# Low stress development of poly(methylmethacrylate) for high aspect ratio structures

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Magnetic head fabrication for $>100$ Gbit/in.$^2$ areal density requires minimum lithographic feature size $<0.15$ $\mu$m, with aspect ratios of 8:1–10:1. Electron-beam lithography can provide adequate resolution for research and development of magnetic heads, and at 100 kV can provide greater than 10:1 aspect ratios in 1–3 $\mu$m thick single-layer resist poly(methylmethacrylate). Poly (methylmethacrylate) (PMMA) is well known for withstanding the rigors of plating baths, but at these thicknesses requires a nonswelling, low-stress developer such as the LIGA mixture (also known as "GG Developer (U.S. Patent No. 4,393,129)"). In this work we present the results of isopropyl alcohol:water development for thick PMMA, and describe the dependence of resist contrast on the temperature of the developer. We also demonstrate the advantage of ultrasonic agitation during development. These development techniques have brought resist profiles in PMMA to the theoretical limit predicted by Monte Carlo simulations. © *2002 American Vacuum Society.*
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## I. INTRODUCTION

Rapidly decreasing dimensions of magnetic read/write heads, along with improvements in magnetic media, servo controls, and error correction, have lead to dramatic increases in the areal density of magnetic disks.[1] This storage density has sustained annual increases of 60% during the last 5 yr, largely due to shrinking dimensions in the read/write head.[1] Current commercial disk drives have a storage density of 17 GBit/in.$^2$ with minimum write head track width or pole tip features of 0.60 $\mu$m. Requirements for the 3–5 yr range include 0.15 $\mu$m wide pole tips for $>100$ GBit/in.$^2$ disks. In addition, sufficient confinement of magnetic fields requires the pole tip to have an aspect ratio of 8:1–10:1, which is achieved by plating magnetic material through the resist. Magnetoresistive read/write heads for magnetic disks are fabricated with the same techniques and equipment as integrated circuit semiconductors, with feature sizes down to the submicron range.

Lithographic minimum feature size for magnetic head production has to date lagged behind that of semiconductors. Although photolithography for heads is still dominated by *I*-line steppers, the rate of decrease in feature sizes is much more rapid than in the semiconductor industry. Critical dimensions for heads are expected to overtake those of semiconductors by 2006. To sustain a 60% annual areal density growth, head development is turning to electron-beam lithography for rapid prototyping and process development.

Figure 1 shows a schematic of a magnetoresistive thin-film head, shown in cross-section and also from the air bearing view; that is, the view of the read/write head as seen from the disk platter. The top yoke of Ni–Fe [Fig. 1(b)] requires a high aspect-ratio plating stencil. For sufficient transmission of magnetic flux, this upper pole must have an aspect ratio around 8:1. Resist for plating Ni–Fe must then have an aspect ratio greater than 10:1 in 2–3 $\mu$m resist, presenting a challenge for lithography. Write head pole tips currently shipping with 0.6 $\mu$m features are expected to shrink to 0.15 $\mu$m for production of 100 GBit/in.$^2$ disks by 2005.

Pole tips are fabricated by plating Ni–Fe through a patterned polymer. The choice of polymer is influenced by the following requirements: (1) the polymer must have good adhesion to the plating seed layer to avoid metal "underplating" beyond the line edge; (2) the plating stencil must remain stable in the acidic plating bath; (3) the polymer must be easily removable after plating; (4) additives such as solvents and acid catalysts must not react with the seed layer; (5) plasma cleaning of the trench, if necessary, must not oxidize the seed layer to the extent that the surface is no longer conducting; and (6) the polymer film must have low stress and must not swell or crack during development.

Poly(methylmethacrylate) (PMMA) works well with Au plating baths, and is similarly well suited to plating Ni–Fe. Epoxy resists as SU8 are precluded because of the difficulty in stripping the resist. Requirement 5, oxidation of the seed layer, is a concern when oxygen is used to transfer a pattern through a planarizing polymer; but fortunately use of PMMA avoids the issue by providing a 10:1 aspect ratio in a single layer of resist. Requirement 6 precludes the use of the e-beam resist ZEP (Nippon Zeon Co.) in a single-layer scheme, since $>2$ $\mu$m thick films of ZEP swell and crack during development. PMMA is one of the few materials which satisfies all these requirements, and provides the simplicity of single-layer resist processing.
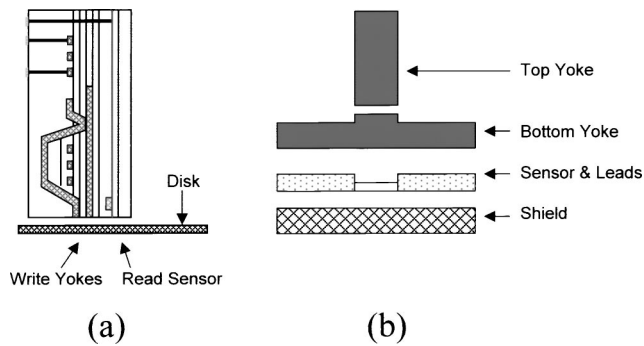
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FIG. 1. Magnetoresistive head (a) as a cross section with the magnetic disk spinning in/out of page, (b) viewed from the air bearing surface; that is, looking up from the disk. The top yoke of Ni–Fe requires a high aspect-ratio plating stencil.



FIG. 2. Cross section and top surface of 2 $\mu$m thick PMMA after exposure of lines and development for 10 min in 1:9 MIBK:IPA. Swelling of the resist has closed off the lines at the top surface.

Multilayer resist schemes may also meet these requirements. A typical combination is a thick bottom layer of hard-baked novolak photoresist, covered with a thin image transfer layer of $SiO_2$ or Ge, covered with a thin imaging layer. The pattern is written in the top layer and then transferred down using reactive ion etching. While the use of a thin imaging layer is necessary when using 248 nm photolithography, 100 kV electron beam exposure tools have such a large depth of focus that we can avoid the complexity of multilayer resist processing. This process simplicity is the primary advantage of electron-beam resist over photolithography for rapid development of magnetoresistive heads.

In this article we will present a comparison of PMMA development techniques and their effects on the dimensional control of high aspect-ratio structures.

## II. COMPARISON OF DEVELOPERS

For a comparison of resist contrast in various developers, 950 K molecular weight PMMA was exposed with a dose bracket pattern using 100 kV electrons at a beam current of 170 nA. Three types of developers are compared: mixtures of methyl isobutyl ketone (MIBK) and isopropanol (IPA), the "LIGA" developer,[2] and mixtures of IPA and water.

One of the best developers for thick PMMA is the "LIGA" mixture[2] consisting of 2-(2-butoxyethoxy) ethanol, morpholine (tetrahydro-1,4-oxazine), ethanolamine (amino-ethanol), and water. The LIGA mixture provides a nonswelling developer which works well for both x-ray and electron-beam exposure. Unfortunately, the components are highly toxic, carcinogenic, and mutagenic.

The second candidate is the widely used solvent/nonsolvent combination MIBK:IPA. MIBK is a strong solvent for PMMA, and IPA dilutes and weakens the developer. Although commonly referred to as the "nonsolvent," IPA is more precisely a very weak solvent for low molecular weight PMMA. At lower doses the electrons break up the polymer into low molecular weight components, which are preferentially dissolved by developer. At much higher doses a competing reaction crosslinks the PMMA chains to form a negative-acting resist. By itself, IPA cannot fully develop thick PMMA at any dose, since the electrons begin to
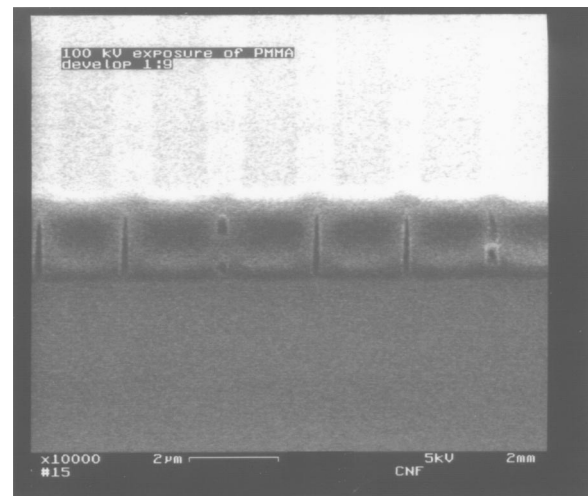
crosslink the polymer before the average molecular weight is low enough for dissolution. Although IPA has been used for high resolution development of very thin (40 nm) PMMA layers,[3] more typically MIBK is mixed with the IPA to open a window between positive acting (chain scission) and negative acting (crosslinking) behavior. For PMMA of thickness less than roughly 1 $\mu$m, this combination provides resolution in the 10 nm range for the thinnest layers. Unfortunately MIBK causes the resist to swell, and narrow lines (slots) in thick PMMA layers ($\gtrsim$2 $\mu$m) will close off as they develop, as shown in Fig. 2. The resist cross section shown in Fig. 2 is the result of developing a 2 $\mu$m thick film of PMMA in 1:9 MIBK:IPA for 10 min. This very dilute mixture has developed the lines down to the substrate, but has swollen shut the top surface. This swelling exaggerates the undercut resist profile and reduces resolution. Other high-resolution developers, such as mixtures of MIBK, MEK, and Cellosolve[4] work well for thin resist ($<$1 $\mu$m) but will cause similar swelling problems in thick layers of PMMA. Since any strong solvent is likely to swell the unexposed resist, we consider next what other additive might give IPA a slight improvement.

The third developer candidate is the unlikely combination of IPA and water. Taken separately, neither IPA nor water is an effective solvent of PMMA. In fact, water has no effect at all on exposed or unexposed PMMA. The mixture of water and IPA acts as a so-called cosolvent, with a solvent strength larger than either separate component. The mechanism of this effect is uncertain, but has been attributed to a modification of the alcohol molecule in the presence of water or alternatively to the interaction of water with the PMMA carbonyl group.[5] In either case the presence of the highly polar water molecule improves the solvent action of IPA.

Contrast measurements using these three types of developers are shown in Fig. 3. Samples of 1.7 $\mu$m thick PMMA were exposed at 100 kV and developed for 4 min in each developer. The popular mix of 1:3 MIBK: IPA provides a contrast[6] of 4.2 LIGA developer provides a slightly higher
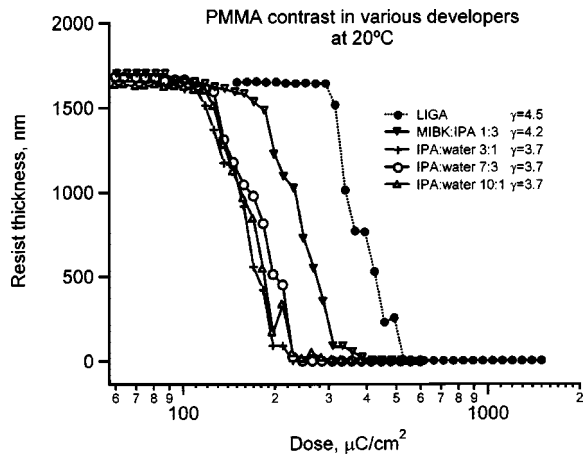
FIG. 3. PMMA thickness vs dose for comparison of contrast (g) and sensitivity for development in MIBK:IPA 1:3 (10 min), the LIGA mixture (4 min), and various ratios of IPA:water (4 min). All measurements were taken at 20 °C. Exposures conducted at 100 kV.

contrast of 4.5, with a sensitivity at half thickness of 350 $\mu C/cm^2$. Various mixtures of IPA and water provide higher sensitivity, 160 $\mu C/cm^2$ at half thickness, but the lower contrast of 3.7. Figure 3 also shows that the contrast and sensitivity of PMMA in IPA/water developer remains unchanged over a broad range of mixture ratios, from 10% to 25% water in IPA. Other researchers have found more pronounced differences in contrast and sensitivity as a function of IPA/water ratio, when using lower voltage electrons and much lower molecular weight PMMA.[7] For 950 K molecular weight PMMA exposed at 100 kV, our measurements show that IPA/water has the practical benefit that contrast and sensitivity are relatively insensitive to solvent mixture.

## III. TEMPERATURE DEPENDENCE OF CONTRAST

We can match or even exceed the LIGA developer contrast (4.5) by cooling IPA/water developer, at the price of lower sensitivity. Figure 4 shows the contrast and sensitivity for 3:1 IPA: water at temperatures from 0 to 20 °C. At 10 °C the sensitivity matches that from LIGA developer, and the contrast is higher, 5.0. At 0 °C the contrast is 6.1 and the
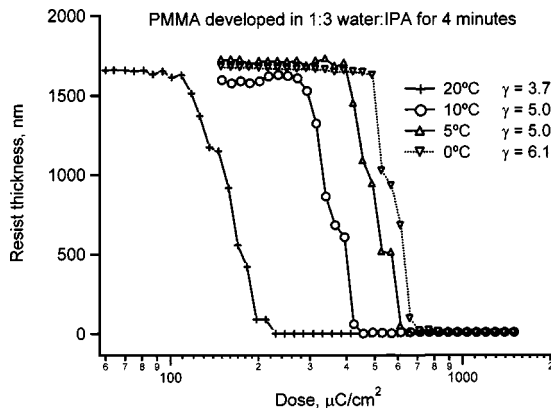


FIG. 4. Temperature dependence of contrast and sensitivity for PMMA developed in 1:3 water:IPA for 4 min.
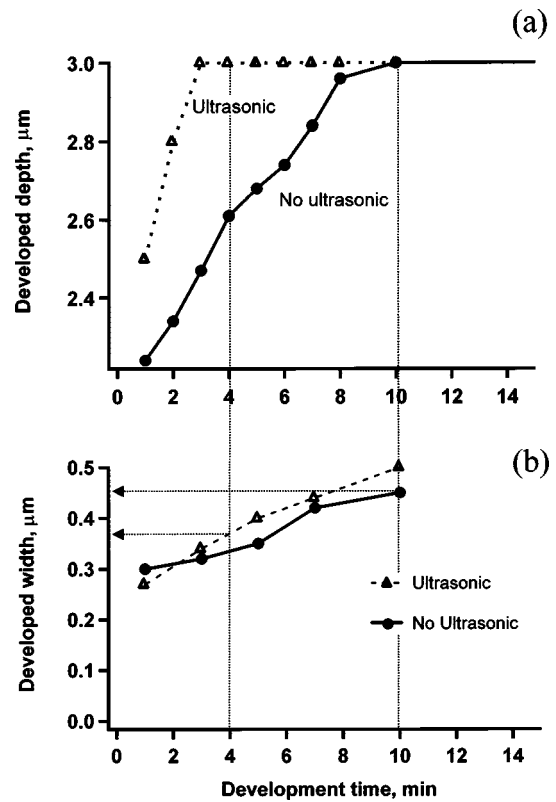
FIG. 5. (a) Developed depth of narrow lines vs time with and without use of ultrasonic agitation during development in IPA:water 3:1. Lines are fully developed after 4 min when using ultrasonic agitation, but require 10 min without. Vertical lines are shown at these two development times. (b) Developed width of narrow lines vs time, with and without ultrasonic agitation, showing the improvement in linewidth due to the shorter development time.

sensitivity has dropped significantly to 560 $\mu C/cm^2$. LIGA developer can also be cooled to increase contrast,[8] but the resist becomes even less sensitive. By cooling IPA/water to 10 °C we can operate in a contrast/sensitivity regime similar to that of 20 °C LIGA developer.

## IV. DEVELOPMENT WITH ULTRASONIC AGITATION

A problem with the development of high aspect ratio profiles is the lower dissolution rate for exposed resist in deep structures. Lavallée *et al.*[9] have reported that holes in PMMA with a diameter less than 100 nm cannot be cleared well with IPA/water developer. Yasin *et al.*[10] have solved this problem in thin layers of PMMA by using ultrasonic agitation during development. While it has been shown that ultrasonic agitation is helpful in clearing the exposed resist[11] and results in high resolution patterns in thin PMMA,[10] it has not been shown that this improves resolution in thick resist. We show here that ultrasonic agitation does improve resolution in thick resist by considering the effect of development time on linewidth.

Figure 5 shows the development rate in 3:1 IPA/water of 3 $\mu m$ thick PMMA, exposed with a pattern of narrow lines at 100 kV. The plot shows the developed depth versus time of narrow, widely spaced lines (as-defined width of 0.1 $\mu m$, pitch 2 $\mu m$) developed either with or without ultrasonic agi-
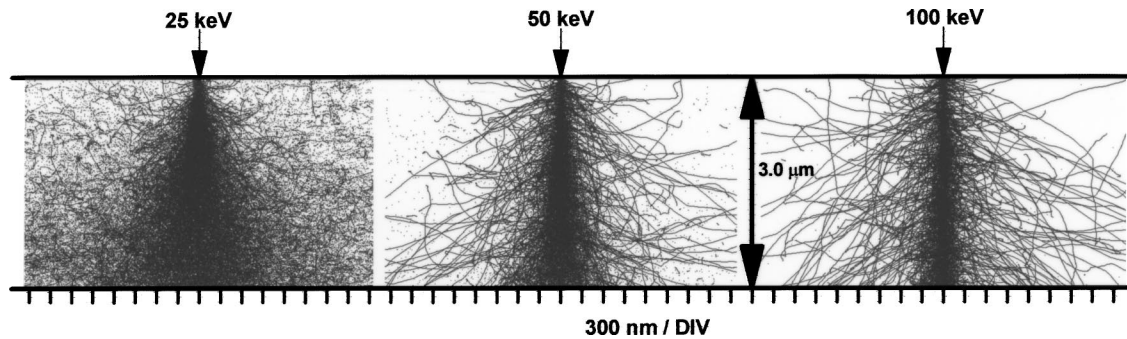
FIG. 6. Monte Carlo simulation of the secondary electron distribution at 25, 50, and 100 keV, using 6000, 15 000, and 30 000 electrons, respectively. The distribution shows that the maximum achievable aspect ratio in 3 $\mu$m thick resist at 100 keV is about 10:1, and drops of significantly for 50 keV exposure to about 5:1, and in the range of 2:1–3:1 at 25 keV.

tation. While the clearing dose for large features is 1 mC/cm$^2$, an exposure for narrow lines of 4.2 mC/cm$^2$ was used to minimize development time. Using simple dip development, the time needed to clear 3 $\mu$m deep trenches was 10 min. Ultrasonic agitation reduced this time to 4 min. By measuring the developed linewidth as a function of development time [Fig. 5(b)] we see that the shorter development time reduces linewidth by 18%; that is, from 0.45 to 0.37 $\mu$m.

## V. SIMULATIONS AND RESULTS

The maximum achievable aspect ratio is limited by the so called forward scattering of the primary electron beam as it passes through the resist towards the resist–substrate interface, neglecting the effect of backscattered electrons for the exposure of an isolated resist line. The aspect ratio in thick resist is defined here as the ratio of the total resist thickness to the width of the exposed line at the resist–substrate interface, since the actual developed linewidth is a function of the position in the resist. The linewidth at the resist–substrate interface is also the most critical linewidth as far as the magnetic head device is concerned. The developed positive resist line profile shows a lightly reentrant resist profile, as seen in Fig. 7, which results in a narrower linewidth at the top of the resist. The diameter of the finely focused electron beam at the top of the resist is typically less than 10 nm and spreads less than 10 nm over a 3 $\mu$m resist thickness due to depth of focus effects. However, the width of the exposure profile in the resist is primarily determined by elastic scattering of the primary electrons and the range of the fast secondary electrons generated as the primary electrons interact with the resist. The fast secondary electron distribution in 3 $\mu$m thick PMMA resist has been simulated with Monte Carlo modeling.[12] Figure 6 shows the secondary electron distribution at 25, 50, and 100 keV primary electron energy using 6000, 15 000, and 30 000 electrons, respectively. The distribution shows that the maximum achievable aspect ratio in 3 $\mu$m thick resist at 100 keV is about 10:1, and drops of significantly for 50 keV exposure to about 5:1, and in the range of 2:1–3:1 at 25 keV. This trend is in agreement with previ-

ous work on the fabrication of x-ray masks.[13] Experimental results using IPA/water ultrasonic development at 5 °C show that we are operating near the predicted limit, with an aspect ratio of 10:1 (Fig. 7).
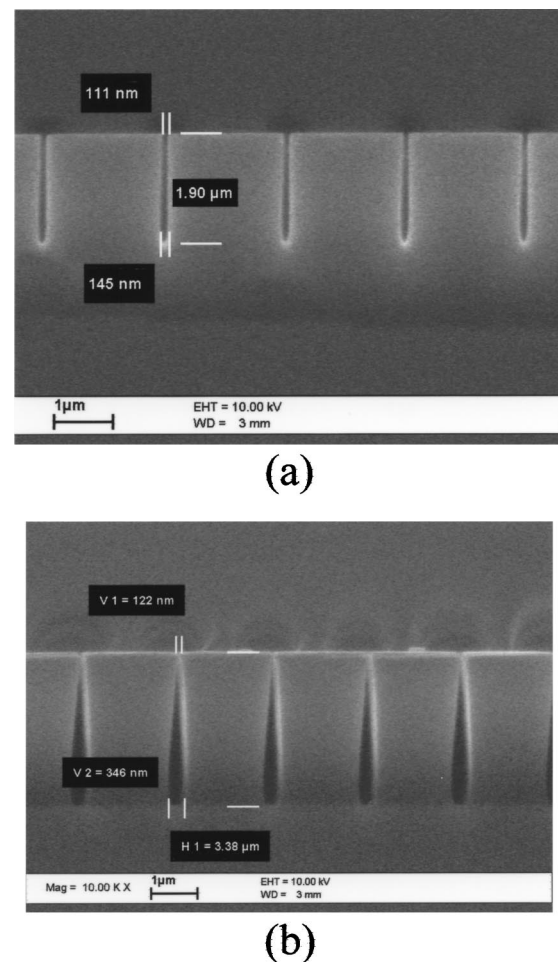


(a)



(b)

FIG. 7. PMMA resist profiles after development in 3:1 IPA:water, with ultrasonic agitation, for (a) 1 min and (b) 10 min. Lines were exposed with 20 passes spaced at 5 nm (100 nm as defined) with ~8 nm diam spot at 100 kV. Micrographs were taken with low current (~10 pA) and fast acquisition times (~2 s) to avoid resist deformation. Using a linewidth measured at the bottom, the aspect ratio width:depth is: (a) 13:1 and (b) 10:1.

## VI. SUMMARY

Magnetic head requirements for high aspect ratio pole tips have been met using single-layer PMMA exposed at 100 kV. We have demonstrated 14:1 aspect ratios in resist, using cooled mixtures of IPA and water and ultrasonic agitation. These resist profiles are useful for the fabrication of magnetic pole tips, and for such applications as high density interconnect lines. IPA/water development matches the resolution and contrast of the LIGA developer, without the use of highly toxic chemicals. Temperature control of the developer provides a convenient way to trade off between contrast and sensitivity. We have demonstrated that ultrasonic development improves the linewidth and aspect ratio of resist profiles. Monte Carlo simulations show that we are approaching the limit of aspect ratio for 100 kV e-beam exposures.

## ACKNOWLEDGMENTS

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