) contain more pixels than the lines of the pattern. The pixels can overlap when they reach the photoresist due to spherical aberrations of the lens (as shown previously in Figure 2.2). Each pixel overlapping with its neighbors increases

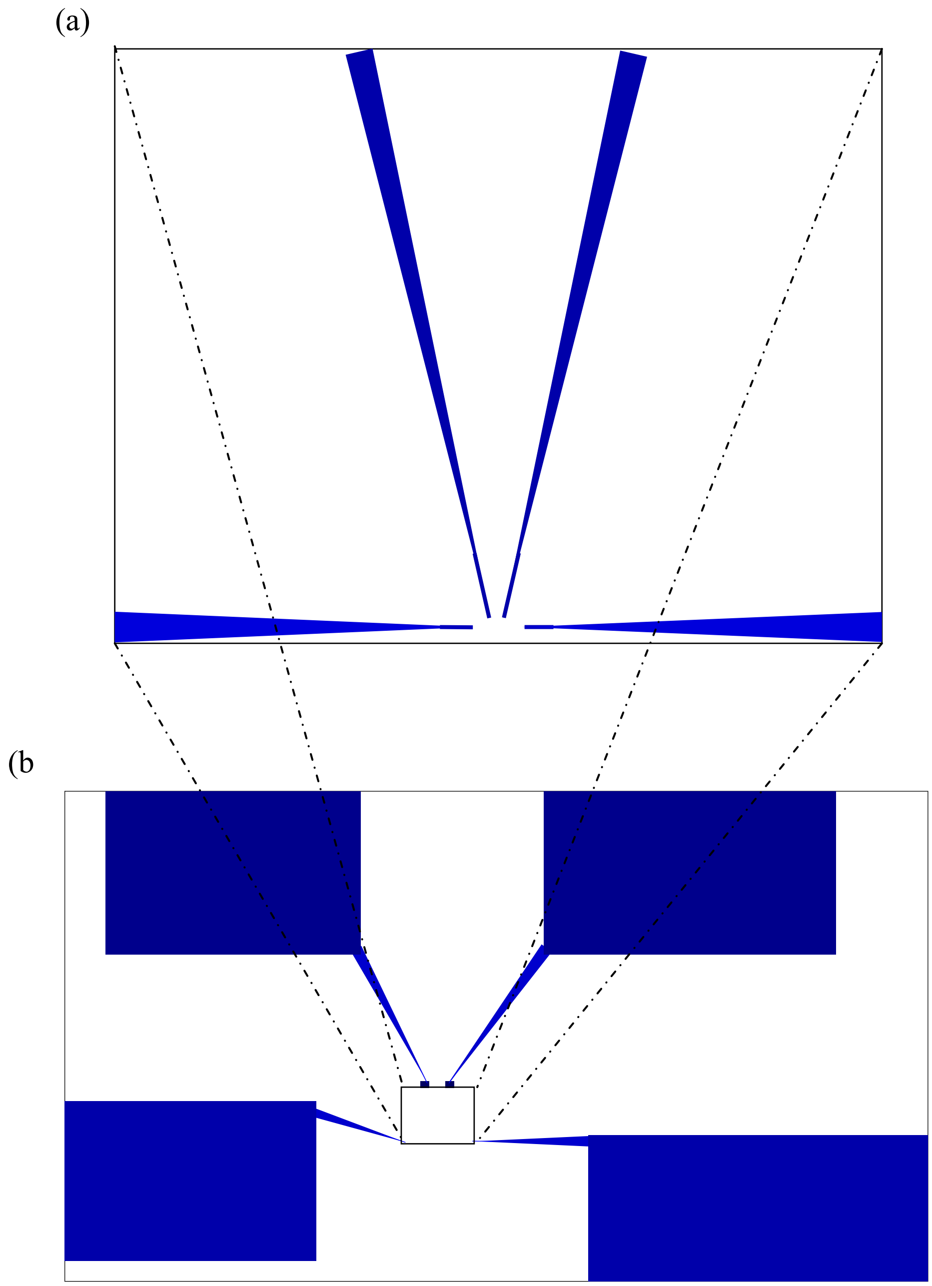

Figure 4.1: (a) Sample of a PowerPoint slide for the 50x magnification part of the pattern. The lines are angled away from each other to decrease chance of overexposure. The 50x magnification part of the pattern is exposed first. (b) Sample of a PowerPoint slide for the 5x magnification part of the pattern. The dashed lines indicate the alignment of the 50x magnification part of the pattern near the center. In the experiment, the pattern is multiple shades of blue, as discussed in the text, and the background of the slides is black.

the total intensity at each point on the large feature. A darker shade of blue lowers the total intensity and reduces the chance of overexposure.

As explained before (Section 3.2), complex patterns were created by using the 5x magnification immediately after the 50x magnification. A gap in the 5x magnification pattern allowed it to connect to the 50x magnification pattern without covering the smaller pattern (Figure 4.1b). It seemed logical that this gap would be in the center of the pattern. Early test runs proved otherwise. The center of the 50x magnification pattern appeared left of the center of the 5x magnification pattern. Specifically, it was 0.69" left and 0.08" above the center using the length in PowerPoint. Even with this knowledge, the lines did not always match up, as seen in Figure 4.2. This alignment problem could be caused by the different lens size for the 5x and 50x magnifications. The 5x magnification has a bigger lens, which allows it to receive light from wider angles. This

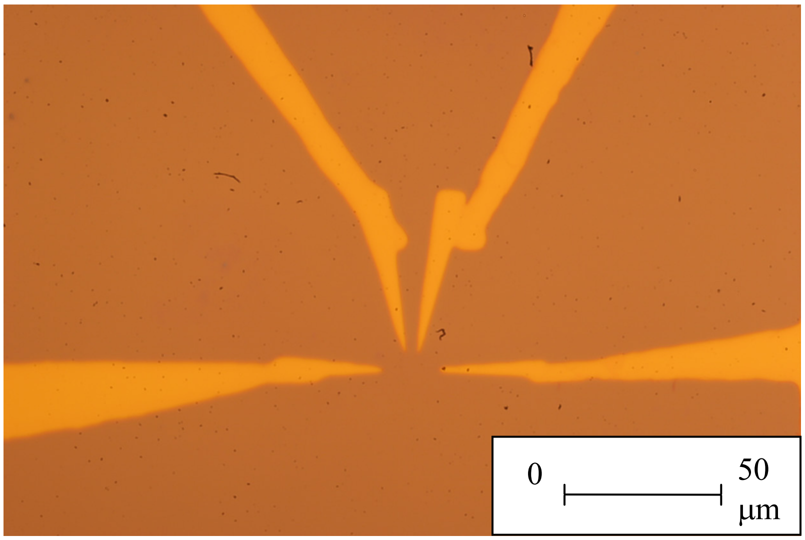

Figure 4.2: Image of the pattern at 50x magnification. Parts of the 5x magnification pattern do not always line up with parts of the 50x magnification pattern. Also, the smallest part of this pattern was measured to be ~1 μm using *ImageJ*.

may cause spherical aberrations that center the light at a different point than the 50x pattern.

Another alignment issue occurred when making the 50x magnification pattern connect to a sample of graphene. The red pattern was superimposed on the graphene and aligned properly, but exposure with the blue pattern developed above and to the right of the sample. This may be due to the fact that blue light and red light come from different places within the projector. The projector has three light sources for red, blue, and green, which can be combined to make all the different colors. Blue light and red light do not come from the same source, and due to the aberrations explained before they hit the photoresist in different places. Moving the red images 1.0" up and 0.1" (PowerPoint measurements) to the right solved the problem. The blue slides remained unchanged.

After perfecting the exposure technique, the next step was metal deposition. Sometimes the metal did not stick to the chip during lift off. This happened because the patterns had straight lines. If excess metal stuck to one part of the line during lift off, then it would peel the whole line off. Changing the lines to triangles (as seen in Figure 4.1a) solved this issue. If a piece of excess metal sticks to part of these triangular lines, then it will peel off a thin line rather than the whole thing.

In some of the earlier tests metal did not stick to the chip because surfactant was not used. When the nickel used in these tests did not stick during the lift off process, gold was used along with the surfactant Triton X-100 [13]. The surfactant helped gold stick to the layer of silicon dioxide as well as the graphene. Mixing the surfactant with distilled water decreased the viscosity of the surfactant and made it easier to apply to the chip. In this experiment, a ratio of 1 drop of surfactant was mixed with 1 mL of distilled water.

After developing the chip, one drop of the mixture is applied to the pattern with a dropper. Once the chip is then rinsed in distilled water, it is ready for metal deposition. Triangular lines and Triton X-100 increased the success rate of lift off.

The smallest feature in Figure 4.2 is ~1 μm. We used *ImageJ*, a free computer program, to measure the feature size, since measuring by hand is impractical. The program measures the length based on the number of pixels in the picture. To convert this length to real units (mm), a picture of the real unit is needed (Figure 4.3). *ImageJ* measured 0.1 mm to be 321.4 pixels. Now this conversion factor can be used for any other picture, as long as it is the same size as the original picture (720 x 480) and it is taken under the same conditions as the original. The equation is

$$\frac{0.1(mm)}{321.4}x = y\,(mm) \tag{1}$$

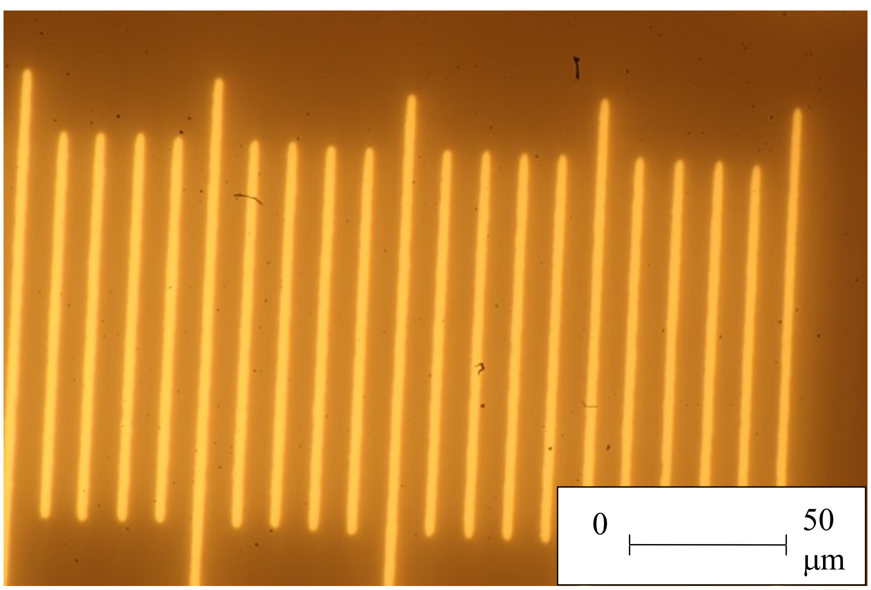

Figure 4.3: Image of 1.0 mm slide (only 0.2 mm visible). Each line represents 0.01mm, or 10 μm. *ImageJ* can measure the distance in pixels, which is used as a conversion factor between pixels and mm.

where x is the number of pixels measured in *ImageJ* across a feature of width y. In Figure 4.2, the smallest part of the pattern has $x = 3.727$. Therefore $y = 0.00116$ mm or 1.16 μm.

The results of this experiment show that many different factors can affect the feature size of a pattern. Multiple shades of blue throughout the pattern help control exposure. Line style affected exposure and metal adhesion. This experiment needed surfactant to ensure that the metal stuck to the chip during lift off. All these factors played a part in decreasing the minimum achievable feature size to 1.16 μm.

5. CONCLUSION

This experiment shows that building a low cost, maskless photolithography apparatus is possible. Substituting a projector and a microscope for a lithography machine decreases the cost by millions of dollars. Using a computer to make the patterns has proved invaluable. The computer allows the experimenter to change the pattern as needed. Since the pieces of graphene used in this experiment are not uniform, the pattern needed slight alterations for each one. Buying a new mask each time for a conventional photolithography apparatus would get expensive.

The equipment in this experiment was relatively inexpensive, but it still resulted in a very small feature size. While 1 μm does not come close to the record of ~50 nm, it is more than small enough for the purpose of this experiment. The 1 μm line width will allow the 50x magnification pattern to fit on most pieces of graphene with ease.

Although this experiment accomplished many of our goals, altering some parts of the apparatus could improve the results. Using a smaller wavelength of light could expose the photoresist better than the blue light. As seen in Figure 2.1a, the spectrum of blue light used in the experiment has wavelengths slightly larger than the peak sensitivity of the photoresist.

Adjusting the path of the light could also improve the results. Ideally, the light would travel from point to point like a single particle. In reality, all parts of the pattern do not follow the same path. Spherical aberrations may cause some of this, but other adjustable factors in the experiment affect the path too. The focal point of the light exiting the projector should coincide with the distance between the projector and mirror.

If unfocused light hits the mirror, then the light will stay unfocused throughout the rest of its path. Moving the projector forward or backward can focus the light to a point as it hits the mirror.

The angle of the mirror also affects the path of the light. The mirror should redirect the light straight down into the microscope; otherwise, the path of light may pass through the edge of the lens in the microscope. The spherical aberrations have a greater effect on the image produced when the light travels through the edge of the lens. Having the image focused close to the center of the lens allows for a more streamlined path and focused image. These changes to the setup of the machine may lead to decreasing the smallest feature size.

Future work could include the changes described above in order to find the absolute minimum feature size of this maskless photolithography apparatus. The tests run in this experiment involved multiple lines near each other. Exposing a single line may result in smaller features. This eliminates the possibility of overexposure due to the closeness of other lines.

As mentioned before, this experiment aimed to make electrical leads to study graphene. Future work would include depositing metal leads onto a sample of graphene and connecting the sample to a circuit. This experiment has proven that leads can be made small enough for this purpose.

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References

[1] Wikipedia contributors, 'ASML Holding', *Wikipedia, the Free Encyclopedia* (Wikimedia Foundation, Inc., 2012) <http://en.wikipedia.org/w/index.php?title=ASML_Holding&oldid=487144309> [accessed 15 April 2012].

[2] 'MTI Provides Lab Equipment and Advanced Crystal Substrates', *MTI Provides Lab Equipment and Advanced Crystal Substrates* <http://www.mtixtl.com/> [accessed 16 April 2012].

[3] Geim, A. K., and K. S. Novoselov, 'The Rise of Graphene', *Nature Materials*, **6** (2007), 183–191 <doi:10.1038/nmat1849>.

[4] Soldano, Caterina, Ather Mahmood, and Erik Dujardin, 'Production, Properties and Potential of Graphene', 2010 <http://arxiv.org/abs/1002.0370>.

[5] Qazi, Muhammad, Thomas Vogt, and Goutam Koley, 'Trace Gas Detection Using Nanostructured Graphite Layers', *Applied Physics Letters*, **91** (2007), 233101 <doi:10.1063/1.2820387>.

[6] Bullis, Kevin, 'Graphene Transistors - Technology Review', *Technology Review* <http://www.technologyreview.com/computing/20119/>.

[7] Brunner, Timothy, 'Why Optical Lithography Will Live Forever', *Journal of Vacuum Science & Technology B*, **21** (2003), 1071-1023.

[8] Brueck, S. R. J., and Mark Schattenburg, 'Interferometric Lithography - A Nanotechnology Enabler'.

[9] 'Chem 421 - The Chemistry of Photoresists' <http://chem.chem.rochester.edu/~chem421/polymod2.htm> [accessed 19 March 2012].

[10] 'EIKI LC-XNB5M LCD Projector' <http://www.aboutprojectors.com/EIKI-LC-XNB5M-projector.html> [accessed 1 May 2012].

[11] Crisp, Peter, 'Microposit S1813 Photoresist', *Docstoc.com* <http://www.docstoc.com/docs/6461552/Microposit-S1813-Photoresist> [accessed 29 April 2012].

[12] 'List of Density and Acoustic Impedance Values for Commonly Used Materials.' <http://www.inficonthinfilmdeposition.com/en/densityandacousticvalues.html> [accessed 29 April 2012].

[13] Zhang, Y, Nathan W Franklin, Robert J Chen, and Hongjie Dai, 'Metal Coating on Suspended Carbon Nanotubes and Its Implication to Metal-tube Interaction', *Chemical Physics Letters*, **331** (2000), 35–41 <doi:10.1016/S0009-2614(00)01162-3>.