The Lithographic Effect of Electron Beam on Poly(methyl Methacrylate) in a Scanning Electron Microscope: Minimization of Line Width by the Dose and Beam Current

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Synopsis

The lithographic effect of electron beam in line exposures in scanning electron microscopy (SEM) on poly(methyl methacrylate) (PMMA) was evaluated using the line width in a film deposited on a silicium substrate and from the line profiles in a PMMA plate. It was found that the effect of the dose on dimensions of the exposed structures in line exposures is not unambiguous, in contrast to area exposures, but that at constant dose and beam width the line dimensions increase with beam current. Sensitivity in line exposures (line sensitivity) is smaller than in area exposures (area sensitivity). The effect of beam current on the line width increases with decreasing dose; at doses close to line sensitivity it is the strongest. The increasing effect of a beam on the polymer with increasing current at constant dose is explained through the increasing range of thermal degradation due to exposure. A qualitative explanation is based on simplified calculations of the thermal conditions in the resist film during and after the exposure.

INTRODUCTION

In connection with the application of electron lithography to submicron structures, resolution conceived as the minimal line width which can be obtained in the polymer using an electron beam of constant width becomes an important characteristic of the resist-lithograph system.

The line width at a constant beam width is affected predominantly by the chemical structure of the polymer, and also by exposure conditions and by conditions used in the development of the exposed structures.[1,2] Further effects worthy of mention include thickness of the resist layer,[1,3] material of the substrate,[4] and pre-exposure treatment of the resist film.[5]

Exposure conditions include the dose and energy of incident electrons, namely the accelerating voltage. The effect of these two quantities was experimentally checked with the PMMA resist.[6] Particular attention in both experimental and theoretical studies, has been paid to the effect of the dose on the width and profile of lines,[1,6-9] assuming an unequivocal effect of the dose on the dimensions of line structures, as ensues from theoretical exposure models for electron-sensitive resists.[7,10]

The dose D depends on the beam current I, the exposure time t, and the surface area of the exposed line S according to the relation

$$D = \frac{I \cdot t}{S} \tag{1}$$

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Hence, the required dose may be applied in various ways; at various currents and times according to (1). The aim of this study is to verify whether the assumption regarding the unequivocal effect of the dose on the dimensions of exposed structures in line exposures is indeed valid.

EXPERIMENTAL

The line width was investigated using a PMMA resist film deposited by centrifugal casting from a 6% solution of PMMA (M_w = 800,000) in dioxan as a layer ~ 0.9 μm thick on silicium substrate; the line profiles were examined on a PMMA plate produced by Madreperla, Italy ($M_w = 2.1 \times 10^7$) ~ 0.9 mm thick. The resist layers were baked at 150°C for 30 min.

The samples were exposed in a scanning electron microscope JSM 35 manufactured by JEOL (Japan). The beam width in the exposure of the film on a Si substrate was 1.4 μm, in the case of plates it was 2.1 μm, the accelerating voltage in both experiments was 15 kV. The lines were exposed in the resist film at currents 2.5×10^{-10}, 2.5×10^{-9}, and 7.5×10^{-9} A to doses $5.5 \times 10^{-5} - 7 \times 10^{-4}$C cm^{-2} and in the case of the PMMA plate, to dose 7×10^{-5}C cm^{-2} at currents 3.5×10^{-9} and 7.5×10^{-9} A. The exposed structures were developed in isobutylmethyl ketone and isopropyl alcohol in the volume ratio 1:1 at 20°C for 2 min with constant stirring of the developer.

The line width in the films and the profile dimensions in PMMA plates were determined from SEM micrographs made after development with a JSM 35 microscope. The micrographs also showed whether the film has been developed to the substrate; the smallest dose, which is needed in this case, is defined as the line sensitivity. To explain the effect of temperature, PMMA plate was subjected to thermogravimetric analysis (Fig. 1).

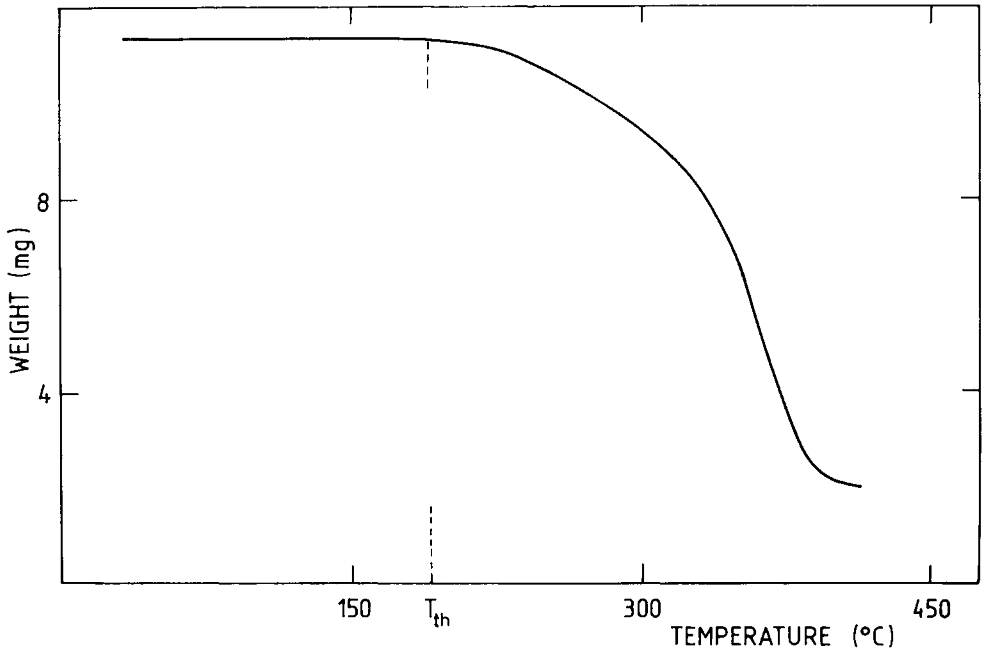

Fig. 1. Dependence of the PMMA weight on temperature during thermostating in nitrogen. Heating rate 15°C/min; T_{th} is the threshold temperature of depolymerization.

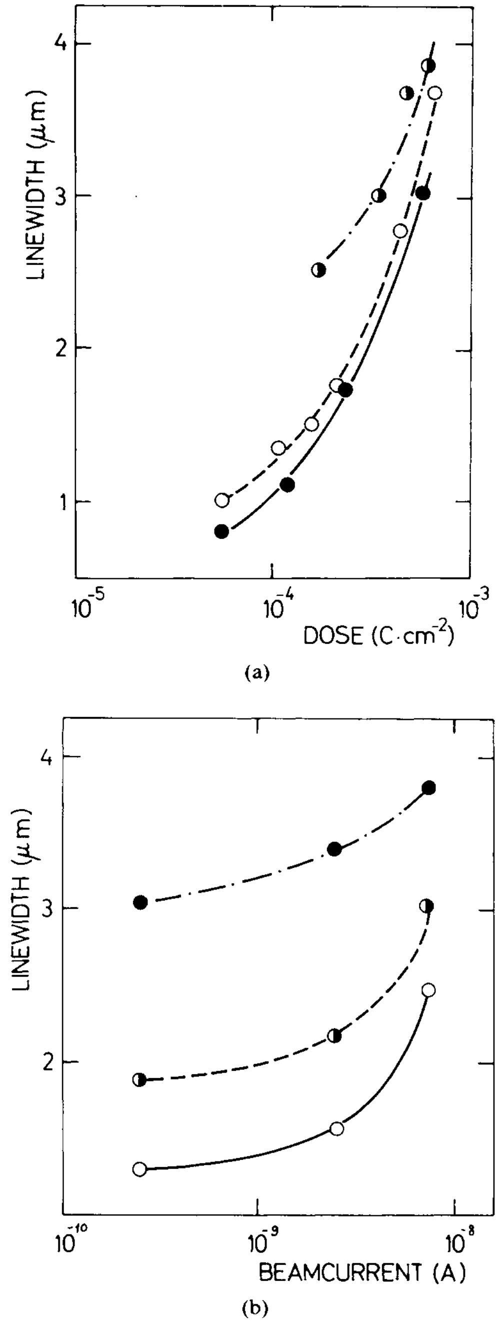

Fig. 2. Effect of dose and current on line width in a resist film. Beam width 1.4 μm (a) dependence on dose for currents 2.5×10^{-10}(●—), 2.5×10^{-9}(o---), and 7.5×10^{-9}(◒-.-) A. (b) Dependence on current for doses 1.6×10^{-4}(o—), 3×10^{-4}(◑---), and 6×10^{-4}(●-.-) C cm^{-2}.

RESULTS

Effect of Dose and of Electron Beam Current in PMMA Resist Film

The results are plotted in Figure 2(a) and (b). As expected, the line width increases with increasing dose, but a constant line width w_n cannot be guaranteed at the constant dose D. With increasing current I [and thus proportionately to the decreasing exposure time according to Eq. (1)] the lines become broader.

The line sensitivity lay in the range $7 \times 10^{-5} - 1 \times 10^{-4}$C cm^{-2}, but no dependence on current could be observed. The area sensitivity with the same developing procedure used was 5×10^{-5}C cm^{-2}. The decrease in sensitivity in line exposures may be explained by a slower removal of the polymer during the development of line exposures compared with area exposures and by a more effective utilization of the dose in the case of area exposure due to the proximity effect.

The curves in Figure 2(a), (b) show that the effect of current on the line width increases with decreasing dose. For example, at the dose 1.5×10^{-4}C cm^{-2} (and thus a dose close to the line sensitivity) an increase in the current from 2.5×10^{-10} to 7.5×10^{-9} A brings about an increase in the line width by about 70%, while at 6.5×10^{-4}C cm^{-2} the respective increase is only by 30%. Thus, it is obvious, that in reaching narrow lines when small doses close to line sensitivity are used a decrease in the current is particularly important.

Effect of the Electron Beam Current at Constant Dose on the Line Profile in the PMMA Plate

Measurements of the profile dimensions of several lines provided average line dimensions at dose 7×10^{-5}C cm^{-2} for currents 3.5×10^{-9} and 7.5 ×

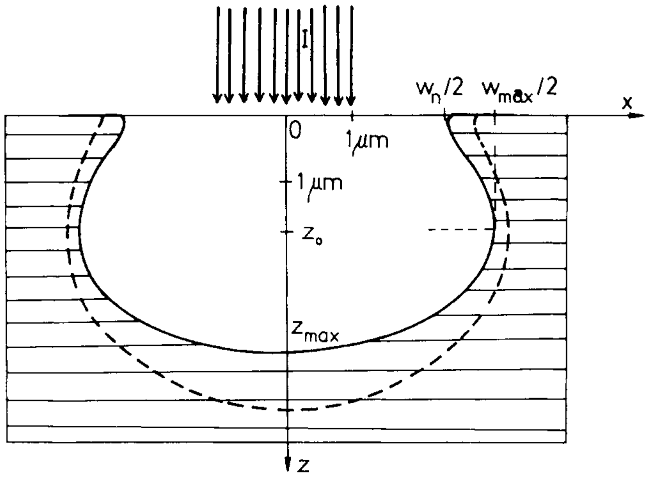

Fig. 3. Average line profiles in the PMMA plate at currents 3.5×10^{-9}(—) and 7.5×10^{-9}(– – –) A at a constant dose 7×10^{-5}C cm^{-2} and beam width 2.1 μm. Meaning of symbols in the text.

TABLE I
Dimensions of Line Profiles in the PMMA Plate[a]

	Currents (A)	
Profile parameters (μm)	3.5×10^{-9}	7.5×10^{-9}
$Z_{\max}$	3.3	3.8–4.4
z_o	1.8	1.8
w_n	4–5.1	4.4–6
$w_{\max}$	5.8–6.2	5.5–6.7

[a] Dose, 7×10^{-5} C cm^{-2}; currents, 3.5×10^{-9} and 7.5×10^{-9} A; beam width, 2.1 μm.

10^{-9} A (Fig. 3). The dimensional parameters of the profiles are given in Table I. Both Figure 3 and Table I show that the effect of electron beam on the resist is stronger at a higher current. The neck width w_n, the maximal line width $w_{\max}$ and the maximal line depth $z_{\max}$ are larger at a higher current, the increase of the effect of the electron beam at the higher current being more pronounced in the direction of the current. Only the position of the center with the scattered energy maximum $z = z_0$ is 1.8 μm in both cases.

DISCUSSION

Exposure of PMMA samples to the electron beam results in radiation degradation, and, due to local heating of the polymer, also in thermal degradation and depolymerization. The loss in weight of PMMA due to thermal depolymerization in nitrogen can be seen in Figure 1. The threshold temperature of depolymerization T_{th} is ~ 180°C. However, thermal degradation of PMMA takes place at lower temperatures (100–120°C),[11,12] which raises the solubility of the polymer. The calculation of the dependence of temperature $T(t, x, y)$ on time (t) and the coordinates (x, y) in the resist near the point of incidence of the beam 0 (Fig. 4) is based on the thermal balance of heating caused by passage of the electric current I and of heat losses due to heat removal to the surroundings:

$$c \cdot \frac{dT}{dt} + \operatorname{div}(\lambda \cdot \operatorname{grad} T) = b \cdot I^2 \qquad (2)$$

where c is the specific heat of the polymer, λ is the thermal conductivity of

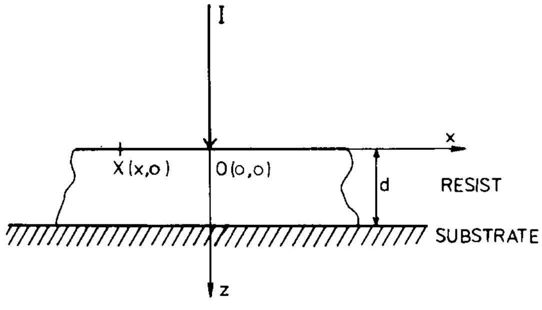

Fig. 4. Geometrical arrangement for the calculation of thermal conditions in the resist film caused by exposure.

the polymer, b is a constant depending on the specific resistance of the polymer and on the geometry of the electron beam.

Using this equation, and simplifying assumptions, we calculated relations for the time dependence of temperature of the resist film on the surface during and after exposure in the line center in the point 0 (o, o) and at a distance x from the line center in the point X (x, o) (Fig. 4).

The following simplifying assumptions are made in the calculation of the surface temperature of the resist film in the line center: the electron beam is infinitely thin, the temperature of the substrate and its surroundings is T_o, the temperature gradient in the direction of passage of the current is constant due to the small thickness of the polymer, heat removal in the direction parallel to the surface is neglected (with respect to the small conductivity and resist thickness d). Also, c, λ, b are assumed to be independent of temperature. Under such assumptions, we have from Eq. (2) for the increase in temperature T_1 (t, o, o) on the resist surface in the line center during the exposure

$$T_1(t, o, o) = \frac{b \cdot c \cdot d^2}{\lambda}\left(1 - \mathrm{e}^{-\lambda/c \cdot d^2 \times t}\right) + T_o \tag{3}$$

and for the decrease in temperature T_2 (t, o, o) on the resist surface in the line center after completion of the exposure [the required dose D at the current I is related to the exposure time $t_{D,\,I}$ by relation (1)] we obtain

$$T_2(t, o, o) = \left\{T_{\underline{1}}\left(t_{D,\,I}, o, o\right) - T_o\right\}\mathrm{e}^{-\lambda/c \cdot d^2(t - t_{D,\,I})} + T_o \tag{4}$$

For the temperature $T_3(t, x\, o)$ on the resist surface at a distance x from the line center after the end of exposure we have from Eq. (2)

$$T_3(t, x, o) = e^{-x/\sqrt{2} \cdot d} e^{-\lambda/c \cdot d^2(t - t_{D,\,I})} . \left\{T_1\left(t_{D,\,I}, o, o\right) - T_o\right\} + T_o \tag{5}$$

The functions $T_1(t, o, o)$, $T_2(t, o, o)$, and $T_3(t_{D,\,I}, x, o)$ can be seen in Figure 5(a), (b) for three currents: $I_o, 2I_o, 3I_o$. The curve $D =$ const. in Figure 5(a) shows the maximal temperature which is reached for a certain constant overall dose delivered equally distributed over various exposure times. This allows us to determine the exposure times $t_{D,\,I_o}$, $t_{D,2I_o}$, $t_{D,3I_o}$, needed to reach dose D at currents I_o, $2I_o$, $3I_o$, and the maximal temperatures at the end of exposures. These maximal temperatures obviously increase with current. The hatched areas limited by the curves $T_1(t, o, o)$, $T_2(t, o, o)$, and the straight line $T = T_{th}^d$, where T_{th}^d is the threshold temperature of thermal degradation, are related with the degree of thermal damage of the sample in an exposure to constant dose at different currents.

The curves $T_3(t_{D,\,I}, x, o)$ [Fig. 5(b)] start at the temperatures reached at the end of exposure in the line center at constant dose by using various currents: I_o, $2I_o$, $3I_o$, and indicate a drop in temperature with increasing distance from the line center. If T_{th}^d is the threshold temperature at which degradation becomes apparent during development, then the distances x_{I_o}, x_{2I_o}, x_{3I_o} show the range of heat damage to the polymer. It can be seen in Figure 5(b) that at constant dose and increasing currents the range of heat damage increases.

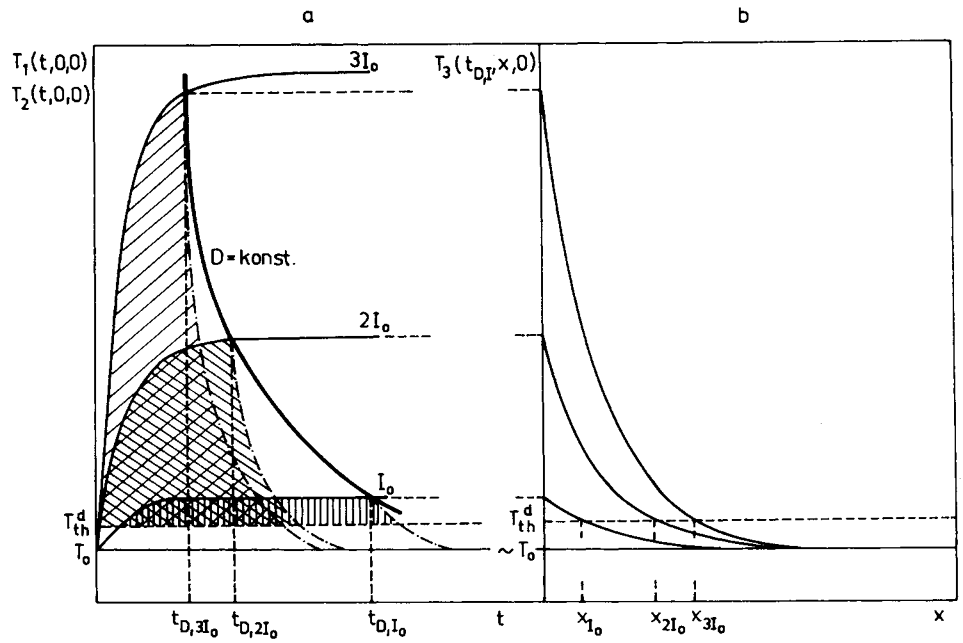

Fig. 5. Time dependence of temperature on the resist surface in the line center during exposure and after (a) and dependence of temperature on the distance x from the line center at the moment of end of exposure (b). (*a*) Function $T_1(t, o, o)$ [Eq. (3)—)] and $T_2(t, o, o)$ [Eq. (4)- – · – · –], respectively, express the rise in temperature during exposure at currents I_o, $2I_o$, and $3I_o$ and decrease in temperature after exposure. The curve D = const. (——) determines the dependence of temperature at the end of exposure to constant dose D at various currents on the exposure time. The currents I_o, $2I_o$, $3I_o$ have the corresponding exposure times t_{D,I_o}, $t_{D,2I_o}$, $t_{D,3I_o}$. T_o is the temperature of surroundings, T_{th}^{d} is the threshold temperature of thermal degradation. The hatched areas are related to the degree of thermal damage to the polymer. (*b*) Functions T_3 $(t_{D,I}, x, o)$ [Eq. (5)] represent the decrease in temperature of the resist surface at a distance x from the line center at the moment of end of exposure by currents I_o, $2I_o$, $3I_o$ at constant dose D. The distances x_{I_o}, $x_{2I_{ox}}$, x_{3I_o} are ranges of the thermal damage to the polymer.

For the PMMA plate the solution to Eq. (2) becomes more complicated. It can be said, however, that heat removal is smaller due to the larger thickness of the polymer, and thus the heat damage to PMMA is more strongly current-dependent. On the surface, i.e. in the points (x, o) (cf. Fig. 4), the polymer is heated only by the heat flow from the line center while in the points (o, z), it is heated by the passage of the current. This may explain the greater range of heat damage due to the stronger current in the direction of passage of the beam.

CONCLUSIONS

The results obtained in this study indicate that the effect of electron beam on PMMA is current dependent at a constant dose and constant beam diameter. This phenomenon is related to the thermal effect of the beam on the polymer and may be expected for polymers in which solubility increases as a result of thermal depolymerization and degradation.

The effect of electron beam on the polymer is predominantly marked in line exposures, where the dimensions of the exposed structures can be compared with the line broadening caused by the heat damage to the polymer. In area structures, due to the size of the exposed field the effect of current at constant dose on the field size after development can be neglected.

The effect of current at constant dose is particularly operative in exposures to small doses approaching line sensitivity. In the line exposure of PMMA to a dose of 1.5×10^{-4}C cm^{-2} with increasing current of a beam with a constant diameter from 2.5×10^{-10} to 7.5×10^{-9} A the lines are broadened by 70%.

Sensitivity in line exposures is smaller than in planar exposures (1×10^{-4} compared with 5×10^{-5}C cm^{-2}).

These findings are to be respected in the lithographic production of submicron structures.

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