Hexane-based development of PMMA

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Polymethyl methacrylate (PMMA) is among the oldest and most common resists for electron beam lithography due to its low cost, high resolution, and ease of use. Historically, the most common developers for PMMA have been mixtures of isopropanol (IPA) and 4-methyl-2-pentanone (methyl isobutyl ketone, MIBK). Recent advances have demonstrated that using various mixtures of alcohol and water yields better contrast, sensitivity, and line edge roughness compared to MIBK-based development[1]. In this work, we aim to find a new development chemistry for PMMA using only solvents with very low surface tension. This may allow high aspect ratio structures that are normally prone to collapse on drying after development to remain stable. Since hexane has the lowest surface tension of common solvents, we use Hansen solubility parameters[2,3] to explore solvent mixtures of primarily hexane that we expect to exhibit similar solubility of PMMA compared to common developers.

Hexane, IPA, and methanol are all poor solvents for PMMA, with relative energy differences (RED), based on their Hanson solubility parameters, of 1.3, 1.7, and 1.0 respectively. RED greater than 1 predicts poor solubility. However, mixtures of those three solvents can have a RED of ~0.7, similar to MIBK and IPA mixtures commonly used for PMMA development. A mixture of 43% hexane, 43% methanol, and 14% IPA was tested. A contrast pattern consisting of 150 μm squares was exposed, developed for 1 minute in this solvent mixture, and remaining resist thicknesses were measured by reflectometry. Preliminary results show no dark erosion with a dose to clear of ~2000 $\mu C/cm^2$. Work is ongoing to improve contrast and determine the efficacy of hexane-based developers to avoid feature collapse during drying.

[1] Leonidas E. Ocoloa. Development characteristics of polymethyl methacrylate in alcohol/water mixtures: a lithography and Raman spectroscopy study. Nanotechnology 27 035302 (2016)
[2] Charles M. Hanson. The three dimensional solubility parameter and solvent diffusion coefficient. Danish Technical Press, (1967)
[3] Abhinav M. Gaikwad et al. Identifying orthogonal solvents for solution processed organic transistors. Organic Electronics 30 (2016)

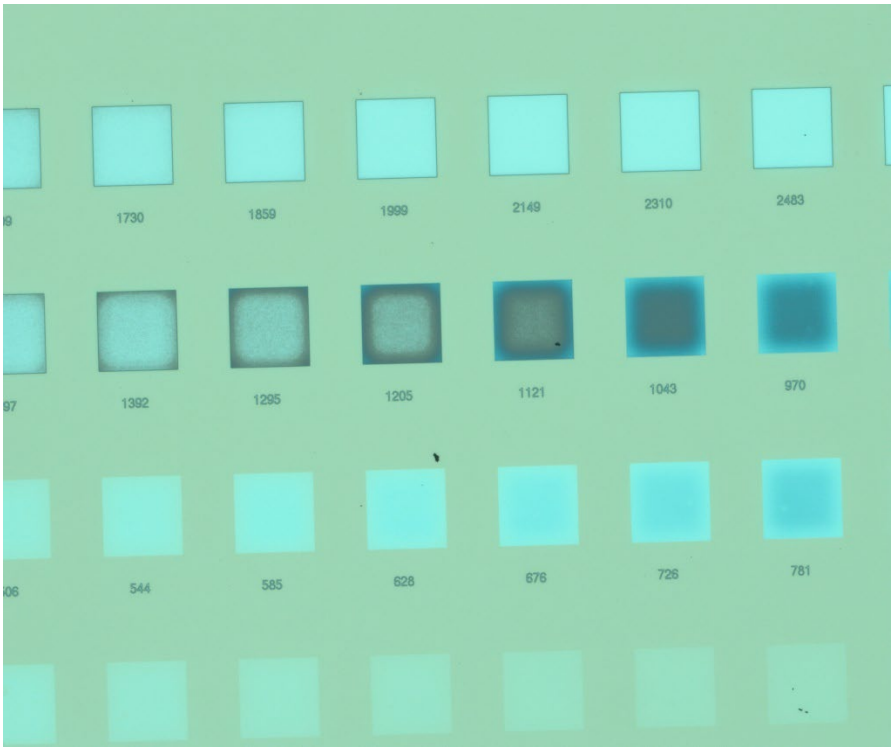

Figure 1: Optical image of contrast pattern developed with hexane:methanol:IPA mixture

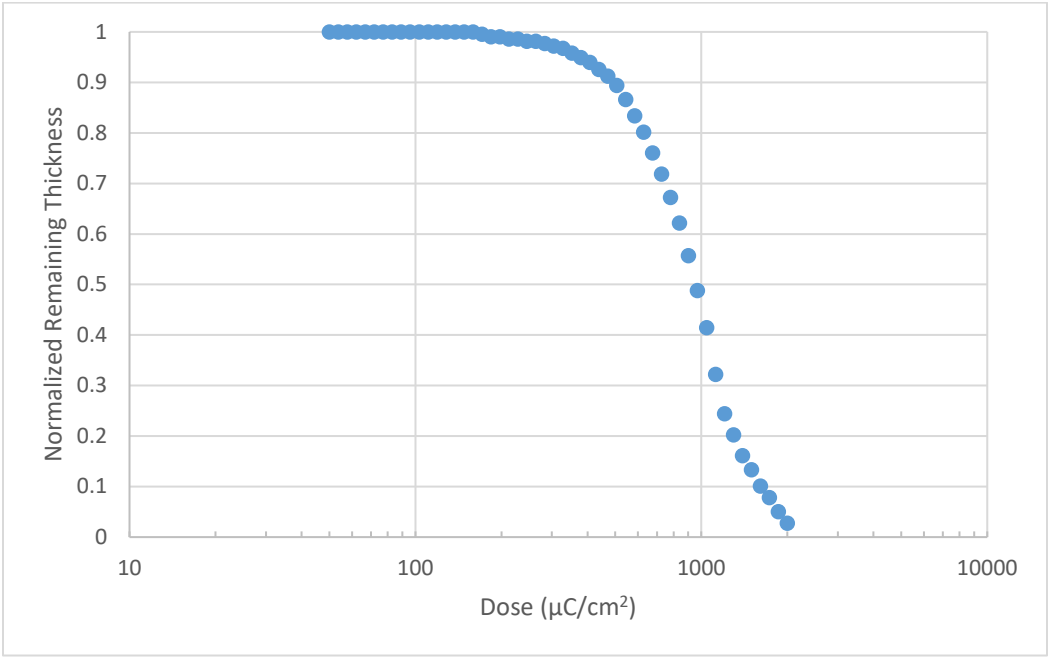

Figure 2: Contrast curve of PMMA developed in hexane:methanol:IPA mixture