Optimal temperature for development of poly(methylmethacrylate)

Bryan Cord, a Jodie Lutkenhaus, and Karl K. Berggren
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139-4309

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The authors have investigated a range of poly(methylmethacrylate) (PMMA) development temperatures as low as −70 °C and characterized their effect on the resolution of PMMA as an electron resist. The results show that cooling, in addition to reducing the sensitivity of the commonly used positive-tone mode of PMMA, also increases the sensitivity of its less commonly used negative-tone mode. They have shown that the resolution-enhancing properties of cold development peak at approximately −15 °C as a result of these competing sensitivity changes. At lower temperatures, the high doses required to expose the resist produce significant cross-linking of the polymer, altering its solubility properties and sharply degrading the contrast. If the correct development temperature is used, however, sub-10 nm features are readily achievable in PMMA-based scanning electron-beam lithography. © 2007 American Vacuum Society. [DOI: 10.1116/1.2799978]

INTRODUCTION

The relatively recent discovery that cold development of poly(methylmethacrylate) (PMMA) resist substantially enhances its contrast has provided scanning electron-beam lithography (SEBL) with a correspondingly substantial resolution boost.1–3 Using cold development, structures with dimensions on the order of 10–15 nm can be readily fabricated on relatively inexpensive 30 keV SEBL tools. Unfortunately, extending SEBL past this resolution and into the sub-10 nm regime has proven difficult, even when cold development is used. While development temperatures as low as −17 °C have been previously studied,4 no published work exists examining the behavior of PMMA at lower temperatures. The resolution-enhancing effect of cold development seems to improve with decreasing temperature, leading to speculation that development in the temperature regime between −17 and −80 °C (the approximate developer freezing point) may increase resolution even further and allow arbitrary sub-10 nm patterning with SEBL. Unfortunately, our detailed investigation of this temperature regime has shown that, below a certain temperature, cold development actually reduces the resolution of PMMA substantially, with maximum resolution occurring in a very narrow temperature range.

Cold development, a cheap and simple process where an electron resist is simply developed below room temperature, has been a key recent breakthrough in SEBL resolution enhancement. When used with chain-scission-based electron resists (such as PMMA and ZEP), cold development has the effect of “freezing out” the polymer chains that have been partially exposed at the edges of a feature due to scattering of the primary beam. These partially exposed chains readily develop away at room temperature, but become locked in place when developed below a certain threshold temperature (thought to be the glass transition temperature, but possibly the theta/Flory temperature at which the polymer becomes uncoiled), reducing feature bias and enhancing resist contrast and resolution, particularly at the lower beam voltages used on less-expensive SEBL tools.4 These advantages come at the expense of a decrease in sensitivity (requiring a higher electron dose to cause enough chain scission for the resist to develop away at reduced temperatures) and a corresponding increase in exposure time. Despite this reduction in sensitivity, the ease of use, low cost, and demonstrable resolution enhancement have made cold development an invaluable tool in the electron-beam lithographer’s toolbox.

Using a combination of thermoelectric chillers and dry-ice baths, we have investigated the resolution of PMMA in our 30 keV Raith-150 SEBL tool at development temperatures ranging from 15 to −70 °C, a much wider range than any previous work. The results show a well-defined limit to the resolution-enhancing effect of cold development. Below a certain temperature, the dose required to fully expose the resist is so high that cross-linking of the polymer during exposure becomes significant, altering the morphology of the PMMA molecules and sharply degrading the contrast. As a result, when using a standard developer solution of 3:1 isopropanol:methyl-iso-butyl-ketone (IPA:MIBK), a development-temperature “sweet spot” can be defined at approximately −15 °C, a point cold enough to cause maximum freeze-out of partially exposed resist but not so cold that it pushes the exposure threshold into the cross-linking regime. Fortunately, we find that fabrication of features smaller than 10 nm is both possible and relatively straightforward at this temperature.

EXPERIMENTAL SETUP

PMMA was the only electron resist used in this work, although we expect the results also apply to the ZEP resist family since the exposure mechanisms of the two resists are similar. All samples were exposed on a Raith-150 SEBL tool at an accelerating voltage of 30 keV and developed in a 3:1 solution of IPA:MIBK at various temperatures.

aElectronic mail: bcord@mit.edu
Contrast measurements were performed by exposing a series of $20 \times 100 \ \mu \text{m}^2$ bars in a 160-nm-thick PMMA film at various doses, and developing for a fixed time. The thickness of the resist remaining after development was then measured using a profilometer. At higher electron doses, significant postexposure contraction of the PMMA film was observed, resulting in a reduction in thickness even before development.

The mechanism of this contraction is unknown, but is thought to be due to the local density of the polymer being increased by severe cross-linking. As a result, accurate measurement of the amount of resist removed during development required the thickness of the exposed features to be measured both before and after the sample was developed, rather than assuming an identical initial thickness for each bar. It should be noted that this effect was negligible (within the measurement uncertainty) for all temperatures at which quantitative data were taken; it only becomes significant at extremely low temperatures where full development is nearly impossible.

Figure 1 shows the contrast curves measured for PMMA at development temperatures ranging from 15 to $-65 \ ^\circ \text{C}$. As expected, the sensitivity of the resist decreased as the temperature was reduced. Correspondingly, the curves measured at $-20 \ ^\circ \text{C}$ and below show incomplete development occurred at higher doses, where cross-linking of the polymer film reduced the development rate and caused the PMMA to behave as a negative-tone resist. The sensitivity of this negative-tone behavior showed a temperature dependence opposite that of the positive-tone PMMA sensitivity; at low temperatures its onset occurred at lower exposure levels. As the development temperature was reduced, the positive- and negative-tone dose thresholds were observed to approach one another and eventually intersect, at which point full development of the resist was impossible (Fig. 2).

This effect can be explained by examining the behavior of PMMA during electron-beam exposure and development. In the ideal case, a film of long PMMA polymer chains undergoes localized chain scission when exposed to an electron beam, resulting in a reduction of the average chain length and molecular weight in the exposed region. When placed in mild organic solvents, the solubility of PMMA is highly

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dependent on its molecular weight, leading to its character-
istically high contrast as an electron-beam resist. This
simple model is sufficient in most typical SEBL situations,
but fails to take cross-linking, a parallel process by which
two PMMA chains are fused together during electron-beam
exposure, into account. At the doses typically used to expose
PMMA for room-temperature development, chain scission
dominates and cross-linking events are negligible. At the
higher doses required to fully expose PMMA at temperatures
below −20 °C, however, cross-linking, rather than scission,
starts to play a larger role, increasing the molecular weight
and reducing the development rate to the point that negative-
tone behavior is observed in the resist. The common mini-
mum shared by all the curves in Fig. 1 indicates by the gray
bar shows the approximate dose at which this crossover
from positive-tone to negative-tone behavior occurs.

The contrast of PMMA at the various development tem-
peratures can be calculated from the data in Fig. 1 by using
the formula \( \gamma = \left[ \log \left( \frac{E_f}{E_i} \right) \right]^{-1} \), where \( \gamma \) is the contrast, \( E_f \) is
the dose at which the resist is completely developed away,
and \( E_i \) is the dose at which the resist thickness is 75% of its
predevelopment value. As previously discussed, the prede-
velopment thickness of the resist had to be measured sepa-
ately, as some thickness reduction occurs during exposure at
extremely high doses, but this turned out to be negligible in
the temperature regime in which it was possible to measure
contrast. The contrast values for the 15 to −30 °C tempera-
ture range are plotted in Fig. 3. In the range between 15 and
−15 °C, cold development provides the resist with a notice-
able increase in contrast. At −20 °C and below, however, the
contrast drops off sharply and the benefits of cold develop-
ment quickly disappear.

The explanation for this behavior once again lies in the
fact that PMMA undergoes significant cross-linking when
exposed to high electron doses. Cross-linking fundamentally
alters the morphology of the PMMA molecule, changing the
PMMA molecules from linear to branched polymers in addi-
tion to increasing the molecular weight. The solubility/
molecular weight relationship critical to the high contrast of
PMMA relies on the fact that PMMA is a linear molecule;
adding a significant percentage of cross-linked, branched
polymers to the film complicates the dissolution of the ex-
posed resist during development. At the doses required to
develop PMMA in 3:1 IPA:MIBK at temperatures below
−20 °C, the positive- and negative-tone dose regimes are
very close together and a significant amount of cross-linking
has taken place in the exposed PMMA, resulting in a de-

\[ \text{FIG. 3. Resist contrast function } \gamma \text{ as a function of temperature, derived from }
\text{the slope of the contrast curves in Fig. 2. Three temperature regimes are visible in the plot: In region I, contrast is degraded by development of }
\text{partially exposed resist at the edges of the exposure area. In region II, these }
\text{partially exposed polymer chains are frozen in place, enhancing contrast. In }
\text{region III, the presence of increasing amounts of cross-linked PMMA hin-
\text{ders the development process of highly dosed resist and sharply degrades }
\text{the contrast. From this chart, the optimal range of development temperatures }
\text{appears to fall between 0 and −15 °C, with optimum contrast occurring at }
\text{−15 °C.}
\]
increased dependence of the dissolution rate on electron dose and a correspondingly sharp drop in the contrast below −20 °C.

Using these contrast measurements, it is possible to define three distinct temperature regimes of PMMA development. The “warm” regime between 5 and 15 °C is the range where cross-linking is negligible, but resolution is limited by development of the partially exposed resist at the edges of the exposed area. In the “cold” regime between 5 and −20 °C, this spurious development is decreased but cross-linking is still negligible, leading to optimal resolution. In the “too cold” regime, between −20 °C and about −50 °C, an increasing amount of cross-linking in the exposed resist negates the contrast boost from freeze-out of the partially exposed resist and sharply decreases the contrast. Below about −50 °C, the sensitivity of PMMA is so low that it becomes impossible to develop the resist at all; the competition between chain scission and cross-linking will not allow the molecular weight to be reduced enough for any dissolution to occur.

RESOLUTION MEASUREMENT

Contrast measurements are not always a good indicator of real-world resolution, so we attempted to pattern extremely fine structures in each of the first three temperature regimes to determine the dependence of lithographic resolution on temperature. Several silicon substrates were coated with 30 nm of evaporated SiOx and 85 nm of PMMA, and then exposed using a pattern consisting of an array of 1 × 1 μm² gratings of single-pixel lines at pitches ranging from 20 to 100 nm. The array was repeated for a wide array of doses over a total area of approximately 300 μm². The samples were then developed in 3:1 IPA:MIBK for 30 s at various temperatures. Directly imaging PMMA in a scanning electron microscope (SEM) is problematic, so a two-step reactive ion etch process was used to transfer the exposed pattern into the substrate before imaging. A CF4-based etch was first used to pattern the SiOx layer, which was then used as a hard mask for a Cl2 etch of the underlying silicon. The resulting trenches were then examined with a SEM (Fig. 4).

The results of this experiment correlated qualitatively with the contrast measurements in Fig. 3, with the minimum achievable linewidth decreasing with temperature down to about −15 °C, then sharply increasing at −30 °C. The micrographs of the −30 °C sample in Fig. 4 also show significant nonuniformity and bridging, symptoms of sloped resist profiles resulting from the low contrast. At −15 °C, sub-10 nm linewidths were readily achievable at pitches of 40–100 nm. Interestingly, the minimum yieldable grating pitch was not significantly affected by development temperature. Further work is required to understand the origin of this effect, which may be related to resist adhesion, our etch process, or some other factor.

CONCLUSION

The central result of this work is that developing PMMA in 3:1 IPA:MIBK at reduced temperatures gives an increase in lithographic resolution only up to a point: below −20 °C, the doses required to expose the resist are so high that cross-linking in the exposed PMMA becomes significant, reducing solubility and degrading the resist contrast. The optimum development temperature is the point where maximum freeze-out of the partially exposed chains at the edges of the feature occurs, but the sensitivity is still high enough to avoid cross-linking during the resist exposure process. This high-contrast “sweet spot” occurs at approximately −15 °C; for maximum resolution, PMMA should always be developed at or near this temperature when using 3:1 as a developer. When PMMA is developed at the proper temperature, sub-10 nm features are readily achievable with a 30 keV SEBL tool, a resolution that can be difficult to achieve on even a high-end 100 keV SEBL system using conventional development techniques.

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