

50 nm resolution, defect-free, electron-beam resists produced with monomer/polymer multilayer films

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Recent technological advances in very large scale integration (VLSI) are beginning to outstrip the technology used to produce these circuits. Ultraviolet and optical lithography techniques are producing resist patterns with resolutions approaching the expected minimum. Application needs demand that this minimum be improved to achieve more features per unit area of circuit. We have achieved a potentially major breakthrough towards improving the resolution of resist patterns. Through the use of monomer/polymer multilayers, line resolutions produced by way of a novel computer-controlled electron beam technique is now possible. The relative ease and high reliability of multilayer formation ensures uniform films of a thickness an order of magnitude less than spin cast film thicknesses. The high electron sensitivities of these films enables excellent degradation (or polymerization) upon exposures to an electron beam. Final pattern resolution, for both positive and negative resists, is an order of magnitude higher than conventional resist resolutions, offering possible improvement in circuit capability. Morphological studies of these multilayer films provide unique information on domain size and structure. The ultimate morphology of these films is shown to be dependent on deposition conditions as well as the substrate used.

1. Introduction

1.1. Current problems in photoresists

Conventional photoresists produce patterns with resolutions of about 2000 nm, through exposure to optical or uv radiation. This pattern resolution is rapidly approaching its theoretical limits. With the advent of very large scale integration (VLSI), it is becoming necessary to obtain patterns with higher resolutions than those obtained now in order to further miniaturize circuits.

Typical commercial resists, such as poly(methylmethacrylate) and poly(cinnamic acid), are deposited by precipitation from solution on a spinning wafer. Defect-free films are guaranteed only when the film thickness exceeds $1\ \mu\text{m}$ [1]. At thicknesses of less than $1\ \mu\text{m}$, pinholes (poorly covered regions of the wafer surface) appear, providing films unacceptable for high resolution (submicron) patterns.

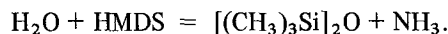
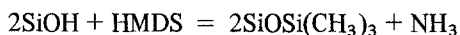
This required film thickness results in a minimum line resolution. As the exposing irradiation passes through the resist film, a portion of it eventually reaches the substrate and, due to Compton's effect, is backscattered. The energy lost by the irradiation is scattered in an oblong pear-shaped volume roughly equal to the penetration depth [2]. This backscattering exposes more film than desired, producing lower line resolutions than anticipated. Final line resolution is thus directly dependent on the film thickness, for thicker films lead to more backscattering. Therefore, thinner films would enable the production of higher resolution patterns, providing the size of the radiation beam is small enough.

1.2. Advantages of the electron beam

The introduction of thinner films into current resist production techniques would offer little

impurities were present and the contact angle of water with the surface approached zero. Clean chips were stored between sheets of Fisher lens paper and unclean ones were cleaned again.

The cleaning procedure was insufficient in providing a silicon surface of adequate quality for deposition. Silicon has a tendency to form silicon hydroxide from hydroxy groups and adsorb water, causing part of its surface to be hydrophobic and others hydrophilic. Such a non-uniform substrate surface has proven to be detrimental to good multilayer formation (Fig. 3). Dark areas (pinholes) form in the film, making it unfit for high-resolution work. Treatment of the silicon surface for 5 min with hexamethyldisilazane (HMDS— $[(\text{CH}_3)_3\text{Si}]_2\text{NH}$) removes both surface water and hydroxy groups by the following reactions:



The surface is completely covered by hydrophobic $\text{Si}(\text{CH}_3)_3$ groups with all other products being volatile. In addition, unreacted HMDS is also evaporated, leaving a uniform surface enabling proper deposition. This treatment did not completely remove all pinholes, but it did lead

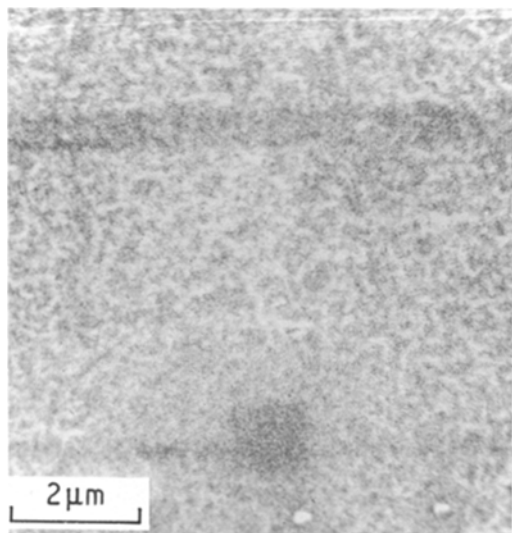


Figure 3 Example of pinhole-containing multilayer film. The pinholes range in sizes of up to $0.5\ \mu\text{m}$, leading to a film insufficient for submicron lithography. The high electron sensitivity of ODAA is illustrated by the dark square at the bottom of the figure. This area was focused on for 3 sec and in that time underwent a high degree of degradation.

to a decrease in the number and size of the pinholes, thereby supplying ample films for high-resolution work.

Such treatment proved to be unnecessary when GaAs was used as the deposition substrate.

2.3. Deposition environment

All depositions were carried out in an environmentally controlled dust-free room with a temperature of $23.3 \pm 0.5^\circ\text{C}$. The film balance used was a commercial MGW Landa-Filmwaage Preparative Film Balance, designed for continuous isotherm measurement, control and compression of a monolayer to a constant film pressure. An X - Y recorder displayed the pressure and molecular area, and a digital readout displayed the surface pressure of the monolayer and the temperature of the subphase. Constant pressure is controlled by a feedback loop circuit between the floating Langmuir pressure balance and the movable barrier. A constant temperature circulator maintains a constant temperature in a thin layer of water near the surface (-0.5°C).

The subphase consisted of doubly distilled tap water. The first reaction flask removed inorganics while the second flask contained potassium permanganate (KMnO_4) to ensure oxidation of any organic contaminants. The final pH of the water ranged from 6.9 to 7.1 and remained constant for several weeks if stored in a closed glass flask. Even if the distilled water was exposed to the atmosphere, the pH would drop to no lower than 6.3 (the drop being due to the adsorption of CO_2).

The passing of the substrate through the water surface was accomplished by a pneumatic dipping device. The uptrip and/or downtrip velocities of the device could be controlled physically, with speeds ranging from 1 to $1000\ \text{mm}\ \text{min}^{-1}$. The pneumatic dipper offered advantages over electric motor-driven dipping devices in that movement was fluid and no hesitations were present at any time.

2.4. Formation of monolayers and multilayers

All solutions were deposited dropwise on a clean water surface via a micropipette. Drops typically measured $10\ \mu\text{l}$ in volume with monomer concentrations in the range of $0.5\ \text{mg}\ \text{ml}^{-1}$ in heptane. Isotherms were always run preceding deposition procedures, and were very reproducible due to accurate volume delivery.

A typical isotherm [1] (plot of surface pressure against molecular area) of alpha-octadecyl acrylic acid (ODAA) reaches a local maximum of surface pressure equal to 46 dyn cm^{-1} . This rapid pressure rise is expected of amphiphilic molecules as the close-packing distance of the upright molecules is approached [11]. Further attempts to compress the film beyond this packing distance lead to what is termed film collapse, or the transformation from the monolayer state to that of the usual bulk crystallite state. Previous work [13] has shown that the best deposition for certain monolayers occurs at a surface pressure of about 10 dyn cm^{-1} below the characteristic collapse pressure. Depositions were, therefore, usually carried out under a surface pressure of 36 dyn cm^{-1} .

Other dipping conditions were determined by experimentation (discussed later). Typical values for deposition were 18.2 dyn cm^{-1} , a dipping speed of 4 mm min^{-1} (uptrip and downtrip), and sub-phase $\text{pH} = 3.5$.

2.5. Resist patterning

A novel computer-controlled electron beam lithography technique was used to pattern the ODAA resist. A JEOL JEM-100B electron microscope was coupled with a digital VC-100 digital computer to allow complete control of the lithographic process. The program assumes a 1000×1000 grid and activates the beam by on/off controls and sets the X - Y position. The software permitted complete flexibility in the operation of the program. Variables such as beam current, pattern shape, pattern definition, and number of passes could be determined and set by the operator.

The coupling of the computer to the microscope completed the necessary adjustments in the software of the system. Unfortunately, the scope was not equipped with a sample holder that allowed secure placement of the silicon chip within the chamber. At first, silver paint was used to fasten the silicon chip in the scope, but the paint volatilized somewhat and caused chamber contamination. The problem was solved by designing a new sample holder (Fig. 4). The new holder was made out of light-gauge brass and made to hold the chip between the clips while still providing enough pressure by the clips to secure the chip. The holder was designed to attach to the scope sample entry unit and was inserted into the scope from there.

The lithographic exposure could result in either polymerization or degradation of the ODAA resist,

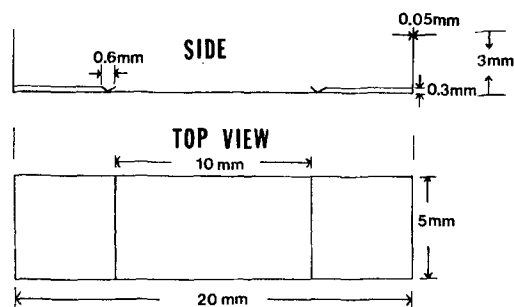


Figure 4 Design of new sample holder for the electron microscope. The holder is made of small gauge brass and the silicon chip is placed under the clips. This device allowed exposure of a majority of the film to the electron beam while properly securing the chip.

producing either a negative or a positive resist, respectively. The type of resist received depended upon the treatment prior to introduction into the microscope. All films were deposited pure, as monomers, with no sensitizers added (which are required in most conventional resists). Initial results illustrated that when the film received a small dose of irradiation from a small uv source, it polymerized slightly. This slight polymerization provides enough long-range order to render the ODAA film stable in the microscope chamber. Any exposure to electron irradiation of such a film produced a negative resist. Treatment of a multilayer film with high doses of irradiation (up to 4.8 Mrad) essentially completely polymerized the film. A positive resist results upon exposure of this type of film to the electron beam.

Post-pattern treatment of these films is usually necessary in order to dissolve away any soluble fractions of the film. When it was required, the films were placed in ethanol for a predetermined length of time to develop the pattern and make it sharper.

2.6. Deposition variables

The quality of the film deposited on the substrate is dependent upon the conditions at which the deposition was done. Major variables in the Langmuir-Blodgett deposition technique are dipping speed, temperature, surface pressure, and possibly pH and type of substrate used. Each of these parameters were varied over a substantial range to determine the effect of film formation. In all cases, the type of deposition received was the alternating Y-structure [14-16]. The films were compared to one another with

respect to domain size, number, and orientation, and ease of deposition.

3. Results and discussion

3.1. Morphology

The morphology of the final multilayers is determined by the spreading conditions of the monolayer. It has been shown [17] that domains in the monolayer continue to grow until the solvent has completely evaporated. These domains are a general phenomena of all multilayers. By controlling the evaporation rate, the domain size can be varied as desired [18]. Once the evaporation is finished, the domain size in the monolayer remains the same.

Deposition of the monolayer onto a substrate has a detrimental effect upon the domain size. In most cases, passing the substrate through the monolayer surface disrupts the domains and breaks them apart. Multilayer domains are therefore probably smaller than those in the original monolayer. This disruption of domains has been known to be effected by the dipping conditions. Through variation of the deposition parameters, we hope to determine the optimum conditions for forming ODAA multilayers from its monolayer. This work should also show that desired morphology can be obtained by changing dipping conditions.

3.1.1. Substrate dependency

Little difference could visually be seen between deposition of ODAA on $\langle 111 \rangle$ silicon and that on $\langle 100 \rangle$ GaAs. In both cases, deposition was smooth

and uniform and no problems seen in the final film.

Magnified views showed that the films differed significantly on the microscopic level (Figs. 5 and 6). Differential interference contrast optical microscopy (also called the Nomarski method) is a relatively new method in the study of thin films. The interference method is superior to phase contrast as only the surface layers of a specimen are examined and surface reliefs are possible, similar to scanning electron microscopy. Its main use has been in the field of metallurgy for studying grains in metal surfaces.

One can think of the fundamental domains in a monolayer as similar to metal grains. Both boundaries represent regions of misalignment of perfect crystals. The Nomarski method yields a wealth of information when applied to the study of multilayers.

Multilayer domains on Si consist of anisotropic rods of about $2\ \mu\text{m}$ by $1\ \mu\text{m}$ in size. The domains are seen to exist throughout the film, not just at the external portions of the film. The aspect ratio of the domains is 2, which is expected, for ODAA is a paraffin-like material and paraffin has an aspect ratio of 2, owing to its unit cell. The domain packing is more or less biaxially aligned. This alignment is not characteristic of any epitaxial effect between film and substrate. Rather this biaxial packing is merely a consequence of any dense organization of anisotropic rods.

The same biaxial alignment exists in multilayers on GaAs (Fig. 6). However, the alignment is much more ordered in this case, as indicated by the

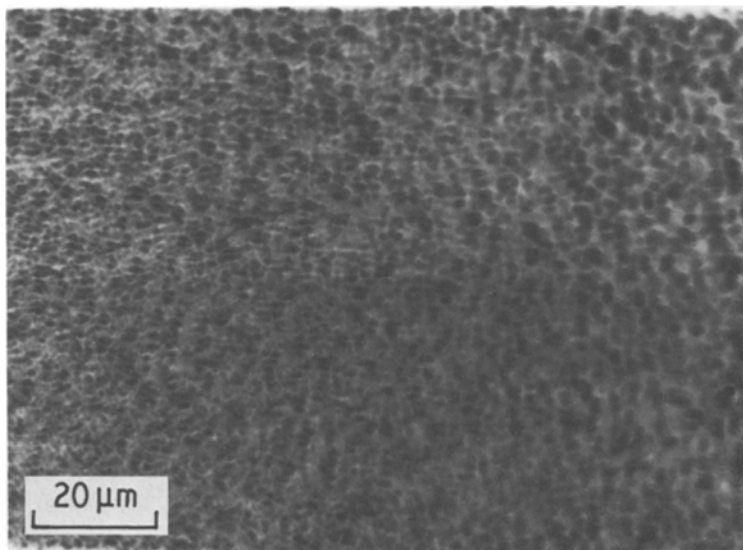


Figure 5 Differential interference contrast optical micrograph of ODAA on silicon. Domain sizes averaged $2\ \mu\text{m} \times 1\ \mu\text{m}$, and exhibited little orientation.

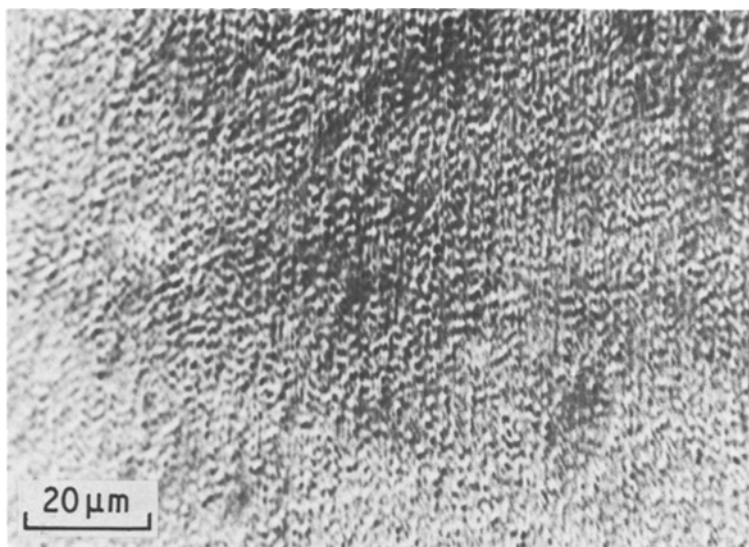


Figure 6 Differential interference contrast optical micrograph of ODAA on gallium arsenide. Domain sizes averaged $1.5 \mu\text{m} \times 0.75 \mu\text{m}$. Higher degree of orientation (lines) indicate possible epitaxial effect.

arrows in Fig. 6. This rather high degree of orientation indicates a possible epitaxial effect between $\langle 100 \rangle$ GaAs and the ODAA film. The domain size has now been decreased ($1 \mu\text{m} \times 0.5 \mu\text{m}$).

3.1.2. Temperature

Of the operational variables present in the Lauda balance, temperature would be expected to have the greatest impact on the final film morphology. Monolayers have been known to undergo large changes in viscosity with slight changes in temperature. This change in viscosity leads to a change in the isotherm of the monolayer [1], ultimately affecting deposition.

The quality of film deposition is highly dependent on the fluidity of the monolayer (Table I). At lower temperatures, higher viscosities cause film fracture as the flexibility of the monolayer is removed. Higher temperatures lead to a reduction in viscosity, effectively reducing the stability

TABLE I Effect of temperature on crystal size

Temperature ($^{\circ}\text{C}$)	Domain size (μm)
7.0	(unstable monolayer)
9.8	1.5×0.8
13.2	2.0×1.0
16.0	2.0×1.0
20.2	1.5×0.8
22.9	1.0×0.5
26.0	1.0×0.5

At lower temperatures (higher viscosities) the domains become smaller because the film is more brittle. The domains are also smaller at higher temperatures due to the increased thermal energy of the monolayer. The best deposition temperature appears to be 16 to 18°C .

of the monolayer. Smaller domain sizes result, due to a lack of stability in the film. At temperatures in between, domain characteristics appear to be at an optimum.

3.1.3. Surface pressure

The orientation was affected little, if any, by varying the surface pressure of deposition. Domain size decreased with decreasing pressure in increments of 2 dyn cm^{-1} from 37 dyn cm^{-1} to 31 dyn cm^{-1} (Table II). Below 31 dyn cm^{-1} , the domain size remained roughly the same, but the number continued to decline. This could easily be seen visually, as less film was deposited at lower surface pressures (Table II).

3.1.4. pH of subphase

The only true difference in deposition through variation of the subphase pH occurs at a pH of

TABLE II Effect of surface pressure on crystal size

Surface pressure	Domain size (μm)	% Coverage
25	1.0×0.5	40
27	1.0×0.5	50
29	1.0×0.5	65
31	1.0×0.5	85
33	1.5×0.8	95
35	2.0×1.0	100
37	2.0×1.0	100

Higher surface pressures lead to larger domain sizes, probably due to an increase in the orientation of the molecules. Also listed is the visible % coverage of wafers versus the surface pressure. More of the substrate is covered as the surface pressure is lowered, due to the less destructive effect of the substrate.

about 5.5, which is related to the extent to which the ODAA is ionized. Dissolution of the ODAA monolayer tends to occur if the pH of the subphase is higher than 5.5. In these cases, we observed that dissolution led to smaller domain sizes.

3.1.5. Dipping speed

Deposition of any monolayer onto a substrate would be expected to decrease in quality and quantity as the dipping speed increases. At higher dipping speeds, the monolayer does not have enough time to flow and deposit as in Fig. 1. Rather, pinholes form as the increased pressures caused by the dipping speed fracture the film. The domains that are deposited are quite small after being fractured during deposition. As the dipping speed is decreased, these pressures are easier to overcome and the domain size becomes larger (Table III) in a defect-free film. This relationship continues until a critical dipping speed is reached, below which no change in film morphology can be detected. For ODAA, this dipping speed appears to be about 4 mm min^{-1} .

3.2. Positive resists

Initial problems in the resist area were concerned with obtaining films of sufficient quality for high-resolution work. Such films would need to be nearly defect-free at a thickness much less than $1 \mu\text{m}$.

We decided to concentrate on films composed of 20 layers of ODAA, which would make the films about 69 nm thick. These films were deposited at 36 dyn cm^{-1} , subphase pH of 3.5, dipping speed of 4 mm min^{-1} (both uptrip and downtrip), and a temperature of 18.2°C . Typical early films (Fig. 3) contained pinholes, due to the defects present in the substrate surface prior to dipping. Hydrophobic areas of the substrate surface lead to tail

TABLE III Effect of dipping speed on crystal size

Dipping speed (mm min^{-1})	Domain size (μm)
2.6	2.0×1.0
3.9	2.0×1.0
4.9	1.5×0.8
7.7	1.3×0.7
10.7	1.3×0.7
16.2	1.0×0.5

Slower dipping speeds enable the monolayer to conform to the substrate much more readily, thereby causing the least destruction of crystal sizes. Depositions done at higher dipping speeds fragment the domains, causing smaller domain sizes.

attachment of the monolayer while no molecules would deposit during the first downtrip in the areas of hydrophilicity. This phenomenon causes stresses in early monolayers resulting in poorly covered regions of the wafer surface. The detrimental effect of these pinholes can be seen in the fuzzy appearance of the degraded lines. Pretreatment of the silicon surface with HMDS essentially eliminates these pinholes, providing ample films for submicron work.

The degradation of a polymer film by the electron beam renders the exposed material soluble in a developer, producing what is known as a positive resist. Positive patterning of the ODAA resist was accomplished after varying the operational parameters in a concerted manner to obtain optimum results (Fig. 7). A beam with an effective diameter of 250 nm was used to draw these 300 nm wide lines, which converts to a 20% Compton backscattering effect.

Increasing the resolution down from 300 nm was done at higher magnifications, for the magnification controlled the beam diameter. 50 nm resolution lines were received (Fig. 8) at a magnification of 10 000 and a proximity effect of 100%. Besides better resolution, this pattern had the added advantage that it was written in one-third the time needed to write the previous one. At this resolution, the electron sensitivity of the ODAA multilayers was determined to be in the range of $10^{-6} \text{ C cm}^{-2}$, making it much more sensitive than pure conventional resists. The resolution obtained is slightly better than in previous work with multilayer films [19].

3.3. Negative resists

Polymerization of the monomer resist material (negative resist) by the electron beam proved to be more difficult than positive resist work. The length of exposure during the pretreatment period had to be just long enough to slightly polymerize the film. If the pretreatment period was too short, the required exposure in the electron microscope became too long to be practical. However, if the films were polymerized to an exceedingly high degree before exposure to the electron beam, degradation began.

The best treatment results were achieved through exposure of the film to 250 mW cm^{-2} uv lamp for 1 h at a distance of 10 cm. Once the proper exposure was determined, negative resist patterning became rather simple (Fig. 9). Typical

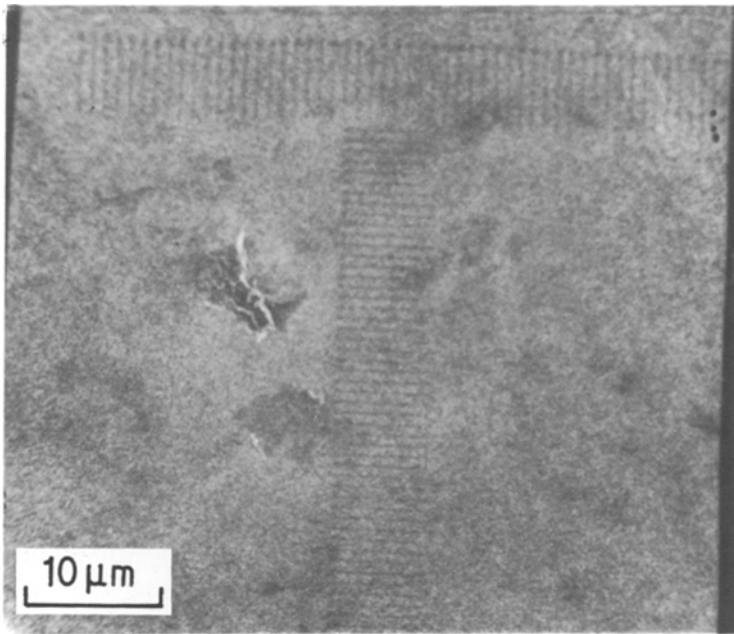


Figure 7 Positive resist pattern of ODAA. Written with an effective beam diameter of 250 nm, resolution of the lines is 300 nm (resulting in a 20% backscattering effect). No development was necessary.

resolutions obtained were 1000 nm. Shorter exposure times than positive resists were needed in order to obtain this resolution.

The poorer resolution obtained by the negative resist as compared to a positive resist at the same magnification is an indication of the Compton backscattering problem. The patterns in both Figs. 7 and 9 were written with a beam of a 250 run effective diameter. The high electron sensitivity of the monomer led to wider lines as the material

was polymerized by the backscattered electrons. While the resolution was decreased somewhat in the positive resist, the polymer was not sensitive enough to react on exposure to the backscattered electrons as extensively as the monomer. Thus, the detrimental effect of backscattering is less significant for positive resists, leading to better resolutions than in negative resists.

This factor holds true even at higher resolutions (Fig. 10). The best negative resist results have

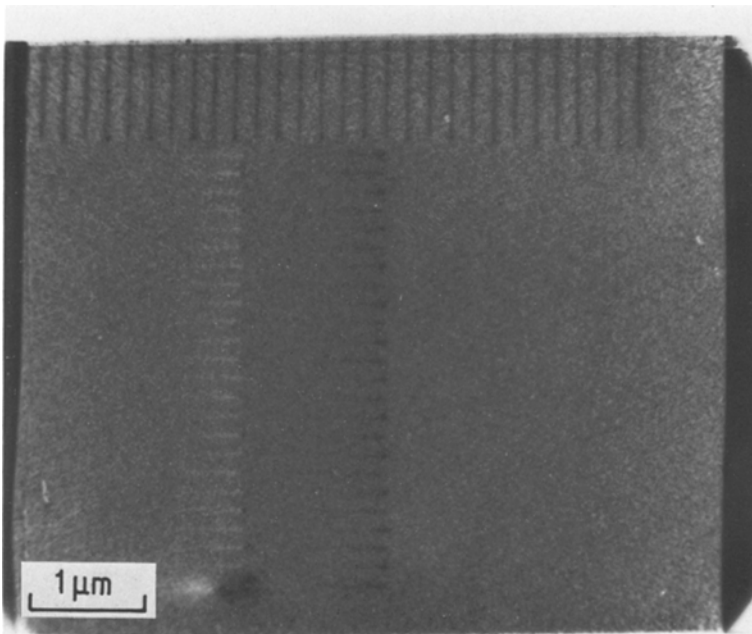


Figure 8 Positive resist pattern of ODAA with a resolution of 50 nm. Effective beam diameter used was 25 nm, with a backscattering effect of 100%. No development was necessary.

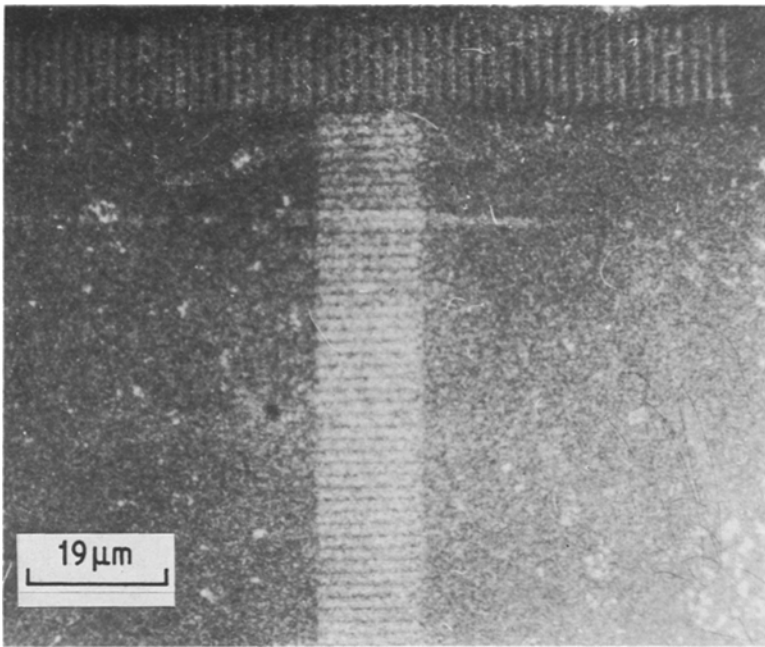


Figure 9 Negative resist pattern of ODAA with a resolution of 1000 nm. This pattern was written by an electron beam with an effective diameter of 250 nm and a backscattering effect of 300%.

typically been 80 nm, as compared with 50 nm normally received for positive resists. Since a 25 nm effective diameter electron beam was used, we see that the backscattering effect is still greater for negative resists than positive resists, though not by as much as before.

4. Conclusions

The need to develop a new resist capable of

submicron lithography has led to several advantageous innovations related to resist technology.

1. A computer-controlled electron lithographic system has been designed to produce resist patterns. Such a system eliminates the need for a mask and greatly increases the accuracy of the patterns. Operational variables of the program allow any pattern to be produced. Final pattern resolution is determined by the operator, by means of adjusting

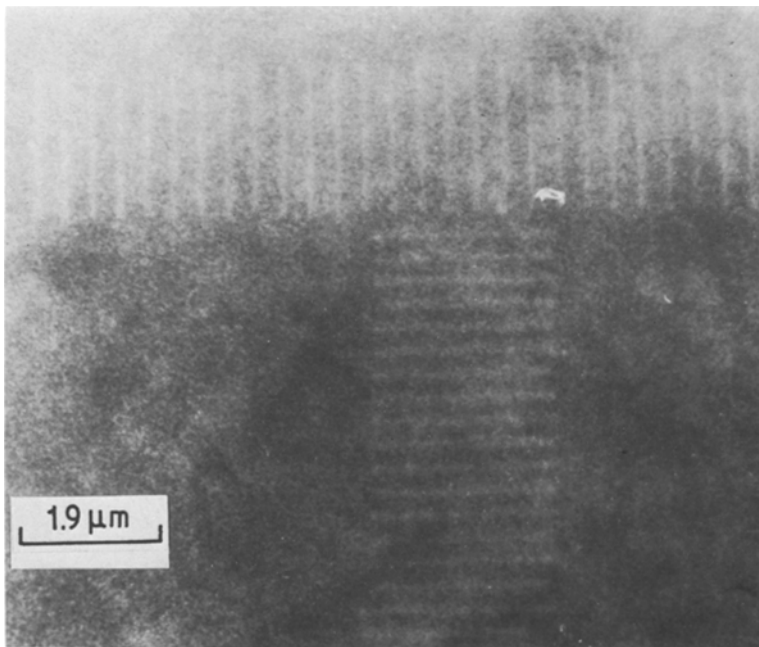


Figure 10 Negative resist pattern of ODAA with a resolution of 80 nm. The effect beam diameter was 25 nm. Backscattering effect was 220%.

the magnification. Beam diameters of down to 5 nm are possible.

2. A new holder for silicon chips permits easy placement of the films in the electron microscope while still permitting a large portion of the film to be exposed. This new holder is made of brass, which unlike most metals, does not affect the electron beam or its manipulation.

3. Quality multilayer deposition on the SiO surface is possible through the pretreatment of the surface with hexamethyldisilazane. If no pretreatment is done, pinholes in the range of $1\ \mu\text{m}$ appear in the film, which is thus inadequate for high-resolution work. Electron micrographs show that after treatment hydrophilic portions are eliminated and excellent, virtually defect-free films are formed on the treated surfaces.

4. Final morphology of multilayer films is dependent upon dipping conditions as well as spreading conditions. Manipulation of the dipping conditions may prove useful in obtaining a certain required film morphology. Domain size and orientation are also possibly affected by the substrate used for deposition, with possible epitaxial effects.

5. Langmuir–Blodgett films of alpha-octadecyl acrylic acid are excellent electron beam resists, offering several advantages over conventional and other electron beam resists:

(a) higher resolutions are obtained (60 nm compared with $> 500\ \text{nm}$);

(b) because the alpha-octadecyl acrylic acid multilayers exhibited an electron sensitivity in the range of $10^{-6}\ \text{C cm}^{-2}$, no sensitizers are needed as are usually required with conventional resists;

(c) both positive and negative resists can be made from the same material, while normal resists require special treatment to become one or the other;

(d) a lower energy electron beam can be used. The high contrasts normally required in high-resolution lithography are then unnecessary;

(e) development of such a positive resist is not

necessary, though it usually is advantageous;

(f) results indicate that the lithography can be done at a variety of accelerating voltages (20 to 100 kV). The accelerating voltage has a minimum effect on the final line resolution ($< 10\%$ difference for the full range of accelerating voltages).

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