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A Procedure to characterize electron-beam resist using a scanning electron microscope and study of process optimization of an electron beam imaging system using experimental design methods

Randall C. Pyles

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A PROCEDURE TO
CHARACTERIZE ELECTRON-BEAM RESIST
USING A SCANNING ELECTRON MICROSCOPE
AND
STUDY OF PROCESS OPTIMIZATION
OF AN ELECTRON BEAM IMAGING SYSTEM
USING EXPERIMENTAL DESIGN METHODS

by
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B.S. Temple University
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A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science in the Center for
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Date: 4/20/82
A procedure is established which will enable the study of contrast and sensitivity characteristics of electron-beam resist materials. The imaging system includes an electron beam-sensitive resist coating on an oxidized silicon substrate exposed with a scanning electron microscope (SEM) and developed in a suitable solvent. The results correlate with published data. A chemically amplified electron-beam resist imaging system is studied using a three level, three factor Box-Behnken design. The effects of postbake temperature, postbake time, and development time on contrast and sensitivity are presented.
ACKNOWLEDGEMENTS

Successful completion of this thesis owes recognition to support from several sources. Supplies of electron-beam resist material are particularly appreciated from Eastman Kodak Research Laboratories, Mead Imaging Technologies, and the Shipley Company. Graciously acknowledged is the use, during a portion of this project, of a Nanospec film thickness measurement instrument in care of Mr. John Guild of the Eastman Kodak Research Laboratories. Special thanks are given to Mr. Bruce Smith for continued support throughout the second phase of this project and to Mr. Richard Holscher for his assistance and technical guidance in the operation of the MEBES system at RIT.
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INTRODUCTION

Resist History

There has been exponential growth in the applications of high technology during the past two to three decades. Solid-state devices and microelectronics have become an integral part of daily life. Microelectronic applications have dictated that devices become faster, reach higher levels of performance, and increase packaging density without raising costs and decreasing reliability. The accomplishment of these goals requires ever more complex designs. These designs have evolved into very large-scale integration (VLSI) of electronic devices [Lai, 1985].

The trend of increased design complexity has put severe demands on the fabrication industry to manufacture integrated circuit devices with submicron dimensions. "Lithography is a key technology for producing LSIs with increased speed and packing density" [Sakakibara, et al., 1981, p. 1279]. The fabrication process can not totally overcome the limitations of the transfer of pattern definition onto the semiconductor material.

The cornerstone of the lithography process is the resist material. The resist "serves to protect portions of surfaces of the substrate wafers during certain steps of processing..." [Schnabel & Sotobayashi, 1983, p. 298]. "A photo-resist is an
image-wise layer formed from a light-sensitive material by exposure to a master pattern, so as to produce a protective stencil on a surface and allow modification of the surface in such a way as to give a complementary or corresponding image" [Hepher, 1964, p. 181]. Generally, photoresists are polymers which are sensitive in the deep blue and ultraviolet regions of the electromagnetic spectrum. Patterned areas of the photoresist will change in solubility when exposed. Insolubility of the resist material in the exposed areas describes a negative-acting resist. The opposite action is also possible. In a positive-acting resist, the exposed areas become soluble and develop away. A schematic representation of patterning negative and positive resists is illustrated in Figure 1.

![Schematic of Lithography Using Negative and Positive Resists](image)

Figure 1
Present-day lithography techniques evolved from early photo-etching processes, which were applied to the printing industry. This evolution was made possible by continued success in development of resist chemistry. The characteristics of the resist have been found to be the most important elements in a lithographic system.

"Historically the photo-resist is of considerable significance and it is generally accepted that the first camera picture ever to have been recorded was made by Niepce with a photo-resist method" [Hepher, 1964, p. 181]. In 1826 J.N. Niepce discovered that a layer of bitumen, a complex hydro-carbon prepared from asphalt, coated on a silvered glass substrate was photosensitive and capable of producing an image when exposed to light for several hours [Hepher, 1964]. The bitumen was inherently photosensitive because of a certain degree of unsaturation in the molecular bonding. The long exposure to short wavelengths of light removed the saturation due to molecular crosslinking. The exposed regions became insoluble in a mixture of oil of lavender and mineral spirits. With this technique he was able to create the world's first permanent images and to use these images to etch designs on several mediums. In practice, he had used to his advantage the change in solubility of a material upon exposure to light. This is the fundamental characteristic assumed in resist methods used in microelectronic fabrication. This behavior
found wide-spread acceptance; however, the length of the exposure was unreasonable.

Niepce's discovery never reached the importance of the development of a photoetching process which used gelatin sensitized with chromium salts as the resist. In 1852, W.H.F. Talbot received a British patent for this process, which he applied to etching copper [DeForest, 1975]. It was found that many natural colloids and resins could be photo-crosslinked when sensitized with dichromate salt. The availability of the materials used and the decreased exposure times made this system much more practical than Niepce's method. Hence, it has continued to receive attention as a useful resist system. It was found, however, that the coated layer was unstable and had a tendency to become insoluble in the dark, and that only water-soluble colloids responded well to dichromate sensitization. Also, the developed image was found to be poorly resistant to etching chemistry and not impermeable to water [Hepher, 1964; DeForest, 1975; Pyles, 1985]. Efforts to overcome these drawbacks continued.

Extended research spawned an array of alternate configurations. These include resists with water-insoluble resins to provide etch-resistant images and spectral sensitization with dyes to increase the light sensitivity of the system to include longer wavelengths [DeForest, 1975]. Alternate sensitizers have been investigated also [Hepher, 1964].
The first "modern" photo-resist systems were based on cinnamic acid derivatives, which are inherently photosensitive. Cinnamic acid derivatives are not able to form uniform coatings themselves, but are appended as side groups on polymers to increase their film-forming capability [DeForest, 1975]. These resins act as carrying agents and do not add much to the solubility changes. However, very stable coatings can be formed. These systems were found to be several times faster than the dichromated colloids. They also have a wide development latitude and show excellent resistance to water-based etchants [Pyles, 1985].

The initial discovery of the sensitivity of cinnamic acid was made at the turn of the century. Research in these systems increased in the 1930s and 1940s and led to the synthesis of cinnamic acid esters of polyvinyl alcohol. This system provides a polymer with photosensitive side groups. In the early 1950s Kodak marketed KPR (Kodak photoresist), a poly-vinyl cinnamate material based on this system [Pyles, 1985]. KPR is typical of cinnamate systems with outstanding dark reaction stability. The release of this system dramatically influenced the expansion of modern photo-resists. This began an age of large expansion in the electronics industry with a corresponding evolution of resist systems designed to meet it.

This era included the evolution of positive working
resist systems. The most notable are compounds based on novolac or m-cresol novolac resins and diazonaphthoquinone sensitizer. "Such materials are coated from an organic solvent and, after exposure to light, are treated in aqueous alkali which removes the light struck areas leaving the remaining parts to form a positive image with good resistance to acid etching solutions" [M. Hepher, 1964, p. 189]. These compounds have formed the basis for the most popular positive resist systems.

The imaging reaction mechanism is such that upon exposure to light nitrogen is released and an intermediate ketene is formed. In the presence of water, an indene carboxylic acid results following a molecular rearrangement by the Wolff mechanism. The carboxylic acid exhibits solubility in aqueous base developers [Blevins, et al., 1987; Goncher, et al., 1988]. These systems comprise the backbone for the microelectronics industry in terms of positive optical resist chemistry. The exposure reaction of this nature is indicated in Figure 2.

Electron-Beam Resists

To meet the demand for continuing miniaturization of integrated circuitry, resist materials have been designed to be used with non-optical exposure technologies.

Electron-beam resists are almost exclusively organic
Diazonaphthoquinone-novolac Exposure Reaction

Figure 2

copolymers of high molecular weight. In general, both crosslinking and chain scission events occur to different degrees in the same polymer. When both occur in relatively equal amounts, the resist has very poor characteristics. The early work in electron-beam lithography used optical resist, but it was soon discovered that simple non-light-sensitive polymer and copolymer materials were electron beam sensitive, and the present electron resists have evolved from this discovery.

Positive Resists

Electron beam exposure that causes predominantly chain scission to occur in polymer molecules results in a positive resist image. The chain scission causes the molecular weight
to decrease and allows removal by a solvent.

A notable group of positive resist materials is the methyl-acrylate family. Perhaps the best known example is poly(methylmeth-acrylate), PMMA, which is a common material known under the trade names of Lucite and Plexiglass [Brewer, 1980]. PMMA is a positive resist which has received considerable attention in electron-beam applications. It is a single homogeneous material that has excellent characteristics, including resistance to wet chemical etchants and excellent film forming properties. PMMA has been studied by a number of workers who found it to be capable of excellent (<<1\mu m) resolution upon electron-beam exposure [Chandross, et al., 1981]. However, it was found that the sensitivity of PMMA is too low to be used as a production resist, and PMMA has poor dry etch durability. The other family members of this group are made by replacing the side radical or by making a copolymer. This has been done to try to increase sensitivity while retaining the other excellent properties.

The search continued for a more sensitive positive resist. The polyolefin sulfone family has been found to be highly sensitive to electron beam exposure. Poly(1-butene sulfone), PBS, has the best resist properties of the group. PBS is much faster than PMMA and sensitive enough to be commercialized as an electron-beam mask-making resist. As a result, PBS is the most dominant positive electron-beam resist
on the market today [Gozdz, 1987]. The biggest disadvantage of PBS is that the resolution and dry etch resistance is poorer than PMMA.

**Negative Resists**

Until 1981 there was great emphasis on the search for and study of positive working electron resists, but in 1982 this changed, and more attention was directed to negative working resists [Roberts, 1984]. Crosslinking occurs in the exposed areas of a negative resist material. This results in an increase in molecular weight and a corresponding decrease in solubility.

"Intense investigation in this field led to the conclusion that polystyrene has outstanding characteristics when compared to other polymers; and so this polymer gained prominence and took a position similar to that taken by PMMA among positive resists. A serious disadvantage affixed to polystyrene refers to its rather low radiation sensitivity and many attempts were taken to improve radiation susceptibility" [Schnabel & Sotobayashi, 1983, p. 331].

Several derivatives of polystyrene have been investigated in the search for increased sensitivity. Poly(chlormethyl-styrene) has emerged as a highly sensitive resist with excellent etch resistance and resolution compared to PMMA. This has led to its increased use throughout the industry.

Epoxy based resist systems using glycicydyl methacrylate
and related copolymers have also been found to have superior negative resist characteristics and therefore have gained wide acceptance [Blevins, et al., 1987]. Monomers with other desirable resist properties, particularly adhesion, have been joined with the high sensitivity of the glycidyl monomer to form good resists. The copolymer of glycidyl methacrylate and ethyl acrylate (COP) has been found to be highly sensitive to electron exposure and have good film forming properties. The problem with these systems has been the need for post curing and poor resistance to dry etching.

Other polymers were formed with glycidyl methacrylate and allyl methacrylate, another monomer that is sensitive to electron beam exposure. This polymer was studied at the Eastman Kodak Research Laboratories and is one resist material that was also studied in this research project [Tan, et al., 1984]. This copolymer shows high sensitivity and resolution, good resist properties, and good dry and chemical etch resistance. In general, the negative resist systems do not exhibit the resolution of PBS or the numerous acrylate based positive resists.

Chemically Amplified Resists

The resist materials previously discussed each have their advantages, but there is not one which has properties of high resolution, high sensitivity, and high resistance to dry
etching. Researchers at the Rohm and Haas Company stated that it was their intent to develop a resist material that had good performance characteristics in all of these areas. [Liu, et al, 1988] The result was the development of a three-component negative resist with chemical amplification. The chemical amplification of this material results from a formation of an acid upon electron-beam exposure. During the post exposure baking the acid catalyzes the bonding between the resin base and the crosslinking material. Each catalyst molecule can react more than once and contribute to many crosslinking reactions, hence amplification occurs. [deGrandpre, et al, 1988; Lamola, et al, 1991]

The Rohm and Haas and Shipley Companies have succeeded in marketing a version of this resist under the trade name Microposit SAL 601-ER7. The chemistry of this resist includes a novolac based polymer resin, an aminoplast acid activated crosslinking component, and a photoacid generator. They claim that this material provides the high performance they sought in contrast, sensitivity, and dry etch resistance properties. The Shipley has also developed and markets the SAL 605 electron beam resist material. This is an improved version of SAL 601-ER7, which is formulated for increased sensitivity and includes a contrast enhancing dye. [Fedynyshyn, et al., 1990]
Negative vs. Positive Resist

The decision to use negative or positive resist will depend on the application and an analysis of the advantages and disadvantages of both. In general, the advantages of negative resists are higher sensitivity, spectral sensitization, good adherence and coating, and lower cost. However, negative resists are sensitive to oxidation, they require organic developers which cause pollution, and their resolution is limited because they tend to swell during development. Positive resists provide better resolution, less pollution and better step coverage of wafer topology. The disadvantages of using a positive resist are poor adhesion and slower speed.

Exposure Technology

Originally it was thought that performance levels and density requirements of the new generation of devices could not be achieved by using photolithography for pattern definition. Therefore, investigation of alternate patterning techniques began to take place. Alternate techniques include short wavelength lithography, X-ray lithography, ion-beam lithography, and electron-beam lithography. Recently it has been shown that certain optical techniques surpass the resolution that was originally thought possible [Fuller, 1987; Pike, 1987]. This has been brought about by developments in
resist technology, higher numerical aperture lenses, excimer laser sources, and advances in process techniques.

Although optical lithography continues to advance beyond original expectations, it is important to continue research into alternate techniques. These alternate techniques are also advancing and finding roles in integrated circuit manufacturing.

Through extended research and advancements, electron-beam lithography has found a niche in the production of integrated circuits. During its infancy, the process was looked upon as a potential replacement for optical lithography techniques. Since then, its limitations have been recognized and electron-beam techniques emerged to fill specific roles.

"The basis of this technology is a finely focused electron beam that is both deflected over a surface and blanked on and off under computer control. The electron beam exposes the resist where it strikes..." [Brewer, 1980, p. 13]. The resist will then be developed as in photolithography to leave a patterned image. Both positive and negative resist materials have been developed with electron beam sensitivity.

The application of electron-beam technology to lithography techniques stemmed from the apparent limitations of photolithography. One of these limitations is the minimum resolution obtainable through exposure. Typically, resolution can be calculated as follows: [Fuller, 1987; Oberai, 1987]
\[ R = \frac{k \lambda}{NA} \]

where: 
- \( k = 0.8 \) for production resolution limits
- \( \lambda \) = wavelength of light used for exposure
- \( NA \) = numerical aperture of the lens system

"...When higher resolution is demanded and the linewidth is reduced to the point that it is comparable to the wavelength of the light used for exposure, diffraction effects from the mask openings and reflection effects within the resist degrade the quality of the replicated image of the mask" [Brewer, 1980, p. 7]. "Electrons, like photons, possess particle and wavelength properties; however, their wavelength is on the order of a few tenths of an angstrom, and therefore the resolution is not limited by diffraction considerations. Therefore, minimum linewidths with electron-beam are less than photolithography" [Thompson, et al., 1983].

This theory is logical, but it is more difficult to apply in practical situations. "Due to the serial nature of writing, reductions in image size and increases in wafer size have tended to decrease the throughput in terms of wafers per hour.... Notwithstanding the limited throughput, electron-beam technology has been the critical technology in mask writing, early development devices, and now more than ever in application-specific integrated circuits (ASIC)" [A.S. Oberai, 1987]. Although its resolution is potentially higher than
photolithography, the technique is too slow for most production applications. Electron-beam techniques have been given an active role in making masks used in optical lithography, direct-write specialty applications, device prototype development, and proximity flood exposure techniques.

Electron-Beam Exposure Systems

True electron-beam exposure systems are descendants of scanning electron microscopes (SEM), which were introduced in the 1960s. Along with the developing acceptance of electron-beam lithography came the need for exposure systems specifically designed for this application. Since the 1960s, the SEM technology has been expanded and refined to permit high precision electron-beam image "writing" rather than specimen "reading". However, the basic building blocks of the system have remained the same.

There are two main exposure philosophies which have been investigated during the development of electron-beam imaging systems as lithography tools. These categories could be used to describe the main branches of a "family tree" of electron-beam exposure systems [Thompson, et al., 1983]. These categories can be separated into those systems which rely on a "projection" of electrons or a direct "scanning" of the electron beam to expose the substrate.
Exposure Strategies

Projection

The development of projection systems was explored mainly to solve the low throughput problem that plagues electron-beam systems. In this approach, the whole wafer is exposed at one time, rather than drawing an individual feature with a scanned electron beam. One type of projection system employs ultra-violet irradiation of a masked photocathode to create the electrons which expose the substrate. Another reported projection system is designed to reduce the image of large metal masks by demagnification of the electron beam with electromagnetic lenses [Elliott, 1982]. There are inherent problems with these systems which limits their practical applications, but these continue to be addressed.

Scanning

The most mature electron beam exposure technologies involve the scanning of an electron beam over a sensitized substrate. The design of these units most closely resembles a SEM. There are two primary writing strategies which are in use with scanning imaging systems. These strategies differ in the way the substrate is addressed by the beam. The electron beam can be controlled by raster or vector methods. In the raster method, the electron beam scans the entire substrate. The beam is then turned on or off at different positions in order to expose the desired areas. This method allows for
less complex addressing control than the vectoring systems. However, the exposure times are limited by the fact that the entire substrate needs to be scanned. In the vectoring method, the beam is directed only at the particular areas which need to be exposed and is blanked as it travels from one area to another. This requires more complex beam control systems, but the exposure times can be reduced because little time is lost as the beam travels over areas which do not need to be addressed.

In addition to the scanning method, there is also an option to adjust the shape of the electron beam. This is particularly useful in the vector scanning systems. This allows for several options to be used to expose or fill in a given area. The beam can be programmed to outline a given feature. Then the shape can be optimized in order to expedite exposing the entire structure. This increases the speed of the system since fewer addresses are needed to complete the image.

**Equipment**

An electron-beam imaging system can be described as a combination of four main subsystems: 1) a computer that provides a means for data input and pattern control, 2) the electron-optical column including the electron source, 3) the elements that provide the beam control and pattern execution, and 4) miscellaneous support equipment including vacuum pumps.
and power supplies for the system [Brewer, 1980; Thompson, et al., 1983]. Figure 3 shows a simple diagram of an electron-beam exposure system based on the main subsystems.

![Electron Beam Exposure System Diagram](image)

**Figure 3**

**Computer**

The computer that services the electron-beam imaging hardware is typically very powerful. High speed computing power and large amounts of memory are needed to process and store the quantities of data necessary to expose a wafer or mask. The wafer and mask designs are typically developed using computer-aided-design (CAD) software. One of the computer's functions is to decode the CAD files which control the exposure of the designed features. There are several
tasks that the computer performs as part of this function. The computer transfers the pattern data from the CAD format to a decoded format which the computer can process. It also controls the hardware-exposure-control activities such as beam deflection and blanking, stage movement, and loading and unloading substrates.

As a part of the exposure-control tasks, the computer may correct for proximity effects. Proximity effects result from the distribution of electrons as they scatter when traveling through the resist and backscatter when they enter the substrate. These scattered electrons are undesirable, since they tend to expose areas outside the area intended. Therefore, the total energy absorbed by an area in the resist is dependent on the "proximity" of adjacent exposures [Brewer, 1980]. Compensation for proximity effects may be executed by prior programming to adjust the exposure. This correction can also be performed in the CAD system prior to decoding the pattern data.

In addition to exposure control, the computer also processes the registration data needed to align the substrates to the successive mask levels in direct-write applications. Fiducial marks are placed on the substrates or stage as points of reference so that adjustments can be made to account for beam drift caused by process-induced distortion, vibration, electronic noise, mechanical inaccuracy, etc. [Brewer, 1980;
At the alignment-mark areas the electron beam is used more as an analytical tool rather than an exposure device. Detection of the registration marks can be achieved by creating a difference in the signal-to-noise ratio by increasing the amount of backscattered electrons. This can be done by etching an area of the substrate or depositing a material with a different atomic weight. Once the fiducial marks are located, the beam deflection parameters are corrected through various algorithms. A computer is well suited to monitor signal changes, perform the beam correction algorithms, and implement the necessary mechanical adjustments.

**Electron Optical Column**

The heart of any electron-beam lithographic system is the electron optical column. The components of the column include the electron source, which produces a primary electron beam; the electromagnetic lenses and apertures, which focus the primary beam on the target and provide a means of beam blanking; and a beam deflection unit, which is used to position the beam precisely and accurately over the scan field. Depending on the purpose and design of a particular system, it is possible to configure these elements in a variety of ways.

**Electron gun**

The purpose of the electron gun is to generate a beam of
electrons which can be focused onto a target by the remaining elements of the electron optical column. The gun consists of an electron source and electrodes used to accelerate the electrons to the desired beam energy. An electrical potential, established between a cathode and anode, attracts negatively charged source electrons to the anode. This voltage difference is known as the "accelerating voltage". The electrode arrangement is designed so that the traveling electrons pass through an aperture in the anode and into the lens system.

Electron sources can be classified into two groups, depending on the method used to emit the electrons. Thermionic sources rely on heating a material above a temperature beyond which electrons are emitted from the surface. [Thompson, et al., 1983] A field emitter source consists of a high electrical field surrounding a very sharp tip of material. The electrical field extracts electrons off the source material.

There are three materials which are predominately used as thermionic sources. These are tungsten, lanthanum hexaboride (LaB₆), and thoriated tungsten. The tungsten material is typically bent to form a tight radius in order to create a small emitting area at the tip. The tungsten hairpin is popular for use in electron microscopes because of its uniformity, current stability, tolerance to vacuum variations,
ease of fabrication, and maintainability. However, the life and relative brightness of these sources is lower than the other materials. [Elliott, 1985]

The work function of the LaB₆ material is much lower than tungsten. Therefore, the brightness is an order of magnitude greater at lower operating temperatures. [Brewer, 1980; Thompson, et al., 1983] These sources must be used under higher and more stable vacuum pressures to achieve longer life potential.

A tungsten surface which has been carburized at high temperatures becomes thoriated tungsten. These sources also have a lower work function than tungsten. The brightness and life increase under lower operating temperatures. These materials require more stable vacuums and, because of the additional processing, are more difficult to manufacture.

A field emitter source is typically a tungsten rod with a very precisely polished tip. The relative brightness and life of this source is considerably higher than thermionic sources. However, these sources are more complicated to fabricate and they require very high vacuum conditions.

**Lenses**

Because electrons are charged particles, their traveling path can be altered as they pass through magnetic fields. The magnetic fields in an electron optical column are created by
electromagnetic lenses. The lenses are basically a length of wire wound around an iron core. The magnitude of an electrical current applied to the wire is proportional to the magnetic field strength of the lens. The amount that the electron beam is effected by the lenses is related to the field strength of the lens, the velocity of the electrons, and the relative angle between the electron path and the magnetic field lines. [Postek, et al., 1980]

The lens section of the electron optical column consists of a series of electromagnetic lenses and apertures which shape, demagnify, and focus the electron beam. There are several sections of the lens system which can be grouped by task. The condenser lens follows the electron gun and is the first to effect the beam. This lens may be made of several lenses which demagnify the beam through a focal point. There is usually an aperture in this area which blocks stray electrons and thereby homogenizes the beam.

Following the condenser lens series is an assembly of deflection lenses. The function of this group is to deflect the beam over the scan field on the target. This assembly may also include a mechanism used to blank the beam and lenses which correct for aberrations and astigmatism created in the entire lens system.

Finally, there is an objective lens that demagnifies the beam to a focal point on the target surface.
Beam Control

The exposure system must employ a mechanical stage system in addition to the deflection lens assembly in order to control the beam and expose the entire substrate. The stage uses either roller bearings or an external air bearing to enable x-y motion. The stage should be made from non magnetic materials, since distortion of the beam pattern could result otherwise.

Typically, a step and repeat mode is used to expose a portion of the substrate in the target area while the stage remains stationary. The stage is stepped to an adjacent area so that the next section of the substrate can be exposed. This process is continually repeated until the entire substrate is exposed. An alternate method would be to expose the substrate while the stage is under continuous motion.

In either method, a registration system is used to repeatedly locate the stage accurately in the proper position. The registration system must provide a means for detection and feedback of a known reference point either on the stage or the substrate. There are two popular methods to perform this task. As described previously, the signal-to-noise ratio changes of the electron backscatter at the substrate surface can be detected. Also, a laser interferometry technique can be used to monitor the target position.
Support Equipment

There are several reasons why an electron-beam system must be operated under a high vacuum. The column must be kept extremely clean. Dirt that has been deposited on the walls of the column or that is suspended in the beam path can become charged and deflect or block the beam. Air present in the system will cause fast oxidation of the filament which would result in extremely low life. Also, air molecules will scatter the beam electrons.

A pumping system is used to create the vacuum necessary in the exposure instrument. More than one pump is used in order to attain the high vacuums required. A mechanical, or roughing, pump is used initially during the pump down cycle to reach the range of $10^{-2}$ torr. These pumps could be used to reduce the pressure further, but their efficiency is decreased as the vacuum increases. This would require a very long time to reach the working pressure. Therefore, a diffusion pump is used in combination with the roughing pump. Once the roughing pump decreases the vacuum to a specific pressure the diffusion pump will activate and continue to reduce the pressure to the required point.

Electron-beam systems require capable power supplies. The supply used to power the computer must be filtered and highly regulated in order to reduce the chances of inaccurate data being entered into the system or lost altogether by power
surges or irregularities. The high voltage power supply used for the electron gun must be stable and capable of the required current to alleviate any beam fluctuations.

Because of the high resolutions and tolerances expected in electron-beam systems, they must be used in tightly controlled environments. Normally these units are operated in a clean-room atmosphere where the cleanliness, temperature, and humidity levels are monitored and maintained. Other environmental considerations would be vibration isolation and suppression of electromagnetic interference.

**Scanning Electron Microscope**

The exposure system used for Phase I of this experiment is a Stereoscan S600 Scanning Electron Microscope manufactured by Cambridge Instruments. It is designed as a stand-alone analytical instrument with accompanying support equipment and is not interfaced to any computer system. A cross section of this SEM is found in Figure 4.

The electron gun of this system uses a fixed hairpin tungsten filament as the electron source. The potential of the electron gun can be selected at either 1.5, 7.5, 15, or 25KeV. The gun assembly also contains alignment coils which are used to adjust the beam relative to the optical axis.

A double condenser lens and an objective lens configuration is used in the electron optical column. The
Scanning Electron Microscope

Figure 4

condenser lens tube contains the spray apertures used to clean up the beam. The scanning coil assembly is located in the objective lens tube. This assembly includes the stigmator, micro-shift, and deflection coils. The chosen final aperture is also located in the objective lens tube.

Just below this final lens assembly is the specimen chamber. Access to this chamber is obtained through a rectangular opening at the side of the electron optical column. The specimen stage is a complex mechanical device and is an integral part of the column. The stage provides facilities for specimen mounting and orientation. The stage
is capable of X, Y, Z, rotation, and tilt movement of the specimen. External controls used to execute these movements are located on a front plate which also provides a means to seal the column once the stage is inserted into the specimen chamber.

The main beam control is available by manually adjusting the specimen relative to the beam. There is also a means of providing slight adjustment to the electron beam using the micro-shift controls.

This SEM has an automatically controlled vacuum system. The vacuum system includes a rotary roughing pump, diffusion pump, and associated control units. The control assemblies contain various valves, gauges, and control logic with feedback to enable the vacuum system to operate automatically. The SEM is also equipped with an optional dry nitrogen back filling system to help protect the vacuum system from dirt and moisture.

Power is supplied to the instrument through a standard domestic socket. However, the SEM has power supplies to provide power levels necessary to operate all internal systems.

For a more detailed description of this SEM instrument it is recommended that the reader reference the Stereoscan S600 operating manual [Cambridge Instruments].
Mask Making Electron-Beam Exposure System

A mask making electron-beam exposure system (MEBES) was used as the exposure source for the study of chemically amplified resist material in Phase II of this project. The unit was designed and built by ETEC specifically for mask making.

This unit is interfaced to a Data General Nova computer system. The computer system runs with RDOS operating language. It is supported with several software packages and routines. These packages include "MEBES " which interprets a job for the hardware, "CHECKSPEC" and "CHECKPAT" which are used to verify the job deck and pattern being exposed. "ASOP" is used to set the operation parameters of components in the electron optical column.

A cross section of the MEBES electron optical column is depicted in Figure 5. The electron optical column is composed of the electron gun assembly, the condenser lens system, the deflection assembly, and the objective lens system. The gun assembly uses a thermionic tungsten hairpin filament as the electron source. The potential of the electron gun is set to 10KeV. This gun outputs approximately $3 \times 10^5 \text{ A/cm}^2 \cdot \text{sr}$ source brightness. The gun has centering coil control used to adjust the beam. A spray aperture is included to assist in cleaning up the beam. The beam spot size can be adjusted between 0.25 and 1.0 $\mu$m. This system is capable of 45 nA beam current with
a maximum dose of 1.1 $\mu$C/cm².

The condenser lens system includes a double lens configuration, a limiting aperture, energizing coils, and the beam blanking system. The deflection assembly houses the stigmator and deflection coils which are used to control the beam scanning. The objective lens performs the final beam focusing.
Vacuum stage controls are used in the writing chamber to provide X-Y stage movement. A cassette loading system is mounted adjacent to the exposure chamber to allow multiple substrate exposures without breaking the vacuum. A loading chamber is provided to isolate the loading system from the exposure chamber via a separate vacuum system and a trap door. This system has tooling and fixtures capable of accepting 5"x5" mask masters or silicon wafer substrates. A complex valve and gauge system is used to maintain vacuum control in the electron optical column and substrate chambers. Ion, roughing, and diffusion pumps are used to provide the various degrees of vacuum throughout the system.

A detailed description of MEBES and other electron beam machines can be found in Brewer's text [Brewer, 1980].

Objective

The presented overview of electron-beam lithography gives some insight into the complexity of this technology. Because of its complexity and role in current integrated-circuit manufacturing it is important to promote study and research in this area. This work is intended to advance activity in this field by providing a comprehensive literature survey, initiating electron-beam imaging studies at R.I.T., and promote continued research using the latest available equipment with statistically design experiments.
It is the published opinion of several individuals that the future of microelectronic fabrication will involve a mix and match of the several lithographic techniques previously mentioned [Pike, 1987; Doane, 1987; Burggraaf, 1987]. The optimal process will be one in which the assets of the different techniques will be used to the greatest advantage for a particular application. The role of electron-beam lithography will be even more firmly entrenched in the fabrication process.

One objective of this research project is to develop a procedure to evaluate electron-beam resist materials exposed by a scanning electron microscope. The process parameters will be outlined in detail. Characteristic curves for the resist used in the experiment will be generated and analyzed in accordance with the methods described herein. The results will be correlated with other experimental values and published data. Performance of this experiment will promote a working knowledge of an unconventional electron-beam lithography technique. This will further enable a comparison between optical and electron-beam technologies.

Another objective of this project is to contribute data to the continued study of a novel chemically amplified electron beam resist material. A statistically designed experiment will be performed using a MEBES I exposure system. The data will be analyzed using computerized response surface
methods to determine the optimal value of the process parameters studied.

This work could pave the way for further characterization experiments and theses to follow. Some of this work has already been introduced, and continued studies in this area at R.I.T. are rapidly progressing past points originally conceived when this project was started.
METHODS

The research for this project was undertaken in two stages. Prior to the undertaking of this study, electron-beam images had never been generated at R.I.T. The initial hypothesis was that the electron beam from a scanning electron microscope (SEM) could be used as an exposure source for resist material. The SEM was available for use at the time, whereas a computer controlled, direct write or mask making electron-beam system was not. The first stage of this research involved the use of the SEM as an exposure tool to study electron beam resist material. Background work in this area included course work in analytical techniques using the SEM, practice in SEM maintenance and operation, and instruction in photolithography theory and integrated circuit processing methods.

A delay in the presentation of this work resulted in the availability of a MEBES I system. This presented an opportunity to study a novel chemically amplified resist using the MEBES as the exposure tool. A statistically based matrix was designed and followed to study the effects of post exposure bake time, post exposure bake temperature, and development time on the contrast and sensitivity of the imaging system. Computerized software modelling was used to analyze the data with the intention of developing optimum
Feasibility Study of SEM Exposure

Because electron-beam exposures with a SEM had not been previously achieved by close associates, it was necessary to perform a feasibility study to determine if experimental projects could be based on this type of work. The purpose of the study was to determine if an electron-beam image could be acquired using the SEM as the exposure source.

KMPR820 Samples

The first few attempts at obtaining an electron-beam image with the SEM were done with Kodak Micro Positive Resist 820 (KMPR820) photoresist. This is a novolac-based positive optical resist. It was expected that this resist would be sensitive to electron-beam exposures in addition to actinic radiation. Silicon wafer samples with KMPR820 photoresist were prepared using prior knowledge of coating parameters. A 0.5 μm thickness of the KMPR820 was obtained using a spin coating method. A 30 minute pre-bake at 90°C followed the spin coating. The SEM was set to 25 KeV with 10,000X magnification at the second to largest spot size. Two samples were exposed at three places for times of 120, 210, and 300 seconds. The wafer samples were then developed using parameters and solutions recommended by Kodak. No electron-beam images resulted from these first attempts.
EK-75 Samples

The Eastman Kodak Company generously donated a sample of an experimental electron-beam resist, EK-75, to be used during this study. This is a methyl methacrylate copolymer negative resist material. The coated resist thickness of 0.6 - 0.8 \( \mu m \) was recommended by Kodak, based on their knowledge and experience with the material. The coating parameter combination required to result in the desired resist thickness was developed empirically by performing a spin speed matrix. A spin speed of 2500 rpms was used to obtain a resist thickness of 0.7 \( \mu m \). The coated samples were pre-baked at 90\(^{\circ}\)C for 20 minutes prior to mounting on the specimen holder. Once a sample was placed on the specimen mounting stub, it was baked again at 90\(^{\circ}\)C for 10 minutes in order to cure the conductive silver paste used to adhere the sample to the specimen holder and to complete the pre-bake of the resist material. The first sample was exposed at 15 KeV with a magnification of 1,000X and the next to the largest spot size. The sample was exposed at three areas with times of 60, 120, and 180 seconds. This was dip developed in a solution of 1:1 methyl isobutyl ketone and methanol and rinsed in DI water. This resulted in three independent square areas of resist material. This study determined that the SEM was capable of being used as an exposure tool for electron-beam resist research and resulted in the first electron-beam images.
obtained at R.I.T. This determination enabled work to proceed on the first phase of this project.

PHASE I

Characteristic Curves

The characteristic curve used to determine the contrast and sensitivity of a resist imaging system is generated by plotting the electron dose received by the resist material during exposure versus the resulting resist thickness in the exposed region after development. In order to gather this data, many samples are exposed so that each receives different amounts of electron dosages, while all other parameters remain unchanged. It is expected that the post development resist thickness will vary with the amount of exposure. In general, increased exposure will result in increased thickness for negative resists. The opposite is true for positive resist materials.

The dose, or in optical terms, the exposure, is the product of the beam intensity and the time this intensity is irradiating a given area on the coated substrate. The electron-beam intensity is a function of the beam current per unit area. This is usually expressed in A/cm². The exposure dose is expressed in electron charge per unit area (C/cm²). The dose calculation is derived as follows:
\[ D = \frac{I \cdot t}{A} \text{ C/cm}^2 \]

\begin{align*}
I &= \text{beam current (A or C/t)} \\
t &= \text{time (sec)} \\
A &= \text{area (cm}^2) \\
\end{align*}

The exposure area used to calculate the dose during phase I was approximated with a theoretical calculation of the beam exposure area based on the active image area of the SEM cathode ray tube (CRT) and the magnification setting during exposure. This calculation assumes that the image on the CRT is proportional to the area which is being scanned by the electron beam. The calculation becomes:

\[
\frac{\text{CRT Area (cm}^2)}{\text{Area}} = \frac{\text{CRT Area (cm}^2)}{\text{magnification}^2}
\]

where one side of the square CRT measured at 4.0" or 10.16 cm and the CRT Area is then 103.2 cm².

Typically the characteristic curve is a plot of normalized film thickness as a function of the log dose. Figure 6 indicates an example of this curve for a negative resist material. The sensitivity is determined from this curve and is defined in this experiment as the dose required to obtain 50% of the initial film thickness following development.

The useful sensitivity for a positive resist is defined
Characteristic Curve Example for Negative Resist

Figure 6

as the dose required to produce complete solubility in the exposed region, while not affecting the unexposed substrate. This is illustrated in Figure 7. The contrast for both negative and positive resist is determined by extrapolating the slope of the straight portion of the characteristic curve.

Electrometer/Faraday Cup

In order to plot characteristic curves of Dose vs. Resist Thickness for electron-beam resist materials, it is necessary to measure the beam current striking the substrate surface.
Characteristic Curve Example for Positive Resist

Figure 7

This current is used to calculate the Dose. The current created by the electron beam is very small. There are very sensitive ammeters, or electronmeters, which are specifically designed for this purpose. A Faraday cup is used to collect the charged electron particles inside the vacuum chamber. The electrons travel through coaxial cable to the electronmeter and are measured in the form of a current.

An electronmeter was available via donation from an industrial affiliate of the microelectronics program. A Faraday cup was fashioned by drilling a hole into a specimen mounting stub and covering the opening with thin copper foil.
A small pin hole was placed in the foil to allow the electrons an opening to enter. Figure 8 shows a cross section of the Faraday cup.

![Faraday Cup Cross Section](image)

Figure 8

The cup was mounted in the stage in the same way a specimen would be mounted. The coaxial cable connecting the Faraday cup to the electronmeter is a factory installed option that is connected to the stage and exits the vacuum chamber at the base of the electron optical column. The electronmeter was used during the feasibility study and initial exposure trials. The electronmeter was subsequently replaced with a current-to-voltage converter circuit.

Before using the electronmeter to measure the electron
beam current the unit had to be serviced. Two units were available, but only one would function. The batteries were replaced at a relatively high expense. The donated electronmeter is an outdated instrument and requires specially made batteries. In addition, the reliability and accuracy of the unit was questioned. Based on these considerations, a decision was made to retire this unit and replace it with a current-to-voltage conversion circuit. The performance of this circuit is well understood, and it is more accurate and trustworthy. Figure 9 shows the schematic of this circuit.

![Current-to-Voltage Schematic](image)

**Current-to-Voltage Schematic**

**Figure 9**

The theory of the circuit is simple. The small current created by the electron beam is passed through a high value resistor. According to Ohm's Law the product of the current and resistance is a voltage. This voltage is amplified and
can be measured using a standard digital voltmeter. There is a choice of two different resistor values. The gain factor can be adjusted by accessing either of these resistors with a switch. By knowing the measured voltage, the amplification factor (gain) of the conversion circuit, and Ohm's Law, the input current can be calculated as follows:

\[ I = \frac{V}{R} \quad \text{(Ohm's Law)} \]

Considering circuit gain the basic equation would become:

\[ I = \frac{V \times \text{gain}}{R} \]

Substituting these known values of the particular current-to-voltage converter circuit

\[
R = 100\text{M ohm} \\
\text{Gain} = (1 + \frac{10\text{K ohm}}{1\text{K or } 100 \text{ ohms}})
\]

the current calculation becomes,

\[
I_{in} = \frac{V_{out}}{(100\text{E}6) \left[ 1 + \left(10\text{E}3 / 1\text{E}3 \text{ or } 100\right) \right]}
\]

A measurement of the electron beam current can be made by placing the Faraday cup into the vacuum chamber and operating the SEM as if to view a specimen. The gun parameters are set to the same values which would be used during an exposure. With the magnification set to a low value, the opening of the Faraday cup is manually positioned in the center of the beam.
by adjusting the stage. The magnification is increased until the entire beam is being focused at a point inside the cup. The cup traps the electrons which are amplified by the detection circuit, and a measurement of voltage created by the beam current can be made.

Substrates

Silicon wafers with 1,0,0 crystal orientation were chosen as substrates for this experiment. This choice was made to facilitate sample preparation. The doping parameters of the wafers was considered not important, as this would not effect the results of the experiment.

Silicon Dioxide

In an attempt to keep all parameters as close to an actual application as possible, silicon dioxide \((\text{SiO}_2)\) was grown on the surface of the wafers using a wet process. The oxide was grown in a furnace set at 1100°C for 30 minutes with a water flow rate of 1.5 l/min. The targeted oxide thickness was 4000Å - 5000Å. The final oxide thickness was determined using a Nanospec Automatic Film Thickness (AFT) Measurement System. A minimum of three measurements were taken across the surface of representative wafers. These measurements were averaged. The index of refraction for \(\text{SiO}_2\) used in the measurement was 1.45 for all trials.
Resist Coating

One positive resist, PMMA, and two negative resists, Kodak Micro E-Beam Resist ZX-784 and COP, were chosen for this experiment. Copies of the manufacturers' data sheets can be referenced in the Appendix. These materials were spun onto the oxidized silicon substrates using a puddle and spin method. A series of spin coatings was performed with each material in order to establish the spin speed required to meet the desired film thickness. The series was made by varying the spin speed while keeping the other parameters constant, and measuring the resulting resist thickness. Curves were created by plotting the spin speed versus the resist thickness. The spin speed used to prepare the exposure samples was determined by reading the appropriate spin curve and matching the recommended resist thickness to the spin speed. The desired film thickness in all cases was 0.6 μm. While creating these curves all other coating parameters were kept constant.

The puddle and spin method of resist coating is a manual technique. A model EC-101 spinner manufactured by Headway Research was used in coating the resists. A wafer was placed on the spin chuck and vacuum was initiated in order to hold the wafer in place. A laboratory syringe was used to dispense 0.5 ml of resist material onto the center of the wafers. The wafers were then spun at the preset speed for 20 seconds. The
wafers coated with the negative resists were prebaked in a conventional convection oven at 90°C for 30 minutes, as recommended by the manufacturers. It was recommended that the wafer samples to be used with the PMMA material be pretreated with hexa-methyldisilizane (HMDS) prior to coating the resist. A 0.25 ml quantity of HMDS was applied to the center of these wafers and spun at 2000 rpms for 20 seconds. The HMDS was allowed to dry for 30 seconds prior to dispensing the PMMA. The PMMA was prebaked at 170°C for 30 minutes, as recommended.

Due to the absence of a readily available Nanospec AFT measurement instrument, the resulting resist thicknesses for the spin series were determined using a laser interferometry technique developed at R.I.T. This method involves monitoring the power of a HeNe laser reflected off the resist-coated side of a wafer while the resist is being dry etched in a plasma asher. Wafers are oriented in the chamber of a Plasmaline 200 such that a laser can be directed off the coated surface and through the glass viewing port on the chamber door. A detector from a radiometer is positioned to be illuminated by the reflected beam. The reflected beam power is measured by the radiometer, and the radiometer output is plotted as the resist material is ashed away. Light is reflected from both the resist-wafer interface and from the resist-air interface. The beam power oscillates over time in a sinusoidal fashion in relation to the superposition of the destructive and
constructive interference of the two reflected beams. The number of sinusoidal cycles is proportional to the resist thickness by the equation:

\[ t = \frac{\lambda N}{2n} \]

where

- \( t \) = resist thickness
- \( N \) = number of cycles
- \( \lambda \) = wavelength of light (632.8 nm)
- \( n \) = index of refraction of the resist

Therefore, the resist thickness on a wafer can be calculated after determining the number of interference cycles and knowing the index of refraction of the resist. The indexes of refraction used are 1.51, 1.50, and 1.49 for ZX-784, PMMA, and COP respectively. It has been found that this method is quite accurate. However, there are several problems with this technique. The resist layer on the sample is destroyed during the measurement and, therefore, can not be used for exposure. Also, the throughput of this process is slow, so it takes a long time to measure many samples.

**Sample Preparation**

Once the proper spin speed was identified, wafers were coated with the appropriate thickness of electron-beam resist using the puddle and spin method. Through trial and error on
initial experimentation, it was determined that a dehydration bake of the wafers just before resist coating is advisable. This helped promote adhesion of the resist material to the silicon and decreased scumming during development of the exposed image. A 10 minute bake was made at 55°C in a convection oven. The coating parameters were kept the same as those used during spin characterization of the individual resists. Prebake temperatures also remained the same. Prebake time was shortened by 10 minutes for the PMMA and COP resist samples. These 10 minutes were made up during the curing of the conductive silver paint used to adhere the samples to the mounting stubs. The ZX-784 samples were prebaked for the full 30 minutes.

Because the specimen size is limited by the configuration of the stage, coated wafers needed to be sized down. The 1,0,0 crystal orientation of the wafers allowed the wafers to be broken into pieces without shattering the entire wafer. The resulting samples were likely to have straight sides. Rounded sides were evident on samples which came from areas at the perimeter of the wafer.

Samples were also prepared by dicing wafers using a diamond saw. The dicing was done prior to resist coating. This technique resulted in rectangular and uniform samples. However, this procedure made it very difficult to develop a coating process because the samples were unconventionally
sized relative to the equipment available. The time and effort required to prepare a process using this cutting method did not seem well spent. As a result, only broken wafer samples were used for this experiment.

The samples were adhered to the mounting stubs with colloidal silver conductive paint. This provided a means of stabilizing the sample and supplied a conductive path to ground in order to alleviate excess charging of the sample during exposure. The silver paint on the mounted sample was thermally cured in a convection oven. This expelled any solvents which could outgas and contaminate the vacuum chamber of the SEM and increased adhesion of the sample. Curing of the PMMA and COP samples was done for 10 minutes at the relevant pre-bake temperatures. This curing also served to complete the pre-bake for these samples. Because the ZX-784 samples were coated and exposed on different days, the pre-bake was completed as part of the coating process. The silver paint curing was done at 55°C for 10 minutes in a convection oven prior to exposure. It was found that the ZX-784 resist is susceptible to moisture contamination, but curing in this manner provided a means to dehydrate the resist coating.

Exposure

As previously mentioned, exposure was performed with a Cambridge Instruments Stereoscan 600 Scanning Electron
Microscope. Matrices were performed with each resist material by varying the exposure. It was intended that exposure time be the only parameter varied to form the matrix for each resist. The Kodak ZX-784 was exposed with 15 KeV, the maximum spot size, and 20X magnification. Fifteen KeV, the maximum spot size, and 100X magnification was used to expose the PMMA resist. The exposure parameters for the COP resist were 15 KeV, maximum spot size, and 50X magnification. The exposure times were measured to the nearest second using a hand held stop watch.

Post Exposure Treatment

The exposed ZX-784 samples were vacuum cured for 10 minutes before being removed from the SEM.

Prior to development each sample was removed from the mounting stub. The samples were twisted off the stub by hand. It was found that the wafer samples may break if they are pried off the stub. The residue of the conductive paint on the back of the samples was cleaned off with cotton tipped swabs moistened with acetone. The developer bath is quickly contaminated if this operation is not performed. Care was taken not to allow acetone to contact the exposed side of the sample, as it would dissolve the resist coating. The acetone on the back side of the samples was blown dry with nitrogen after the cleaning to ensure full evaporation.
Development

All exposed samples were developed using a dip and swirl method. While being held with forceps, the samples were dipped into glass beakers containing a developer bath. The sample was agitated in the bath using a random swirling motion in order to keep fresh developer moving across the exposed area. The samples were then rinsed and blown dry with nitrogen. The temperature of the developer baths was maintained at room ambient (approximately 20°C).

The ZX-784 samples were developed in a solution of 1.2 to 1 ratio of methyl isobutyl ketone (MIBK) to ethanol for 60 seconds. The samples were rinsed in isopropanol for 10 seconds and then 10 seconds in deionized (DI) water prior to nitrogen drying.

An ethanol and MIBK solution was also used to develop the PMMA and COP samples. However, the ratio of MIBK to ethanol was 1.75 to 1 and the development time was shortened to 30 seconds. The PMMA samples were dipped in DI water for 2-5 seconds before and after the 10 second isopropanol rinse. The DI water dip was omitted for the COP development.

Since these samples would not be subjected to further processing, it was felt that post-baking the developed samples was not necessary.
Resist Thickness Measurement (Post Development)

The remaining resist thickness of the imaged samples was assessed using a Nanospec AFT measurement instrument. Oxide thickness of representative samples and the index of refraction of the resist material was fed into the computer of the measurement system. The index of refractions used were the same as those used with the laser interferometry measurements. At least three measurements were made on each sample. The average of these values was used to plot the characteristic curves.

PHASE II
Statistical Design

The SAL 601 manufacturer's product literature indicates that control of the post-exposure bake process is critical to achieve optimum imaging sensitivity and linewidth [Shipley, 1988]. This literature also indicates that the contrast of the system is related to the development time. The work published by Liu, et al. [Liu, 1988] states that their results demonstrate that postbake time and postbake temperature and the interaction between the two variables certainly effect the resulting sensitivity. This work also proves that the contrast is a function of the development time. In this experiment, the postbake time, postbake temperature, and development time will be varied to study their effects to the
resulting sensitivity and contrast.

It is therefore hypothesized that the contrast and sensitivity of the SAL 601 imaging system is dependent on the postbake time, postbake temperature, and development time. To study these relationships a three factor, three level \((3^3)\) experiment was designed as a statistical approach. It is economical to use an incomplete factorial design rather than perform experimental trials at all combinations of factor levels. The Box-Behnken design was chosen as the strategy to study these relationships since it offers the ability to determine the linear, quadratic, and interactive effects of these variables [Box, Behnken, 1960]. This is an efficient three factor design and has been proven over a wide range of practical problems [Lucas, 1976]. The three factor level of this design uses 13 of the 27 points from the full factorial with two extra replicates at the center point, for a total of 15 points. The geometric character of this design is such that all points, except the center points, are at the midpoints of the edges of a hypercube whose dimension is the number of factors. All of these points lie on a single sphere and are equally spaced from the center. This property is associated with rotatability. The geometry of a three factor design is illustrated in Figure 10. The replicated center points provide a means to measure the inherent experimental error and are sufficient to predict the variance as a function
Three Factor Box-Behnken Design Geometry

Figure 10

of the distance from the center. This design also lends itself to computer modeling and response surface analysis methods used to determine the process parameter values which optimize the imaging system performance.

The levels of the independent variables was determined through discussions with associates who have had previous process experience with the imaging system and through analysis of product literature. It is predicted that the optimum response levels will be obtained by processing the independent variables within the boundaries established in
this experiment. To meet Box-Behnken design criteria the independent variable levels will be quantitative and equally spaced from a center value. The levels and unit values chosen are summarized as follows:

Postbake temperature: 110, 115, 120 °C
Postbake time: 40, 70, 100 seconds
Development time: 5, 8, 11 minutes

The response variables are a unit less contrast number and a sensitivity value in C/cm². These values are derived from characteristic curves developed from data obtained at each experimental trial. The tabulated representation of the independent variables in the factorial format is shown in Table 1. It should be noted that trials 13, 14, and 15 are the replicates of the center point.

The mathematical model assumed for this quadratic three-factor experiment accounting for interactive effects can be expressed as

\[ Y_{ijk} = u + A_i + B_j + C_k + AB_{ij} + AC_{ik} + BC_{jk} + AA_{ii} + BB_{jj} + CC_{kk} + e_{ijk} \]

where

- \( A_i \) = the estimated effect of the \( i \)th level of factor \( x_1 \)
- \( B_j \) = the estimated effect of the \( j \)th level of factor \( x_2 \)
- \( C_k \) = the estimated effect of the \( k \)th level of factor \( x_3 \)
- \( Y_{ijk} \) = the response measured at the \( i \)th level of \( x_1 \), the \( j \)th level of \( x_2 \), and the \( k \)th level of \( x_3 \)
- \( e_{ijk} \) = the estimated error effect at the \( i \)th level of \( x_1 \), the \( j \)th level of \( x_2 \), and the \( k \)th level of \( x_3 \).
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<td>115</td>
<td>100</td>
</tr>
<tr>
<td>6</td>
<td>11</td>
<td>115</td>
<td>40</td>
</tr>
<tr>
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<td>5</td>
<td>115</td>
<td>100</td>
</tr>
<tr>
<td>8</td>
<td>5</td>
<td>115</td>
<td>40</td>
</tr>
<tr>
<td>9</td>
<td>8</td>
<td>120</td>
<td>100</td>
</tr>
<tr>
<td>10</td>
<td>8</td>
<td>120</td>
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<tr>
<td>11</td>
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<td>110</td>
<td>100</td>
</tr>
<tr>
<td>12</td>
<td>8</td>
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</tr>
<tr>
<td>13</td>
<td>8</td>
<td>115</td>
<td>70</td>
</tr>
<tr>
<td>14</td>
<td>8</td>
<td>115</td>
<td>70</td>
</tr>
<tr>
<td>15</td>
<td>8</td>
<td>115</td>
<td>70</td>
</tr>
</tbody>
</table>

Unrandomized Experimental Schedule

Table 1

A detailed description of the test hypothesis are as follows:

1. $H_0$: $A = 0$
   $H_1$: $A > 0$
2. $H_0$: $B = 0$
   $H_1$: $B > 0$
3. $H_0$: $C = 0$
   $H_1$: $C > 0$
4. $H_0$: $AB = 0$
   $H_1$: $AB > 0$
5. \(H_0: AC = 0\)  
\(H_1: AC > 0\)

6. \(H_0: BC = 0\)  
\(H_1: BC > 0\)

7. \(H_0: AA = 0\)  
\(H_1: AA > 0\)

8. \(H_0: BB = 0\)  
\(H_1: BB > 0\)

9. \(H_0: CC = 0\)  
\(H_1: CC > 0\)

All hypotheses are to be tested for significance at the \(\alpha = .05\) level using analysis of variance and the F statistic. The pure error of the model based on the data of the center points will be separated from the total experimental error to enable a lack of fit determination. The hypotheses to be tested are [Montgomery, 1991]

\[H_0: \text{the model fits the data}\]
\[H_1: \text{the model does not fit the data}\]

The lack of fit will be tested using the F statistic at the \(\alpha = .05\) level. An attempt to eliminate the bias error will be made by randomizing the order of the trials. Precision error will be minimized by having the same operator perform the experimental tasks, using standard measurement techniques on the same equipment, taking an average of three readings of resist thickness at the same exposure level, and using the same software program to plot characteristic curves.

A solution to the experimental model for both contrast and sensitivity will be derived using stepwise multiple regression. The nonsignificant factors will be removed in
stepwise fashion until the null hypotheses of the coefficients tested at the \( t = .025 \) level are rejected (the coefficients are significant). The solution to the model will be used in response surface plotting to determine the optimum responses within the experimental boundaries.

**Characteristic Curves**

Characteristic curves will be plotted to determine the response variables in the same manner as previously described. However, because this phase of the experiment is performed on a MEBES exposure tool rather than a SEM elements in the dose are calculated slightly differently. The same basic dose equation applies except the area and time determinations are particular to MEBES specifications. The electron beam can be diverted to measure current using a Faraday cup built into the electron column. The area used in the dose formula is itself calculated using the radius of the spot size which is measured in the Faraday cup (Area = \( \pi r^2 \)). The time is derived from the scan frequency of the MEBES (20 MHz). Therefore, the dose calculation using the MEBES becomes

\[
Dose = \frac{\text{current}}{\pi r^2} \cdot \frac{1}{20 \text{ MHz}}
\]

**Substrates**

Chrome coated quartz glass mask blanks were used as
substrates for this phase of the experiment. These blanks were coated with approximately 1500Å of chrome prior to resist coating. These were chosen to emulate real applications of this process and because proper tooling was available to facilitate processing.

Resist Coating

The only resist used in this portion of the experiment was the Shipley SAL 601. Copies of the manufacturers' data sheet can be referenced in the Appendix. This material was applied using the same puddle and spin method outlined previously. A spin speed matrix was performed to determine the proper parameters which result in the desired 0.6 µm initial film thickness. A Nanospec ATF instrument was used to determine the resist thickness. The "positive resist on silicon" program with an index of refraction of 1.64 was used during all resist thickness measurements. A syringe was used to dispense 0.5 ml of resist material prior to spinning at 5000 rpm for 30 seconds. No pretreatment was used. The coated substrates were prebaked on a hotplate for 90 seconds at 85°C.

Exposure

A Perkin-Elmer MEBES I was used to make the exposures of these plates. Each exposure trial contained enough data to
plot a characteristic curve. The same pattern was exposed with various dose levels at 39 separate locations on the substrate. The individual pattern is shown in Figure 11 and the repeat pattern is shown in Figure 12. The minimum dose was calculated using the equation mentioned above. The repeat patterns were made in increments of the minimum dose level by writing over the same pattern. The second repeat pattern would be written over twice. Therefore, it would have twice the dose of the first pattern and so forth up to 39 patterns.

Individual Exposure Pattern

Figure 11
The exposures were made at a voltage of 10 KeV with a beam current of 8.99 nA at a spot size of .45 μm.

**Post Exposure Bake**

Each sample was postbaked on a hotplate at the temperature and for the time called for in the random experimental schedule. The time was monitored with a digital lab timer.

**Development**

All exposed samples were developed using an emersion technique. The samples were placed in the bottom of a glass
pan containing Shipley MF-319 developer solution. The pan was agitated from side to side during the development cycle. Development time was in accordance with the experimental schedule. Following development, the samples were rinsed in DI water for approximately one minute before being spun dry for 45 seconds.

Resist Thickness Measurement

The resist thickness of the repeat patterns on the substrates was measured using the Nanospec ATF. The Nanospec was programmed in the same fashion as that used during the spin matrix. Three readings were taken in the hour glass shaped area and then averaged before plotting the data. The resist measurements were taken at the least exposure dose first and progressed toward the highest level. The readings on a plate were considered complete once the readings leveled off.
RESULTS

Phase I

Sample Parameters

The resulting silicon dioxide thickness on the wafers used for the ZX-784 samples was 4600Å. The oxide on the COP and PMMA samples was 2000Å thick.

Spin Trial Data

The data accumulated during the spin parameter evaluation trials are shown in the following tables.

<table>
<thead>
<tr>
<th>Spin Speed (rpm)</th>
<th>Thickness (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000</td>
<td>0.733</td>
</tr>
<tr>
<td>3000</td>
<td>0.576</td>
</tr>
<tr>
<td>4000</td>
<td>0.525</td>
</tr>
<tr>
<td>5000</td>
<td>0.419</td>
</tr>
</tbody>
</table>

ZX-784 Spin Speed Data

Table 2
The spin speed data are also presented in the following plots.
ZX-784 Spin Curve

Figure 13

PMMA Spin Curve

Figure 14
The resist thickness for ZX-784 before imaging was 8496 Å. This was achieved using a spin speed of 2500 rpm. The initial coated thickness of the COP material was 6606 Å at a spin speed of 4000 rpm. A spin speed of 1000 rpm resulted in an initial resist coating of 6586 Å thick for PMMA.

**Exposure Data**

The exposure data collected for the three resist materials are shown in the following tables. The Dose is calculated in the same way described previously in this document. The normalized resist thickness was calculated to indicate the relative thickness changes in relation to
exposure time.

<table>
<thead>
<tr>
<th>Time (sec)</th>
<th>Dose (C/cm²)</th>
<th>Resist Thickness (Å)</th>
<th>Normalized Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.3974 x 10⁻⁸</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>4.7948 x 10⁻⁸</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>1.1987 x 10⁻⁷</td>
<td>842</td>
<td>.1127</td>
</tr>
<tr>
<td>15</td>
<td>3.5961 x 10⁻⁷</td>
<td>3530</td>
<td>.4725</td>
</tr>
<tr>
<td>30</td>
<td>7.1922 x 10⁻⁷</td>
<td>5022</td>
<td>.6720</td>
</tr>
<tr>
<td>45</td>
<td>1.0788 x 10⁻⁶</td>
<td>6018</td>
<td>.8056</td>
</tr>
<tr>
<td>60</td>
<td>1.4384 x 10⁻⁶</td>
<td>6640</td>
<td>.8880</td>
</tr>
<tr>
<td>90</td>
<td>2.1577 x 10⁻⁶</td>
<td>6889</td>
<td>.9220</td>
</tr>
<tr>
<td>120</td>
<td>2.8769 x 10⁻⁶</td>
<td>7320</td>
<td>.9799</td>
</tr>
<tr>
<td>150</td>
<td>3.5961 x 10⁻⁶</td>
<td>7417</td>
<td>.993</td>
</tr>
<tr>
<td>180</td>
<td>4.3153 x 10⁻⁶</td>
<td>7470</td>
<td>1</td>
</tr>
<tr>
<td>360</td>
<td>8.6306 x 10⁻⁶</td>
<td>7489</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Area = 0.667383 cm²
Beam Current = 1.6 x 10⁻⁸ amps

ZX-784 Exposure Data
Table 5
<table>
<thead>
<tr>
<th>Time (sec)</th>
<th>Dose (C/cm²)</th>
<th>Resist Thickness (Å)</th>
<th>Normalized Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>6325</td>
<td>1.0</td>
</tr>
<tr>
<td>15</td>
<td>$9.956 \times 10^{-6}$</td>
<td>5773</td>
<td>.9127</td>
</tr>
<tr>
<td>30</td>
<td>$1.991 \times 10^{-5}$</td>
<td>3363</td>
<td>.5317</td>
</tr>
<tr>
<td>45</td>
<td>$2.987 \times 10^{-5}$</td>
<td>1630</td>
<td>.2577</td>
</tr>
<tr>
<td>60</td>
<td>$3.983 \times 10^{-5}$</td>
<td>509</td>
<td>.0805</td>
</tr>
<tr>
<td>90</td>
<td>$5.974 \times 10^{-5}$</td>
<td>532</td>
<td>.0841</td>
</tr>
<tr>
<td>120</td>
<td>$7.965 \times 10^{-5}$</td>
<td>428</td>
<td>.0677</td>
</tr>
</tbody>
</table>

Area = 0.01032 cm²

Beam Current = $6.85 \times 10^{-9}$ amps (or C/cm²)

PMMA Exposure Data

Table 6
<table>
<thead>
<tr>
<th>Time (sec)</th>
<th>Dose (C/cm²)</th>
<th>Resist Thickness (Å)</th>
<th>Normalized Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>$3.319 \times 10^{-7}$</td>
<td>5542</td>
<td>.8397</td>
</tr>
<tr>
<td>5</td>
<td>$8.297 \times 10^{-7}$</td>
<td>5529</td>
<td>.8377</td>
</tr>
<tr>
<td>10</td>
<td>$1.659 \times 10^{-6}$</td>
<td>6084</td>
<td>.9218</td>
</tr>
<tr>
<td>15</td>
<td>$2.489 \times 10^{-6}$</td>
<td>6416</td>
<td>.9721</td>
</tr>
<tr>
<td>20</td>
<td>$3.319 \times 10^{-6}$</td>
<td>6393</td>
<td>.9686</td>
</tr>
<tr>
<td>30</td>
<td>$4.978 \times 10^{-6}$</td>
<td>6491</td>
<td>.9835</td>
</tr>
<tr>
<td>45</td>
<td>$7.467 \times 10^{-6}$</td>
<td>6489</td>
<td>.9832</td>
</tr>
<tr>
<td>60</td>
<td>$9.956 \times 10^{-6}$</td>
<td>6516</td>
<td>.9873</td>
</tr>
</tbody>
</table>

Area = 0.04128 cm²

Beam Current = $6.85 \times 10^{-9}$ amps

COP Exposure Data

Table 7

The data presented in these tables are also plotted in the following graphs to create the characteristic curves of the imaging system. The log Dose was calculated before plotting these curves, but the tabulated data are not presented. These graphs were used to determine the contrast and sensitivity of each system.
Characteristic Curve
ZX-784 Resist

Figure 16

PMMA Characteristic Curve

Figure 17

70
The experimental contrast and sensitivity of each imaging system are summarized in the following table.

<table>
<thead>
<tr>
<th></th>
<th>ZX-784</th>
<th>COP</th>
<th>PMMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitivity</td>
<td>40 (\mu)C/cm(^2)</td>
<td>1.8 (\mu)C/cm(^2)</td>
<td>45 (\mu)C/cm(^2)</td>
</tr>
<tr>
<td>Contrast</td>
<td>0.7</td>
<td>0.7</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Contrast and Sensitivity Summary

Table 8
### Process Parameter Summary

#### Resist Material

<table>
<thead>
<tr>
<th>Trade Name</th>
<th>ZX-784</th>
<th>COP</th>
<th>PMMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>glycidyl methacrylate co allyl methacrylate</td>
<td>glycidyl methacrylate (methyl meth acrylate)</td>
<td></td>
</tr>
</tbody>
</table>

| Refractive Index | 1.51 | 1.49 | 1.50 |

#### Substrate

<table>
<thead>
<tr>
<th>Material</th>
<th>SiO₂/Si</th>
<th>SiO₂/Si</th>
<th>SiO₂/Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si Crystal Orientation</td>
<td>1,0,0</td>
<td>1,0,0</td>
<td>1,0,0</td>
</tr>
<tr>
<td>SiO₂ Thickness (Å)</td>
<td>4600</td>
<td>2000</td>
<td>2000</td>
</tr>
</tbody>
</table>

#### Resist Coating

<table>
<thead>
<tr>
<th>Deposition Method</th>
<th>Spin</th>
<th>Spin</th>
<th>Spin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount Deposited (ml)</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Spin Speed (rpms)</td>
<td>2500</td>
<td>4000</td>
<td>1000</td>
</tr>
<tr>
<td>Spin Time (sec)</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Initial Thickness (Å)</td>
<td>8496</td>
<td>6606</td>
<td>6586</td>
</tr>
</tbody>
</table>

#### Preexposure Treatment

<table>
<thead>
<tr>
<th>Adhesion Promoter</th>
<th>none</th>
<th>none</th>
<th>HMDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount Deposited (ml)</td>
<td>---</td>
<td>---</td>
<td>0.25</td>
</tr>
<tr>
<td>Spin Speed (rpms)</td>
<td>---</td>
<td>---</td>
<td>2000</td>
</tr>
<tr>
<td>Spin Time (sec)</td>
<td>---</td>
<td>---</td>
<td>20</td>
</tr>
</tbody>
</table>
Prebake Conditions:

<table>
<thead>
<tr>
<th>Method</th>
<th>convection</th>
<th>convection</th>
<th>convection</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>90</td>
<td>90</td>
<td>170</td>
</tr>
<tr>
<td>Time (min)</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>ambient</td>
<td>ambient</td>
<td>ambient</td>
</tr>
</tbody>
</table>

Exposure Parameters

<table>
<thead>
<tr>
<th>Radiation Type</th>
<th>electron</th>
<th>electron</th>
<th>electron</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exposure Tool</td>
<td>Cambridge Stereoscan 600 SEM</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Radiation Mode</td>
<td>Scanning beam for all</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Radiation Energy (KeV)</td>
<td>15</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Magnification</td>
<td>20X</td>
<td>50X</td>
<td>100X</td>
</tr>
<tr>
<td>Beam Current (amps)</td>
<td>1.6x10^-8</td>
<td>6.85x10^-9</td>
<td>6.85x10^-9</td>
</tr>
<tr>
<td>Exposure Environment</td>
<td>vacuum</td>
<td>vacuum</td>
<td>vacuum</td>
</tr>
<tr>
<td>Vacuum Curing</td>
<td>10 min</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>Image Area (cm^2)</td>
<td>0.667</td>
<td>0.413</td>
<td>0.010</td>
</tr>
</tbody>
</table>

Development Parameters

<table>
<thead>
<tr>
<th>Method</th>
<th>dip/swirl</th>
<th>dip/swirl</th>
<th>dip/swirl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution</td>
<td>1.2:1</td>
<td>1.75:1</td>
<td>1.75:1</td>
</tr>
<tr>
<td></td>
<td>methyl isobutyl ketone/ethyl alcohol for all</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>22</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Time (sec)</td>
<td>60</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Rinse</td>
<td>isopropanol/ DI water</td>
<td>isopropanol isopropanol</td>
<td>DI Water</td>
</tr>
<tr>
<td>Rinse Time</td>
<td>10 sec/ 10 sec</td>
<td>10 sec</td>
<td>10 sec/ 2-5 sec</td>
</tr>
</tbody>
</table>
Phase II

Exposure Data

The exposure data was plotted as characteristic curves for each experimental trial using Harvard Graphics software. The contrast and sensitivity was determined using the same techniques outlined earlier in this report. The individual characteristic curves can be found in Appendix B. Table 9 summarizes the trials of independent variables and the associated responses.

Statistical Analysis

Informal analysis of the data is useful prior to detailed statistical analysis. Trends in the responses are evident when comparisons of the average of response values are made at different factor levels. Results of these analysis are summarized in Tables 10 & 11 below.

<table>
<thead>
<tr>
<th>PEB Temp (°C)</th>
<th>Sens</th>
<th>PEB Time (sec)</th>
<th>Sens</th>
<th>Devel Time (min)</th>
<th>Sens</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>1.06</td>
<td>40</td>
<td>1.04</td>
<td>5</td>
<td>.95</td>
</tr>
<tr>
<td>115</td>
<td>.88</td>
<td>70</td>
<td>.89</td>
<td>8</td>
<td>.89</td>
</tr>
<tr>
<td>120</td>
<td>.80</td>
<td>100</td>
<td>.80</td>
<td>11</td>
<td>.88</td>
</tr>
</tbody>
</table>

Average Sensitivity (µC/cm²) as a Function of Factor Level

Table 10
<table>
<thead>
<tr>
<th>Trial</th>
<th>Develop Time (min)</th>
<th>Postbake Temp (°C)</th>
<th>Postbake Time (sec)</th>
<th>Contrast $V_1$</th>
<th>Sensitivity $V_2$ (μC/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11</td>
<td>120</td>
<td>70</td>
<td>1.54</td>
<td>.60</td>
</tr>
<tr>
<td>2</td>
<td>11</td>
<td>110</td>
<td>70</td>
<td>1.90</td>
<td>.90</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>120</td>
<td>70</td>
<td>3.16</td>
<td>1.2</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>110</td>
<td>70</td>
<td>2.25</td>
<td>1.0</td>
</tr>
<tr>
<td>5</td>
<td>11</td>
<td>115</td>
<td>100</td>
<td>2.28</td>
<td>.90</td>
</tr>
<tr>
<td>6</td>
<td>11</td>
<td>115</td>
<td>40</td>
<td>3.34</td>
<td>1.1</td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>115</td>
<td>100</td>
<td>1.13</td>
<td>.63</td>
</tr>
<tr>
<td>8</td>
<td>5</td>
<td>115</td>
<td>40</td>
<td>2.14</td>
<td>.925</td>
</tr>
<tr>
<td>9</td>
<td>8</td>
<td>120</td>
<td>100</td>
<td>1.33</td>
<td>.60</td>
</tr>
<tr>
<td>10</td>
<td>8</td>
<td>120</td>
<td>40</td>
<td>1.24</td>
<td>.80</td>
</tr>
<tr>
<td>11</td>
<td>8</td>
<td>110</td>
<td>100</td>
<td>2.41</td>
<td>1.0</td>
</tr>
<tr>
<td>12</td>
<td>8</td>
<td>110</td>
<td>40</td>
<td>2.58</td>
<td>1.35</td>
</tr>
<tr>
<td>13</td>
<td>8</td>
<td>115</td>
<td>70</td>
<td>2.33</td>
<td>.96</td>
</tr>
<tr>
<td>14</td>
<td>8</td>
<td>115</td>
<td>70</td>
<td>3.15</td>
<td>.80</td>
</tr>
<tr>
<td>15</td>
<td>8</td>
<td>115</td>
<td>70</td>
<td>2.70</td>
<td>.78</td>
</tr>
</tbody>
</table>

SAL-601 Data Summary

Table 9
The trend in sensitivity is to increase as all of the independent variables are increased. This is what is expected based on the literature [Shipley, 1988] [Fedynyshyn, et al., 1990]. Changes in development time do not have as much effect as the postbake parameters. It is unclear that a maximum sensitivity value has been reached since no peak in this data is indicated.

<table>
<thead>
<tr>
<th>PEB Temp (°C)</th>
<th>Contrast</th>
<th>PEB Time (sec)</th>
<th>Contrast</th>
<th>Devel Time (min)</th>
<th>Contrast</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>2.29</td>
<td>40</td>
<td>2.33</td>
<td>5</td>
<td>2.17</td>
</tr>
<tr>
<td>115</td>
<td>2.44</td>
<td>70</td>
<td>2.43</td>
<td>8</td>
<td>2.24</td>
</tr>
<tr>
<td>120</td>
<td>1.82</td>
<td>100</td>
<td>1.79</td>
<td>11</td>
<td>2.27</td>
</tr>
</tbody>
</table>

Average Contrast as a Function of Factor Level

Table 11

The trends of the contrast are less distinct because there is less range between the data averages. The data indicates that the greatest contrast is obtained when processing between the maximum and minimum postbake factor levels. In fact, the peak contrast value is found close to the nominal postbake factor levels. Increasing the development time corresponds to an increase in contrast. This effect is also expected based on the literature.
This statistical analysis was performed using Statgraphics version 5.0 software. This software package was chosen because it has routines written specifically to assist the user in the design and analysis of $3^3$ Box-Behnken experiments. The results of the ANOVA for the dependent variables sensitivity and contrast are shown in Tables 12 & 15.

### ANOVA for sensitivity - Box-Behnken Design

<table>
<thead>
<tr>
<th>Effect</th>
<th>Sum of Squares</th>
<th>DF</th>
<th>Mean Sq.</th>
<th>F-Ratio</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: postbake t</td>
<td>.1378125</td>
<td>1</td>
<td>.1378125</td>
<td>14.16</td>
<td>.0639</td>
</tr>
<tr>
<td>B: postbake t i</td>
<td>.1365031</td>
<td>1</td>
<td>.1365031</td>
<td>14.02</td>
<td>.0645</td>
</tr>
<tr>
<td>C: develop t i</td>
<td>.0081281</td>
<td>1</td>
<td>.0081281</td>
<td>.84</td>
<td>.4659</td>
</tr>
<tr>
<td>AB</td>
<td>.0056250</td>
<td>1</td>
<td>.0056250</td>
<td>.58</td>
<td>.5337</td>
</tr>
<tr>
<td>AC</td>
<td>.0625000</td>
<td>1</td>
<td>.0625000</td>
<td>6.42</td>
<td>.1268</td>
</tr>
<tr>
<td>BC</td>
<td>.0022562</td>
<td>1</td>
<td>.0022562</td>
<td>.23</td>
<td>.6823</td>
</tr>
<tr>
<td>AA</td>
<td>.0149079</td>
<td>1</td>
<td>.0149079</td>
<td>1.53</td>
<td>.3414</td>
</tr>
<tr>
<td>BB</td>
<td>.0027502</td>
<td>1</td>
<td>.0027502</td>
<td>.28</td>
<td>.6532</td>
</tr>
<tr>
<td>CC</td>
<td>.0008079</td>
<td>1</td>
<td>.0008079</td>
<td>.08</td>
<td>.8031</td>
</tr>
<tr>
<td>Lack-of-fit</td>
<td>.2545688</td>
<td>3</td>
<td>.0848563</td>
<td>8.72</td>
<td>.1046</td>
</tr>
<tr>
<td>Pure error</td>
<td>.0194667</td>
<td>2</td>
<td>.0097333</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total (corr.)</td>
<td>.64389000</td>
<td>14</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

R-squared = 0.574406  R-squared (adj. for d.f.) = 0

$F_{1, 2, \alpha=.05}=18.51$  $F_{3, 2, \alpha=.05}=19.16$  $F_{1, 2, \alpha=.25}=2.57$

ANOVA for Sensitivity

Table 12

The ANOVA for sensitivity shows that all factors are insignificant at the 5% level and that the null hypotheses are rejected. The lack-of-fit test is also rejected and indicates that the model is inadequate. At the 10% level the postbake time and postbake temperature factors become significant ($F_{1, 2, \alpha=.10}=8.53$), but the lack-of-fit test is still rejected.
The lack-of-fit indicates that this model is adequate at the 25% level \( F_{3,2,\alpha=.25}=3.15 \).

Further analysis of the data is performed to confirm the lack-of-fit to a regression of the variables to sensitivity. Statgraphics was used to run the quadratic multiple regression on the full model in an effort to ultimately determine the coefficients of the mathematical model so that predictions of the response are possible. The analysis of regression variance is summarized below.

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>DF</th>
<th>Mean Square</th>
<th>F-Ratio</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>0.357888</td>
<td>9</td>
<td>0.0397653</td>
<td>0.761684</td>
<td>.6602</td>
</tr>
<tr>
<td>Error</td>
<td>0.261035</td>
<td>5</td>
<td>0.0522071</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total (Corr.)</td>
<td>0.618923</td>
<td>14</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

R-squared = 0.578243  
R-squared (Adj. for d.f.) = 0  
Std. error of est. = 0.228489  
Durbin-Watson statistic = 1.7878

Analysis of Regression Variance for Sensitivity

Table 13

Since the F number, 0.762, is less than \( F_{9,5,\alpha=.05}=2.02 \) the null hypothesis for regression is accepted. This model can not be used with confidence. A detailed regression for all the factors is shown below in Table 14.
Model fitting results for: sensitivit

<table>
<thead>
<tr>
<th>Independent variable</th>
<th>coefficient</th>
<th>std. error</th>
<th>t-value</th>
<th>sig. level</th>
</tr>
</thead>
<tbody>
<tr>
<td>CONSTANT</td>
<td>29.312662</td>
<td>63.669273</td>
<td>0.4604</td>
<td>0.6646</td>
</tr>
<tr>
<td>postbaketi</td>
<td>-0.039113</td>
<td>0.090134</td>
<td>-0.4339</td>
<td>0.6824</td>
</tr>
<tr>
<td>postbake</td>
<td>-0.504167</td>
<td>1.097076</td>
<td>-0.4596</td>
<td>0.6631</td>
</tr>
<tr>
<td>developm</td>
<td>0.899468</td>
<td>0.905794</td>
<td>0.9930</td>
<td>0.3663</td>
</tr>
<tr>
<td>postbaketi^2</td>
<td>0.000037</td>
<td>0.000132</td>
<td>0.2821</td>
<td>0.7892</td>
</tr>
<tr>
<td>postbake^2</td>
<td>0.002292</td>
<td>0.004756</td>
<td>0.4818</td>
<td>0.6503</td>
</tr>
<tr>
<td>developm^2</td>
<td>0.002338</td>
<td>0.013212</td>
<td>0.1770</td>
<td>0.8665</td>
</tr>
<tr>
<td>postbaketi*postbakeet</td>
<td>0.00025</td>
<td>0.000762</td>
<td>0.3282</td>
<td>0.7560</td>
</tr>
<tr>
<td>postbake*developm</td>
<td>0.000125</td>
<td>0.001269</td>
<td>0.0985</td>
<td>0.9254</td>
</tr>
<tr>
<td>postbake*developm</td>
<td>-0.008333</td>
<td>0.007616</td>
<td>-1.0941</td>
<td>0.3238</td>
</tr>
</tbody>
</table>

R-SQ. (ADJ.) = 0.0000  SE= 0.228489  MAE= 0.116444  DurbWat= 1.788
Previously: 0.9509  0.212956  0.118997  1.709
15 observations fitted, forecast(s) computed for 0 missing val. of dep. var.

Detailed Analysis of Regression Variance for Sensitivity

Table 14

The t statistic is used here to evaluate the significance of each individual variable. This table confirms that each variable is insignificant.

The ANOVA for contrast indicates that several factors would be significant at a more liberal 25% confidence level. However, the lack-of-fit is the most significant and the second order model would be rejected entirely. In addition, the R^2 statistic indicates lack-of-fit to the model. The
relatively low value of the F ratio for development time loosely confirms the informal analysis that this is less significant than the postbake parameters.

<table>
<thead>
<tr>
<th>Effect</th>
<th>Sum of Squares</th>
<th>DF</th>
<th>Mean Sq.</th>
<th>F-Ratio</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>A:postbakete</td>
<td>.4371125</td>
<td>1</td>
<td>.4371125</td>
<td>2.59</td>
<td>.2487</td>
</tr>
<tr>
<td>B:postbaketi</td>
<td>.5778125</td>
<td>1</td>
<td>.5778125</td>
<td>3.43</td>
<td>.2054</td>
</tr>
<tr>
<td>C:developtim</td>
<td>.0180500</td>
<td>1</td>
<td>.0180500</td>
<td>.11</td>
<td>.7777</td>
</tr>
<tr>
<td>AB</td>
<td>.0169000</td>
<td>1</td>
<td>.0169000</td>
<td>.10</td>
<td>.7846</td>
</tr>
<tr>
<td>AC</td>
<td>.4032250</td>
<td>1</td>
<td>.4032250</td>
<td>2.39</td>
<td>.2621</td>
</tr>
<tr>
<td>BC</td>
<td>.0006250</td>
<td>1</td>
<td>.0006250</td>
<td>.00</td>
<td>.9576</td>
</tr>
<tr>
<td>AA</td>
<td>.6617026</td>
<td>1</td>
<td>.6617026</td>
<td>3.92</td>
<td>.1861</td>
</tr>
<tr>
<td>BB</td>
<td>.6308103</td>
<td>1</td>
<td>.6308103</td>
<td>3.74</td>
<td>.1926</td>
</tr>
<tr>
<td>CC</td>
<td>.0304641</td>
<td>1</td>
<td>.0304641</td>
<td>.18</td>
<td>.7167</td>
</tr>
<tr>
<td>Lack-of-fit</td>
<td>3.9304250</td>
<td>3</td>
<td>1.3101417</td>
<td>7.77</td>
<td>.1162</td>
</tr>
<tr>
<td>Pure error</td>
<td>.3372667</td>
<td>2</td>
<td>.1686333</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total (corr.)</td>
<td>6.92524000</td>
<td>14</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

R-squared = 0.383748
R-squared (adj. for d.f.) = 0

\[ F_{1,2,\alpha=.05}=18.51 \quad F_{3,2,\alpha=.05}=19.16 \quad F_{1,2,\alpha=.25}=2.57 \]

ANOVA for Contrast

Table 15
DISCUSSION

Phase I

Feasibility Study

In retrospect, there are many factors which could have contributed to the failure of obtaining images. During further experimentation it was discovered that correct sample preparation is extremely important. It was found that achievement of electron-beam images is highly dependent on correct sample placement within the vacuum chamber of the SEM. It is believed that inaccurate sample placement in the specimen chamber is the primary cause for failure to obtain images on the first trials. At the time, it was believed that either the 820 resist is not as sensitive to electron-beam exposure as was originally referenced in the literature or that the exposure parameters of the SEM were not set properly. The steps taken to solve these problems were to obtain a resist material that was designed for electron-beam exposure and to continue further experimentation in order to gain experience setting the exposure parameters of the SEM. The success of the further experimentation is believed to be a result of more experience using the SEM for resist exposures, rather than directly related to switching from an optical resist to an electron-beam resist material.
Spin Curve Data

The experimental spin curve for the ZX-784 material indicates extremely close accuracy to the published data sheets (see Appendix). However, the initial resist thickness of the ZX-784 material was thicker than what would be expected from the spin trial data at the corresponding spin speed. It is possible that part of the error can be attributed to errors associated with the laser interferometry method which was used to measure the resist thickness during the spin trials. The majority of this error can not be explained. The added initial resist thickness should have had some effect on the sensitivity and contrast results of the imaging system. The initial thickness for the PMMA and COP material was as predicted from the experimental spin curves.

Characteristic Data

Comparisons of the experimental sensitivity and contrast values to published values are tabulated below for each individual resist material.
### Comparison of Characteristic Data for ZX-784

#### Table 16

<table>
<thead>
<tr>
<th></th>
<th>Sensitivity</th>
<th>Contrast</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental</td>
<td>40 μC/cm²</td>
<td>0.7</td>
</tr>
<tr>
<td>Published</td>
<td>46 μC/cm²</td>
<td>&gt; 1</td>
</tr>
<tr>
<td></td>
<td>(Kodak Data Sheet, 1984)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50 μC/cm²</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>(Tan, 1984)</td>
<td></td>
</tr>
</tbody>
</table>

### Comparison of Characteristic Data for COP

#### Table 17

<table>
<thead>
<tr>
<th></th>
<th>Sensitivity</th>
<th>Contrast</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental</td>
<td>1.8 μC/cm²</td>
<td>0.7</td>
</tr>
<tr>
<td>Published</td>
<td>0.4 μC/cm²</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Mead Data Sheet)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.4 μC/cm²</td>
<td>0.9-1.2</td>
</tr>
<tr>
<td></td>
<td>(Brewer, 1980)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.3 μC/cm²</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Elliott, 1985)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.7 μC/cm²</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Watts, 1984)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sensitivity</td>
<td>Contrast</td>
</tr>
<tr>
<td>------------------</td>
<td>------------------</td>
<td>----------</td>
</tr>
<tr>
<td>Experimental</td>
<td>45 μC/cm²</td>
<td>1.5</td>
</tr>
<tr>
<td>Published</td>
<td>40 μC/cm²</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Hunt Data Sheet)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40 μC/cm²</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Thompson, 1983)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40-80 μC/cm²</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Brewer, 1980)</td>
<td>2-3</td>
</tr>
<tr>
<td></td>
<td>50 μC/cm²</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Elliott, 1982)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>80 μC/cm²</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Blevins, 1987)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>80 μC/cm²</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Watts, 1984)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100 μC/cm²</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Schnabel, 1983)</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td>56 μC/cm²</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Schnabel, 1983)</td>
<td></td>
</tr>
</tbody>
</table>

Comparison of Characteristic Data for PMMA

Table 18

Data Analysis

There are many variables in the determination of the contrast and sensitivity of a resist imaging system which can explain the disparity between the indicated experimental and published values. The most obvious would be differences in the processing parameters during the various research. The biggest variances would result from dissimilarities in
accelerating voltage and the development parameters. There may also be differences in the way particular researchers define and calculate the contrast and sensitivity values. The majority of the referenced research does indicate that the accelerating voltage used to obtain the given values was different to that used during this experiment for each resist. However, it is not always clear what development parameters were used nor how the characteristic values are determined.

There are also experimental variations in this research which would promote inaccuracies compared to other research. The most evident anomaly would be in the exposure data for the COP resist which resulted in a deformed characteristic curve. The plotted data indicate that the doses used to expose these samples are in the shoulder portion of the characteristic curve. Therefore, a complete picture of the COP imaging system was not obtained and the sensitivity and contrast parameters determined from this curve can only be approximated at best. The incomplete exposure data for this system is attributed to the fact that the increased sensitivity of COP in relation to the other resists was not fully taken into account. Although the magnification of the scanning beam was decreased to cover greater substrate area in order to decrease the exposure dosage, this decrease was not enough to make up for the order of magnitude difference in sensitivity between COP and the other resists. It is felt that the accomplishment
in obtaining complete data for the ZX-784 and PMMA materials verifies the process procedure and that incomplete data for the COP trial would not jeopardize the success of this project.

The other main experimental variation which would contribute to inaccuracies would be the curve fitting of the exposure data used to create the characteristic curve. The "connecting the dots" of any plotted data is always subject to interpretation and will present variances when determining the contrast and sensitivity. The use of computers for curve fitting has taken away some of the human element. However, there are several different algorithms available which could be used in these types of graphs. In addition, the choice of just where and how to draw the linear portion of the characteristic curve will also add to variance in contrast values.

A more detailed examination of the characteristic data indicates very close matching of the experimental sensitivity values to published data for the ZX-784 and PMMA systems. There are several factors which advanced the accuracy of these systems. The main element was close contact with representatives of Eastman Kodak whom developed and studied the ZX-784 material in detail. A second factor was that more time was taken to optimize the developer solution to the coating and exposure parameters for these samples. The main
parameters of the process procedure were worked out while using this material and then duplicated to obtain data for COP and PMMA.

Inspection of the contrast data comparison indicates somewhat lower than published values. These differences can be mainly attributed to not completely optimizing the exposure and development parameters. This is indicated by the fact that the resist thickness for PMMA never cleared but leveled off at the higher doses.

A comparison of the experimental values acquired during this project shows that the PMMA has a relatively high contrast compared to the negative resists. This was expected based on the general characteristics of positive versus negative resists. The general relationship of the experimental values to one another holds true when compared to the relationship of the published values.

Phase II

Evaluation of Statistical Data

The statistical data proved that a worthwhile second order model could not be fit to the data presented and that responses could not be predicted with a reasonable amount of certainty. The F tests indicated that a significant relationship could not be determined between the independent
variables and the responses within the area of study. The effect of the factors could not be separated from the effects of the experimental error. As result, this experiment is not sensitive enough to provide meaningful response surface analysis to optimize this imaging process.

It is highly possible that the separations between the levels of the independent variables was not enough to provide the variances needed to make confident judgements about the data. Based on the available literature and discussions with users of this resist material it was assumed that the levels chosen would provide a broad range of responses and that the optimum combination could be determined. Without further study it can not be statistically determined if the process optimum falls inside or outside the experimental space.

A lack of significant effects could be a sign that this experiment was performed within the process latitude of the SAL-601 material. Process variations within the experimental space did not significantly alter the imaging characteristics.

The product literature states that the post-exposure bake process is the most critical step to control for optimum results. A build up of random experimental error throughout the postbake process may have caused effects to be masked. The temperature variation across the hotplate used to post-exposure bake the substrates is the most likely source of error.
Although coefficients for the mathematical model can not be assigned based on the data resulting from this experiment, the model should not be discarded entirely. The boundaries of this model can be expanded to encompass a process range where significant effects can be determined. The contrast data presented indicates that the peak occurs at the experimental center point. This is recommended as a starting point of independent variables for further contrast studies.

Recommendations for Further Work

The completion of phase I of this work and the presentation of an initial process outline has provided a tool for which many further electron-beam studies could be based. Since this procedural technique is developed using an unconventional exposure source, it would be expected that most further work along the lines presented would be undertaken primarily at R.I.T. Additional electron-beam resist studies using this proposed methodology were initiated. Further studies could include any combination of process parameter examinations with relation to resist characteristics. Many of these could follow classic resist characterization outlines.

An alternative to additional resist characterization would be to modify the hardware to include computer control of the exposures. More specifically, a computer could be interfaced to the SEM in order to control the beam deflection
and stage to produce more useful patterns. This step has already been taken by researchers at the University of Rochester. [McIntyre, et al., 1989] This would result in a relatively low cost exposure system which can create useful electron-beam images. This would also expand the research options by offering opportunities for further hardware and software improvements.

Some of these offered options are interim and remedial to work with a system which has been designed specifically for electron-beam imaging for the purpose to output a mask or integrated circuit. Phase II of this project expanded characterization knowledge of the MEBES I and SAL-601 imaging system. Plenty of opportunity exists to further this phase of work. Certainly, the statistical data needs improvement by broadening the factor levels to obtain a functional mathematical model of the imaging system. The search for maximum sensitivity should be continued in the direction indicated by the trends. The scope of this work can be increased with studies of other members of the Shipley chemically amplified resist materials and associated developers.
CONCLUSION

In Phase I of this work a procedure has been developed which has enabled the study and characterization of electron-beam resist materials. The process parameters of this characterization are summarized in detail. This outline allows a complete analysis of the process and indicates the unconventional exposure system used to create the latent images in the resist materials. Characteristic curves for three different electron-beam resist systems were generated and analyzed. It was found that the sensitivity and contrast of these systems compare favorably with previously published data for the same resist materials, which proves that what is presented is a viable approach. It is known that other projects at R.I.T. utilizing the SEM as the exposure tool for electron-beam resist studies have been initiated based upon work performed as part of this research.

A novel chemically amplified electron-beam resist material was studied in Phase II of this project. A statistically designed experiment was formulated, performed, and analyzed. No statistical effects could be proven. Trends in the sensitivity data do follow published results although the region of the maximum was not found. The maximum contrast is within the experiment boundaries.
APPENDIX A

RESIST DATA SHEETS
KODAK Micro E-Beam Resist ZX-784 is a novel, negative-working microresist for use with e-beam exposure devices, primarily for the generation of hard-surface masks on chrome. This resist has high sensitivity and high resolution. It withstands high processing temperatures well and has good resistance in dry-etching applications.

**Features**
- With a resist thickness of 0.6 μm, the sensitivity of this resist 4.6 x 10⁻⁷ coulombs/cm².
- The contrast γ can be expected to be greater than 1.0 (See Figure 1.) γ = (log D₀/D₁)⁻¹
- Resolution of 1.0 μm lines and spaces can be obtained using a resist thickness of 0.6 μm.
- The resist displays excellent adhesion on silicon and on most metals.
- The resist has good resistance to both chemical etching and dry etching.
- This resist is not sensitive to visible light and therefore, it can be handled under ambient lighting conditions.
- The resist is filtered to an absolute value of 0.2 μm.

**Storage and Handling Recommendations**
KODAK Micro E-Beam Resist ZX-784 has a shelf life of 1 year or more under normal handling conditions. The resist should be stored at room temperature. Exposure to high humidity conditions should be avoided, and refrigerated storage is not recommended.

**Physical Properties**
- Specific Gravity (25°C) 1.018
- Solids 23 - 24%
- Viscosity (cSt) 15 - 25
- Water Content 0.5%
- Flash Point 121°F CC Seta flash
- Ash Content < 0.02%
- Refractive Index
  - Liquid Resist 1.4287
- Total Metal Ion Content 10 ppb

**Process Guidelines**
- **Coating**—A coating of 6000 A of material of 18.5% solids can be obtained by spinning at 3000 to 3500 rpm. (See Figures 2 and 3.) KODAK Micro E-Beam Thinner ZX-987 may be used to dilute the resist if required.
- **Prebake**—Prebake in a convection oven for 30 minutes at 90°C.
- **Exposure**—See Figure 1. Sensitivity = 4.6 x 10⁻⁷ C/cm²

**Development**
- Developer—KODAK Micro E-Beam Developer ZX-984
  - Full strength
- Development Time—40 seconds
- Development Temperature—22°C
- Resist Thickness—0.6 μm
- Rinse—Use KODAK Micro E-Beam Rinse ZX-989 for 10 seconds
- **Conditions for processing in an APT spray processor**
  - 1st cycle—developer 40 sec. spin speed 1
  - 2nd cycle—developer and rinse 5 sec. spin speed 1
  - 3rd cycle—rinse 10 sec. spin speed 1
  - 4th cycle—spin dry 30 sec. spin speed 3
- **Postbake**—In a convection oven for 30 minutes at 170°C or for 30 minutes at 180°C
- **Etching**—Use conventional wet-etching techniques or dry-etching techniques.
  - For wet etching, use a chrome bath (cerc ammonium nitrate/acetatic acid). For plasma etching use CF₂O₂ at 0.7 torr and 100 watts. The etch rate ratio vs SiO₂ is 0.3 to 0.5
- **Stripping**—Use and O₂ plasma or NU-Terg stripper at room temperature.

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PRELIMINARY PROCESSING INFORMATION

P (GMA-co-EA) Negative Electron Resist

1. Spinning speed: 3500 rpm gives approximately 6000 Å film thickness.

2. Prebake: 90-120 °C for 30-90 min. in vacuum.

3. Exposure: 4.0 x 10^-7 C cm^-2 gives approximately 70% of the initial film thickness after developing.


5. Rinse: Spray MEAD Rinse II for 15 sec. with overlap of 5 sec. between developer and rinse.

6. Postbake: 120-180 °C for 30-120 min.

7. Strip: Ozone, plasma or dichromate-H2SO4 solution (e.g., Allied Chemical RT-1 stripping solution.)

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INTRODUCTION

MEAD PMMA is a one component, high resolution, positive working resist with wide process latitude and excellent film forming characteristics for electron beam (E.B.) and deep u.v. (DUV) exposing. Aspect ratios of 7:1 are achievable in sub-micron images with MEAD PMMA in DUV. MEAD PMMA is made to order as to solids content and molecular weight.

PRIMING

Prior to coating, wafers should be thoroughly cleaned, dehydration baked and primed with Olin Hunt HMDS as follows:

For manual HMDS application
1. Dip in HMDS for 30 seconds
2. Nitrogen blow dry

For automatic HMDS application
1. Spray HMDS for 4 seconds at 500 RPM
2. Spin dry for 15 seconds at 5000 RPM

COATING

The spin speed charts below will provide a starting point for resist application. MEAD PMMA should be static dispensed and spun at the determined speed for 30-40 seconds. The amount of resist used will vary with the wafer size, however, a pool of resist about the size of a fifty-cent piece (4 ml) would be sufficient for a 4 inch wafer.

The charts which follow give coating thickness as a function of spin speed. A key contributing factor to the thickness attained is the solids content of the resist. Below please note the curves for various solids content PMMA.
PREBAKE

Wafers may be baked in a conventional slow recovery oven or a quick recovery oven. The recommended temperature for both is 160° - 180°C. The bake time in the conventional oven is 30 minutes while the time may be reduced to 20 minutes in the quick recovery oven.

EXPOSURE

Radiochemical conversions culminate in main chain scission caused by exposure to DUV (below 300 NM) or electron beams. It is strongly recommended that an exposure matrix be performed on site due to the variation in exposure tools.

For electron beam exposure the following values have been demonstrated:

<table>
<thead>
<tr>
<th>KEV</th>
<th>uc/CM²</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>50</td>
</tr>
<tr>
<td>15</td>
<td>40</td>
</tr>
<tr>
<td>20</td>
<td>30</td>
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</tbody>
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DEVELOPING AND RINSING

Developing may be accomplished using a dip, spray or spray-puddle technique. In each case it is recommended that MEAD PMMA Developer be used during the developing cycle and that MEAD PMMA Rinse be used for rinsing.

**SPRAY DEVELOPING TECHNIQUE**

1. Spin wafer at 500 RPM
2. Dispense MEAD PMMA Developer for 30-45 seconds at 500 RPM at 25°C*.
3. Dispense MEAD PMMA Rinse for 30-45 seconds at 500 RPM at 25°C.
4. Spin dry at 5000 RPM for 30 seconds.

**DIP DEVELOPMENT TECHNIQUE**

1. Immerse wafer in MEAD PMMA Developer for 30 seconds at 25°C.
2. Remove from developer and immerse in MEAD PMMA Rinse for 30 seconds at 25°C.
SPRAY PUDDLE TECHNIQUE

1. Spin wafer at 500 RPM.
2. Dispense MEAD PMMA Developer for 3-4 seconds.
3. Stop wafer from spinning while continuing to dispense MEAD PMMA Developer for 2 seconds.
4. Allow the wafer to remain static for 25-40 seconds.
5. Dispense MEAD PMMA Rinse for 30-45 seconds at 500 RPM at 25°C.
6. Spin dry at 5000 RPM for 30 seconds.

*NOTE: Temperatures of 25°C have been recommended for small geometries and for tighter C.D. However, room temperature processing of PMMA is commonplace. The constant temperature recommendation is in the interest of optimizing the process.

POSTBAKE

Postbake may be accomplished between 90-120°C. It is recommended that postbake occur at 110-120°C for 30 minutes in a conventional oven and for 20 minutes in a quick recovery type.

STRIPPING

Non-phenolic strippers like Olin Hunts Microstrip 2001 should be used.

MATERIAL SAFETY DATA SHEETS

MSDS are available from MEAD Technologies, Inc., P.O. Box 748, Rolla MO 65401. MSDS for Olin Hunt HMDS or Microstrip 2001 are available from Olin Hunt Specialty Products Inc., 5 Garret Mountain Plaza, West Paterson, NJ 07424, attn: Microelectronics
APPENDIX B

SAL-601 CHARACTERISTIC CURVES
Characteristic Curve
SAL-601 Trial 2

Normalized Resist Thickness

Log Dose (C/cm²)

70 sec @ 110 C Postbake, 11 min Develop
Characteristic Curve
SAL-601 Trial 3

Normalized Resist Thickness

Log Dose (C/cm²)

70 sec @ 120 C Postbake, 5 min Develop
Characteristic Curve
SAL-601 Trial 4

Normalized Resist Thickness

Log Dose (C/cm²)

70 sec @ 110 C Postbake, 5 min Develop
Characteristic Curve
SAL-601 Trial 5

Normalized Resist Thickness

Log Dose (C/cm²)

100 sec @ 115 C Postbake, 11 min Develop
Characteristic Curve
SAL-601 Trial 6

Normalized Resist Thickness

Log Dose (C/cm²)

40 sec @ 115 C Postbake, 11 min Develop
Characteristic Curve
SAL-601 Trial 7

100 sec @ 115 C Postbake, 5 min Develop
Characteristic Curve
SAL-601 Trial 8

Normalized Resist Thickness

Log Dose (C/cm²)

40 sec @ 115 °C Postbake, 5 min Develop
Characteristic Curve

SAL-601 Trial 9

Normalized Resist Thickness

Log Dose (C/cm²)

100 sec @ 120°C Postbake, 8 min Develop

1.0E-07

1.0E-06

1.0E-05
Characteristic Curve
SAL-601 Trial 10

Normalized Resist Thickness

Log Dose (C/cm²)

40 sec @ 120 C Postbake, 8 min Develop
Characteristic Curve

SAL-601 Trial 11

Normalized Resist Thickness vs Log Dose (C/cm²)

100 sec @ 110°C Postbake, 8 min Develop
Characteristic Curve
SAL-601 Trials 13, 14 & 15

Normalized Resist Thickness

Log Dose (C/cm²)

--- Trial 13  --- Trial 14  --- Trial 15

70 sec @ 115 C Postbake, 8 min Develop
REFERENCES


