High resolution electron beam lithography using ZEP-520 and KRS resists at low voltage

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(Received 28 May 1996; accepted 16 August 1996)

ZEP-520 and KRS resist systems have been evaluated as candidates for use in low voltage electron beam lithography. ZEP-520 is a conventional chain scission resist which has a positive tone for over two orders of magnitude in exposure dose. KRS is a chemically amplified resist which can be easily tone reversed with a sensitivity $\sim 8\ \mu\mathrm{C/cm^2}$ at 1 keV. Both resist systems are shown to have sensitivities $\sim 1\ \mu\mathrm{C/cm^2}$ for positive tone area exposures to 1 keV electrons. A decrease in contrast in 50 nm thick resist layers is seen when exposure voltage is lowered from 2 to 1 keV, indicating nonuniform energy deposition over the resist thickness. High resolution single pass lines have been transferred into both Si and SiO_2 substrates at both low and high voltages in each resist system without using multilayer resist masks. The ZEP-520 and KRS resists are shown to have resolutions of 50 and 60 nm, respectively, at 1 kV, within a factor of 2 of their high voltage resolutions under identical development conditions. A cusp shaped etch profile in Si allows high aspect ratio 20 nm wide trenches to be fabricated using these resists on bulk Si. Low voltage exposures have been used to pattern gratings with periods as small as 75 and 100 nm in ZEP-520 and KRS, respectively. Low voltage exposures on SiO_2 show no indications of pattern distortion due to charging or proximity effects. *© 1996 American Vacuum Society.*

I. INTRODUCTION

A major improvement in the throughput of high resolution electron beam lithography is necessary to make this process commercially competitive with photolithography in a production environment. Arrays of microcolumn electron beam sources operating at low voltages have been suggested as a way to dramatically increase throughput both by increasing the number of direct write electron beams as well as reducing the beam current necessary for exposure of resist materials. We have characterized two high sensitivity resist systems as candidates for use with low voltage electron beams. The first, ZEP-520, is a commercially available chain-scission-type positive resist.[1] The second, KRS, is a chemically amplified positive resist system developed at IBM.[2] High sensitivity and chemically amplified resists are now rivaling polymethylmethacrylate (PMMA) as candidates for high resolution electron beam lithography at both low ($\leqslant$5 keV) and high ($\geqslant$50 keV) energies. In comparison to PMMA the high sensitivity of these resists may substantially increase the throughput of any direct write electron beam lithography system.

The goals of the microcolumn project have been outlined in previous papers.[3,4] In order to achieve a throughput over 25 eight inch wafers per hour, it is anticipated that arrays of microcolumns will operate in parallel, with nanoampere beam currents and 25 nm resolution at 1 keV. A successful electron beam resist for use with the microcolumns would have a critical area dose near 1 $\mu\mathrm{C/cm^2}$, be capable of producing high resolution (<100 nm) patterns suitable for the next generation of nanoscale devices, and have an etch resistance allowing high aspect ratio patterning of bulk semiconductors from very thin resist layers with low defect densities.

In our previous work we have examined both a variety of processes using PMMA and P(SI–CMS) resists.[5,6] While both these systems were able to produce high resolution features, the PMMA based processes required critical doses over 10 $\mu\mathrm{C/cm^2}$, and the P(SI–CMS) resist was not able to be patterned at high resolution using a 1 keV electron beam. The limited range of the low voltage electrons in resist materials requires all the patterning to occur in very thin layers (<100 nm). This means that multilayer or top surface imaging processes are beneficial.[7] The ZEP-520 and KRS resist systems could also be used in a multilayer process to extend the maximum etch depth and increase the aspect ratio of features, but their higher etch resistance has allowed us to transfer these patterns directly into Si and SiO_2 in this study.

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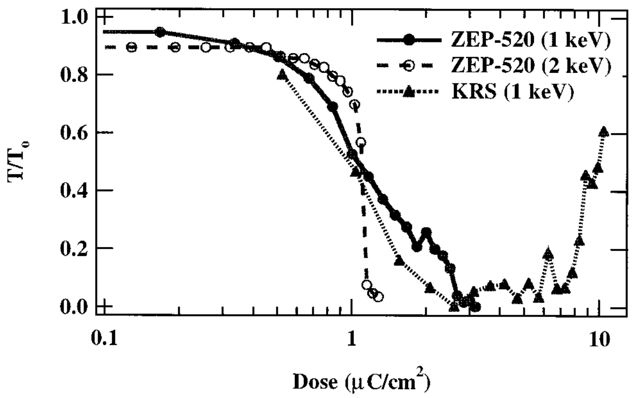

FIG. 1. Normalized thickness after development vs dose for 1 and 2 keV exposures of ZEP-520, and 1 keV exposure of KRS. The ZEP-520 shows a significant loss of contrast at 1 keV. The KRS reverses tone near 10 μC/cm^2. Unexposed resists were ~50 nm thick.

TABLE I. A summary of critical single pass line dose and area dose for a variety of resist systems characterized for high resolution electron beam lithography using low accelerating voltages. All the resist systems were capable of producing features smaller than 80 nm. Ranges indicate a variation of development parameters.

Resist system/tone	1 keV line dose (pC/cm)	1 keV area dose (μC/cm^2)
ZEP-520/Positive	10	1
KRS/Positive	12	1–3
KRS/Negative	220	8
PMMA/Positive	100–1200	5–20
PMMA/Negative	15 000	2000
P(SI–CMS)/Negative	140 (required 2 keV)	2

II. RESIST PROCESSING

ZEP-520 is a copolymer of α-chloromethacrylate and α-methylstyrene, which has been used to pattern features as small as 10 nm with high energy (70 keV) exposures by Kurihara *et al.*[8] A variety of developers[9,10] have been explored for use with ZEP-520. We have used a xylene solution, which provides very high sensitivity with good contrast. ZEP-520 thinned in chlorobenzene enables us to spin uniform layers ~50 nm thick without surface priming. A two minute, 170 °C prebake is used before electron beam exposure, and samples were developed in the xylenes for either 30 or 60 s. Typical sensitivity plots for both 1 and 2 keV exposures (see Fig. 1) show a critical dose $D_{0.5} \sim 1$ μC/cm^2.

KRS was originally designed as a deep-UV (DUV) resist system which uses polyhydroxystyrene partially protected with an extremely acid-labile ketal group. This protecting group has a low deblocking activation energy and an extremely high reaction rate. Therefore the chemical amplification occurs rapidly after exposure at room temperature *without a postexposure bake*, in contrast to most chemically amplified resist systems.[2] This resist also contains triphenyl sulfonium triflate as an acid generator and a proprietary additive. KRS has shown excellent performance with 50 keV electron beam exposure producing vertical sidewalls in 0.8 μm thick resist for trenches as small as 0.15 μm.[2,11] KRS films, ~50 nm thick, can be spun on hexamethyldisilazane vapor primed silicon surfaces. A 3 min prebake at 90 °C is used. The thin positive resist layers are developed in 0.1*N* TMAH (tetra-methyl ammonium hydroxide) for 15 s. The 1 keV KRS sensitivity plot (Fig. 1) shows a $D_{0.5} \sim 1$ μC/cm^2.

KRS can be tone reversed with a modest increase in dose (Fig. 1). When the area dose is greater than 8 μC/cm^2, exposed areas cross link. Applying a postexposure bake of 120 °C and developing for 30 s in 0.1*N* TMAH completely removes the unexposed regions resulting in negative tone. It should be possible to pattern KRS in both positive and negative tones on a given wafer in a single resist processing step, if the regions of positive and negative tone can be separated spatially enough to allow a DUV exposure of the negative tone regions instead of the post exposure bake. In comparison, the ZEP-520 resist system remains positive tone even for doses (>150 μC/cm^2) two orders of magnitude greater than the critical dose.

Extremely thin resist layers are necessary when working with a 1 keV electron beam due to the limited penetration depth of electrons in the resists. The 50 nm thick layers are comparable to the 1 keV electron ranges in these materials, resulting in nonuniform exposure of the full depth of the resist. We have discussed exposure uniformity in our previously published Monte Carlo simulations where 2 keV electrons are seen to deposit energy more than twice as deep into the resist as 1 keV electrons.[6] This causes a dramatic reduction of resist contrast γ shown in Fig. 1 when the beam energy is lowered from 2 keV ($\gamma \sim 25$) to 1 keV ($\gamma \sim 0.7$). A similar loss of contrast is seen with PMMA and KRS resists. Nonuniform exposure with depth is believed to be the reason high resolution features were not achieved at 1 keV with the P(SI–CMS) resist, which has even shorter penetration depths than the other systems due to its Si content. Thinner resist layers would produce unreasonably large defect densities. An optical study of pinholes in the 50 nm thick ZEP film measured ~2060 pinholes/cm^2, about five times the density on control samples coated with 400 nm thick ZEP or 1.3 μm thick Shipley 1813 photoresist. Both ZEP-520 and KRS can successfully pattern both single pass lines and large areas at 1 keV. Table I has a summary of doses for a variety of resists using a 1 keV beam.

III. PATTERN TRANSFER

Resist patterns were exposed on both Si and SiO$_2$ substrates at low and high voltages. The exposure tool is a thermally assisted field emission digital scanning electron microscope (Leo [Zeiss] DSM 982, SEM) controlled by an external pattern generator. The DSM 982 reduces the noise in low voltage operation by operating the upper portion of the column 8 keV above the final beam energy. The spot size of the focused electron beam is less than 10 nm at 1 keV, and less than 3 nm at 30 keV.[12] Resist patterns were directly transferred into the substrate. To maximize etch selectivity we use an electron cyclotron resonance (ECR) high density plasma etching system without rf power, which reduces sput-

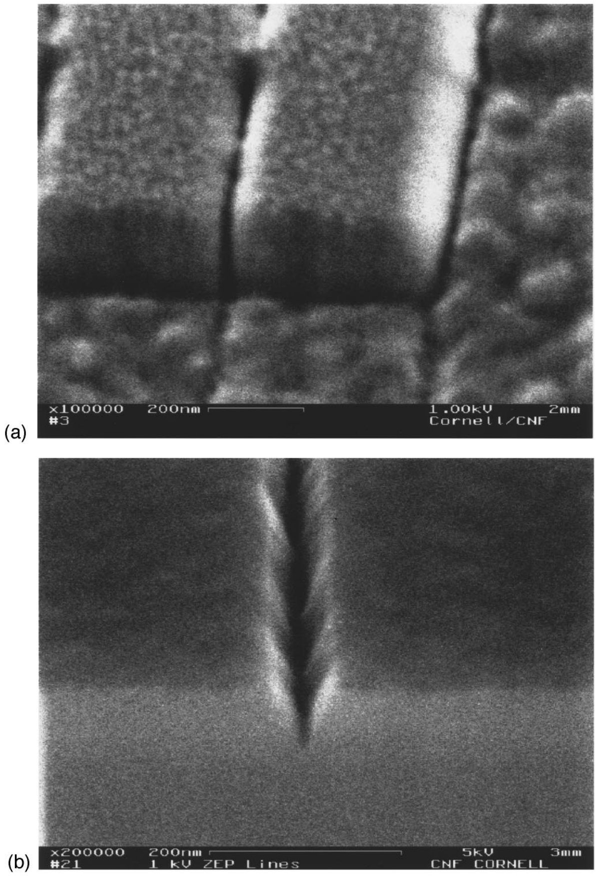

FIG. 2. Two different Si trenches patterned by ECR etching of 1 keV exposures of ZEP-520 resist. The top image (a) shows an edge of a 20 nm wide, 100 nm deep trench (line dose 7.5 pC/cm). The lower image (b) shows the cusp-shaped etch profile in a cleaved cross section of a trench (line dose 26 pC/cm).

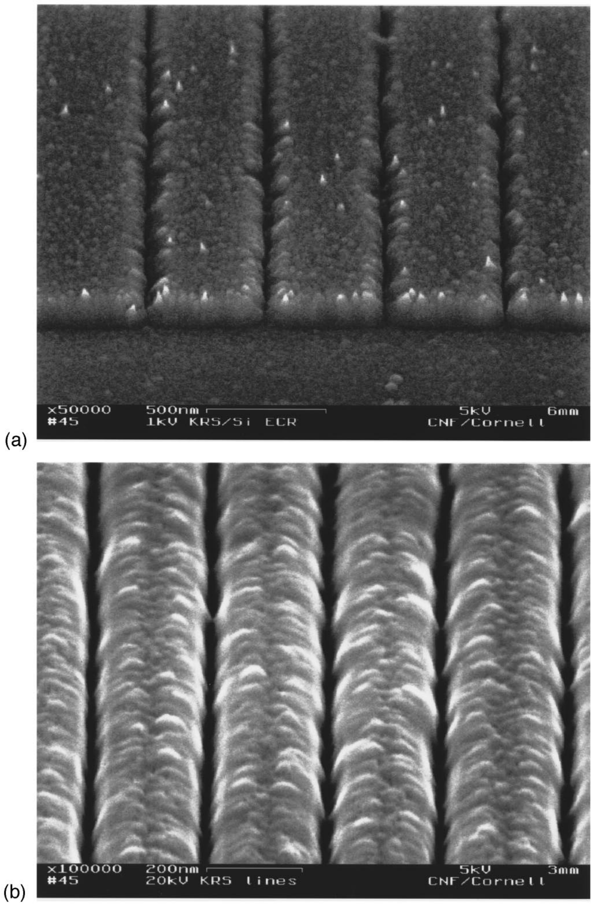

FIG. 3. Single pass lines etched into Si using the two step ECR etch, for KRS resist exposed at 1 keV (a) and a 20 keV (b) with line doses of 11 and 175 pC/cm, respectively.

tering. Despite a lower selectivity, patterns on SiO_2 were transferred with a conventional reactive ion etching (RIE) plasma etch to achieve vertical sidewalls.

ECR plasma etches using 400 W of microwave power (2.45 GHz), 2 mTorr of pressure, and 9.8/2 sccm flows of Cl_2/BCl_3, have achieved a selectivity of 3:1 for silicon over ZEP-520 resist. The Si etch rate is ~100 nm/min. The anisotropy and etch profile of these etches can be excellent, as demonstrated by a 20 nm wide trench over 100 nm deep [Fig. 2(a)]. However, the etch profile is not always reproducible. High aspect ratio features often result in cusp-shaped profiles, as shown in the cross section in Fig. 2(b). Native SiO_2 can have a significant etch resistance, and the best results are achieved by stripping this oxide with buffered HF. Thin SiO_2 layers can be used as a bilayer for a two step ECR etch. We have transferred resist patterns into the Si native oxide with a Cl_2/BCl_3 etch, and followed this with an introduction of O_2 into the plasma, enhancing the selectivity of the etch for Si over SiO_2. This strips the remaining resist, but continues etching Si using the native oxide as a mask. The results of this two step etch using KRS resist patterned at 1 and 20 keV are shown in Fig. 3. High Si:SiO_2 etch selectivity has been used in a complete tone reversal process reported by Kurihara *et al.*[13] This process is compatible with 1 keV patterning of 50 nm thick ZEP-520.

The patterns on 100 nm thick thermal SiO_2 were transferred from both ZEP-520 and KRS using a conventional RIE parallel plate plasma at 13.56 MHz (rf) with a power density of 0.17 W/cm^2. The gas flow was 42/8 sccm of CF_4/H_2 with a chamber pressure of 15 mTorr. This etch has a 1:1 selectivity for SiO_2 to ZEP-520 at an etch rate of 20 nm/min. With KRS, the selectivity improved to 4:3. In both cases the etch has a nearly vertical sidewall profile. The 150 nm thick layer of resist and SiO_2 should maximize any deleterious effect on 1 keV exposures due to charging. Figure 4 shows vertical etch profiles in SiO_2 from a cross section of 30 keV single pass lines patterned in ZEP-520, and an end view of trenches patterned in KRS at 1 keV.

IV. RESOLUTION

High voltage exposures of KRS [Fig. 3(b)] and ZEP-520 [Fig. 4(a)] were performed to determine resolution limits using the same thicknesses and development as the low voltage exposures. The 20 keV KRS single pass lines on Si (line dose 175 pC/cm) appear to be ~30 nm wide, and can be distinctly resolved with a 100 nm period. The 30 keV ZEP-520 single pass lines on SiO_2 (dose 30 pC/cm) are ~35 nm

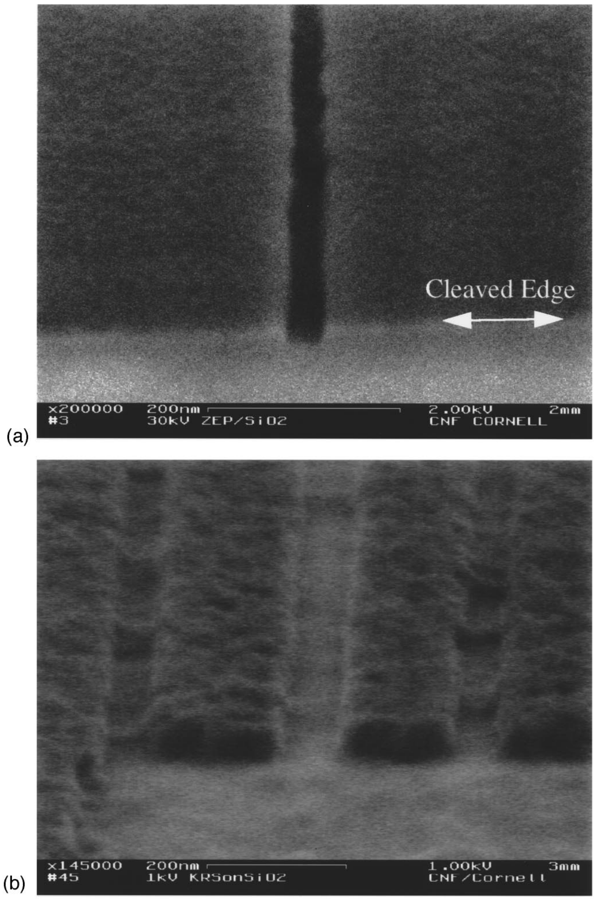

FIG. 4. Examples of the vertical sidewalls achieved using conventional RIE to transfer patterns from ZEP-520 (a) and KRS (b) into SiO_2. The ZEP-520 was exposed at 30 keV (line dose 30 pC/cm) and is shown in a cleaved cross section. The KRS pattern has single pass lines on each side of a finite-width line, and was exposed at 1 keV (line dose 18 pC/cm).

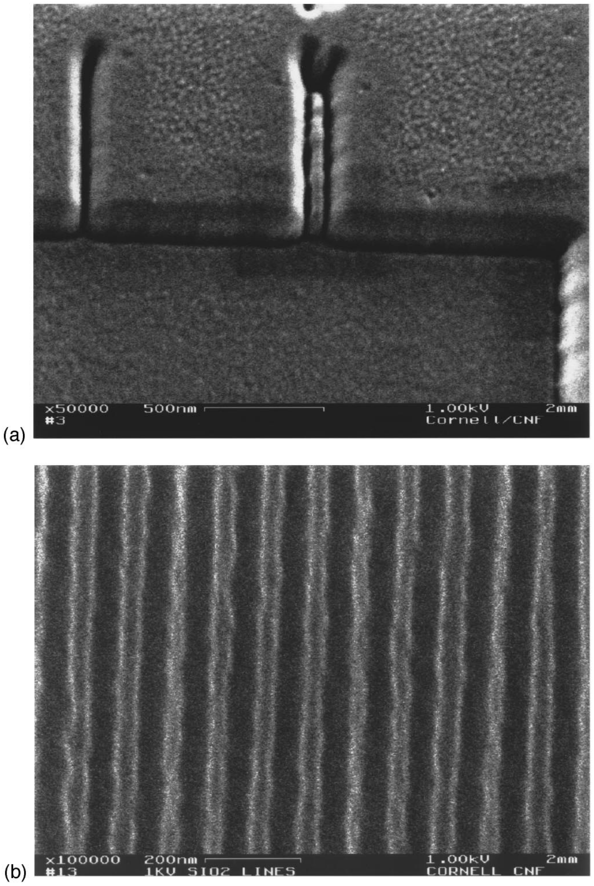

FIG. 5. Two examples of the narrow spacing possible using ZEP-520 on both Si (a) and SiO_2 (b) substrates. The lines in Si are spaced 80 nm apart and were patterned at 2 keV (line dose 22 pC/cm). The grating in SiO_2 has a 100 nm period and was exposed at 1 keV (line dose 15 pC/cm).

wide. The expected beam size at these voltages is ~5 nm, suggesting the resolution is limited by the resist/developer system. ZEP-520 exposed at 70 keV developed in hexyl acetate has demonstrated 10 nm resolution.[8] We exposed KRS at 50 keV (IBM V6 *e*-beam writer) revealing 50 nm exposed regions and 20 nm spaces.

The low voltage resolution of ZEP-520 patterns etched into Si is seen in Fig. 2(a) which shows a 20 nm wide trench patterned with a single pass line (dose 7.5 pC/cm) at 1 keV. Similar 20 nm lines (dose 22 pC/cm) with an 80 nm separation have been patterned at 2 keV [Fig. 5(a)]. In contrast, the cross section [Fig. 2(b)] of a 1 keV (dose 26 pC/cm) single pass line etched into Si appears to be 60 nm wide at the surface. In SiO_2, 1 keV single pass lines (dose 15 pC/cm) become vertical trenches 50 nm wide [Fig. 5(b)]. Similar gratings etched in SiO_2 have been resolved with a 75 nm period leaving unexposed regions of ZEP-520 as small as 20 nm. The 20 nm trenches in Si may be smaller than the features patterned in ZEP-520 exposures due to the etch profile. The proximity of trenches in Si and SiO_2 suggests the low voltage minimum exposable feature is $<$50 nm, not far from the high voltage resolution.

The 1 keV KRS single pass lines etched into Si [dose 11 pC/cm, Fig. 3(a)] also have the cusp-shaped ECR etch profile, with widths ranging from 30 to 100 nm. Gratings of single pass lines (dose 10 pC/cm) can be resolved with periods down to 100 nm [Fig. 6(a)]. Figure 4(b) shows the profile of etched SiO_2 for a finite-width (10 nm) line centered between two single pass lines (dose 18 pC/cm). The two single pass lines appear to be 60 nm wide, while the finite-width line is 75 nm wide. The 1 keV minimum exposable feature size of KRS resist was ~60 nm. This is comparable to the resolution we achieved at 1 keV using KRS in negative tone exposures (dose 220 pC/cm) as an etch mask for Si as seen in Fig. 6(b).

The decrease in resolution with the lowering of beam energy is due to the electron scattering in the resist. Monte Carlo calculations show that the 1 keV electrons are scattered laterally up to 25 nm in the resist, much more than the higher energy electrons. Lower energy primaries have a higher cross section for large angle scattering, decreasing their pennetration depths, but allowing them to deposit almost all of their energy into secondaries generated in the resist layer. The increase in sensitivity with decreasing energy is due to high efficiency with which low energy primaries deposit their energy into the resist. Ultimately, the solu-

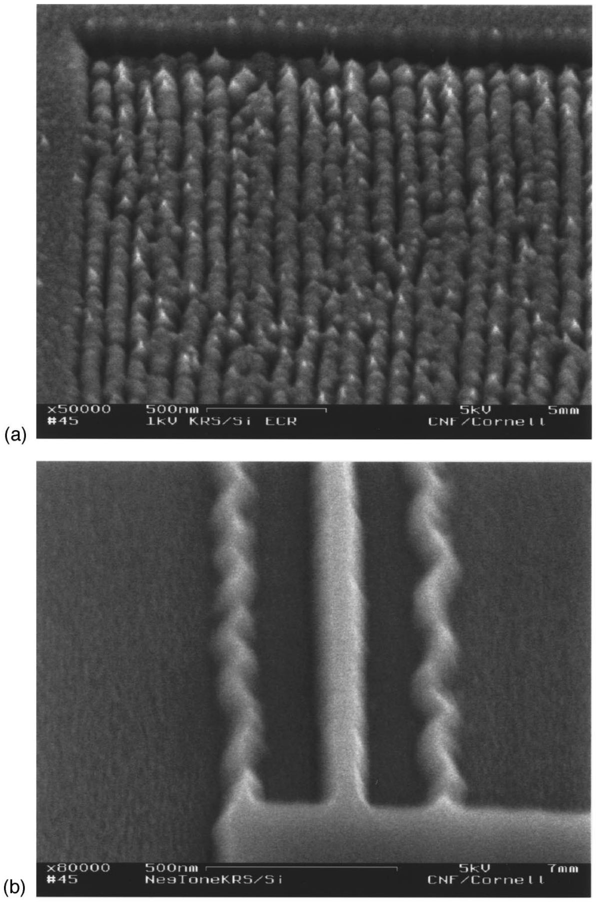

FIG. 6. Positive (a) and negative (b) tone exposures of KRS resist transferred into Si. The positive tone pattern is a grating of single pass lines (line dose 10 pC/cm) with 100 nm period. The negative tone image is of the same pattern as Fig. 4(b).

bility changes in the resists are dominated by interactions with low energy secondaries, regardless of primary energy.

V. CONCLUSIONS

The 50 nm thick layers of ZEP-520 and KRS resists are excellent candidates for high throughput low voltage microcolumn based electron beam lithography. Sensitivities are at the target goal of 1 μC/cm^2, and high resolution performance has been demonstrated. There were no obvious indications of proximity or charging effects when writing small period gratings with either resist. The low voltage resolutions are larger than the high voltage resolution limits, and are understood to be limited by lateral scattering in the imaging layers of the low energy primary electrons and the associated production of secondaries over lateral dimensions comparable to the resist layer thickness.

In ZEP-520, 50 nm lines have been written on a 75 nm period and patterned into SiO$_2$ substrates at 1 keV. A distinguishing feature of this resist is a consistant tone over a wide range in dose, enabling uniform high sensitivity development even from a nonuniform electron beam energy deposition. KRS can be exposed in positive or negative tone, by varying dose. Positive tone exposures can pattern 60 nm lines on a 100 nm period at 1 keV, and negative tone patterns have been written with 80 nm lines on a 125 nm pitch. The possibility exists to use both positive and negative tones on a single layer of KRS when combined with a DUV photolithographic exposure defining the positive and negative regions.

ACKNOWLEDGMENTS

D.M.T. would like to thank M. J. Lercel for many insights regarding ECR etching of Si and use of the electron beam pattern generation system. This work was funded by the Advanced Research Projects Agency under Contract No. F4920-93-C-006 and was performed in part at the Cornell Nanofabrication Facility which is supported in part by the National Science Foundation under Grant No. ECS-8619049.

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