Development Characteristics of Polymethyl Methacrylate in Alcohol/Water Mixtures

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Poly methyl methacrylate (PMMA) is the most widely used resist in electron beam lithography. This paper reports on the study of development characteristics of PMMA in methanol, ethanol and isopropanol (IPA) mixtures with water as developers. We have found that ethanol/water mixtures at a 4:1 volume ratio are an excellent, high resolution, non-toxic, developer for exposed PMMA and GL-2000 resist.

Ethanol is much less hazardous than both methyl isobutyl ketone (MIBK) and IPA (traditional PMMA developers), as it has been historically consumed by cultures all around the world as part of alcoholic beverages. As a developer, ethanol had been used in combination with other solvents [1] or as "95%" ethanol [2, 3]. No detailed study of ethanol-water mixtures as a developer for PMMA has been previously reported as far as we have investigated.

We also have found that the proper methodology to use so that contrast data can be compared to techniques used in polymer science is not to rinse the developed resist but to immediately dry with nitrogen. Samples were prepared from a single 4" silicon wafer coated with 260 nm of 950K PMMA, baked at 180 ^{o}C for 3 min. The electron beam exposures were carried out on a JEOL 9300FS 100 KV tool. A series of 200 μm x 150 μm rectangular areas were exposed using a non-linear dose array comprising of 60 doses that covered a dose range from 100 μC/cm^2 to 3300 μC/cm^2. Each contrast curve was fit to an empirical equation modified from prior work [4]: $NRT = C_o - e^{-\boldsymbol{S}(D-\boldsymbol{D_c})}$ where: NRT is the normalized resist thickness; C_o is a constant ~ 1; $\boldsymbol{S}$ is a factor related to resist contrast; $\boldsymbol{D}$ is dose; and $\boldsymbol{D_c}$ is the dose to clear. Figures 1 and 2 show the $\boldsymbol{Dc}$ and $\boldsymbol{S}$ as a function of alcohol volume concentration. Figure 3 shows an example of high resolution results using ethanol / water developer at a 4 to 1 ratio. Our results show that ethanol/water developer has lower dose to clear and higher contrast than IPA/water developer.

Details on the interpretation of these plots, comparison to cosolvency data and preliminary Raman spectra analysis will be discussed. Our results show how powerful simple lithographic techniques can be used to study ternary polymer solvent solutions when compared to other techniques found in the literature. The impact of the understanding these interactions may open doors to a new family of developers for other electron beam resists that can reduce the toxicity of the waste stream. We have already tested Ethanol:Water in 4:1 volume ratio on GL-2000-12 resists (similar to ZEP 520A) with good resolution. Other resists to follow.

References:

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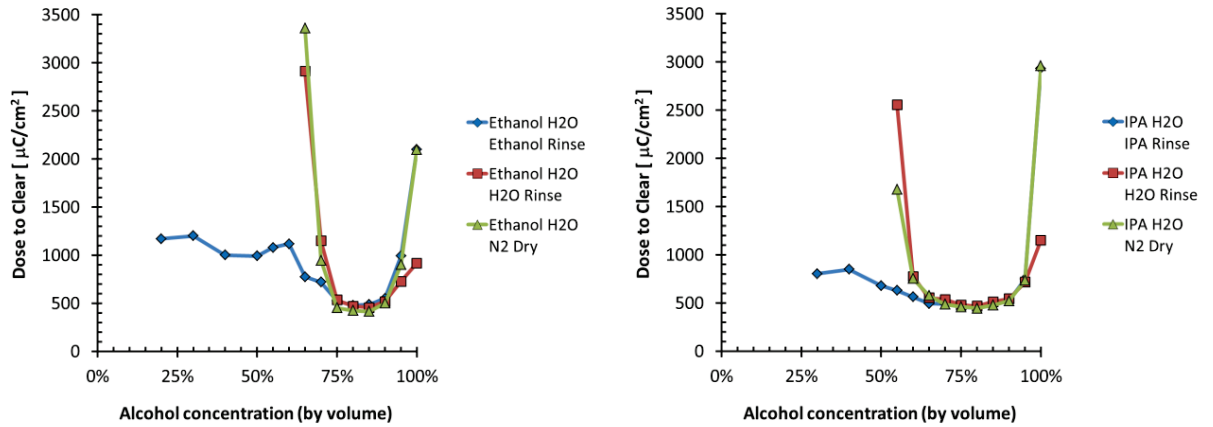


Figure 1. Dose to clear of ethanol/water and isopropanol/water developers under no rinse (N2 dry) or rinse with alcohol or water vs alcohol volume concentration. (Left) Ethanol data. (Right) Isopropanol data.

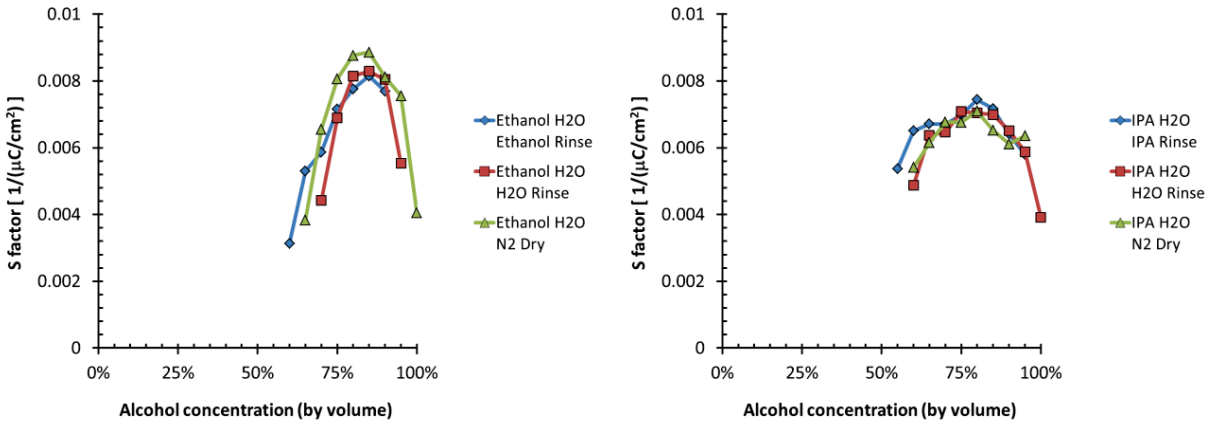
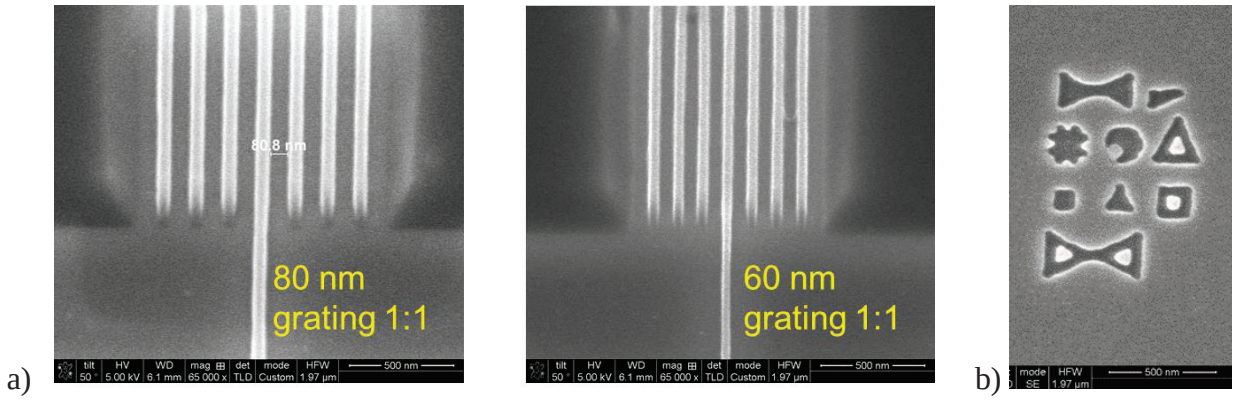


Figure 2. S-factor (or contrast) of ethanol/water and isopropanol/water developers under no rinse (N2 dry) or rinse with alcohol or water vs alcohol volume concentration. (Left) Ethanol data. (Right) Isopropanol data.



a) b)

Figure 3. (a) Developed PMMA using 80% (v) ethanol – water mixture for 20 s at room temperature. (b) Arbitrary features exposed in GL-2000-12, developed in same ethanol – water developer for 30 s at room temperature. Scale bar on all micrographs is 500 nm.

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