AN ELECTRON BEAM LITHOGRAPHY SYSTEM: SETUP AND CHARACTERIZATION

by

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B.Eng., McMaster University, 1992

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF APPLIED SCIENCE

in

THE FACULTY OF GRADUATE STUDIES

DEPARTMENT OF ENGINEERING PHYSICS

We accept this thesis as conforming to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA

October 1994

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Date 15 OCTOBER, 1994

ABSTRACT

An electron beam lithography system was realized by externally controlling a Hitachi S-4100 field emission scanning electron microscope with a computer. Associated facilities were established for applying resist layers to substrates and for developing and etching exposed patterns. Procedures for the system's use were developed and optimized as it is anticipated that many researchers will use the system in the future.

The system's performance was characterized with importance being placed on those issues that impacted on the goal of achieving sub 50 nm resolution with high pattern uniformity. The results were found to depend on many parameters including the resist thickness, resist composition, development time, and the specific pattern that was written. Resolutions of ~50 nm with feature spacings of ~200 nm were achieved in polymethylmethacrylate (PMMA) resist layers ~200 nm thick. Indications are that moving to thinner resist layers, shorter development times, and higher contrast developers will enable better resolution to be achieved in the future. Nonuniformities on the order of ~10 nm over ~5 μ m scales have been achieved on both line and dot array patterns. These patterns were emphasized because of their applications in distributed feedback semiconductor lasers, and in the construction of artificial atom arrays. Systematic and random noise limitations were encountered that require further investigation to improve the uniformity beyond this level.

Several patterning and processing concerns were also investigated to provide data important for the design of devices that incorporate nanometre scale structures. The most important issues are a limitation on the overall pattern size due to a fluctuating beam current, and a rotation effect that changes the orientation of the patterns on the substrate as the beam energy and working distance are varied.

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ACKNOWLEDGEMENT

First and foremost, I would like to thank my supervisor, Dr. Jeff Young, whose never ending assistance and insight were instrumental to the results achieved so far. I would like to thank him as well for the research experience he has given to me. I would also like to thank Dr. Tom Tiedje for the use of his equipment and facilities, as well as Dr. Mike Jackson who provided some assistance in this regard as well. Special thanks go out to Christian Lavoie who taught me how to use the electron microscope and to both him and Shane Johnson for the loan of some substrates early on to perform experiments with. Vighen Pacradouni also deserves a mention, for proof-reading portions of the thesis. As well, I would like to give a big thank-you to to Manoj Kanskar who arrived somewhat late in the work, but whose experience, knowledge and assistance contributed to immediate improvements in the results.

Chapter 1 Introduction

A great deal of research and development is being directed to control material structure on smaller and smaller length scales. In industry, this push is motivated by the desire to fit more devices into a given area, allowing both higher device performance and lower cost. In addition, structures on smaller length scales show unique features that lead to new devices and allow one to view properties that can not be seen on larger length scales. Current state of the art silicon technology is based on 0.5 micron minimum feature sizes and much of the groundwork has been laid for introducing 0.3 micron devices within the next few years. Growth techniques such as molecular beam epitaxy (MBE) and metal-organic chemical vapour deposition (MOCVD) allow the material structure to be controlled down to ~ 2 nm in one dimension, and the push to control material structure on similar length scales in two and three dimensions continues. Distributed feedback (DFB) lasers employ gratings with pitches on the order of 0.25 microns, chosen to act as Bragg reflectors for the infrared light which they emit [Ref. 1]. Several new transport phenomena have been demonstrated in conductors fashioned into "wires" and "dots" with characteristic length scales less than 0.15 microns, where the structure of the device begins to modify the quantum mechanical wavefunction of the conduction electrons [Ref. 2-3]. Further reductions in size are expected to lead to additional control over material properties and new applications for these materials, such as the creation of structures with a photonic band gap [Ref. 4-5].

Various techniques are being pursued to accomplish the goal of smaller feature sizes, including deep ultraviolet (UV) extensions of optical lithography, as well as electron beam, ion beam and X-ray lithographic processes. Each of these techniques has its advantages and disadvantages, and the "best" one depends on what one wishes to make and in what volumes. Optical lithography in the deep UV is attractive for large volume processes, as this technology is an extension of the UV technology already in place. X-ray lithography holds promise for giving the same resolution capability as electron beam lithography, but it is still in the development stage. Deep UV and X-ray techniques also require masks that need to be manufactured by electron-beam lithography. These considerations make UV and X-ray techniques better for high volume processing. Ion beam lithography is attractive from the perspective that the ions do not penetrate far into the substrate and scatter over a small volume, possibly providing better resolution than electron beam systems. The ion beam currents available at this time are small, however, meaning that it will take much longer to write patterns with ion beams than by using the other methods.

Electron beam based systems have the flexibility of allowing one to write the pattern directly on the sample, although some systems are also being designed in an effort to imitate the optical techniques and allow exposure through masks. The ability of beam-driven systems to directly write on the sample makes them attractive for a research environment where new designs are constantly being tried and great flexibility is required of the system, while large throughput is not. The lower throughput of the electron beam systems is due to three features: the beam operation needs to be done in a vacuum, they are time limited by the beam currents that are available to expose the sample, and even if the beam current is high enough, the patterns are defined using individual points, or pixels, which limits the speed with which the beam can be moved across the sample by the microscope's scanning circuitry.

The flexibility and superior resolution of the electron beam process when compared to the optical processes in use are precisely what is useful in our lab. We want to fabricate two

dimensionally textured optical waveguides to extend the basic principle behind DFB lasers, and arrays of "quantum" wires and dots (artificial atoms) with dimensions less than 50 nm. Recent results indicate that these goals are achievable, with feature sizes at least as small as 10-25 nm on 50 nm pitches having been demonstrated [Ref. 6-7]. Such structures represent new classes of materials whose ground state and dynamical optical and electrical properties await discovery and exploitation. With these long term goals in mind, we began developing the electron beam lithography system described in this thesis. The majority of the thesis is devoted to describing the system that has been developed and summarizing our efforts to characterize its performance.

The electron beam lithography process is, in many ways, an extension of optical lithography. The basic single pass procedure is illustrated in Figure 1-1 and involves coating the substrate with a resist layer, exposing the resist, developing it, and transferring the resulting pattern to the underlying substrate. The substrate may be cleaned before spinning on the resist layer. The sample is then baked and, if multi-layers of resist are needed, returned for another coating of resist. The sample is exposed by writing directly on the sample with the electron beam. The resist layer is then developed and post-baked. Pattern transfer is accomplished by etching or lift-off and the resist layer is then stripped off the substrate. At this point, the sample can be returned for further pattern definition when additional pattern transfer steps are necessary.

The thesis is divided into three main chapters. Chapter 2 reviews the basic principles involved in each aspect of the lithographic process. Chapter 3 describes the apparatus (hardware and software) and the processes that were developed to implement the electron beam lithography capabilities in a Hitachi S-4100 scanning electron microscope. Chapter 4 describes the procedures used and the results obtained in characterizing the system's performance. This primarily consisted of determining the system parameters required to achieve sub 50 nm



Figure 1-1. Block diagram of a single pass process for lithography pattern definition and transfer. Dashed lines and boxes indicate optional steps that may not be present in all processes due to variation in materials and procedures.

resolution and pattern uniformity on the order of 10 nm. Since it is anticipated that the system will be used by many researchers, detailed operations procedures are included in Appendix A.

2.1 Introduction

This chapter deals in detail with practical and theoretical aspects of the lithographic process. There are many general references available on the lithography process [Ref. 8-12], which is quite well understood on a semi-quantitative level. However, due to the complicated mechanisms involved in electron scattering and polymer breakdown, an empirical approach is necessary for developing a functional "system".

This chapter follows the lithographic process outlined in Figure 1-1: initial cleaning, spin-on of resist/pre-bake, exposure, development and post-processing, and pattern transfer which includes etching, lift-off, and removal of the resist. Included in the exposure section is a general outline of electron microscope operation and a discussion of the electron scattering processes. The chapter is summarized in a table listing the parameters identified in each section.

2.2 Lithographic Process

2.2.1 Initial Cleaning

Initial cleaning of samples depends on their prior processing history and the type of contaminant(s) present. For example, a particle on the surface of the sample will cause resist thickness variations during resist application, change the dose and development characteristics in its vicinity, and affect the transfer of the pattern to the substrate. This is especially evident when

one compares the relevant length scales. A particle may be several micrometres in size, while the resist thickness for nanolithography is typically about 200 nm at its largest, and pattern features can extend well below 100 nm in size.

Preventing as many contaminants as possible from coming into contact with the sample is obviously preferable to cleaning it, since contamination from the cleaning process is also possible. Ensuring that a clean environment exists that minimizes airborne particles, that the wafer is thoroughly cleaned during processing steps such as etching, and keeping the time that a sample is exposed to the room environment to a minimum helps in this regard. There may, however, be times when contamination is unavoidable due to processing considerations.

How contaminants are dealt with depends on their composition. Contaminants can be separated into three broad categories [Ref. 8, p.182]: organic films, inorganic films, and particulates. Examples of inorganic films that may be undesirable are unwanted oxide films, salts, and water stains, while particulates can come from many sources including humans, airborne particles, dirty equipment, storage containers, contaminated cleaning solutions, and previous processing steps. Generally, these are removed by using etching techniques. On GaAs, sulphuric acid or ammonium hydroxide can be used to remove surface contaminants and oxides without etching the substrate. For deeper contamination some of the substrate may also need to be etched away. This may not be a feasible option in some cases such as those involving regrowth on a patterned substrate. Etching of the substrate may also increase the roughness of the surface of the sample.

Organic films come from a variety of sources such as machinery oils or greases, people handling the substrate, and polymer films from previous steps or contaminated chemicals. Two methods of cleaning these types of contaminants are the use of a solvent-rinse system and/or ashing the surface with an oxygen plasma (see Section 2.3.3). A solvent-rinse system may include: an acetone rinse, possibly heating the acetone and doing multiple rinses followed by one or more rinses in methanol to dissolve the remaining acetone, deionized water to dissolve the methanol and, finally, blowing the remaining fluid off the sample with a clean gas such as nitrogen. The purpose of multiple rinses is to ensure that the final rinse in a step is in as clean a solution as possible. Once cleaned, the sample is moved to the next step, the application of the resist coating.

2.2.2 Spin-on of Resist/Pre-Bake

Application of thin, uniform coatings of resist is critical to future process steps. Uneven resist coatings could result in parts of the pattern developing while others remain undeveloped. As well, good adhesion of the resist to the substrate is required so that it can withstand the processing necessary to transfer the pattern to the substrate.

The spin coating method is a widely used method for coating thin layers on planar substrates. It is very flexible in that the basic technique and apparatus can be used in the application of a variety of resists to a number of different substrates. It involves placing a few drops of the coating material in the centre of a sample and spinning the substrate at a speed from 1000-10,000 rpm for a period of time long enough to reach a steady state in thickness and for the resist to be nearly dry. The substrate is then baked to remove the remaining solvents and to relieve stress that may build up in the film during the spinning process, due to shearing.

When the resist is in a fluid state, particulates are more likely to stick when they strike the surface. Since this occurs when applying the resist solution, spinning, and baking, particular care

must be taken to minimize exposure to particulates during these processes. Operating in as clean and dust-free an environment as possible while applying and spinning the resist solution onto the sample minimizes this problem. For the pre-bake, the substrate is placed in a clean, glasscovered container.

For a Newtonian fluid, where the volumetric flow rate change is zero, the thickness of the steady state resist layer is expected to follow a relationship like [Ref. 8; 13]

$$\delta = K \left(\frac{\nu}{\omega^2} \right)^{\frac{1}{3}}$$
(2-1)

where δ is the film thickness, υ is the kinematic viscosity, ω is the rotation speed, and K is a constant that depends on the volume fraction of resist to solvent and the substrate size. This equation does not account for effects such as the evaporation of the solution the resist is dissolved in, in which case the viscosity is no longer constant. K depends on the substrate size because as this size decreases, the coating becomes thicker, holding all other parameters constant. For samples less than a centimetre wide, uneven coatings result as the area influenced by edge effects becomes comparable to the wafer area. The thickness behaviour becomes more complex with low viscosity fluids at higher rates of rotation or for long times, but this regime has also been solved theoretically [Ref. 13]. Since the viscosity increases with increasing solid percent, diluted solutions and higher spin-on speeds result in thinner coatings. Thinner coatings are desirable to reduce the scattering of electrons in the resist which leads to broader developed linewidths, as is discussed in the exposure and development sections below.

The pre-bake is done at a temperature high enough to relieve the stress in the resist layer and to evaporate the remaining solvent, but low enough not to damage the coating. For polymers this is typically done above the glass transition temperature, usually referred to as T_g , at which point the material starts to flow. For polymethylmethacrylate (PMMA), a typical bake temperature is 175 °C (Appendix A). This is typically done for about 2 hours in an oven, although longer times on the order of 12 hours have been used [Ref. 14]. The reasoning behind using a longer bake time is that it should relieve more stress in the layer and promote better adhesion. If the stress releases during development or pattern transfer it could result in the resist shifting or detaching from the sample, which would destroy the desired features. Once the prebake is complete, the sample is ready for exposure.

2.2.3 Exposure

Exposure of a lithographic pattern consists of two main processes: delivering the current into a focussed spot which is raster-scanned to create a pattern, and the interaction of the electrons with the resist and substrate which cause the resist to change. This change is then used to develop, or selectively remove, the resist coating, as discussed in the next section. The electron microscope will be discussed first, and this is followed by a description of the mechanisms that cause the resist to change upon exposure to high energy electrons.

2.2.3.1 Electron Microscope Fundamentals

A schematic diagram of the four main components of a scanning electron microscope (SEM) is shown in Figure 2-1. These components are an electron source, a beam deflection system, electromagnetic lenses, and apertures. The figure is more typical of a field emission system such as the one used in the present work, than a thermal emission system. Thermal

emission systems generally have more condenser lenses in the column to reduce the larger initial spot size.

The role of the source is obvious. The top, condenser, lens is used to provide a demagnified image of the source, approximately 1 nm in diameter, which is imaged by the objective lens onto the target. The primary role of the objective lens is to allow flexibility in the "working distance" between the sample and the scan coils. Larger apertures called "spray diaphragms" are placed throughout the system to collect stray electrons. The beam limiting apertures control the maximum angle, α , of the beam through the system. The angle α on the sample is shown in Figure 2-1(c). The apertures affect the beam aberrations through the dependence of the aberrations on α (spherical aberration $\propto \alpha^3$, chromatic aberration $\propto \alpha$, and astigmatism $\propto \alpha$).

The following parameters all directly affect the quality of the features obtained using the SEM to expose the resist layer on a substrate: the electron energy, the spot size (of diameter d_s, on the sample), the average current at the sample, the current stability at the sample, and the rotation angle between the beam scan directions and translation stage scan axes. Theoretical considerations (Section 2.2.3.2) and the information gained through the development process described in Chapter 4 have led to the following optimal settings. The electron energy is particularly important for limiting the range of forward scattered electrons (see Section 2.2.3.2) in the resist layer and so was always set at 30 keV, the maximum allowable energy for the S-4100 SEM. For many applications the orientation of the pattern with respect to the crystallographic planes of the sample is very important. It is therefore convenient to have the beam axes coincide with the X,Y translation axes of the sample holder. This is accomplished by setting the working distance to ~19 mm (see Chapter 4). With the electron energy and working



Figure 2-1. (a) Field emission scanning electron microscope column, corresponding to the column of the Hitachi S-4100 SEM: (1) Electron source, (2) Beam paths showing the effect of successive apertures in the column, (3) Apertures, (4) Condenser lens, (5) Deflection coils, (6) Objective lens, (7) Specimen. (b) Magnetic lens detail showing how the magnitude of the axial magnetic field component, B_z , varies in the lens region. (c) Detail showing geometry of beam aperture angle, α , at the sample.

distance fixed, the only remaining control is through the aperture sizes and the extraction current. The apertures are usually set to the smallest available diameter to minimize the aberrations due to non-paraxial trajectories in the lenses, as well as helping to form the smallest spot size. This does limit the current and, hence, increases the time required to expose a pattern. Together, the smallest final aperture setting (20 μ m diameter in the S-4100 SEM) and working distance (19 mm) fix the aperture angle (-0.53 mrad (0.03°)). The extraction current is adjusted as high as possible to minimize exposure times while maintaining an acceptable period between tip flashes, after which the system must be allowed to stabilize for about 2 hours before it is again usable for lithographic purposes. An emission current of 10 μ A has been found to be optimum.

With these "standard" settings the average current and spot size on the sample along with the stability of the current - both short term (seconds) and long term (hours) - are determined primarily by the electron source characteristics. The rest of this section therefore describes the two principle sources used in SEMs and compares their characteristics with regard to lithographic applications. This section also includes a brief explanation of why the beam scan axes depend on the working distance.

Electron sources are generally characterized by their brightness, β , which has units of A·cm⁻²·sr⁻¹. For a given extraction voltage this becomes a constant of the system, expressed as

$$\beta = \frac{j}{\pi \alpha^2} = constant$$
 (2-2)

where j is the current density in A·cm⁻² and α is the beam half angle *at any image of the source, regardless of specific lens or aperture arrangements.* The beam half angle at the specimen, α , is shown in Figure 2-1(c), for the image at the sample surface. Although the brightness is constant at all points in the system, apertures restrict the beam angle and lower the current available at the sample. The relevant parameters at the sample are the final beam spot size d_s , the specimen current I_s and the beam angle at the specimen α_s , determined by the lens elements and usually restricted by the final aperture in the system. Substituting the specimen values into Equation 2-2 and using the definition of the current density, j, as current divided by area, we find that at the specimen,

$$\beta = \frac{I_s}{\pi (d_s/2)^2} \frac{1}{\pi \alpha_s^2} = \frac{4 I_s}{\pi^2 d_s^2 \alpha_s^2}$$
(2-3)

From Equation 2-3 it is seen that the current, spot size and beam angle are not independently variable. Fixing the spot size and beam angle with the column apertures and lenses limits the available beam current on the sample, for a given brightness.

Electron sources typically operate in either one or a combination of thermal and field emission modes [Ref. 11, p.7-20; 15, p.13-20]. These processes are illustrated schematically in Figure 2-2. For thermionic emission the electrons must overcome the workfunction, Θ , of the material to be emitted. The value of Θ is affected by the crystal orientation of areas on the tip and the composition of any surface layer of atoms covering the tip which can raise or lower the work function. Thermionic emission sources use a tip with the temperature raised to just below the melting point of the material to give as many electrons as possible enough energy to overcome the work function. Emitted electrons are then accelerated down the column by the potential difference between the tip and the other system components. Field emission occurs when the potential gradient, caused by a strong applied electric field, is large. This reduces the potential barrier width, b in Figure 2-2(2), so that tunnelling, which depends exponentially on b, can occur. Field emission occurs at energies close to the Fermi energy in the tip, below the



Figure 2-2. Thermionic and field emission of electrons. (1) Thermionic emission of electrons, which must overcome the work function, Θ , at the interface between the metal and vacuum, with a small electric field applied. (2) Field emission of electrons by quantum mechanical tunnelling through a potential barrier of width b. This is made possible by a much higher electric field in the vicinity of the interface.

energy level of the workfunction. There is a much larger density of electrons available at the Fermi energy than at the top of the workfunction, where thermal emission occurs. Two anodes are generally used in field emission microscopes to get fields of the required strength, on the order of 10^9 V·cm⁻¹. One anode is used to extract the current while the second accelerates or decelerates the electrons to yield the required final beam energy.

Since higher current corresponds to reduced pattern write times, having a high brightness is desirable. Field emission sources have much higher brightness, on the order of $10^8 - 10^9$ $A \cdot cm^{-2} \cdot sr^{-1}$ when compared to thermionic sources whose values are in the $10^5 - 10^6 A \cdot cm^2 \cdot sr^{-1}$ range (both at $E \approx 20 \text{keV}$) due to the large amount of current extracted in the tunnelling process [Ref. 8, p.69]. Another advantage of field emission tips is their smaller source sizes ($\approx 100 \text{ nm}$) which means that fewer condenser lenses are needed to demagnify the source image to the required small probe size. The main disadvantage of field emission sources is their greater current noise when compared with thermionic sources. This is particularly relevant to lithography applications of the SEM, where the feature size written in the resist is often a very sensitive function of the dose of incident electrons.

Thermionic sources, using a heated tip, have much more stable beam currents than the field emission sources. The field emission tip current suffers from both short term fluctuations and long term drift. The short term fluctuations are a result of diffusing surface atoms changing the structure of the tip and are also due to changes in the number and type of atoms or molecules adsorbed onto the tip [Ref. 11, p19; 16, p.3]. Long term downward drift is also noted, due to the build up of excess atoms on the tip surface which must then be cleaned off by flashing (running a higher current through the tip for a short time). To reduce these effects and prevent damage to the tip from ionized atoms in the large electric field around the field emission tips, they must be operated in a much higher vacuum than the thermal tips. The life cycle of the tip is illustrated schematically in Figure 2-3, which shows the atoms building up on the tip resulting in the final condition when flashing is required. Some systems heat the field emission tip to an intermediate temperature of about 1000 K in an attempt to avoid adsorption of atoms and molecules onto the tip and to reduce the noise associated with this. The result of this noise is a variation of exposure dose while writing patterns and it imposes strong limits on the uniformity of large patterns.

Once emitted, the electron beam is focussed on the specimen by the lenses in the column. These components set the final spot size and beam aperture which, in turn, fix the current through their relationship to the source brightness. The beam angle is limited at the same time using small apertures, as shown in Figure 2-1(a) & 2-1(c). Typical lenses are cylindrically symmetric, weak field magnetic lenses with a bell-shaped magnetic field on the beam (z) axis as shown in Figure 2-1(b). The magnetic field is designed so that it is confined to a small volume



Figure 2-3. Process of gas adsorption on a field emission tip. (a) Condition of tip after desorbing atoms (flashing). (b) Unstable current portion as atoms adsorb onto tip. (c) More stable regime where atoms occasionally desorb from and adsorb onto the tip. A gradual decrease in the emission current is seen. (d) Multiple layers of atoms form and more adsorption and desorption occurs (nearing the point where tip needs to be flashed again) [Ref. 16, p.3].

and all the components are kept at earth ground so that the radial and angular components of velocity are due entirely to the magnetic fields.

For a weak magnetic lens the lens equation 1/f = 1/p + 1/q is used [Ref. 11; 15] to describe the imaging system. The resulting magnification of the spot is given by M = q/p, where f is the focal length, p is the source image to lens distance and q is the lens to final image distance. If the demagnification of the source image is large then p »q and f ~q which implies M ~ f/p. Under the weak magnetic lens approximation, the electrons are assumed to have constant velocity and to not vary radially in the field region. In this case the focal length becomes [Ref. 11; 15]

$$\frac{1}{f} = \frac{e}{8m_o V (1 + E/E_o)} \int_{-\infty}^{+\infty} B_z^2(z) dz$$
(2-4)

where f is the focal length (m), V is the potential difference across the anode and cathode (V), E is the beam energy (keV), $E_0=m_0c^2=511$ keV, the axial component of magnetic field shown in Figure 2-1 (b) is $B_z(z)$ (T), e is the electron charge (1.602 X 10⁻¹⁹ C), and m_0 is the electron rest mass (9.11 X 10⁻³¹ kg).

The function of the first lens in the system, the condenser lens (shown in Figure 2-1) is to demagnify the initial spot image. The initial spot image occurs at a point called the "cross-over", where the electron trajectories first cross-over each other after the electrons are emitted from the tip and are accelerated by the electric field in the tip region. The last lens in the system, the objective lens, also has an effect on the spot size, but its main function is to focus the spot on the specimen, or set the working distance. Decreasing the condenser lens magnetic field strength results in an increase of the magnification. At a set energy, increasing the working distance leads to a larger magnification and an increase in the spot size at the specimen. At large working distances and low energies, the assumptions p = q and those of the weak lens assumption, constant velocity and radial distance in the magnetic field region, start to break down. Although the magnetic field strength can be varied to compensate for changes in beam energy, this has limits due to a particular microscope's design. As the focal length of the lenses vary (especially the objective lens), the distance between the image plane of the condenser lens and the object plane of the objective lens also varies. All of these effects will increase the beam spot size at the specimen at large working distances.

The apertures, Figure 2-1, are used to limit the beam angle and hence also affect the final beam current. Typically, the final aperture is used as the limiting aperture in the system and an aperture near the final lens sets the beam half-angle by $\alpha \approx d/2f$ where d is the aperture diameter and f is the focal length of the final lens. Larger beam apertures, while they increase the beam

current, also increase the beam aberrations as the aberrations depend on the beam angle [Ref. 11-12; 15]. These aberrations ultimately limit the spot size. The major, but correctable, aberration is due to beam astigmatism, or the beam focussing at different points along different axes in the plane of the specimen. This is corrected by using additional beam shaping elements in the column. Spherical aberration, or the focussing of the beam at different points on the beam axis is inherent in the lens design and is not correctable. Also, electrons of different energy will focus to different places on the beam axis, an effect called chromatic aberration. Although small beam apertures decrease these effects, it is not possible to eliminate them entirely. A system is optimized to minimize the effects of these uncorrectable aberrations and the result is that it is not possible to arbitrarily increase the beam angle to get large current and small spot sizes at the same time.

A rotation of the source image is also introduced by the motion of the electrons through the magnetic fields. The rotation angle, ϕ , is given by the expression [Ref. 15]

$$\phi = \sqrt{\frac{e}{8m_o V \left(1 + E/E_o\right)}} \int_{-\infty}^{+\infty} B_z(z) dz$$
(2-5)

This rotation affects the lithographic process due to the necessity of placing the deflection system before or in the final lens. The scanning coils are also electromagnetic and the process of scanning the beam across the sample changes the rotation equation from its value without scanning. This results in a net rotation between the screen (or lithography pattern) and the motion of the sample on the microscope stage. This becomes important if the pattern is to be written along a specified crystallographic direction for processes such as cleaving and etching. Since the rotation depends on the integral of the axial component of magnetic field and inversely on the beam energy, changing the working distance or beam energy changes the rotation angle.

There are thus several trade-offs to be considered when operating the microscope for lithographic purposes. The final current and spot size depend on the beam energy, condenser lens setting, working distance or objective lens setting, and, for field emission sources, there are noise considerations as well. The optimum parameters are determined by considering the electron scattering processes in the material. Electron-material interactions are the subject of the next section.

2.2.3.2 Electron Beam and Material Interactions

After impacting on the surface, the electron beam interacts with both the resist coating and the underlying substrate. To understand the subsequent exposure and development processes, the nature of this interaction and the parameters it depends on are needed. As will be discussed below, some of these parameters are: the impacting beam energy, the substrate and resist composition (atomic number, atomic weight, density), and the thickness of the materials. The mechanism by which the impacting electrons alter the resist is also important. The basic process will be presented here and more detail on the scattering and polymer breakdown mechanisms can be found in Appendix B.

Upon entering the thin resist layers, the high energy electron beam spreads slightly due primarily to inelastic small angle (forward) scattering. This scattering is illustrated schematically in Figure 2-4(1). The result of this process is that energy is deposited in a small area that grows in diameter as the beam travels through the resist layer. After traversing a thin resist layer, the electrons continue losing energy through inelastic scattering processes, but also experience

elastic scattering, which typically occurs at relatively large angles with a distribution depending on the scattering cross-section (see Appendix B). Some of these electrons reenter the resist, at lower energy, where they give up more energy to the polymer layer over an extended range, on the order of the penetration depth in the substrate [Ref. 10, p.61; 17, p.43]. This process is illustrated in Figure 2-4(2). Regardless of the method by which energy is transferred to the resist layer, the resulting material modifications are usually taken to depend only on the local energy density deposited in the layer.



Figure 2-4. Schematic illustration of scattering processes in the resist and substrate. (1) Small angle forward scattering. (2) Large angle scattering and backscattering from the substrate.

Although the exact distribution of deposited energy is complex, a very useful

approximation describes the radial dependence in the form [Ref. 8; 10; 12; 15; 17]:

$$E_{abs}(r) = \frac{B}{1+\eta_{E}} \left(\frac{1}{\zeta_{f}^{2}} e^{-\left(\frac{r}{\zeta_{f}}\right)^{2}} + \frac{\eta_{E}}{\zeta_{b}^{2}} e^{-\left(\frac{r}{\zeta_{b}}\right)^{2}} \right)$$
(2-6)

where $E_{abs}(r)$ is the areal energy density absorbed, B is a constant depending on the materials and initial electron energy and flux, ζ_f and ζ_b are the half-widths of the forward and backscattered distributions, and η_E is the ratio of backscattered to forward scattered contributions to the total energy absorbed. These parameters are determined both empirically and by using numerical simulations. The first term is due to the forward scattered primary electrons as they traverse the resist layer, while the second is of much larger range and is due to the diffuse, backscattered electrons. For Equation 2-6, reported values for a 0.5 µm film of PMMA on a silicon substrate are: ζ_{f} -0.08 µm and ζ_{b} -2 µm at 20 keV while at 50 keV the values are ζ_{f} -0.04 µm and ζ_{b} -9 µm [Ref. 18, p.43]. The 20keV silicon substrate values for η_E are in the range 0.5-1.1 [Ref. 15, p.312]. This illustrates the basic results of the scattering process, that higher beam energies result in smaller forward scattering ranges in the resist while the same conditions increase the backscattered range by large amounts. These backscattered ranges are much larger than the submicron features of the pattern and lead to a proximity effect, where closely spaced pattern features contribute to the absorbed energy dose of other pattern elements.

It is important to realize that the incident dose specified by the lithography control software is in terms of the charge incident on the resist layer (beam current times exposure time). This does not relate directly to Equation 2-6, and an additional conversion factor must be introduced for this purpose.

Thus, for an isolated dot exposure, the total energy deposited in the resist as a function of radial distance from the exposure point can be expressed by replacing the constant B in Equation 2-8 by another constant dependent on the material parameters, beam energy and beam current times exposure time. For a given exposure time, the developed spot size will be

approximately given by the radius at which the deposited dose falls below the critical value that is needed for the resist to be developed.

2.2.4 Development and Post-processing

2.2.4.1 Development

The development process transfers the exposed pattern into the topology of the resist. Procedurally, it is similar to the initial cleaning; immersing in the developer for a specified time, followed by one or more rinses, and blowing the remaining fluid off the developed wafer with a gas such as nitrogen. A resist and developer combination is typically characterized by two figures, the sensitivity and contrast. Figure 2-5 illustrates both of these for a positive resist, which is one where the exposed areas are developed away. A negative resist is defined by the opposite effect: the exposed areas remain after developing. Further details on this may be found in Appendix B.

For a positive resist the sensitivity is given by the dose necessary for the resist to develop all the way through to the substrate. For a negative resist it is usually defined as the point where 50-70% of the resist in the exposed area is left. A resist with low sensitivity will not be good as it will take too much time to expose, while one with too high a sensitivity will have two problems. One is that it may be too volatile, with its chemistry changing uncontrollably between the time it is applied and stripped off, and the second is that the exposure time may be so small that too few electrons are needed to expose it, leading to large statistical fluctuations.



Figure 2-5. Typical development curve used in determining contrast and sensitivity for a positive resist.

The contrast, $\gamma_{pos},$ is defined by the slope of the line in Figure 2-5 through

$$Y_{pos} = \frac{1}{\left(\log D_{pos} - \log D_{pos}^{0}\right)} = \left[\log \frac{D_{pos}}{D_{pos}^{0}}\right]^{-1}$$
(2-7)

where the symbols are defined in Figure 2-5. A larger contrast means that the developer is more discriminating in its removal of molecular fragments and provides a sharper cut-off between the solubility of higher and lower molecular weight polymers in the resist.

The contrast and sensitivity of the resist depend on many factors and must be quoted with

reference to specific molecular weight resists, exposure conditions, resist thickness, substrate, developer/rinse composition and times, the temperature, and any additional processing conditions, such as developing with ultrasonic vibration. Typical values for PMMA are a sensitivity of 50-80 μ C/cm² and a contrast of about 2 [Ref. 10, p.96,227]. The contrast and sensitivity also depend on the distribution of molecular weights in the resist. Ideally, this distribution should be narrow, initially far above that which the developer will easily dissolve and, when exposed, entirely below the molecular weight where the developer will selectively remove the resist. Usually, the contrast and sensitivity are quoted for large exposed areas. Features that cover less area could require larger doses to develop entirely through to the substrate. Since longer development times will remove unexposed resist as well as the exposed regions, shorter development times are preferable. Another parameter that affects this is the development temperature, which increases the rate at which polymer is removed and reduces the necessary exposure time.

The important issue is that the doses used to define the sensitivity and contrast fundamentally relate to the absorbed energy dose described in the previous section, and not the incident dose used during exposure which is expressed in terms of the measurable charge incident on the resist.

2.2.4.2 Post-Processing

Post-processing typically refers to a post-bake to remove any remaining solvents from the development process and to promote adhesion for subsequent pattern definition steps. However, some literature using thin layers of PMMA to create fine patterns on GaAs report that post-

baking was avoided so that the profiles were not degraded from thermal flow [Ref. 6]. Degradation at temperatures as low as 50 °C was noted by these researchers. Instead, they placed the sample in a desiccator for more than a day. A post-bake may therefore not be advisable for thin patterns with fine features. We have not noticed any effects due to post baking on large feature patterns (greater than 150 nm) and have not attempted to post-bake on smaller featured patterns.

2.3 Pattern Transfer

2.3.1 Etching

There are two main types of etching; wet chemical etching and dry etching. Only wet chemical etching will be discussed below and for further information on both types of etching there are several books available [Ref. 19-21].

Wet chemical etching on GaAs involves two reactions. The first oxidizes the surface and the second removes this oxide layer and is categorized according to whether a base or acid is used. Factors to be considered are how much the etchant attacks the masking layer, whether the etchant tends to smooth or roughen the surface as it etches, the safety and ease of use of the chemicals, and whether enhanced etching at the mask edges occurs. As well, whether the etchant is isotropic or anisotropic is important for some applications. Isotropic etches etch different crystal planes at the same rate, while anisotropic etches etch different crystal planes at different rates. This is illustrated in Figure 2-6. In a diamond or zinc-blende crystal, the (111) planes generally have lower etch rates than other planes due to the higher density of atoms in these
planes. In GaAs these rates also depend on the direction from which they are approached; a Ga face is designated (111)A and an As face (111)B, with the (111)A planes typically having a slower etch rate. Further considerations within an etch system are the ratio of acid or base to oxidizer, and the overall concentration and temperature of the solution.



Figure 2-6. Illustration of different etch profiles that typically occur when etching features in different directions on a GaAs substrate with an anisotropic etch.

The typical method used is to have one container with etchant and one or more rinse solutions. The advantage of multiple rinse solutions is that the one closest to the etchant can be disposed of each time and refilled with fresh H_2O at the end of the line. This ensures that the last rinse is always uncontaminated.

2.3.2 Lift-off

Lift-off involves patterning the substrate with an undercut resist profile and then evaporating a layer of material on the substrate. The remaining resist is then stripped off, leaving the material in a patterned shape on the substrate. This is used, for example, to pattern metallic contacts on a substrate. The resist profile is important in this process, and the upper edge must be narrower than the lower edge in order for the metal to deposit in a way that will allow the resist to be removed. The required profile is illustrated in Figure 2-7 and shows the areas of resist that are still exposed where the resist stripper can access and dissolve the resist and "liftoff" the remaining metal.



Figure 2-7. Illustration of resist profile needed for the lift-off process.

2.3.3 Strip-off of Resist

Removing the resist is typically done with a solvent, such as acetone for PMMA, that the resist will dissolve in. A similar procedure to the initial cleaning procedure is used. Another method, called ashing, involves etching the surface with an oxygen plasma. This has the

advantage that it leaves no residue, which the solvent process may leave on the surface. A disadvantage is that it does not remove metallic ions well, which the wet stripping process does. However, a plasma stripping process can be followed by a wet stripping process to remove metals [Ref. 22].

2.4 Summary

A large number of parameters have been identified in this chapter as having an effect on the final pattern quality. These parameters are summarized in Table 2-1.

| Process | Parameters |
|------------------|--|
| Initial Cleaning | Contaminant Type |
| Spin-on Coating | Rotation Speed Substrate Size/Shape Coating Composition Coating Properties |
| Pre-Bake | Resist Properties (T _g) Bake Temperature Bake Time |
| Exposure | Accelerating Voltage Beam Spot Size Beam Current Current Stability Substrate Composition Substrate Thickness Resist Properties/Thickness Resist Contrast/Sensitivity Pattern Geometry Vacuum Conditions |
| Development | Developer Properties Exposure Development Time Temperature Agitation During Process |
| Post-Processing | Bake Temperature Bake Time Development Process Resist Properties |
| Etching | Resist Composition Substrate Composition Etchant Composition Temperature Time |
| Strip-off Resist | Resist Composition Stripper Properties Agitation Temperature Time |

Table 2-1. Parameters affecting the lithographic patterning process.

3.1 Introduction

This chapter, together with Appendix A, describes the configuration and usage of all the hardware and software components of the lithography system. The components, discussed in Section 3.2, include a photoresist spinner used to apply the resist coatings onto the substrates, an oven to bake the photoresist, the chemicals and related storage and handling equipment, and the exposure system. A block diagram of the exposure system appears in Figure 3-1 below. The exposure system consists of a field emission scanning electron microscope (SEM); a computer with an interface board equipped with digital-to-analog (DAC) and analog-to-digital (ADC) converters; an interface between the two; and software to design and control the exposure process, called the Nanometer Pattern Generation System (NPGS). The methods used to characterize the specimen current stability, the resist thicknesses, and the topography of the developed resist layers are described in Section 3.2. Section 3.3 describes the characterization techniques used to study the system and its application to electron beam lithography. More specific procedures for the lithographic process can be found in Appendix A.

3.2 System Components

The following subsections describe the exposure hardware and software and the sample related hardware.



Figure 3-1. Block diagram of the major components of the electron beam lithography design and exposure system. The programs are: DesignCAD (used to design the patterns), MRF (used to create the run files), NPGS, PG, and AL (used to write the patterns). More detailed explanations of the software can be found in Section 3.2.2 and Appendix A.

3.2.1 Exposure System Hardware Components

The exposure hardware system consists of a S-4100 Field Emission SEM, a computer to run the software and control the exposure system, and an interface between the two. Each will be described below, beginning with the electron microscope.

3.2.1.1 Hitachi S-4100 Field Emission SEM

The electron microscope used in this study is a cold cathode field emission SEM, model S-4100 from Hitachi. The microscope was modified by interrupting the signal between the microscope's internal XY scan circuitry and its electron beam column x-y scan controls, as will be described in the interface section below. Operating instructions can be found in the operation manual [Ref. 16]. Proper adjustment of astigmatism and fine focus are particularly important for attempting to obtain the best resolution with the lithography system.

A summary of the microscope's characteristics is provided in Table 3-1. Note that all of these features, together with the image shift, astigmatism correction, and coarse/fine focus controls are set by the user and not the lithographic software described below. Use of the microscope's controls during the pattern exposure should therefore be avoided except where absolutely necessary.

| Performance | Magnification | 20 to 300,000X |
|-----------------|--|--|
| | Resolution | $1.5 \text{ nm} (V_{acc} = 30 \text{kV}, \text{WD} = 5 \text{mm})$ |
| Electron Optics | Accelerating Voltage (V _{acc}) | 0.5 to 30 keV (100 V steps) |
| Parameters | Emission Current (I _{emm}) | 5 to 20 µA (1 µA steps) |
| | Working Distance (WD) | 5 to 35 mm (1 mm steps) |
| Specimen Stage | X, Y Directions | 0 to 25 mm (2 µm steps) |
| | Z Direction (WD) | 5 to 30 mm (2 µm steps) |
| | Tilt | -5° to 45° (0.18° steps) |
| | Rotation | 360° (0.5° steps) |

Table 3-1. Selected Hitachi S-4100 cold cathode field emission SEM specifications. From the S-4100 operating manual [Ref. 16, p.5, 2-17, 2-33].

3.2.1.2 Computer and NPGS Hardware

The computer used to control the pattern exposure is a 80486 50 MHz IBM-AT

compatible running the MS-DOS operating system and equipped with a Data Translation

DT-2823 multi-function board. This board is equipped with 16 digital I/O lines, an internal

clock, two 16-bit analog-to-digital conversion (ADC) inputs and two 16-bit digital-to-analog conversion (DAC) outputs. The board is capable of storing output data for both DACs and then using this data to change both DAC output levels at the same time. This allows the X,Y raster control for the microscope to have both channels simultaneously updated. The digital I/O lines are not used at this time, but could be used in conjunction with the NPGS software to control additional hardware such as a motorized sample stage. There is also a card installed in the computer that can be used in the future if a beam blanker is installed in the SEM, and an adapter to connect the DT-2823 board to three BNC connectors for the X,Y scan outputs and the video signal inputs. This adapter is also equipped with circuitry to allow adjustments of the output voltage ranges from the DT-2823 DACs.

3.2.1.3 Interfacing of Computer and SEM

The electron microscope was easily modified to allow external control of the electron beam scan controls. These changes are illustrated in Figure 3-2. The modifications involved placing a double-pole double-throw (DPDT) switch between the microscope internal scan controls and the magnification circuitry of the microscope, which was accomplished at connector CN-60 [Ref. 23, drawing 6. SG/VA P.C.B. (2/6)], which was available at the rear of the microscope. BNC cables were run to allow the switch to be attached to the front panel of the microscope. BNC cable connections were then made between the NPGS adapter box described above and this connector box on the rear of the microscope. The microscope provides a VIDEO OUT port on its rear panel, and this was connected directly to the NPGS adapter's VIDEO IN connector. Finally, the computer case was grounded to the microscope rear panel.



Figure 3-2. Details of the interface between the NPGS controls and the SEM through the connector box.

The range of signal levels required at the magnification input is ± 10 V. The board was calibrated for this range using the procedure outlined in the NPGS installation guide [Ref. 24], and then the NPGS system was calibrated using the resolution standard supplied with the NPGS system.

3.2.2 Exposure System Software Components

This subsection describes the components of the NPGS software system and explains their relation to each other. A comprehensive description of how to use the system is contained in Appendix A.

The Nanometer Pattern Generation System (NPGS) software, from J.C. Nabity Lithography Systems, consists of three main components. The patterns are designed using a computer aided design (CAD) package called DesignCAD, and the files are saved in an ASCII format readable by the NPGS programs. The exposure conditions are then set in a program called Make Run File (MRF). Finally, the actual exposure is done with the NPGS program and the two programs it calls. One program must be run to generate the pattern (PG) and the other may be run to do alignment (AL) with respect to previously written markers.

DesignCAD is a two-dimensional CAD program. The use of this program is outlined in its accompanying manuals, along with further instructions in the NPGS manual [Ref. 25; 26]. The pattern is designed using absolute units of µm. Different exposures are indicated by the use of different colours in the pattern design, up to a maximum of 16. As well, different drawing layers allow more parameters to be specified. All pattern features are defined or broken down into line segments, whose width is specified in the CAD program. When this file is complete, the MRF program is used to specify the run parameters. The number and names of the patterns are broken into individual exposure points, called pixels, the pixel spacings need to be specified in the program. As well, the magnification at which the pattern is to be written is set in this program.

The pattern exposure is accomplished by running the NPGS or PG software. The NPGS software has the advantage that it calls either PG to write the patterns or AL to align patterns as necessary, but the PG and AL programs can also be run independently. If the run file created by MRF contains both patterns to be written and ones marked for alignment purposes then the NPGS program must be used. The NPGS and PG programs allow for an adjustment parameter to be entered at run time, to adjust the exposure time. This is used to account for the difference between the current entered in the run file created by MRF and the actual measured beam current at the time of exposure. The software also allows for the possibility of automatic stage controls and digital control of the microscope parameters, although the S-4100 is not equipped with these features.

3.2.3 Other Processing Components

3.2.3.1 Photoresist Spinner and Oven

A photo-resist spinner was purchased for applying the resist to substrates. It is a model EC-101D photo-resist spinner manufactured by Headway Research Inc. The spinner is capable of rotation speeds from 500 to 10,000 rpm. It works by holding the substrate onto a chuck using a vacuum and then accelerating the substrate up to a set speed. The spinning then continues for a set time and then stops, after which the vacuum to the chuck is disengaged. A pump was used to provide the vacuum source needed for the spinner to hold the substrate on the chuck (19-25 "Hg). The vacuum chuck that the substrate sits on needs to be slightly smaller than the substrate surface. Chucks were designed and built to handle 5, 10, and 25 mm substrates using stainless steel and Teflon (due to concerns about the chemicals in the resists and those in the cleaning processes) and have a hole in their tops to provide the vacuum connection to the spinner shaft. A VWR Model 1300U oven capable of temperature ranges from 30-200 °C was used, for pre and post bake procedures. It has a warm up period of about 1-2 hours and a temperature stability of ± 5 °C.

3.2.3.2 Glassware, Containers, and Manipulators

As described in Chapter 2, the PMMA resist is above its glass temperature during the bake procedure. Accordingly, glass petri dishes were used to hold and cover the substrates to reduce the chance of particulates coming into contact with it during this procedure. The

substrates are then transferred to plastic wafer containers and, as an additional precaution against UV radiation that can expose the resist, aluminum foil is used to cover this container. Glass beakers and stainless steel tweezers are used to handle the substrate during the cleaning and development procedure, described in Appendix A, due to the nature of the solvents used in this study. The photoresist was handled using disposable pipets, in order to reduce the likelihood of contaminating the equipment used during this procedure. The resist is used directly from the original container, as it was found that the solvent rapidly evaporates from solutions in smaller containers leading to thicker resist layers. These pipets were disposed of in a "sharps" container designed for contaminated glass and other sharp objects. A source of dry nitrogen gas to blow fluids off the substrate after processing is also necessary.

3.2.3.3 Chemical Storage and Disposal

The chemicals used for most of the procedures in this study are flammable liquids: acetone, methanol, isopropyl-alcohol (IPA) and methyl-isobutyl-ketone (MIBK). As well, there is the resist solution, containing polymethylmethacrylate (PMMA) and chlorobenzene. The facilities where these chemicals are used require good ventilation and personal protective equipment must be used when handling these chemicals including gloves, lab coat, and an acidsolvent vapour mask, as appropriate. These are stored in a flammable liquids cabinet and disposed, due to their compatibility, in the same waste container. The only exception is the waste photoresist, which requires a separate container due to the chlorinated solvent (chlorobenzene) that it contains.

3.2.3.4 SEM Sample Holder

The SEM sample holder has four purposes. It must hold the sample securely, allow for translations of the sample, allow the beam current to be measured, and provide space for a standard where the beam astigmatism can be corrected and fine focussing carried out on a sample with known features. The sample holder used in this work consisted of 8 holes for holding up to 4 stubs at a time around a central Faraday Cup. Samples to be patterned are attached to aluminum stubs. Initially this was done with double sided adhesive tabs, but metal clips are now available for this purpose. The metal clips are preferable as the adhesive often sticks to the sample after it is removed. These stubs are then attached with screws to the sample holder. A gold standard, attached to a separate stub, is also inserted in the holder. The Faraday Cup is a metal cup (13.38 mm deep and 3.38 mm in diameter) with a 0.225 mm hole drilled in its top surface to allow the beam to enter and has a small solid angle $(2.22 \times 10^{-4} \text{ sr})$ that an electron from the bottom of the cup can scatter into and escape from the cup. The current measured is then proportional to the true current, with a smaller solid angle trapping more of the beam and providing a current value closer to the true beam current. Experience with the above holder led to the design of two other specimen holders that hold the samples flat on their surface with the astigmatism correction standard at the same level, and they also incorporate a Faraday Cup. They are designed to use metal clips to hold the sample in place and will make it easier to align the substrates so that they are perpendicular to one of the stage motion directions. They are also capable of holding a larger variety of sample sizes. They were not, however, ready in time to assist with this work.

3.3 Characterization Techniques

3.3.1 Sample Current Measurements

It is critical that the current at the sample be known before running the NPGS program, as the exposures are based on the beam current specified in the run files. For sample current measurements, the Faraday Cup described in Section 3.2.3.4 is used. The sample stage in the SEM is not grounded. The current in the beam at the sample surface is measured by attaching a meter to a BNC connector on the outside of the chamber where the stage is normally grounded to the chamber exterior. A Keithley Model 617 Electrometer, capable of measurements down to 0.1 fA, was used to measure the beam current. The connections were found to be a major source of noise and, as a result of this, a connector and cable were purchased that are designed for measuring currents in this range. The signals were then found to be much more stable against motion by the operator and the background noise in the measured signal was reduced from fluctuations in the region of 100-200 fA to a level of 30-50 fA. The GPIB port on the Electrometer was used during the characterization of the beam current over time, under the control of the same computer used for lithography. A program was written to acquire a current reading every 2.5 seconds and to write this data to a file along with other information on the microscope's operating conditions. A 2.5 second time period was chosen after examining the Electrometer's operating manual and is due to its data collection and conversion method. Note that this GPIB connection cannot be used when patterns are being written, as this computer's resources are used entirely by the lithographic system. Should this become desirable, another computer would have to be used to simultaneously write patterns and acquire current data.

3.3.2 Resist Profile Measurements

The resist thickness was measured using a DekTak Profilometer. This equipment scans a tip in one direction across a surface and measures the changes in tip height while scanning. It is capable of measuring height changes down to a few tenths of a nanometre with a horizontal resolution on the order of the tip radius (about 12 microns). The machine uses an optical microscope to position the tip, and it is difficult to find patterns with features less than about 20 microns across, leading to the necessity of exposing larger areas (about 100 microns across) in order to make this machine useful. Resist profile measurements were conducted by exposing the resist, with a dose well above its sensitivity, over an area of about 100 μ m². The resist is then developed and inspected under an optical microscope to ensure it has developed through. The DekTak tip is run over one of these surfaces and the difference between the heights of the developed and undeveloped areas is then measured. Optical methods that use the refractive index of the resist and optical interference to find the resist thickness are discussed as a recommendation for the future (Chapter 5), as these would have the advantage of not requiring the resist to be exposed before the thickness is measured.

3.3.3 Pattern Inspection Methods

Quantitative measures of the developed resist topography played a central role in developing the overall system. Two methods are used for resist inspection, optical methods and the electron microscope. A Nomarski optical microscope, with a resolution of approximately 0.5 µm is used to initially examine the patterns. This provided a quick method of examining

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patterns immediately after development thus providing the option of longer development times if the pattern was not visible. It should be noted, however, that it is not always clear whether a pattern has developed all the way through to the substrate and so this method is only used as a rough guide. The colour of the features can be compared with the beam dump area or an area where the substrate is known to be showing through to gauge whether the pattern is through the resist layer or not. For pattern features smaller than ~0.5 μ m evidence of a pattern may be seen, but it may not be clear that the pattern is through. In both cases, however, the patterns need to be viewed in the electron microscope to quantify their profiles.

The electron microscope, with its superior resolution, was used for the bulk of the pattern inspections. Photographs taken with this instrument played an important role in this process and it is anticipated that the ability to directly record the images onto a computer file would allow even more flexibility (see Recommendations, Chapter 5). Viewing patterns with the electron microscope exposes them more, so redeveloping after viewing them can not be done. Less damage is done to the patterns by viewing at an accelerating voltage of 1.0 keV as compared to 30 keV, but the resolution is also poorer at the lower voltage. The breakdown of the resist leads to two effects. One is that the area viewed becomes a negative resist, making it more difficult to strip the resist off. The second is that the exposed areas can break down to leave a thin carbon layer on the surface that is resistant to etching [Ref. 15, p.29]. Both of these effects have been seen and an example is shown in the system characterization and application chapter, Chapter 4.

Chapter 4 System Characterization and Application

4.1 Introduction

This chapter explains how the system was characterized and how processes were developed to achieve resolutions of less than or equal to 50 nm with uniformity on the order of 10 nm. Issues associated with the need to write large area patterns for DFB lasers are specifically addressed.

In Chapter 2, several parameters were presented that affect the lithography process (see Table 2-1). Due to the large number of parameters and the lack of consistent information in the literature, it was necessary to fix some of these and then vary others to determine optimum conditions for pattern generation. Some of these parameters were fixed due to research needs or equipment limitations, some due to their relation to other processing steps, and others were determined after reviewing the available data on the chosen resist materials.

One of the fixed parameters was the substrate, gallium arsenide (GaAs), chosen because of its importance in opto-electronic applications. The resist, PMMA, was selected for its high resolution, based on information in the literature [Ref. 8-10] and discussions with other researchers. The development/rinse system, MIBK/IPA, was adopted after discussions with the resist manufacturer and from the need to get the lithographic system up and working quickly. There were two choices for the electron beam energy. One was to use a low beam energy to reduce the backscattered electron region to as small an area as possible. The other was to use a high beam energy to produce the smallest spot size and penetrate as deep into the substrate as possible, to reduce the forward scattering as much as possible and lower the amount of electrons that backscatter into the resist. The drawback to high beam energy, as discussed earlier, is that this backscattered area is much larger at high beam energy than at low energy. The latter choice was made due to the extra difficulties expected with low beam energy (very thin resists, larger spot sizes in the SEM at low beam energy), after reviewing the literature [Ref. 27-30]. This resulted in using high beam energy (30.0 keV), large condenser lens settings (15), and the smallest final aperture ($20 \mu m$) to get the smallest beam size impacting on the resist layer and the deepest penetration into the substrate.

After initial trials with generic test patterns that included many types of sub-patterns, it was recognized that the optimum conditions were so pattern specific that each pattern had to be treated separately. Two patterns were therefore adopted for further optimization; 1-D arrays of lines for use in the fabrication of DFB laser structures and 2-D arrays of dots to produce quantum dot arrays. For the lines in DFB lasers, this requires sub 100 nm structures with excellent uniformity and spacings of 250-300 nm. The arrays needed to be more than 100 μ m in size to be successfully cleaved into lasers with the available equipment and the uniformity should be excellent over this entire range so that specific pattern nonuniformity can be introduced into the designs if necessary. For the dot arrays, sub 50 nm features at sub 100 nm spacings would be desirable, with excellent pattern uniformity.

The parameters that were varied during this investigation were the development time, resist thickness, resist molecular weight (M.W.), incident dose, working distance, field of view, and array pitch. The results of the investigation of these parameters are discussed below. The resolution and uniformity of patterns are discussed first, by addressing the issues common to both and then presenting the results of the dose and the proximity effect tests. Pattern resolutions of ~50 nm were reproducibly achieved, and 40 nm features were obtained with less consistency.

Pattern uniformity varied due to proximity effects on the edges of patterns. As well, systematic and random variations of feature size and position, on the order of 10 nm, were found within the patterns. It was found that a combination of thin resist layers and short development times provided the most consistent results with the best resolution and uniformity. Finally, the results of overall process investigations are shown and their relevance to the production of devices is discussed.

4.2 **Resolution and Uniformity**

The results presented below were achieved by optimising several of the above parameters. These were the development time, resist M.W. and thickness, incident doses, and pattern spacing variations (proximity effect). The process also involved conducting investigations into the noise present in the system, both systematic and random. These efforts resulted in features sizes of 50-70 nm being obtained in both line and dot patterns with spacings of 200 nm and above. Results for 60 nm dots on a 200 nm spacing and 50 nm lines on a 1000 nm spacing are shown in Figure 4-1. These illustrate that the resolution is close to the best reported for similar conditions [Ref. 10], but that the uniformity can be improved. This is especially evident in the dot patterns, where the dot size can be seen to change over the area of the pattern. (Note that the larger features in the lower centre region of the picture are damage caused from a region viewed at high magnification, which will be discussed later in the chapter.) Preliminary results show some 40 nm features and results on 100 nm spacings, but more experimentation and characterization needs to be done for these results to be consistent. The 100 nm results also show some systematic nonuniformities which will be discussed in Section 4.2.2.





Figure 4-1. Picture # 100929 shows 50 nm single pass lines written on a 1000 nm spacing. Picture # 100932 shows 60 nm dots written on a 200 nm spacing. Both patterns were written on 175 nm 496K PMMA layers (the dark regions) and developed in the MIBK/IPA/H₂O system for 90/10/10 seconds. These results indicate that going to even thinner resists and shorter development times would result in smaller feature sizes than those achieved, but experiments would need to be conducted to confirm this and to optimize the process under those changed conditions.

The following discussion is separated into two subsections. The first deals with issues that affect the resolution and uniformity of features regardless of the specific patterns being used. The second section quantitatively assesses the resolution and uniformity obtained for 1D and 2D arrays as a function of the array pitch.

4.2.1 Pattern Independent Issues

The resolution and uniformity depend to a large degree on the same parameters, once the fixed parameters are chosen based on the criteria discussed above. The important variable parameters are the resist thickness, incident (exposure) dose, and development time. There is also an important noise source that was traced to the microscope circuitry that has an impact on both the resolution and uniformity. Finally, the effect of working distance will be briefly discussed.

4.2.1.1 Resist Thickness

Initial patterns written with 496K M.W. PMMA resist layers spun on at 2500 rpm were inconsistent and of poor resolution (\geq 150 nm feature sizes). Results improved immediately when the resist was spun on at 5000 and 7000 rpm. A systematic study of the resist thickness dependence on spin-speed was therefore carried out. Resist layers of both 950K M.W. and 496K

M.W. 4% PMMA were spun on to 1 cm by 1 cm GaAs substrates and baked at 170 °C for 30 minutes. The central region of the wafers was exposed by adjusting the final aperture of the SEM to its largest setting and letting the microscope do a scan on its slowest mode (MODE 4) for two minutes, exposing a block approximately 100 µm square. This was calculated to give an incident dose of approximately 100-150 μ C/cm², large enough to expose the areas completely. The beam was then switched to external control while being moved to the next area to prevent large area exposures in the areas between patterns which would have caused the resist to thin in these areas during development. A pattern in the form of a 2 mm by 2 mm square was generated with exposed blocks in each corner and in the middle of the square. The developed patterns were then measured using a Dek-Tak Profilometer and the mean and standard deviations for the 5 patterns on each wafer were calculated. The results are plotted in Figure 4-2. The 496K M.W. PMMA solution gave thinner resist layers than the 950K M.W. PMMA solutions, as expected since the viscosity of its solution is smaller than that of the 950K M.W. PMMA solution. The 496K M.W. PMMA layers had minimum thicknesses of about 150 nm as compared to about 200 nm for the layers from the 950K M.W. PMMA resist solutions. Since the maximum spin speed of the equipment is 10 krpm, to achieve even thinner layers would require that the solution be diluted to less than 4% PMMA. The theoretical considerations presented in Chapter 2 give an expected $\omega^{-2/3}$ dependence of resist film thickness on spin speed. Fits to the data in Figure 4-2 gave exponents of -0.49 and -0.58 for the 950K M.W. and 496K M.W. 4% PMMA curves, respectively. Since the simple theoretical treatment in Chapter 2 does not include evaporation of the film solvent, which would change the viscosity of the solution, or non-Newtonian fluids, and assumes no time dependence, it could be expected that this may not be entirely accurate to describe the actual resist layer thickness profiles.



Figure 4-2. Log-log plot of spin speed (rpm) versus resist layer thickness for two molecular weights of 4% PMMA (in chlorobenzene) at the centre of a 1 cm by 1 cm GaAs substrate. Films were baked for 30 minutes at 170 °C. The solid lines are best fit curves to Equation 2-1, allowing the power to vary from its theoretical value of -2/3. This results in a power law dependence on the spin speed of -0.49 for the 496K M.W. PMMA and -0.58 for the 950K M.W. PMMA.

The uniformity of the resist layer is also expected to have an effect on the lithography results. A nonuniform layer could develop through in some areas and not in others or may result in the same exposure and development conditions producing a pattern at some times and not at others. Although the resist layer profiles were not plotted for the whole wafer it was noted optically that layers spun on at higher speeds looked more uniform as the colour variation across the wafer was much less at higher spin speeds. A cleaning procedure involving a process of acetone/methanol/water followed by blowing off the wafer with dry nitrogen was used. This procedure, along with another nitrogen blow off after mounting the wafer (while it was spinning) was found to reduce the number of visible particulates left on the surface. Spinning on full two inch wafers was also attempted. With these it was found that removing the wafer from its package and immediately mounting it on the spinner chuck, followed by a spinning blow off with nitrogen before applying the resist, gave the best results, with very few visible defects. In addition, smaller wafer pieces (s 7 mm) were found to be less uniform than larger ones during the spinning process. Optical inspections indicated that this was due to the edge effects covering a proportionally larger area of the wafer than in the case of the larger substrates. Finally, it was found that more consistent layers were achieved when using the resist from its original container, rather than from smaller storage containers.

4.2.1.2 Development Time

An ideal developer would remove all of the resist exposed beyond a critical level, leaving the rest untouched. No real developer is ideal, and the sloped transition in Figure 2-5 schematically illustrates the fact that there is a range of doses over which the developer is discriminating. As a consequence, features can be obtained at relatively low doses by extending the development time. Theoretically, this is a way of minimizing the exposure time for large patterns where current fluctuations can start affecting the uniformity. However, it was found that longer development times yielded poor resolution (minimum reproducible feature sizes with tolerable uniformity for 5 minute development times were ~200 nm), and consequently also limited the minimum achievable pitch of line arrays. The features obtained with long development times also tended to have blurred edges. The results are qualitatively consistent with those expected using the developer in a low-contrast regime. The quantitative conclusion is that reductions in exposure time cannot be achieved while maintaining the resolution and uniformity required for DFB laser gratings. The majority of the work was subsequently carried out using development times of 90 s, and corresponding doses (~8 fC/dot for isolated dots and 0.6 nC/cm for lines) that utilize the higher contrast qualities of the developer.

4.2.1.3 Noise From Internal Scan Circuitry

A source of noise affecting both the pattern resolution and uniformity was encountered and eventually traced to the microscope circuitry. It was found that pattern features written with the microscope scan control in the TV SCAN MODE (where the microscope scans full screens in the shortest time) made writing features on 100 nm spacings very difficult. When these patterns came through at all, their features were not well defined when they were viewed with the SEM. As well, patterns showed variations in long lines with a period that was traced to a 60 Hz variation in the exposure conditions. When the 100 nm patterns were written with the SEM in SCAN MODE 4 (the microscope's slowest full screen scan mode), they became well defined, even when the patterns were overexposed and breaking apart. As a result of this, patterns were systematically written to investigate the extent of this effect. Figure 4-3 shows a comparison of two identical dot patterns written with the microscope on the TV SCAN MODE and on MODE 4. It shows that the feature size is smaller for the MODE 4 patterns than for the TV SCAN MODE patterns. They both show through the resist at close to the same dose, but the size of the dots written using the TV SCAN MODE increase more rapidly, the difference between the dot sizes for the two modes being about 20 nm initially and increasing to about 40-50 nm. Only the features for a 400 nm dot spacing are shown in the figure, but a similar trend was found at other spacings as well.

This has an impact on the resolution, as small dose changes just above the breakthrough threshold cause greater changes in the feature size when using the TV SCAN MODE. It thus has an effect on the latitude in the exposure dose, giving a larger latitude in the MODE 4 patterns where the dot size has only increased by a factor of 1.4 with a doubling of dose from 10 to 20 fC while the dots written with the TV SCAN MODE increase by a factor of 2.3 times their original size in the same dose range. As the line spacing is decreased, both the better resolution and extra exposure latitude become very important, as will be discussed in Section 4.2.2. During the pattern writing, the scan circuits in the microscope are not supposed to be coupled to the beam control circuitry that the lithography system drives. However, the scan MODE 4 circuitry has been designed with a low pass filter that removes 60 Hz noise while the TV SCAN MODE has a higher cut-off. This would provide an explanation for the difference in the patterns that is observed, given that there is some extraneous coupling. Although this would not be expected to affect the uniformity of very large features (i.e., at very large doses), the goal of sub 50 nm features on spacings of 100 nm or smaller is affected, since this source of noise affects the ability



Figure 4-3. Dot diameter versus dose for 400nm dot spacing written with microscope on TV SCAN MODE and SCAN MODE 4. These patterns were written on a 225 nm 950K PMMA layer on GaAs, and were developed using MIBK/IPA/H₂O for 90/10/10 seconds.

to write patterns features on small scales. It is not known at this time whether this problem also has an effect on the beam current as well.

4.2.1.4 Working Distance

The SEM working distance is also a parameter that was of concern. To reduce the rotation effect mentioned in Chapter 2, and discussed more in Section 4.3, it was preferable to work at a larger working distance of 15-17 mm. No effects on resolution and uniformity were seen during this study due to changing the working distance. This is likely because the beam spot size, although larger at longer working distances, is still only on the order of 10 nm at a working distance of 15 mm. Since this is less than the smallest resolved features (40 nm) obtained at even the smallest working distance, it is not expected to be a limiting factor for the resolution and uniformity at this point. Another concern was the beam current. Although this would not be expected to change as the working distance is changed because the final aperture in the S-4100 is before the objective lens, it needed to be confirmed. The results of this study are presented in Figure 4-4. The working distance was adjusted while attempting to keep the emission current constant. The plot shows that the beam current remained fairly constant during this time, even though the extraction voltage changed from 4.8 to 4.9 keV when the emission current was adjusted to keep it at 10 μ A.

In summary, a combination of thin resist layers (≤ 200 nm), larger exposure incident doses (0.6 nC/cm for isolated lines and 10-15 fC/dot for dots) and shorter development times (≤ 90 s) gave the best results in terms of resolution, uniformity, and consistency. In addition, these factors were found not to depend on the working distance at the resolutions achieved so far. An



Figure 4-4. Specimen current versus working distance. Distance was varied in 5 mm increments from 20 mm down to 5mm and then from 30 mm down to 20 mm. The extraction voltage jumped for the last three data points due to the need to adjust the emission current at this point to keep it at 10 μ A, and the black line separates the these two groups of points. The specimen current was measured by the method outlined in Chapter 3. Microscope conditions: Accelerating voltage = 30.0 keV, emission current = 10 μ A, aperture settings = 4, condenser lens setting = 15, magnification = 100 000X.

important feature affecting both resolution and uniformity was noise in the beam position and current and improved results were obtained by writing patterns with the SEM in SCAN MODE 4. Further studies need to be done, however, to confirm whether there is any low frequency AC noise on the beam current. The next section presents the results of studies conducted once the above parameters had been identified and analyzed.

4.2.2 Dose Tests and Proximity Effects

4.2.2.1 Resolution

A generic dose test cannot be conducted, due to the proximity effect: the basic pattern design and dimensions must be specified when quoting any doses. In an attempt to achieve the finest resolution and uniformity possible, line and dot patterns were written on GaAs with varying exposures to investigate the dependence of the feature size on the exposure dose. Line and dot spacings were also varied to observe the dependence on the proximity effect.

Figure 4-5 summarizes the dot and line sizes obtained for a number of different array spacings as a function of the incident dose. The proximity effect is manifest for spacings below ~500 nm, where the array spacing has a large influence on the results. The trends are clear and expected due to the increasing influence of adjacent exposures when the feature spacing becomes comparable to the backscattered electron range (see Equation 2-6 of Section 2.2.3.2). As the spacing decreases, the features start breaking through at lower dose, and the feature size increases at a fixed dose.



Figure 4-5. Feature size versus dose for various feature spacings. The patterns were written on a 225nm 950K PMMA layer on a GaAs substrate and were developed in MIBK/IPA/ H_2O for 90/10/10 seconds. Patterns were written with the microscope on the MODE 4 setting and at 1000X magnification. (a) Single pass lines, (b) Dots on a single-pixel square grid.

These results can be understood on a semi-quantitative level by calculating the deposited dose profiles using the "two gaussian" approximation described in Section 2.2.3.2. Assuming a high-contrast developer, the feature size can be estimated by finding the dot radius at which the deposited dose exceeds a critical threshold value. Results of such a simulation are shown in Figure 4-6. These were obtained with $\zeta_f = 25$ nm, $\zeta_b = 1000$ nm, and $\eta_E = 4$ on a fixed field of view, 2 µm by 2 µm. A range of line exposure profiles are shown in Figure 4-7, corresponding to 6 µm long single-pass lines at different spacings, exposed with the same beam parameters as in Figure 4-6. In Figure 4-7, increasing dose corresponds to scaling the amplitude by a constant multiplicative factor, and the feature size corresponds to the position at which the exposure curve crosses a critical level (a horizontal line). Clearly the features tend to break through a fixed horizontal threshold at lower doses as the spacing decreases. In addition, the factor by which the dose can be increased from the break through value to that where the whole pattern is exposed (when the "background" level goes above the threshold), decreases rapidly at smaller spaces. This is why the slopes of the curves in Figure 4-6 increase substantially at smaller spacings.

The results, when combined with the current stability measurements reported in Section 4.3.1, illustrate the limitations that may be expected when writing large patterns. A quantitative discussion of this issue is included in Section 4.3.1, but clearly to achieve ~10% uniformity in feature size at 200 nm spacings, the current must be stable to within ~10% if one works at a dose safely above threshold.

Figure 4-8 illustrates this point in a different way by showing the points where lines first start to come through, where there are equal line and space widths, and where the pattern features are washed out due to overexposure. This is done for the incident line dose as a function of the line spacing. Although these patterns were written with the microscope on the TV SCAN



Figure 4-6. Plot of critical radius versus incident dose normalized to the dose necessary for an isolated dot to develop through the resist. Patterns are fixed area dot exposures using the double gaussian resist exposure model (Chapter 2). $\zeta_f = 25 \text{ nm}$, $\zeta_b = 1000 \text{ nm}$, and $\eta_E = 4$. The numbers represent dot-spacings in nm and all plots take into account the proximity effect by summing the contributions from neighbouring features.



Figure 4-7. Exposure profiles from the line centre (0 nm) to a distance of 100 nm perpendicular to the line using the double gaussian resist exposure model (Chapter 2). Model parameters: $\zeta_f = 25 \text{ nm}, \zeta_b = 1000 \text{ nm}, \eta_E = 4$. The proximity effect is accounted for by summing the contributions from the nearest features (20 for the 200 nm spacing and 4 for the 1000 nm spacing). The horizontal line represents a fixed threshold at which feature spacings start to show through.



Figure 4-8. Line dose versus line spacing showing the doses at which the lines first break through, when there are equal line and space widths, and when the patterns are completely washed out. Patterns were written on a 225 nm 496K PMMA layer on GaAs (n+ Si doped) with the microscope on TV SCAN MODE, and they were developed using MIBK/IPA/H₂O for 5/5/0.25 minutes.

MODE, similar effects with a wider dose latitude are expected for those written on SCAN MODE 4. At a line spacing of 100 nm, the exposure goes from patterns that are not through the resist layer to ones that are overexposed completely in a dose range of less than 0.025 nC/cm. Since variations in the current of only a few percent can easily take the exposure out of this range, it makes it much more difficult to expose patterns at these small spacings.

The results of this study are that a limit of ~50 nm has been reached for line and dot patterns at doses of 0.5 nC/cm for the lines and 5 fC for the dots on a spacing of 200 nm in resist of ~200 nm thickness. This may be improved by going to thinner resist layers, as the following result suggests.

Normally, one would expect that the resolution would be better for a higher molecular weight (M.W.) resist when compared to a lower M.W. resist. It is expected that for the same resist layer thickness and dose the lower M.W. resist will have its M.W. distribution shifted lower than the distribution of the higher M.W. resist in the patterned area. Since lower molecular weights are more soluble than higher ones in the developer, the pattern features should be larger in the lower M.W. resist patten. From Chapter 2, a thinner layer would have less forward scattering in the resist layer and so feature sizes would be expected to improve if all other parameters are held constant. Figure 4-9 shows a comparison of dot and line patterns on a 496K M.W. PMMA layer 175 nm thick with the same patterns on a 950K M.W. PMMA layer 225 nm thick. Both patterns were developed for the same amount of time (MIBK/IPA/H₂O for 90/10/10 seconds). The dot patterns are both on 400 nm spacings and the line patterns on 300 nm spacings. Although the 496K M.W. PMMA layer dots develop through at a lower dose, as would be expected, the feature sizes in this thinner layer follow closely the dot diameters in the 950K M.W. PMMA layer once it starts to develop through. A similar trend is seen in the line


Incident Line Dose (nC/cm)

Figure 4-9. Exposure comparison test of 496K M.W. PMMA 175 nm versus 950K M.W. PMMA 225 nm layers, on GaAs substrate. (a) Dot pattern, 400 nm spacing. (b) Line Pattern, 300 nm spacing. Both patterns were developed in MIBK/IPA/H₂O for 90/10/10 s.

patterns, although here the variation in the starting dose is much less. Thus, thinning the 496K M.W. PMMA compensates for its intrinsic resolution limitations (compared to those of 950K M.W. PMMA). Further thinning is expected to result in further improvements in the resolution.

4.2.2.2 Uniformity

Uniformity is crucial in many applications of finely patterned structures. Variations in the line/space ratio (duty cycle) of DFB gratings leads to inhomogeneous coupling along the length of the grating that can degrade the linearity and linewidth of the laser. Advantages in laser threshold reduction that might be realized by the increased density of states in quantum dot active layers will be lost if different dots have different energy levels due to inhomogeneities.

Uniformity must be quantified on different lateral length scales. Here we limit ourselves to scales from the inter-feature spacing up to ~5 μ m, limited by the resolution of the SEM photographs from which the measurements were taken.

The uniformity was quantified on length scales up to $\sim 2 \ \mu m$ from the photographs of Figure 4-10 and the corresponding data presented in Figure 4-11. Table 4-1 summarizes the data from the studies of these patterns. The two patterns have 100 nm line spacings and are written, with respect to the photographs, from left to right and from the top to the bottom of the pictures. They show two types of uniformity problems: variations in the size of the dots and variations in the spacing.

Measurements of samples on the photograph were made for 5 rows and 10 columns of horizontal and vertical spacings on both samples, as well as vertical and horizontal measurements on the sizes of the dots in the same region. The averages and standard deviations were calculated



Figure 4-10. Picture # 100930 was written on a 496K PMMA layer 175 nm thick, with an intended line spacing of 99.33 nm, an exposure time per point of 157.2 μ s and an incident dose of 2.0 fC. Picture # 100941 was written on a 950K PMMA layer 225 nm thick, with an intended line spacing of 99.33 nm, an exposure time per point of 156.4 μ s and an incident dose of 2.5 fC. Both patterns are 20 μ m squares and were developed using MIBK/IPA/H₂O for 90/10/10 s.



Figure 4-11. Statistical variations in dot positions. (a) Column standard deviations from mean spacing corresponding to the samples shown in Figure 4-9. (b) Horizontal variations from mean position for dots from 950K PMMA sample (100941) in Figure 4-9. (c) Vertical variations in dot position for same sample as in (b). For (b) and (c), different symbols correspond to data points from different rows in the pattern.

and the results are presented in Figure 4-11 and Table 4-1. Table 4-1 shows that the deviations in the dots sizes are on the order of 4-7 nm. This could be due both to variations in current as the pattern is writing and/or small scale noise in the position of the beam during exposure. It could also be due to variations in resist thickness over small distances and requires further investigation for the cause to be conclusively identified.

Figure 4-11 shows the variations from the mean for both the horizontal and vertical directions plotted against the column number for the 950K M.W. sample, and the standard deviations for each row on both samples. The horizontal and vertical deviations show strong correlations between rows, indicating that these are systematic errors. The plot of standard deviation versus row number shows an average of about 10-12 nm, also listed in Table 4-1. The sample set is small, however, and differences between them would be more significant with the use of larger data sets. However, at the field of view that these patterns were written, 98.63 μ m, the smallest voltage resolution from the controlling computer's digital-to-analog board gives a smallest pixel spacing of 4.5 nm when the nonlinearity of the DAC is considered. This nonlinearity results in voltage outputs that can vary slightly from the intended value, corresponding to a loss in resolution from the board of about 1.5 bits. This should be a stable output error, which is consistent with the systematic trend. Noise problems due to other circuitry in the computer can also lead to further degradation of the signal [Ref. 31, p.614-615], reducing the resolution to about 14-bits, or 10 nm at this magnification, consistent with the results in Table 4-1. This leads to the conclusion that these deviations may be due to errors from the D/A system and/or degradation of the signal from the computer, and this will require more investigation. Even assuming no voltage errors in the DAC output, there is a limit of 16-bits resolution from the DAC which, at 1000X magnification (98.63 µm field of view) represents a limit of 1.5 nm.

Reduced variations may be possible by writing the same patterns at higher magnification. If the variations are due to the NPGS system, which is likely, the microscope should scale them when the magnification is increased and the systematic variations should therefore be reduced. Random fluctuations, which from Figure 4-11 appear to be on the order of 5 nm rms, would not be subject to the same scaling factor if they enter the system after the point at which the interface to the microscope is reached. Thus, it is possible that more precise positioning may need to be done at higher magnifications - leading to smaller overall pattern sizes.

| Resist Layer | Dot Size (nm) | H/W (nm) | Spacing (nm) | Pattern σ _H (nm) | Pattern σ_v (nm) |
|-----------------|------------------|---------------|-----------------|--------------------------------|-------------------------|
| 950K | 39 ± 4 | 1.0 ± 0.1 | 94 ± 8 | 8 | 11 |
| 496K | 52 ± 7 | 1.0 ± 0.1 | 90 ± 10 | 14 | 14 |

Table 4-1. Statistical variations on the uniformity of two 100nm spacing patterns. 496K data from Figure 4-9, picture 100930. 950K data from Figure 4-9 picture 100941. The pattern standard deviations are over the whole data set. H stands for horizontal and V for vertical.

Larger scales out to $\sim 5 \,\mu m$ were measured in a dot pattern on a 200 nm spacing written at the same time as those in Figure 4-10. The deviations in pattern feature size and spacing were also measured to be ~ 10 nm. Pattern feature deviations on the line pattern in Picture 100480 of Figure 4-12 were measured to be $\sim 10-20$ nm.

Two other features are important considerations for the uniformity. These are the consequences of the proximity effect and random defects. Examples of these are shown in Figure 4-12. The first picture shows the edge of a pattern. The proximity effect can be seen at the left of the pattern, as the resist lines are thicker (about 190 nm wide) and the pattern is not quite through to the substrate (shown by the dark areas). As one moves into the pattern (to the

right in the picture), the resist lines become thinner (about 130 nm wide). This is due to the lines in the centre of the pattern having more neighbouring lines contributing to their absorbed dose through the proximity effect than lines at the edge of the pattern. If extremely high uniformity is required then this effect needs to be compensated by giving the outside regions higher exposures.

The second picture in Figure 4-12 has some missing pattern features. It shows a pattern of dots that were written and etched in GaAs. The etch was a citric acid/hydrogen peroxide etch consisting of 10 ml 50% (mass percent) citric acid, 1 ml 30% H_2O_2 , and 33 ml of deionized water. It was etched for 2 minutes at 23 °C. Note that significant numbers of the dots, which appeared to be fine when viewing the resist under the SEM, did not etch through to the substrate. This is especially apparent at the edges and is most likely due to the proximity effect in these areas in a similar manner to the lines discussed above, as test patterns on the same wafer with a lower incident dose had even larger numbers of missing dots on the edge of the pattern.

Dots in the middle of the pattern are also missing. At present, the source of this is not known, but there are three likely causes. One is that the writing system is missing these dots, the second could be due to fluctuations in the resist thickness, and the third could be contaminants that are reducing the incident dose in these areas. A method of investigating this in the future is to write multiple versions of an identical dot pattern. Random fluctuations due to resist thickness variations and contaminants should result in dot features shifting from pattern to pattern, while systematic variations would be expected to remain. Finally, note the two black rectangles surrounded by non-etched flat areas. These are where the pattern was viewed to characterize the dot sizes in the resist before etching. This viewing modified the resist in this area, reducing its solubility so it was not removed by the stripper, indicating that it received so much exposure dose in this region that the resist became negative there. The areas surrounding these rectangles



Figure 4-12. Picture # 100480 - 496K PMMA, lines written on a 300 nm spacing (20 μ m pattern). The dark lines on the left edge of the pattern are not all the way through to the substrate and are caused by damage during the viewing process. Picture # 100734 - dot patterns etched in a citric acid/hydrogen peroxide solution on a 300 nm spacing. Note that this sample is tilted at 22.5° with the top side of the picture away from the viewer.

that did not etch are likely to have suffered from the breakdown of the organic resist locally, leaving a carbon layer that would resist the etch.

4.3 Pattern and Device Related Issues

As well as resolution and uniformity, there are several concerns that relate more strongly to the pattern itself and further processing issues. The main areas of concern are the behaviour of the beam current over time, the pattern size that can be written, and the orientation of the pattern on the substrate.

4.3.1 Current Stability

The stability of the beam current over long time scales becomes important as the pattern size increases. Drift in the current causes parts of the pattern to be exposed while others are not and will result in poorer uniformity as discussed previously. A study of the beam specimen current as a function of time was conducted and the results are presented in Figures 4-13 and 4-14. In Figure 4-13, the emission current was held constant by adjusting it whenever it changed from 10 μ A to a value of 9 μ A. This was done from the point where the tip was flashed to the point where the microscope shut off the beam and indicated that the tip needed flashing again. The graph shows the value of the extraction voltage as well. It indicates that the early stages are more unstable and require frequent increases in the extraction voltage to keep the emission current stable. It is thus better to write later in the cycle when the beam is more stable. The variation in the beam current is large, which can lead to a wide variation in exposed pattern



30 s and averaged. This data did not use the program described in Chapter 3. Microscope settings: Accelerating voltage = 30.0 keV, Figure 4-13. Average specimen current versus time, attempting to hold the emission current constant. 3 data points were taken every working distance = 15 mm, emission current = 10 μ A, aperture settings = 4, condenser lens setting = 15, magnification = 300 000X.



Figure 4-14. Specimen current versus time for constant extraction voltage. Data points were taken every 2.5 s using the program described in Chapter 3. Microscope settings are the same as for Figure 4.13.

features due to the varying dose that the fluctuating current causes. Due to this variation, another method was sought to try to get a more stable signal.

In the second method the extraction voltage was held constant, letting the emission current drop over time. The data was taken for 3.8 keV, then the extraction current was adjusted to bring it back up to the set value (10 μ A). At this point the extraction voltage moved upwards and another run was done, with the extraction voltage now at 4.8 keV. This was repeated once more with the extraction voltage now having a value of 5.1 keV. This data is shown in Figure 4-14. The data indicates that writing in the latter stages of the tip cycle provides a more stable long term signal. However, the short term current becomes more unstable as the extraction voltage increases. The column was then baked and data taken after this had less short term noise than the data in Figure 4-13, but had the same long term current drift characteristics.

The maximum write time from Figure 4-14 is about 1 hour when remaining within 20% of the start current. As the current drops, the pattern features would receive less dose, which would cause variation in the feature size. A pattern consisting of a 180 μ m square array of 200 nm lines with centre-to-centre spacings of 20 nm, an incident line dose of 0.6 nC/cm, and a starting current specified in the lithography run files of 10 pA has an exposure time of 16.2 minutes. Referring to Figure 4-14, if one is writing in the later part of the cycle at an extraction voltage of 4.8 keV then the specimen current would have dropped by ~10% in this time. Referring back to Figure 4-5, fluctuations in the beam current of 10% would cause pattern features to change in size by ~10%. If the pattern was written with the extraction voltage at 5.1 keV the shorter term fluctuations during this time are worse and are ~10%. One way to attempt to compensate for this in the pattern design could be to write pattern features such as single pass lines with multiple passes of the beam over the same lines. For example, an array of

vertical lines could be written first left to right and then right to left in an attempt to even out the dose. This would, however, present other possible problems such as drift of the pattern elements, i.e., the lines may not write over each other with each pass through the pattern. The data indicates that it would be better to write large patterns with closely spaced features with a more stable beam source, such as a thermal emission tip, so that the current would remain constant over longer time scales. The trade-offs are that the field emission sources provide smaller spot sizes and larger beam currents than the thermal sources, as discussed in Chapter 2.

4.3.2 Pattern Rotation

As discussed in Chapter 2, there will be an angle between the motion of the sample, accomplished with the micrometer stage, and the direction the pattern is written. This effect depends on the magnetic fields in the objective lens and scanning coils that the scanning beam passes through, and so the rotation effect depends on the working distance. Since cleaving occurs preferentially in the $(01\overline{1})$ and (011) directions on (001) GaAs substrates, this rotation becomes important when attempting to create structures that must be oriented with respect to cleaving planes. In addition, if etching is anisotropic the pattern may again need to be written with a certain orientation on the substrate. Accordingly, the difference between screen and stage motion was characterized for future work in this area. This data is shown in Figure 4-15 where, at an accelerating voltage of 30.0 keV, the zero point was found to be ~19 mm, while at 5 mm the angle was ~23°.

The first photograph in Figure 4-16 consists of a pattern that was written at 15 mm



Figure 4-15. Working distance versus rotation angle between the screen horizontal and the micrometer stage horizontal motion. Measurements were taken by off the screen and from SEM photographs, and were taken by translating a fixed feature from the bottom left of the screen to the right of the screen and measuring the angle between the screen horizontal and the stage translation line found from connecting the point on the right of the screen to the original position at the bottom left of the screen. The inset indicates the direction of the screen and stage axes and how the angle between them is defined.



Figure 4-16. Picture # 100934 - Dot exposure test pattern (written from upper left to lower right). The line across the picture is from translating between patterns and the large white circle is the beam dump. Note that there is an angle between the stage translation direction and the pattern horizontal (\sim 3°). Picture # 100682 - part of a protractor pattern written to assist in characterizing pattern rotations in the SEM.

working distance and shows the angle between the pattern axes and translation axes. It also shows the beam dump where the beam sat before and after the pattern was written and the line from translating between patterns. As well, Figure 4-16 shows part of a 360° protractor pattern that can be used to help characterize the rotation angle. It is translated horizontally across the screen and the angle can then be read off the protractor. As mentioned previously, early work was accomplished at shorter working distances of about 8 mm while later work was conducted at 15 mm working distance in an attempt to reduce the angle of rotation between the screen and stage axes. No fundamental resolution problems have been noted at this time, but the beam spot size at 30 keV and with the apertures on their smallest settings would be about 10 nm or less at 15 mm. As a result, it is not expected that this would be the fundamental limiting factor at this time, since the minimum features are currently on the order of 50 nm.

4.3.3 Field of View

As well as rotation, the total field of view available is an important consideration. For ease of processing, especially when having to cleave around a pattern, as large a field of view as possible is preferred. At a magnification of 1000X, the field of view is 98.63 µm. As discussed in the first part of this chapter, the systematic uniformity problem in the patterns is likely due to the lithography patterning system's digital-to-analog board and the transfer of this signal to the microscope. This nonuniformity in the pattern spacing would limit the field-of-view that can be used. This would place limits on the usefulness of large patterns. For applications like DFB lasers and quantum dot arrays, for example, the nonuniformity would eventually impact on the performance of the devices. This would places limits on the sizes of such devices, and the only way to increase the device size would be to write patterns and align them with respect to each other. This would be much easier with a beam blanker in the system, in which case the exposed beam dump areas and translation axis lines would not exist. As shown in Figure 4-16, this lack of a beam blanker means that before and after the pattern is written the beam must sit in a place off the pattern which has been found to expose an area up to about 6 μ m in diameter. These extra exposure features must be considered when designing the patterns as further processing steps such as etching and metal lift-off will have an effect in these areas as well as in the patterned area.

4.4 Conclusions

Patterns with consistent feature resolutions down to ~50 nm have been achieved on both line and dot patterns at feature spacings down to ~200 nm, on a field of view of 98.63 µm. The proximity effect along with developer sensitivity and contrast currently limit the resolution and studies indicate that using thinner resist layers and shorter development times would give even better resolution. As well, other development systems with higher contrast could be investigated [Ref. 14]. Systematic pattern uniformity variations on the order of 10 nm rms and random variations of 5 nm rms have been found in the patterns. A source for the systematic variations has been tentatively identified and more work is needed in this area to overcome this problem. Limitations on patterns due to beam current stability have been discussed, although more work is needed to characterize low frequency AC noise on the beam current. As well, limitations on patterns from the pattern rotation and field of view have been studied.

Chapter 5 Conclusions and Recommendations

5.1 Conclusions

An electron beam lithography system was implemented using a Hitachi S-4100 SEM and the NPGS electron beam lithography exposure system. Associated facilities were developed to apply a variety of resist layers to substrates and to develop and etch the exposed patterns. Procedures for this system's use were developed and optimized as it is anticipated that many researchers will use the system in the future.

The system's performance was characterized with importance being placed on those issues that impacted on the goal of achieving sub 50 nm resolution with high pattern uniformity. The results were found to depend on many parameters including the resist thickness, resist composition, development time, and the specific pattern that was written. Resolutions of ~50 nm on feature spacings of ~200 nm were achieved in 496K M.W. and 950K M.W. PMMA resist layers ~200 nm thick. Resolutions reported in the literature of about 10 nm on sub 50 nm spacings with 20 nm resist layers indicate that moving to thinner resist layers, shorter development times, and higher contrast developers will enable better resolution to be achieved [Ref. 6-7]. However, since further processing steps such as etching can also etch the resist layers, this may limit the utility of very thin resist layers. Pattern uniformity on the order of 10 nm, viewed over ~5 μ m scales, has been achieved on both line and dot patterns, chosen for their usefulness in the laboratory's research, including the construction and characterization of DFB lasers and arrays of quantum dots. Systematic and random noise limitations were encountered that require further investigation to improve the uniformity beyond this level.

5.2.1 Pre-exposure Processes

Recommendations for the pre-exposure processes fall into three areas: the process environment, the resist layer attributes, and characterization of the resist layer attributes. Since particles on the substrate were found to be a major concern with these thin resist layers a more dust free environment than is currently used is desirable. This needs to be balanced against the necessity of also having a well-ventilated area and one possibility is to place the spinner in a box with a fan attached for exhausting the fumes and with a filter on the air intake. Alternatively, a fume hood could be used, although then the air cleanliness relies on the room air being clean. The entire procedure could then be accomplished in this cleaner area. If necessary, the oven could also be placed within such an enclosure. Concerns with this idea are ensuring that the fumes would not present a safety hazard with the exhaust equipment and/or oven. Ideally all cleaning, spinning and baking would be accomplished in the same enclosure to minimize the exposure, possibly requiring remote handling.

As thinner films were found to be a method of achieving better resolution it would be desirable to have the ability to spin on layers as thin as 20 nm and characterize them. Diluted resist solutions could be used to provide thinner resist layers. As well, there is some requirement for multiple layer resists to provide finer features for lift-off processes. For both of these, it would be useful to be able to optically characterize the thin film thicknesses in a quick manner in the laboratory without needing to go through the exposure and development steps that were done in this work to characterize the film thicknesses [Ref. 32]. By monitoring the resist layer

thickness under identical spin and bake conditions, this would also allow monitoring of the resist solutions over time to identify changes that may occur - thickening of the solutions, for example. With an x-y stage, it would also allow one to examine the spatial variation of thickness over a substrate.

5.2.2 Lithography

Further work in the lithography area can be divided into three main areas: hardware aspects, theoretical investigations, and further characterization. As well, one important feature that would assist all these areas would be the ability to capture images from the SEM. The ability to capture many images easily would allow more detailed characterization of the resolution, uniformity, and topography of imaged features over a much larger area than is currently possible with photographs from limited areas of the samples.

Hardware aspects involve changes, additions, and further characterizations of the system. One thing to consider is re-calibrating the NPGS system with a higher resolution standard than that which was originally used, although this may require that a standard be designed and manufactured using the lithography system if a suitable one cannot be found. A useful addition to the system would be a beam blanker. This would allow the alignment of patterns to be accomplished without the beam dumps and stage translation exposure lines that now occur in the patterns and would be helpful in larger scale work using fine features that may need to be written at higher magnifications. Further characterization of the system involves two areas; noise characterization and vacuum characterization. Noise characterization of the beam current and position in the column is continuing and may require further shielding of the column. As well, it would be useful to have a more accurate idea of the composition of gases in the specimen chamber and the pressure in this area to assess if the vacuum level plays any role in the resolution and uniformity of the lithographic process.

Theoretical investigations could consider the lithographic process in more detail and attempts could be made to improve the models and predict the process with more accuracy. Experimental studies could be conducted in conjunction with this theoretical process.

Further characterization could include several areas. Lithographic tests on much thinner resist layers would, from the above work, be expected to increase the resolution - perhaps at the cost of further processing steps, however. Other development systems could be investigated to compare the sensitivity and contrast of these systems to the one used in this work. As well, other resist types could be investigated (examples: negative resist, inorganic layers).

Further experimental work could be conducted on thin substrates, on the order of 100-200 nm, which are expected to have a small proximity effect due to reduced backscattering from the substrate. This should enable much finer resolution to be obtained. Accomplishing this would require greater uniformity in the patterns and would require more investigation of the limitations, both systematic and random, imposed by the uniformity variations seen in this work and attributed, in the systematic case, to the NPGS system hardware.

5.2.3 Other Processing Recommendations

Only preliminary wet chemical etching work was accomplished for this work, and much more could be done here. Examples are the characterization of the effect of pattern feature size on the etch rate, to more fully investigate the effect of etchants on the resist layer, to investigate the development of etch profiles and, possibly, to investigate the use of an intermediate layer to act as an etch mask under the resist. As well, only the citric acid-hydrogen peroxide etch system was used and other systems could be investigated.

Although not used in this study, other pattern techniques could also be investigated, such as dry etching and lift-off processes, for defining patterns useful in further studies.

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Appendix A Electron Beam Lithography Procedures

This appendix describes procedures for designing lithographic patterns and using the electron beam lithography system that has been described in Chapter 3 to create those patterns in a resist layer. The pattern design, using the DesignCAD program, is discussed in Section A.1.1 followed by a discussion on the creation of the lithography exposure run files using the MRF program in Section A.1.2. The procedure for applying resist coatings to substrates is then covered in Section A.2. Finally, a procedure for using the NPGS System and Hitachi S-4100 SEM to write the lithography patterns is given in Section A.3. All of these procedures assume that the person following them has read and understood the relevant operating manuals for both the equipment and the program software.

A.1 Pattern Design and MRF File Creation

In this section, the design process will be illustrated by using a typical exposure pattern. This pattern and its associated run files were used to generate the test exposures for most of the data presented in Chapter 4.

In general, the pattern characteristics will be dictated by the particular application. Here, the "application" was largely to optimize the system parameters for writing one-dimensional line arrays and two-dimensional dot arrays. This presented two main considerations for the design of the patterns: the line/dot patterns themselves and a sequence of parameter increments. The test grid used for these parameter characterization studies is shown in Figure A-1. The pattern consists of 20 μ m by 20 μ m sub patterns separated by 4 μ m. The crosses in the pattern consist of



Figure A-1. Lithographic dose test pattern.

100 nm wide lines with a high exposure specified: their purpose was to be easily visible when trying to locate the pattern for inspection at low magnification where, depending on the test pattern, it may be very difficult to find the pattern itself. Each sub pattern consisted of an array of lines or dots with a specified linewidth and pitch, along with an exposure that varied between sub patterns.

There are two separate steps involved in generating the set of files needed so that the NPGS program can write the patterns. The first step involves using DesignCAD to specify the absolute dimensions and relative exposures for all the feature elements that make up the pattern, and the second step involves generating a run file that specifies the absolute doses, beam current, and the pixel spacings used when filling the feature elements. Each of these two steps is described separately below.

A.1.1 Pattern Design

Pattern generation consists of designing individual pattern elements, arranging them into a complete pattern, and associating them with different colours and/or layer numbers, each with separate parameters specified in the run file. Each layer of the pattern is composed of a series of feature elements (eg. individual lines or dots, or filled boxes), and they are exposed in the order that they are created with DesignCAD, although this order can be changed within DesignCAD. The simplest way to generate the 16 separate arrays in the dose test pattern of Figure A-1 is to define each as a 20 μ m by 20 μ m filled box with a dose (colour) that depends on its position in the 4 X 4 array. The actual lines or dots within each box are then controlled in the run file where the pixel step sizes used to fill the boxes, Δx and Δy , are specified by the line spacing distance and centre-to-centre distance respectively. Each array thus has the same line or dot spacings, and a different dose. A more general way of generating line arrays with variable linewidths is to define each line as a separate feature element.

No beam dump is used in this pattern, but if necessary it would have been placed in the upper right corner of the pattern where the NPGS program default beam dump point is located. It should be noted that this requires that the X-Y control voltages be set using the DAC0 program included for this purpose to +10 V on both settings which is the standard practice here due to the lack of a beam blanker (see exposure procedure 9.1 in Section A.3).

Once the pattern is drawn, the elements are given different colours corresponding to different exposures. For example, each box in Figure A-1 is given a different colour.

Each layer is like a separate drawing in that it can have both the spacings, the magnification, and the exposure doses (from the colours) set individually when the run file is

created (Section A.1.2). For example, since the crosses of Figure A-1 need different spacings and exposures than the test patterns, they are defined in layer 2 of the drawing, and are placed in positions corresponding to locations between the filled boxes in layer 1.

Which of the particular features above is used depends on the individual pattern, but it should always be remembered that the pattern drawn sets the limits on the highest magnification that can be used to expose the pattern since the pattern must fit entirely into the field of view to be accurately reproduced. Through the number of pattern colours, the pattern also sets the maximum number of separate exposure doses that can be specified in the pattern. At this point, when the pattern design is completed, the run file should be created.

A.1.2 Run File Creation

The run file reads the previously created pattern(s) and sets the conditions for exposing the features specified in those patterns. First, the number of patterns (up to 16) and their names are specified. The individual patterns can then be repeated up to 20 times with a separate offset for each one, allowing a complicated pattern to be repeated without creating a very large pattern file. Once all the patterns are specified, the exposure conditions for each pattern are entered. A sample of portions of a run file are shown in Figure A-2. These correspond to run files used to create the patterns that are the basis of most of the data in Chapter 4. The pattern used corresponds to the one shown in Figure A-1.

The exposure conditions within a pattern are defined by setting the magnification and the beam current. The magnification is determined by the size of the pattern, with relation to the pattern's origin. Once these are set, the other features can be specified. The centre-to-centre and line-spacing distances are set by considering the pattern features. The minimum spacing is determined by the 16-bit resolution on the DAC board in the computer and the magnification specified earlier. This means that the minimum spacing is given by the field-of-view divided by 2¹⁶. Any spacings set will also be rounded to an integer multiple of this value. For lines, the centre-to-centre spacing is made small enough to allow a smooth transition from point to point, while the line-spacing is set to 1/4 of the final desired linewidth. For single pass lines, only the centre-to-centre distance is of concern and the line spacing in a filled polygon structure defines the line pitch. As an example, for the filled square patterns discussed previously, the centre-to-centre spacing were set to 20 nm. In these patterns from Figure A-1, the line spacings were set to be the spacing required between each single pass line, from 100 to 1000 nm. For the dots, the two spacings were made the same allowing a square grid of dots to be generated. The spacings are set independently in layer 2 for the cross patterns as is shown in Figure A-2.

Using the data entered above, the exposures can be specified. Different exposure doses are entered for each colour used in the pattern file. Either an incident dose or an exposure time can be set, and the other one is calculated using the beam current which was previously entered. Two types of dose may be set, line and area doses. Both use the charge deposited, calculated by multiplying the exposure time by the beam current. For line doses, the charge deposited is divided by only the centre-to-centre distance and the units are in nC/cm. For area doses, both spacings are used and the units are in μ C/cm². For dots, the spacings define the pattern and are not directly relevant to the exposure. As such, for single dots the exposure time is the parameter that is specified and the relevant incident dose was found to be in the fC range. The minimum value of the exposure times for systems without a beam blanker is 10 µs and exposure doses below the fC range are only possible if the beam current is reduced from the nominal value of

10 pA. For the individual exposures, the relevant values to enter are either known from previous experiments or must be estimated. If no other data is available the sensitivity for the developer being used should be the starting value. In a test run, most of the exposures should be in this estimated region, with some exposures significantly above and below the sensitivity value to ensure that some pattern features will come through if the exposure settings are not correct. Once these exposures are tried, the results are fed back in to narrow the range and find the optimal dose in the next pattern written. The exposures can be scaled at run time if the beam current is higher than the one specified in the run files, so an exact value is not needed when designing the run file. A good value to take is 5 pA, since the beam current was found to vary between 1 and 10 pA during experiments. The net result of this exposure scaling is, however, to leave the dose unchanged since the exposure scaling factor is calculated by dividing the file's beam current by the measured beam current.

In the run file, different pattern numbers or layers can be used to vary one or both of the spacings and the exposures. In the files corresponding to Figures A-1 and A-2, there are 16 exposures in each pattern written, and ten patterns in a run file. Thus, one run file was used to create a dose test for a specific geometry and then vary the geometric spacing ten times to create test patterns where the line or dot spacings changed from 100 to 1000 nm. There is a great deal of flexibility in what can be accomplished in a combination of patterns and run files and planning ahead before creating these files is crucial to maximize their utility for a particular application.

Run File Name:..... ab408000.rf6 Pause only for 'p' option?.....(y,n) no How many patterns to write?..... 10 Pattern Name #01:..... ab408000 How many times to repeat pattern?...... 1 -Pattern Location:......0,0 Pattern Name #02:..... ab408000 How many times to repeat pattern?...... 1 -Pattern Location:......0,0 Pattern Name #10:..... ab408000 How many times to repeat pattern?...... 1 -Pattern Location:.....0,0 Pattern File: ab408000 (1 of 10) Pattern File: ab408000 (10 of 10) Layer #01:.....(w,p,c,s) w Origin Offset (x,y):.....(µm,µm) 0,0 Center-to-Center Distance:.....(Å) 105.4 Line Spacing:.....(Å) 9993.6 Microscope Configuration #..... 1.000 Measured Beam Current:.....(pA) 5.0 Color #1 (white).....(µsec) 21.1 -Line Dose:.....(nC/cm) 0.100 Color #2 (red).....(µsec) 42.2 -Line Dose:.....(nC/cm) 0.200 Color #3 (green).....(µsec) 63.2 -Line Dose:.....(nC/cm) 0.300 Color #4 (blue).....(µsec) 84.3 -Line Dose:.....(nC/cm) 0.400 Color #5 (brown).....(µsec) 105.4 -Line Dose:.....(nC/cm) 0.500 Color #6 (magenta).....(µsec) 126.5 -Line Dose:.....(nC/cm) 0.600 Color #7 (cyan).....(µsec) 147.6 -Line Dose:.....(nC/cm) 0.700 Color #8 (dark gray).....(µsec) 168.6 -Line Dose:.....(nC/cm) 0.800 Color #9 (light gray).....(µsec) 189.7 -Line Dose:.....(nC/cm) 0.900 Color #10 (light red).....(µsec) 210.8 -Line Dose:.....(nC/cm) 1.000 Color #11 (light green).....(µsec) 231.9 -Line Dose:.....(nC/cm) 1.100 Color #12 (light blue).....(µsec) 253.0 -Line Dose:.....(nC/cm) 1.200 Color #13 (yellow).....(µsec) 274.0 -Line Dose:.....(nC/cm) 1.300 Color #14 (light magenta)......(µsec) 295.1 -Line Dose:.....(nC/cm) 1.400 Color #15 (light cyan).....(µsec) 316.2 -Line Dose:.....(nC/cm) 1.500 Color #16 (white).....(µsec) 421.6 -Line Dose:.....(nC/cm) 2.000

Layer #02:.....(w,p,c,s) w Origin Offset (x,y):.....(µm,µm) 0,0 Magnification:..... 1000 Center-to-Center Distance:.....(Å) 255.9 Line Spacing:.....(Å) 255.9 Microscope Configuration #..... 1.000 Measured Beam Current:.....(pA) 5.0 Color #1 (white).....(µsec) 130.9 -Area Dose:.....(µC/cm²) 100.000 Run File Name:..... ab408001.rf6 Pause only for 'p' option?.....(y,n) no How many patterns to write?..... 10 Pattern Name #01:..... ab408000 Pattern File: ab408000 (2 of 10) Layer #01:.....(w,p,c,s) w Origin Offset (x,y):.....(µm,µm) 0,0 Magnification:..... 1000 Center-to-Center Distance:.....(Å) 2001.7 Line Spacing:.....(Å) 2001.7 Microscope Configuration #..... 1.000 Measured Beam Current:.....(pA) 5.0 Color #1 (white).....(µsec) 200.2 -Line Dose:.....(nC/cm) 0.050 Color #2 (red).....(µsec) 400.3 -Line Dose:.....(nC/cm) 0.100 Color #3 (green).....(µsec) 600.5 -Line Dose:.....(nC/cm) 0.150 Color #4 (blue).....(µsec) 800.7 -Line Dose:.....(nC/cm) 0.200 Color #5 (brown).....(µsec) 1000.8 -Line Dose:.....(nC/cm) 0.250 Color #6 (magenta).....(µsec) 1201.0 -Line Dose:.....(nC/cm) 0.300 Color #7 (cyan).....(µsec) 1401.2 -Line Dose:.....(nC/cm) 0.350 Color #8 (dark gray) (µsec) 1601.4 -Line Dose:.....(nC/cm) 0.400 Color #9 (light gray).....(µsec) 1801.5 -Line Dose:.....(nC/cm) 0.450 Color #10 (light red).....(µsec) 2001.7 -Line Dose:.....(nC/cm) 0.500 Color #11 (light green).....(µsec) 2201.9 -Line Dose:.....(nC/cm) 0.550 Color #12 (light blue).....(µsec) 2398.0 -Line Dose:.....(nC/cm) 0.599 Color #13 (yellow).....(µsec) 2598.2 -Line Dose:.....(nC/cm) 0.649 Color #14 (light magenta)......(µsec) 2798.4 -Line Dose:.....(nC/cm) 0.699 Color #15 (light cyan).....(µsec) 2998.5 -Line Dose:.....(nC/cm) 0.749 Color #16 (white).....(µsec) 3198.7 -Line Dose:.....(nC/cm) 0.799

Figure A-2. Annotated sample run files, corresponding to those used for producing the patterns in Figure A-1. Similar files were used to produce the data and pictures in Figures 4-1, 4-5, & 4-10.

1

A.2 Procedure for the Application of Resist Coatings to Substrates

- (1) Pre-heat the oven to the pre-bake temperature. For PMMA, this must be 160-180 °C. 175 °C was always used in this work to allow the temperature drop to remain above the 160 °C lower limit when the sample was inserted into the oven. Note that the warm up period takes approximately 1.5 hours. Monitor the temperature using the thermometer on the top of the oven.
- (2) Assemble the equipment. This includes: cotton tipped applicators, 4 glass beakers, absorbent pads (to cover the work area), glass dishes to place the substrate in (the number of these depends on the amount of substrates and their size more than one can be placed in a dish, but they should be separated by at least 1 cm from each other), appropriate sized chucks, aluminum foil, disposable pipets and bulbs (2 or 3), gloves, wipes for cleaning the glassware, and personal protective equipment lab coat, goggles, and acid-solvent filter mask (as appropriate). Chemicals and related equipment include: acetone, methanol, deionized (DI) water, waste solvent container, resist, resist waste container, glass (sharps) container.
- (3) Turn on the spinner and allow 5 minutes for the electronics to warm up.
- (4) Replace the aluminum foil over the bowl of the spinner, if necessary. Clean the glass containers used to bake the substrates, if necessary. This may involve an initial cleaning and scrubbing with a cleaner designed for chemistry glassware. The container may then be rinsed with acetone and methanol if this is deemed necessary, and wiped dry.
- (5) Inspect the chuck to insure that the O-ring is present and not damaged. Attach the chuck to the spinner by aligning the chuck's screw with the flat part of the shaft and pushing the chuck onto the shaft. It should fit on smoothly. Tighten the screw until it stops going in do not tighten it beyond this point.
- (6) Put on the protective equipment. Turn on the pump.
- (7) Clean the top of the chuck with acetone using a cotton tipped applicator. These should be only used once, so discard the applicator or break it after use so it won't be accidently used again.
- (8) Spin on procedure
 - (8.1) Clean the sample, if necessary, with acetone, methanol, DI water, and blow off with nitrogen. Spray the sample using a squeeze bottle while holding it with tweezers over a beaker. Note that if using a new packaged clean wafer then this cleaning step may be skipped.
 - (8.2) Place the substrate on the spinner chuck. Centre the piece on the chuck.

- (8.3) Set the speed on the spinner and spin the wafer, resetting the speed if necessary. Use the nitrogen gas used in step 8.1 to blow off the wafer while spinning. Stop the rotation using the rear part of the spin control pedal.
- (8.4) Apply the resist with the disposable pipet. Cover the wafer entirely. When removing the resist from its container, do it quickly and replace the cap immediately to prevent the resist from thickening. Place the first drop in the waste container, as the solution the resist is dissolved in evaporates quickly leaving a more concentrated solution in the bottom of the pipet that may create a thicker or less uniform resist layer. If you will not be using the rest of the solution in the pipet immediately dispose of it using the chlorinated waste container. Similarly, it is recommended that a new pipet be used for each application of resist for the same reason, unless the process is done quickly.
- (8.5) Spin the resist and substrate for 30 to 40 seconds, by which time the colour of the resist layer on the sample should be uniform and have reached a steady state.
- (8.6) Remove the wafer and place it in a glass container. Cover the container.
- (8.7) Clean the holder with acetone and a cotton tipped applicator. Use a new applicator and break or discard it after use.
- (9) Repeat step 8 until all the wafers have been coated. If necessary, replace the chuck following steps 5 & 7. If replacing the chuck, a new pipet should be used in step 8 as the time spent will be too long and the resist will thicken in the pipet affecting the reproducibility of the process.
- (10) Place the glass container(s) containing the substrates into the oven and bake them. The recommended bake time for PMMA is 2 hours. Longer times may be used if there are problems with further processing steps that result in the resist lifting off the substrate. Occasionally monitor the temperature of the oven to ensure it reaches the temperature in step 1 and remains within the limits specified there.
- (11) Turn off the pump and spinner.
- (12) Clean the chuck with acetone and a cotton applicator. Remove the chuck from the spinner and place it in its storage container. Remove and replace the aluminum foil in the spinner bowl. Discard the old foil.
- (13) Clean and store the equipment and chemicals. Put waste chemicals and used pipets into their proper disposal containers.
- (14) When the bake is finished, remove the glass containers from the oven and allow them to cool. Turn off the oven. When the containers have cooled, remove the substrates and place them in storage containers. Cover the storage containers with foil.

A.3 Exposure of Resist Using the Electron Beam Lithography System

At this point, the procedures outlined in A.1 and A.2 should already have been carried out. A substrate that is coated with a pre-baked resist layer should be ready to have a pattern written on it. As well, the NPGS run file(s) and their accompanying pattern(s) should be ready to run with the NPGS program.

- (1) Both 12 and 24 hours before using the microscope to write patterns, the cold trap on the microscope should be filled with liquid nitrogen. As well, fill the cold trap before starting to use it to write the patterns.
- (2) Sample Preparation:
 - (2.1) If necessary, cleave the substrate into a piece of the correct size for further processing. This is accomplished on GaAs by marking the edge where the cleave is wanted with a diamond pencil and applying pressure on this scratch. Unless it hits a defect, the wafer will cleave in one of two directions on a (001) surface, along either the (011) direction or the (011) direction.
 - (2.2) A scribe can be used to mark the edge of the wafer where the pattern is to be written. The advantage of this method is that the pattern will cleave along this mark, if cleaving through the pattern is desired. This is the recommended method. Alternatively, the NPGS manual recommends marking every mm along the edge of the substrate where the pattern will be written with a pencil, by scraping graphite from the pencil which serves as both a reference and something to focus on at the edge of the wafer. Note that this method should not be used if it will contaminate further processes. Neither method should be used if the pattern is to be written so close to the edge that the mark would interfere with the exposure.
 - (2.3) The substrate should now be attached to the holder, ensuring that it lies flat. Although double sided adhesive tabs can be used to attach the wafers to their holders, a better way is to use metal clips. The substrate should be mounted in the vicinity of both the Faraday Cup (used to measure the beam current) and a gold standard (used to correct astigmatism in the beam). Handle the samples and holders with gloved hands only, to avoid depositing oils and other contaminants on them.
- (3) Turn on the microscope, check and record the pressures on the ion pumps (IP1 to IP3), and insert the sample and holder into the specimen exchange chamber following the microscope operating instructions. While pumping down the exchange chamber, check and set all the microscope parameters (accelerating voltage, working distance, emission current, condenser lens setting, and both aperture settings). Also, load the pattern and run files into the computer in the appropriate subdirectory, if this has not already been done.
- (4) Ensure the raster rotation, dynamic focus, and tilt compensation features are switched off.

- (5) Before turning on the beam, use the micrometer control knobs to position the holder so that the sample to be exposed is not under where the beam will be when it is turned on. With the initial micrometer stage settings, the beam is in the centre of the holder. Following the microscope operating instructions, flash the beam and turn it on. Go to low magnification and, taking care not to expose the sample, move the holder until the gold standard is in view. Focus using the Z-micrometer stage and the fine focus control knob only, and follow the procedure for aligning the beam and correcting the astigmatism in it. You should be able to see clear features on the order of a few nm in size when the astigmatism has been corrected. Do NOT use the coarse control as this changes the working distance. Take your time as this is a critical step for the lithographic process and you also need to wait for the beam current to reach a more stable period in its cycle (see the discussion in Chapter 4 for further details).
- (6) Measure the beam current using the Faraday Cup and picoammeter (see Section 3.3.1 of Chapter 3). Record the micrometer X and Y locations for the Faraday Cup.
- (7) Move to the edge of the sample where you wish to write, being careful not to expose too much of the sample, and focus on the edge of the sample using high magnification. Again, use the Z-micrometer and fine focus control knob only. The edge of the substrate will be at an angle to the screen, and must be aligned so that it is parallel to one of the micrometer stage directions. Do this by translating the sample and, using the rotation knob on the stage, adjust its rotation until translating it over distances of a few microns causes very little change in the screen position of the sample edge. Record the location of the position on the edge where you wish to write the pattern. Move back to the Faraday Cup and record the current value again. If the current is not varying quickly during steps 6 and 7, then you are ready to write.
- (8) Record the current and move back to the location where you wish to write the pattern, using the location recorded in step 7. If the current is not the same as the one specified in the run file(s), you can change the run file(s) or use the "e" parameter in the NPGS and PG programs to scale the exposure time as discussed in the NPGS instruction manual. The value of "e" is given by dividing the run file current value by the measured value. For example, if the run file has a current of 5 pA and the measured current is 10 pA then e = 0.5. The scaling parameter is a faster method and should be used, since the beam current is varying with time and this method uses the least amount of time.
- (9) Exposure:
 - (9.1) Switch the microscope X-Y Scan Control Switch from internal to external control. Set the X-Y position to the upper right of the pattern using the DAC0 program. Move to the position where you wish to write the pattern using the X and Y micrometer knobs, keeping in mind that the beam is not off and will expose the resist during this movement and also when the beam sits at the pattern position before writing the pattern.
- (9.2) Keep a separate record of each exposure run. Record the pattern position and write the pattern using the run file, recording the start and stop times. Remember that the pattern location is an offset of the location on the edge of the sample that was recorded in step 7. Monitor and record the current through the sample while writing the pattern along with the time (for example, after each pattern in a run file is written). Note that the current will change once a pattern starts writing and it has been found that it is more stable and consistent to record it while the writing is in progress. Also monitor the extraction voltage and emission current. As discussed in Chapter 4, the most stable current was found to occur by not adjusting the emission current while writing patterns.
- (9.3) When finished writing the patterns, move away from the pattern and off the wafer using the X-Y micrometer controls and then switch back to internal scan control. Since there is no beam blanker installed in the system, make sure that the electron beam does not cross through previously written patterns during this procedure. Record the specimen current, using the Faraday Cup, and the time.

If writing multiple run files or patterns that take a long time to write, move off the wafer and back to the Faraday Cup between pattern files to check the current, recording the start and stop times of this movement and the time the current measurement was taken, along with the beam current value.

- (10) When finished, shut the beam off and remove the sample following the microscope's operating instructions.
- (11) Remove the sample from the holder and place it back in its container. The sample is now ready to be developed.
- (12) Development Procedure:
 - (12.1) Set up the solutions in a row so that you can move in one direction while developing. Fill two 50 ml beakers with about 40 ml of developer (methylisobutyl-ketone (MIBK) in this work), 40 ml of rinse (isopropyl alcohol (IPA) in this work), and, in a 500 ml beaker, about 300 ml or more of deionized water. Place the nozzle to blow off the samples near the water rinse beaker. Place a timer where you can monitor it during the procedure.
 - (12.2) Develop the sample by immersing and agitating it with tweezers (the self-holding kind are recommended) in first the developer (90s), followed immediately by the rinse (10s) and then the water (10s). It is recommended that these times be used to start with, and once good, consistent results are obtained consideration may be given to changing them. At the last step, keep the sample immersed in the water while getting the nozzle ready. Remove the sample and immediately blow the water beads off the surface on both sides. Place the sample in its storage container.

- (12.3) The sample can now be inspected under an optical microscope, to see if the patterns are through. Note that this will not work for features smaller than the microscope's resolution, but it can be a useful tool to inspect the sample and redevelop it if necessary.
- (12.4) Dispose of the used developer and rinse in the waste solvent container. Rinse and wipe dry all the beakers used and place them in their storage locations.
- (13) The sample can now be inspected in the SEM to view the pattern, but keep in mind that this will expose the pattern further and may cause additional problems if further processing is required, as discussed in Chapter 4. For storage, avoid humid areas and keep in mind that light can cause photo-degradation of the resist.

Appendix B Further Details on Beam-Material Interactions and Resist Development

This appendix describes more details on electron beam-material interactions and the effect they have on polymer resists, with special attention paid to the resist used in this work, PMMA. The electron beam lithography models commonly encountered in the literature are also discussed. Electron beam-material scattering and energy loss will be discussed first, followed by a discussion on the effects of the impacting electrons on the resist and, finally, the consequences for resist development.

B.1 Electron Scattering and Energy Loss

To characterize the distribution of energy absorbed in the resist layer, both the scattering and energy loss of the electrons as they travel through the resist and substrate must be described. There are two types of scattering: elastic scattering which involves changes in direction but very small to no loss in energy, and inelastic scattering where the electrons lose energy, and may also undergo small changes in direction. These can be incorporated into a model of the scattering in the resist layer which simplifies the overall process into forward scattering or back scattering [Ref. 8; 10; 15]. Forward scattering events are those that occur as the electrons in the beam initially traverse the resist layer. Scattering in this regime mainly has the effect of broadening the incident beam over a small area, as was discussed in Chapter 2. Backscattered electrons are those that re-enter the resist after undergoing a combination of energy loss and large angle scattering in the substrate. As mentioned in Chapter 2, this results in an interaction area in the resist that is much larger than the one due to forward scattering.

In simulations, the scattering cross sections for the electron are used to determine scattering angles and the lengths the electron travels between collisions. A common method is to use the elastic scattering cross section to find the scattering angle and an inelastic expression for determining the energy loss. In more general terms, there are cross sections corresponding to elastic as well as inelastic processes. For elastic events, the screened Rutherford cross section can be used for elements of low to intermediate atomic number (eg, up to Ge, Z=32) and intermediate beam energies of about 20-50 keV. For more accurate results and outside of this range, exact Mott cross sections are used [Ref. 15; 33; 34]. Some of the inelastic effects that can be considered are: the generation of slow secondary electrons (0-50 eV from conduction electrons) and fast secondary electrons (>50 eV from more tightly bound electrons), inner shell ionizations, and multiple electron excitations (bremsstrahlung radiation and plasma scattering). To be thorough all these effects would need to be included in a model to determine the total scattering cross-section and mean free path. However, the screened Rutherford scattering crosssection can be used to approximately calculate the elastic scattering cross-section [Ref. see 33, p.20; 15, p.81 for greater detail]. The differential screened Rutherford cross section is given by

$$d\sigma_{el}(\theta) = \frac{e^4 Z^2}{16 \left(4\pi \varepsilon_o E\right)^2} \frac{d\Omega}{\left[\sin^2(\theta/2) + \theta_o^2/4\right]^2}$$

$$\theta_o^2/4 = \delta = 3.4 \times 10^{-3} Z^{\frac{2}{3}}/E \quad (E \text{ is in keV})$$
(B-1)

where Z is the atomic number, θ the scattered angle, E the electron energy, e is the electron charge, ϵ_0 the permittivity of vacuum, and δ is called the screening parameter. The total elastic cross section, σ_{el} , is found by integrating over all the angles from 0 to 180° using d $\Omega = 2\pi \sin\theta d\theta$. Similar methods are followed for other relevant cross sections that need to be calculated. As the electron energy increases, the need for relativistic corrections needs to be examined. For Equation B-1, relativistic corrections need to be added at energies higher than about 50 keV.

Using the cross-sections, the mean free path is found from

$$\frac{1}{\lambda_{T}} = \sum_{i} \frac{1}{\lambda_{i}} = N_{a} \rho \sum_{i} \frac{\sigma_{i}}{A_{i}} = N_{a} \rho \sum_{ij} c_{j} \frac{\sigma_{ij}}{A_{j}}$$

$$c_{j} = \frac{b_{j} A_{j}}{\sum b_{k} A_{k}}$$
(B-2)

where λ_{T} is the total mean free path, λ_{i} are the individual process path lengths, and the other values are as defined previously. c_{j} is the mass fraction used for materials that involve more than one element in their composition, where b_{j} is the atomic fraction of the jth element with atomic mass A_{j} . By integrating Equation B-1 to an angle θ_{1} and dividing by the total cross-section σ_{el} , one can get a probability that an electron will scatter from 0° to θ_{1} . For simulations, this is combined with the mean free path λ_{T} to find the angle and distance that an electron scatters to [Ref. 33-34]. The remaining piece needed is an expression for energy loss.

To account for energy loss, the continuous slowing down approximation (Bethe energy loss equation) can be used [Ref. 8; 10; 12; 15; 33-34]. This equation is an approximation that includes the effects of energy loss from all inelastic processes and gives an energy loss per unit length of, in its nonrelativistic form,

$$\frac{dE}{dx} = -7.85 \times 10^4 \frac{\rho}{E} \sum_i c_i \frac{Z_i}{A_i} \ln \left(1.166 \frac{E}{J_i} \right) \qquad (keV/cm)$$

$$J_i = \left(9.76Z_i + 58.8Z_i^{-0.19} \right) \times 10^{-3} \qquad (keV)$$
(B-3)

where the only additional undefined symbol is J_i which is the mean ionization potential for an element with atomic number Z_i . This is used to record the loss of energy as the electron moves through materials in a simulated trajectory and can give, with a large number of simulated trajectories, an idea of the amount of energy deposited in the resist layer and substrate.

Modelling using the above expressions makes attempts to correct for the proximity effect too time consuming and so more analytical models have also been developed, such as the "double gaussian" model presented in Chapter 2. However, the more complicated models use expressions such as those above in Monte Carlo simulations in their attempts to understand the lithography process. These models usually involve thousands of simulated impacting electrons, and follow their trajectories through the resist and substrate, recording the energy deposited in the resist layer. If, as was discussed in Chapter 2, the changes in the resist are taken to be entirely due to the absorbed energy density, the changes to the resist and its development may then be defined using equations of the sort described in the next two sections. The incident dose can then be calculated if enough simulated trajectories are used that a fairly good average of the energy deposited in the resist is built up.

B.2 Resist Modification Mechanisms

The mechanisms causing changes in the molecular weight of resists are described in this section, and an expression for the change in molecular weight as a function of the absorbed energy density (or absorbed dose) is presented.

When passing through the resist and substrate, the electrons loose energy by inducing

ionizations within bonds of the molecules and, at lower levels of energy transfer, non ionizing electronic and lattice excitations within the material. Both of these can induce changes in the material and can also result in the emission of secondary electrons from the ionization process. These secondary electrons can also cause ionizations and excitations. Electrons recombining with the ionized molecules, or cations, can also cause excited states within the molecules. The initial beam energies are much higher than the bond energies and thus do not tend to selectively excite bonds as in photochemistry [Ref. 35; 9, p.139-153]. The bond energies in polymethylmethacrylate (PMMA), for example, are in the range 3.5-4.5 eV [Ref. 35], while typical values of ionisation energies for atoms and molecules are in the range 8-50 eV [Ref. 36, p.36]. The excitations can also result in the emission of photons or phonons. In organic polymers used for electron beam lithography two important overall reactions follow from these ionizations and excitations.

After the molecule is ionized, if the ensuing reactions lead to the formation of bonds elsewhere on the polymer or combination reactions between polymers then a cross-linked network of bonds could form and result in the polymer being less soluble, which leads to the formation of a negative resist. Alternatively, if the reactions lead to the breaking up of the polymer into smaller fragments, called chain scissioning, then the process leads to the formation of a positive resist. Both of these types of reactions usually proceed simultaneously and, although scissioning dominates in positive resists at lower doses, higher doses lead to negative resists in most organic polymers. This is because the scissioning is limited by the number of available bonds, while the cross-linking proceeds continuously and links the scission fragments as well as the unbroken fragments. In addition to the above reactions gaseous molecular fragments can also be produced. Eventually, at high enough doses, a cross-linked, carbonaceous,



Figure B-1. Illustration of the process of chain scissioning leading to the reduction of molecular weight under the influence of ionizing radiation for polymethylmethacrylate (PMMA) [Ref. 35; 36, p.269,302-316]. ● denotes the highly reactive unpaired bonds, or radicals in the process.

polymerized substance is formed on the surface due to the increasing numbers of carbon-carbon double bonds and large fractions of the non-carbon elements leave the material as gaseous fragments [Ref. 15, p.124].

Polymethylmethacrylate (PMMA), the resist used in this work, is a positive electronbeam resist and the process leading to chain scissioning in PMMA is illustrated in Figure B-1. The initial impacting electron ionizes the molecule, leaving a highly reactive unpaired bond on the polymer (called a radical), a radical fragment of the molecule, CO(OCH₃), and an electron that can ionize other bonds if it has sufficient energy. The CO(OCH₃) fragment breaks down into gases and other radicals. The gaseous products formed can escape from the substrate, leaving gaps that assist the solvent in removing the molecular fragments during the development process. The scissioning molecule breaks into two fragments, one of which is a radical. The remaining radical fragment reacts with an electron in a process called hydrogen abstraction to form a double carbon bond which stabilizes the end of the second molecular fragment. The hydrogen atom lost from the molecule during this process can then react with the radicals formed from the CO(OCH₃) fragment. In addition to the scission process illustrated, the process of hydrogen abstraction can occur in PMMA without chain scissioning, forming a carbon double bond with no break in the polymer chain. This is the process responsible for lowering the scissioning efficiency of PMMA [Ref. 35].

The result of these processes in resists is usually characterized by radiation chemical yields described in terms of the number of specified events per 100 eV of energy absorbed: G(x) for cross-linking and G(s) for chain scission events. The final molecular weight is given by the expression [Ref. 37; 9]

$$\frac{1}{M_f} = \frac{1}{M_n^o} + \frac{[G(s) - G(x)]D}{100\rho N_a}$$
(B-4)

where M_f is the fragmented molecular weight and M_w is the initial molecular weight, both in amu (g·mol⁻¹). D is the absorbed dose in eV·cm⁻³, ρ the resist density in g·cm⁻³ and N_a is Avogadro's number. Note that if scissioning is the only process to occur the G(x) values are taken to be zero. Since resists contain a distribution of molecular weights, this expression would need to be modified to account for this in a simulation of the lithography process.

B.3 Resist Development Model

As was discussed in Chapter 2, the developer acts on the resist material with reduced molecular weight. To simulate this, a rate equation incorporating a dependence on the average final molecular rate, $M_{\rm f}$, of the fragments produced by the electron beam-resist interactions of the form

$$R = R_{o} + \frac{B}{(M_{f})^{A}}$$
(B-5)

is often used [Ref. 9, p.168; 17]. In this expression, R is the solubility rate of molecular fragments with molecular weight M_{fr} , and R_{o} , A, and B are parameters that must be empirically determined. When used with expressions for the energy deposited within the resist layer and the resulting change in the molecular weight of the resist, the solubility of fragments in an area of resist that have received a specified incident exposure dose can be modelled. From this, the amount of resist removed as a function of time can be modelled and estimates of the final developed pattern features can be made.

Several people have investigated electron-beam lithography models [Ref. 17; 37-39], but the usefulness of many of the models in predicting electron beam lithography processes is not yet clear, due to both the complicated nature of the reaction mechanisms and the large numerical simulations that must be carried out to model these processes.