A New Method of Evaluation of the Effect of Electron Beam and Developing Process on Positive Polymeric Resists

Z. PELZBAUER and R. WAGNER, *Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague, Czechoslovakia*

Synopsis

A new method of evaluation of the effect of electron beam on the latent changes in degrading polymer resists has been developed on the base of measurement of the developing curve under an interference microscope. An evaluation procedure using the unit parameters (film thickness and development time) has been suggested for the characterization of the sensitivity and contrast of resists.

INTRODUCTION

A quantitative evaluation of the sensitivity of polymers towards electron radiation which causes their degradation or crosslinking is of fundamental importance in the research of polymeric resists used in lithographic techniques, and particularly in the manufacturing of VLSI circuits.[1] Generally, sensitivity is defined as a minimal radiation dose allowing one to obtain the chosen ratio of the rates of dissolution of irradiated and unirradiated domains of the resist.[2] In practice, sensitivity is evaluated in most cases using a characteristic curve, i.e., dependence of the normalized thickness of the irradiated domain after developing on the logarithm of the radiation dose.[3-5] With positive resists characterized by a rise in dissolution due to the degradative effect of radiation, sensitivity is determined by extrapolation from the decreasing characteristic curve as a minimal dose required for obtaining complete dissolution of the resist during development, and the contrast is the negative slope of the descending portion of the curve.[6]

An essential drawback is seen in the fact that the method has not been sufficiently described and standardized in the literature. Usually, reduction of the thickness of unirradiated domains during development is neglected[4]; this reduction is considerable during fast development and may deteriorate the applicability of the resist.[1] Also, the way in which normalization of the irradiated and developed domain is related to the thickness of the unirradiated domain (after development or the original one) does not justify a comparison between the sensitivities of resists of various thickness (dependence on thickness is not ruled out by such normalization).

It has been our aim to suggest a standard evaluation procedure for resists after irradiation, by means of light microscopy in the process of development. The rather demanding measurement of the characteristic curve and its extrapolation are replaced by direct sensitivity measurement using the so-called developing

Journal of Applied Polymer Science, Vol. 29, 1427–1432 (1984)

CCC 0021-8995/84/041427-06$04.00

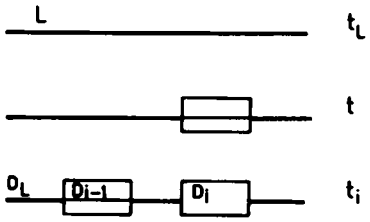

Fig. 1. Scheme of time dependence of the development of a positive resist. Development times $t_L < t < t_i$, exposure doses $D_{i-1} < D_i < D_L$—cf. text.

curve which enables some further important information to be obtained on the effect of electron radiation and developing process on polymeric resists.

EXPERIMENTAL

Film Preparation and Thickness Measurements. The polymeric resist under investigation was poly(methyl methacrylate), $\overline{M}_w$ = 800,000. A filtered solution in dioxane (10 wt %) was spin coated to 2.5 in silicone wafer in order to achieve a uniform thickness of ca. 1 μm. Preexposure baking of the film proceeded at 150°C for 60 min. Film thickness was determined by interference microscopy in incident light (Nomarski interferometer combined with the polarization microscope Zetopan produced by Reichert).

Electron Beam Irradiation. Irradiation was carried out with a scanning electron microscope JSM35 (JEOL), accelerating voltage 15 kV, electron beam 2.5×10^{-10} A (measured with a Keithley electrometer combined with Faraday gauge). The radiation dose D (C·cm^{-2}) was calculated from $D = It/P$, where I is the beam current and t is the time of continuous scanning of the area P. Continuous scanning (distance between lines smaller than their width) was achieved by using a defocussed beam, density 2000 lines/mm. Areas (0.125 mm^2) with graded radiation dose (at the same suitably chosen current controlled by changing the scanning time t) were exposed on the resist at a distance of ca. 5 mm. Areas thus exposed are connected with line L exposed by a dose above 10^{-4} C·cm^{-2}.

Determination of the Developing Curve. In order to determine the developing curve of positive resist, a wafer with the exposed film was placed in a standard thermostated developer in a Petri dish, and the time t was recorded. The dish was placed under the vertical illuminator of the microscope provided

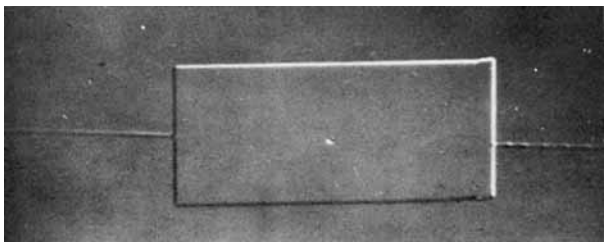

Fig. 2. Exposed domains after completed development, in an interference light microscope.

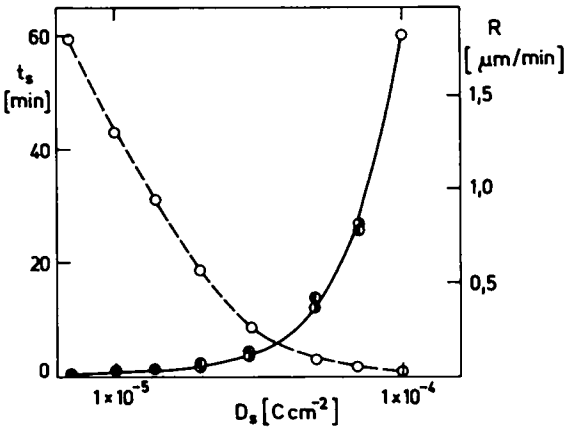

Fig. 3. Dependence of developing time (t_s) and rate (R) on the dose of electron radiation at 15 keV for different thickness PMMA film (M_w = 800 000) developed with MIBK/IPA (1:1 by vol) at 22°C. Thickness: (◑) 0.47; (○) 1; (◐) 1.84.

with the Nomarski device for interference contrast, combined with the Zetopan Pol (Reichert) microscope.

The time dependence of development of the exposed domain is schematically shown in Figure 1. In the first moments after the time t_L, the line L exposed by the dose D_L was developed. After the developing time t, the area exposed by a lower dose ($D_i < D_L$) could already be seen, the line L being still visible inside. The developing time t_i of the area exposed by the dose D_i is indicated by disappearance of the line inside the area (Figs. 1 and 2).

RESULTS AND DISCUSSION

The developing curve of PMMA in the mixture methyl isobutyl ketone, isopropanol (by volume 1:1) at 22°C, i.e., the dependence of the developing time t_s until complete removal of the film irradiated by the dose D_s is given in Figure 3 (broken curve). The same figure shows the plot of the rate of development R as a function of the dose (solid curve), where R has been calculated as the ratio of the initial film thickness z_0 to the corresponding developing time t_s.

The advantage of new evaluation method by means of the developing curve consists in that it enables the sensitivity of the polymer (dose D_s needed for complete removal of the film) to be determined directly as a function of the developing time t_s.

The function $R = f(D_s)$ is important for the deriving of further characteristics. Its analysis (Fig. 3) by the least squares method gave the dependence

$$R = R_{ni} + aD_s^b \tag{1}$$

in which R_{ni} (rate of development of nonirradiated polymer) is 1.34×10^{-2} μm/min and the constants are $a = 1.09 \times 10^9$, $b = 2.20$.

By using the assumption of linearity of the decrease in the film thickness with the developing time confirmed by Greeneich[7] and us (Fig. 3) in this system, it is possible, by means of eq. (1), to describe the dependence of sensitivity on the

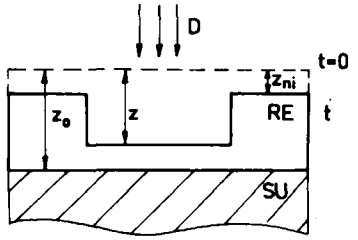

Fig. 4. Reduction of thickness of a positive polymeric resist after irradiation and partial development ($t < t_s$). SU substrate, z and z_{ni} reduction of thickness of irradiated and unradiated resists RE, z_0 original thickness before development ($t = 0$).

developing time t_s and on the initial film thickness z_0

$$D_s = \sqrt[b]{\frac{z_0/t_s - R_{ni}}{a}} \tag{2}$$

For the chosen developing time t_s and the initial film thickness z_0, the so-called characteristic curves, i.e., a decrease in film thickness after exposure and development, can be derived (see Fig. 5) by subtraction of $\Delta z = Rt_s$ from z_0, where R is the experimentally determined dependence $R = f(D_s)$ according to Figure 3 (scheme of thickness reduction is in Fig. 4).

Along with sensitivity, another important characteristic of electron resists is contrast, closely connected with the resolving power. This contrast is generally defined as the absolute value of the slope of a straight line which connects the chosen point A with the point D_s of the characteristic curve (Fig. 6). If the position of point A is expressed by the ordinate $y_A = p(z_0 - z_{ni})$, where the parameter p lies in the range between 0 and 1, the contrast γ_p can be expressed through

$$\gamma_p = \frac{bp(z_0 - z_{ni})}{-\log(1-p)} \tag{3}$$

The dose D_0 for $p = 0.9$ (point A in Fig. 6) is conventionally chosen by us as the beginning of latent changes caused in the polymer by electron radiation. The

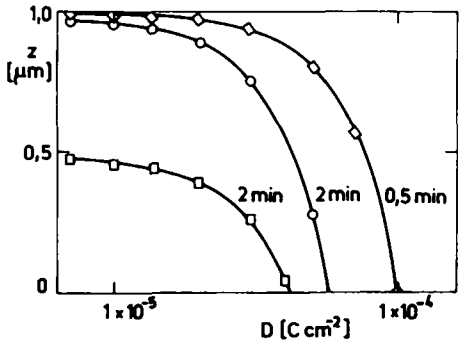

Fig. 5. Characteristic curves of the radiation sensitivity of PMMA for various chosen development times (parameter) and various initial film thicknesses [(◇, ○) 1 μm; (□) 0.5 μm]—derived from R data in Figure 3.

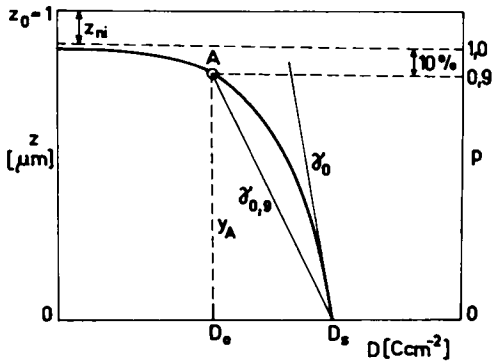

Fig. 6. Scheme of unit characteristic curve and definition of derived characteristic quantities: D_0 = threshold of latent changes; D_s = sensitivity; $\gamma_{0.9}$ and γ_0 values of contrasts.

corresponding contrast in Figure 6 is

$$\gamma_{0.9} = y_A/\log(D_s - D_0) \tag{4a}$$

or, from relation (3),

$$\gamma_{0.9} = 0.9b(z_0 - z_{ni}) \tag{4b}$$

The contrast for $p = 0.9$ is usually lower for positive resists than for $p = 0$ (tangent to the curve in the point D_s), when with respect to relation (3) it becomes

$$\gamma_0 = \frac{b(z_0 - z_{ni})}{\log e} \tag{5}$$

Equations (2)–(5) show that the normalization procedure reported in the literature, in which thickness of the exposed domains after development is divided by the initial thickness, does not rule out the effect of z_0 on sensitivity and contrast. For this reason, we recommend that sensitivity and contrast should be given for the initial film thickness $z_0 = 1$ μm and time of development $t_s = 1$ min. These so-called unit sensitivities and contrasts, as well as the unit characteristic curve, may be calculated from the $R = f(D_s)$ data using the relations given above, or simply derived graphically.

Characteristic quantities evaluated from the unit characteristic curve for poly(methyl methacrylate) irradiated with electrons of 15 keV and developed in MIBK/IPA 1:1 by vol at 22°C are

$$D_0 = 2.72 \times 10^{-5}\ \text{C} \cdot \text{cm}^{-2}$$
$$D_s = 7.75 \times 10^{-5}\ \text{C} \cdot \text{cm}^{-2}$$
$$\gamma_{0.9} = 1.95$$
$$\gamma_0 = 5.00$$
$$z_{ni} = 1.34 \times 10^{-2}\ \mu\text{m}$$

The quantities summarized in the table characterize the polymer reported here as an electron resist and allow us to compare lithographic properties of various materials.

In order to be able to recalculate the data for an other thickness and development time, it is always necessary to confirm experimentally for the given

system that the rate of developing does not depend on the thickness of resist. If this is not the case, i.e., if swelling or a barrier occuring at the resist surface have a retarding effect, the proposed method can be also used, but the parameters have to be derived directly from the experimentally determined unit development curve.

References

1. M. J. Bowden and L. F. Thompson, *Solid State Technol.*, (May), 72 (1979).
2. E. Gipstein, A. C. Ouano, D. E. Johnson, and O. U. Need, *IBM J. Res. Dev.*, **21**, 143 (1977).
3. J. H. Lai and S. Shrawagi, *J. Appl. Polym. Sci.*, **22**, 53 (1978).
4. K. Harada, *J. Electrochem. Soc.*, **127**, 491 (1980).
5. Z. Pelzbauer and R. Wagner, Fifth International Microsymposium on Polymer Morphology, Sofia, 1981, p. 141.
6. R. G. Brault and L. J. Miller, Fifth Photopolymer Conference, Ellenville, N.Y., October 10–12, 1979.
7. I. S. Greeneich, *J. Electrochem. Soc.*, **122**, 970 (1979).

Received June 22, 1983
Accepted September 21, 1983