Investigation of Very Low Temperature Development of PMMA

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Recent work in enhancing the contrast of chain-scission-type electron beam resists has shown potential for exceeding the previously-accepted resolution limits of scanning electron-beam lithography (SEBL). In particular, the investigation of the behavior of PMMA and similar resists when developed below room temperature has yielded substantial improvements in both the contrast and final resolution of low-voltage SEBL.^{1,2} The mechanism behind this contrast enhancement is thought to be a "freeze-out" of polymer chains at the edges of the nominal exposure that are partially exposed due to beam scattering. When cooled below their glass transition temperature, these chains cannot develop away, reducing process bias and resulting in a much smaller final feature size.

While development temperatures down to -17C have been thoroughly investigated, examination of the glass transition data for PMMA suggests that further cooling may lead to even greater resolution enhancement (figure 1). Using a dry-ice-based system, we have been able to develop PMMA at temperatures as low as -70C, very close to the freezing point of the developer.

The low-temperature sensitivity measurements in figure 1 show that, below a temperature of approximately -20C, the development behavior of PMMA changes dramatically. The sensitivity of PMMA at temperatures above this point shows a clear temperature dependence, consistent with the hypothesis that PMMA will develop away when the developer temperature is higher than its glass transition temperature. In the regime below -20C, however, the sensitivity shows no temperature dependence at all, saturating to a fixed point. We believe this behavior to be the result of disentanglement of the exposed PMMA. When enough chain scission events have occurred, the average molecular weight of the PMMA falls below its critical entanglement weight, and the resist readily dissolves in developer regardless of its glass transition temperature.

We will present a new model for PMMA development, based on the interplay of molecular entanglement, polymer reptation, and the glass transition temperature, to fully characterize the low-temperature behavior of PMMA. We will also use this model to examine the contrast enhancement of PMMA at very low development temperatures and identify possible methods for increasing the contrast even further.

¹ W. Hu, K. Sarveswaran, M. Lieberman, G. Bernstein, J. Vac. Sci. Technol. B 22(4), 1711 (2004)

² L.E. Ocola, A. Stein, J. Vac. Sci. Technol. B **24**, 3061 (2006)



Figure 1: Plot of the minimum dose required to develop away a 180 nm thick PMMA layer after 60 seconds of immersion in a 3:1 IPA:MIBK solution at various temperatures. The sensitivity shows a clear temperature dependence above -20°C but saturates to a constant value at lower temperatures.