Effects of molecular weight and plasticization on dissolution rates of thin polymer films

Wendy J. Cooper, Philip D. Krasicky and Ferdinand Rodriguez
School of Chemical Engineering, Olin Hall, Cornell University, Ithaca, New York 14853, USA
(Received 25 October 1984; revised 14 December 1984)

The dissolution rates (DR) in methyl ethyl ketone (MEK) of thin films of poly(methyl methacrylate), (PMMA), were measured using interferometry. Films were spun on silicon-oxide coated wafers. After baking at 155°C for one hour the dry films were about 1 μm thick. PMMA samples with M_n of 6000 to 320 000 were prepared by (a) polymerization and fractionation, and (b) electron beam bombardment of coated wafers. Both preparations resulted in non-linear behaviour when log DR was plotted against log M_n. The irradiated samples uniformly had DR values that were about 2.5 × those of the unexposed samples of the same M_n. Plasticization of PMMA by poly(ethylene oxide), PEO, of $M_n = 4000$ also changed DR in direct proportion to the amount of PEO added. With a weight fraction of 0.2 PEO, the DR was double that for PMMA alone.

(Keywords: dissolution rate; thin films; poly(methyl methacrylate); interferometry; plasticization; resist)

INTRODUCTION

The forefront of the microelectronics revolution is currently occupied by the silicon-integrated circuit. The complexity of circuitry has seen tremendous increases, with the number of components per circuit almost doubling every year since 1959. This has been achieved via increased chip size, decreased feature size, and improved device design[1]. Polymeric materials play an important role in the fabrication of microelectronic devices. The desired electrical characteristics of a circuit are achieved by selectively doping, metallizing or insulating regions of silicon. This is accomplished by lithography, a process in which a pattern is defined in a resist layer (usually polymeric) and then transferred to the silicon beneath. The primary interest of this work lies in the definition of the resist layer, or the development process in lithography.

Once a resist film has been applied to a substrate and irradiated, the next step in lithography is the development process. The production of an image, or pattern, depends on the differential solubility of the exposed and unexposed regions of the polymeric films. Phenomena such as swelling and cracking of the film can cause distortion of the patterns. These effects have been shown to depend on the development solvent used[2–4].

Currently, polymer–solvent pairs are most often chosen on a trial-and-error basis. A good starting point in the evaluation of particular pairs is an analysis of the thermodynamic solubility limit of the polymer in the solvent. This is not sufficient, however, since it has been shown that kinetic factors are also significant[2,3]. The kinetic factors involved are: the diffusion of the solvent into the polymeric film, the subsequent relaxation response of the polymer, and the diffusion of the polymer molecules into the solvent.

These diffusion and relaxation processes are complicated and not yet completely understood. Several workers have examined the permeation of polymer matrices by organic vapours[5], and by the sorption of liquids[6–8]. Also, advances have been made in the development of models to predict the transport of penetrants in glassy polymers based on free volume theories[9] and diffusivity and viscous flow parameters[10].

Various experimental techniques have been developed to observe directly the kinematics of a dissolving polymer[2,11]. Ueberreiter used an apparatus that consisted of a microscope and a sample cell in which a polymer pellet was sandwiched between two glass slides. He used dyes in the solvent or carbon black dispersed in the polymer to aid in the observation of the polymer/solvent interface during dissolution. Using this technique he was able to extract information regarding the diffusion coefficient, surface layer characteristics and was able to observe various types of dissolution behaviour, such as swelling and cracking.

Ouano[11] modified Uebbereiter's apparatus by using optimum angle-of-illumination microscopy rather than dyes to follow the moving layer boundaries. He noted some important factors on which dissolution dynamics depend: polymer tacticity, T_g, thermal history of the polymer, and solvent swelling power. Ouano also did work involving quantitative measurements of the dissolution rate of polymer films. The dissolution rate was measured by removing the film at a predetermined time, drying the sample, and measuring the film thickness. The effects of solvents, polymer molecular weight, and irradiation of the polymer on dissolution under Case II diffusion control were investigated.

Greeneich[4] conducted studies similar to Ouano's. A thin film sample was developed and the thickness of the

Presented at the 1984 annual meeting of the American Chemical Society, 26–31 August 1984, Philadelphia, USA

0032-3861/85/071069-04$03.00
© 1985 Butterworth & Co. (Publishers) Ltd.

film was periodically determined by the interference colour of the partially developed area. His work mainly involved the effect of various solvents on the dissolution rate of irradiated samples.

EXPERIMENTAL PROCEDURE

The polymers studied were PMMA samples obtained from KTI Chemicals Inc., Sunnyvale, CA (Formula 950K, $M_n = 320\,000$, $M_w/M_n = 1.60$) and various molecular weights of PMMA synthesized in the laboratory. The KTI PMMA was a 6% by weight solution of the polymer in chlorobenzene. Polymer mixtures were prepared by adding plasticizer to the KTI solution. The plasticizer (*Table 1*) was Carbowax (Union Carbide Chemicals Inc.).

Free radical polymerizations were carried out at 55°C in acetone and the product was fractionally precipitated using methanol. The initiator was Vazo 52 (*Table 1*) from E. I. duPont de Nemours and Co. Solutions of 8–15% by weight polymer in chlorobenzene were rocked for 24 h to assure uniformity.

All molecular weight measurements were estimated using a Waters Model 201 HPLC with 4 μ-Styragel columns of nominal sizes 500, 10^3, 10^4 and 10^5 Å. The eluting solvent was tetrahydrofuran, THF. Narrow dispersity ($M_w/M_n < 1.1$) PMMA samples obtained from Polymer Laboratory Limited were used as standards in the gel permeation chromatography (g.p.c.) calibration.

Three-inch diameter, SiO_2-coated silicon wafers were spin-coated with the polymer solutions using a Headway Research Model EC-101D spinner. Samples were spun at 1500 rpm for 60 s resulting in a polymer film thickness of about 1.25 μm. The SiO_2 layer on these wafers was found to be about 50–100 Å by ellipsometry[12]. Pre-baking was done in a convection oven at 155°C for one hour to allow film stress annealing and residual spinning solvent removal[13].

Films of KTI PMMA and mixtures were exposed in a modified conventional transmission electron microscope. The beam was broadened to flood the entire wafer uniformly with a flow of electrons. The dosage was varied from 10 μC/cm^2 (C = columns) to 200 μC/cm^2 by varying the exposure time to 50 kV electrons. The current was measured using a Faraday cage.

A laser interferometer was used for solubility rate measurements. With this device, the intensity of reflected light oscillates periodically as the film thickness of polymer on a reflecting substrate decreases. In the case of PMMA dissolving in methyl ethyl ketone (MEK), a nearly symmetrical sinusoidal pattern is obtained with a full period for about each 0.2 μm of polymer removed. Since the films are about 1 μm to begin with, 4 to 6 oscillations in the signal are observed. This is quite enough to characterize the rate of dissolution even when that rate changes slightly during penetration. Some

Table 1 Description of materials

Poly(methyl methacrylate), PMMA (KTI)
$M_n = 320 \times 10^3$, $M_w/M_n = 1.80$, $T_g = 105$°C
Other samples of PMMA (see *Table 2*)
Poly(ethylene oxide), 'Carbowax 4000' (Carbide)
$M_n = 4000$, $T_g = -67$°C, $T_m = 60$°C
Polymerization initiator, 'Vazo 52' (du Pont)
Half-life of 350 min at 55°C:
$[(CH_3)_2CH\text{–}CH_2\text{–}C(CH_3,CN)\text{–}N]_2$

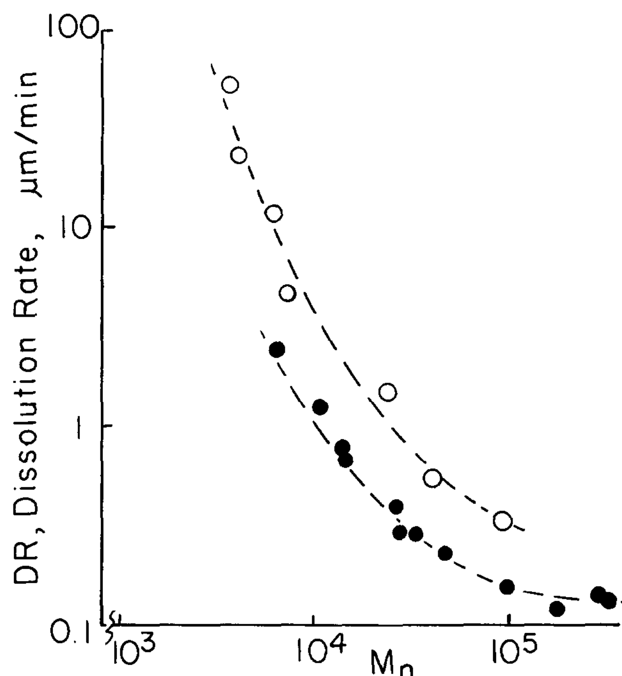

Figure 1 Poly(methyl methacrylate) exposed to the electron beam (○), dissolves more rapidly than unexposed polymer (●) of the same molecular weight. The solvent used was MEK at 17.5°C

workers have used the total time to remove all the polymer in calculating an average rate. The present method can detect the acceleration in dissolution which occurs, for example, when the portion of the polymer film adjacent to the reflective surface has received additional exposure through backscattering of electrons.

The optical principles are similar to those described in the literature[14]. The apparatus used in the present study is simply a 2 mw He–Ne unpolarized laser ($\lambda = 0.6328$ μm) impinging on a coated wafer at an angle of 10° from normal. The photocell signal of the reflected beam is amplified and recorded. The wafer is mounted in a vertical position in such a way that it can be immersed rapidly in a stirred beaker of solvent. The optical measurements commence within two seconds of immersion. While the dissolution rates are several orders of magnitude faster than those reported by Ouano[13] and Greeneich[4], they still are slow compared to the usual cycles used in commercial equipment.

RESULTS AND DISCUSSION

Dissolution rates of exposed and unexposed poly(methyl methacrylate)

Various workers[3,4] have studied the effect of molecular weight on dissolution rate. A range of molecular weights can be obtained by irradiating whole polymers or by synthesizing various molecular weight polymers. *Figure 1* shows our results for the relationship between the dissolution rate and number average molecular weight for exposed and unexposed PMMA samples in MEK. These data represent polymers with a range of polydispersities of 1.2 to 2.2 (*Table 2*). A similar curve was reported by J. S. Greeneich[4] for PMMA samples with a polydispersity of 3. However, Greeneich did not observe any difference between exposed and unexposed polymer of the same molecular weight. He did not measure the molecular weight of the exposed samples directly, but inferred the

Table 2 PMMA samples used in dissolution studies

Unexposed samples		Exposed samples	
$M_n \times 10^{-3}$	M_w/M_n	$M_n \times 10^{-3}$	M_w/M_n
320	1.80	91	1.51
289	1.52	41	1.67
180	1.52	24	1.50
100	1.50	7.5	2.22
80	1.59	6.4	1.95
48	1.51	4.2	1.92
36	1.51	3.9	2.08
29	1.60		
27	1.36		
15	1.52		
14	1.46		
11	1.34		
6.5	1.23		

molecular weights from the time of exposure. The precision lost by not measuring directly may account for the inability to distinguish two separate curves for exposed and unexposed polymer. The solvent used by Greeneich was MIBK. A. C. Ouano[13] has also studied this relationship. He reported two distinct regimes for this relationship at molecular weights less than 100 000, one for exposed PMMA (slope = 1.4) and one for unexposed PMMA (slope = 0.4). Ouano's samples were 'narrow molecular weight fractions', and the solvent used was amyl acetate. The molecular weights of exposed samples were calculated using as a basis the results of a previous dose, chain scissioning study.

The results obtained here more closely resemble Grenneich's results although he reported a common curve for both the exposed and unexposed samples. He found a rather abrupt transition in slope at $M_n = 20\,000$ from 1.5 in the low molecular weight region to a much lower value in the higher molecular weight region. The results found here show a continuous curve for the unexposed samples, but the exposed samples show distinctly higher rates.

Ouano speculated that Grenneich's results were caused by the difficulty in forming a defect-free film for $M_n < 10\,000$. He speculated that the presence of microcracks in the brittle low molecular weight PMMA could result in an anomalously high rate *versus* molecular weight slope for the unexposed samples. This type of phenomenon has been indeed observed by several researchers[4–6] who concluded that cracking is the result of stresses in the polymer film. Stresses exerted on the polymer are a result of osmotic swelling stresses or internal residual preorientation stresses. This study does not support this speculation. The pronounced curvature of the DR vs. M_n relationship is apparent even at molecular weights over 50 000 where tensile strength is high enough that microcracks are unlikely.

The elevation of this curve for the exposed samples could be due to chemical changes upon irradiation. Ouano explained the faster dissolution rate for the exposed samples by postulating the formation of microporosity upon irradiation. It has also been speculated that chemical changes such as the formation of gases and radicals accompany the molecular weight reduction on irradiation. A similar argument was used by Stillwagon to explain the same behaviour when the polymer is poly(butene-1-sulphone)[16]. These volatile species can increase the diffusion coefficient of the solvent and increase the dissolution rate of the polymer. This study found the effect of the postulated microporosity to be significant for both the high and low doses. It may be that Greeneich did not include high enough doses to see this effect.

Both Greeneich and Ouano worked with much slower dissolving systems (by factors of 10 and 100, respectively). However, if the data of the two studies are replotted along with the present results with adjustment of the rate scales, an amazing degree of agreement can be seen (*Figure 2*). Ouano's conclusion that unexposed PMMA can be represented as a straight line with a slope of 0.4 relies almost exclusively on a single point at a M_n of ~10 000. It should be remembered that in a 'most-probable' distribution, about 20% of the sample by weight will have molecular weights below M_n 2000, and, in fact, that a considerable amount of monomer is to be expected when M_n is low. Given PMMA's propensity for depolymerization (obvious when sheet material is cut with a saw), the plasticizing effect of monomer should not be ignored.

Effect of plasticization on dissolution rate

The dissolution behaviour of a plasticized film was studied by adding Carbowax 4000 to the PMMA film prior to dissolution. Carbowax was chosen because it is compatible at low concentrations with PMMA. The major effect of a plasticizer is to lower the glass transition temperature, T_g, of a polymer. T_g values are listed in *Table 1*. The glass transition temperature marks the onset of segmental mobility of a polymer. Plasticization can be implemented in two ways: the addition of a compatible plasticizer directly to a polymer solution or by the

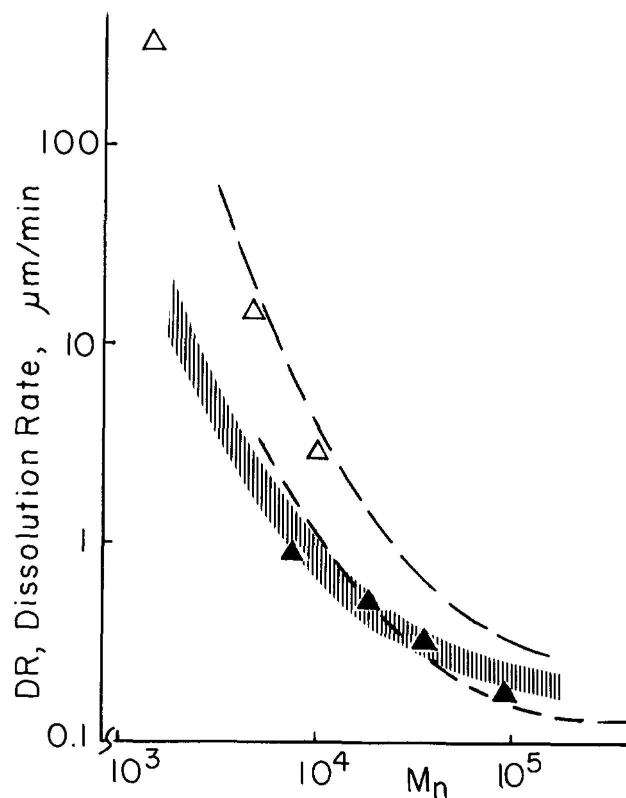

Figure 2 Dissolution rate data of Ouano[13] (triangles) and Greeneich[4] (shaded area) compare favourably with the present results (dashed lines). Ouano's rates have been multiplied by 100 and Greeneich's by 10. Hollow triangles and upper line are for exposed samples. Solid triangles and lower line are for unexposed samples. Greeneich did not distinguish between the two

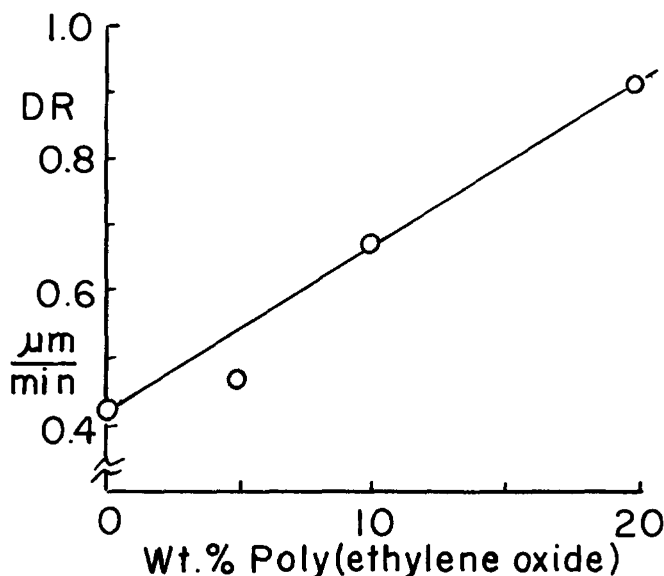

Figure 3 The addition of poly(ethylene oxide) to PMMA in the compatible range increases the dissolution rate linearly. The solvent used was MEK at 27.5°C

addition of a good solvent or swelling agent. Penetrants increase the mean distance between polymer chains and decrease cohesive interactions between chains. This results in an increase in segmental motion of the polymer and an increase in the dissolution rate.

The addition of 20% by weight Carbowax doubled the dissolution rate of the polymer film in MEK compared to the PMMA films (*Figure 3*). The values reported here are an average rate although the dissolution rate did increase as much as ten per cent during the film removal process. For example, with 10% Carbowax, DR initially was about 0.65 $\mu m\ min^{-1}$, but rose to about 0.70 $\mu m\ min^{-1}$ when the last 0.2 μm of the film was being dissolved. A possible reason for a slower dissolution rate near the surface is that some Carbowax may be volatilized during the drying of the resist film leaving a concentration gradient of plasticizer.

CONCLUSIONS

The results of the present study support Ouano's observation that PMMA degraded by electron bombardment dissolves faster than unexposed PMMA of the same measured molecular weight. The cause of the difference may well be microporosity from carbon dioxide and other volatile products of degradation. It takes a relatively large amount of poly(ethylene oxide) (20%) to change DR by a factor of 2. Thus it seems that lowering T_g by very small amounts (less than 1%) of liquid products of degradation is not sufficient to explain the difference between exposed and unexposed polymers of the same molecular weight.

The DR values of exposed and unexposed PMMA remain in the ratio of about 2.5 even at very low molecular weights (less than 10000). It stands to reason that the slope of the DR, molecular weight log–log plot could not conceivably remain constant down to molecular weights where the T_g approaches room temperature. Beevers and White[15] reported a T_g of $\sim$50°C for PMMA of molecular weight 2700. While there is some experimental evidence that DR varies with M_n or M_w to a power of about -0.4 or -0.5, the extension of this to molecular weights at which the polymer is almost liquid seems unlikely.

ACKNOWLEDGEMENTS

The authors thank C. C. Anderson for advice and assistance in polymerizations and molecular weight measurements. The National Research and Resource Facility for Submicrometer Structures at Cornell and the International Business Machines Corporation at East Fishkill both were of assistance.

REFERENCES

1 Thompson, L. F., Willson, C. G. and Bowden, M. J. (Eds.), 'Introduction to Microlithography', ACS Symp. Series 219, American Chemical Society, Washington, D.C., 1983
2 Ueberreiter, K. in 'Diffusion in Polymers', (Eds. J. Crank and G. S. Park), Academic Press, New York, 1968
3 Ouano, A. C. *Polym. Eng. Sci.* 1978, **18**, 306
4 Greeneich, J. S. *J. Electrochem. Soc.* 1974, **121**, 1669
5 Long, F. A. and Thompson, L. J. *J. Polym. Sci.* 1954, **14**, 321
6 Hopfenberg, H. B., Nicolais, L. and Drioli, E. *Polymer* 1976, **17**, 195
7 Sfirakis, A. and Rogers, C. E. *Polym. Eng. Sci.* 1981, **21**, 542
8 Thomas, N. L. and Windle, A. H. *Polymer* 1978, **19**, 255
9 Vrentas, J. S. and Duda, J. L. *Macromolecules* 1976, **9**, 785
10 Crank, J. 'The Mathematics of Diffusion', 2nd Edn., Clarendon Press, Oxford, 1975
11 Ouano, A. C. and Carothers, J. A. *Polym. Eng. Sci.* 1980, **20**, 160
12 Adesida, I., private communication, Cornell University, 1983
13 Ouano, A. C. in 'Polymers in Electronics', ACS Symp. Series 242, (Ed. T. Davidson), American Chemical Society, Washington, D.C., 1984, p. 79
14 Heavens, O. S. 'Optical Properties of Thin Films', Butterworths, London, 1955
15 Beevers, R. B. and White, E. F. T. *Trans. Faraday Soc.* 1960, **56**, 744
16 Stillwagon, L. in 'Polymer Materials for Electronic Applications', ACS Symp. Series 184, (Eds. E. D. Feit and C. Williams, Jr.), American Chemical Society, Washington, D.C., 1982, p. 19