Epoxy silsesquioxane resists for UV nanoimprint lithography

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Ultra-Violet NanoImprint Lithography (UV-NIL) is a promising technique for the low-cost fabrication of nanoscale structures at low temperature and low pressure. However, researchers and industrials are facing important lacks concerning the UV curable imprinting material: only a few are commercially available and their properties and characteristics do not always match the targeted application.
In this paper, we present results on the development of low-viscosity hybrid organic / inorganic UV-NIL resists based on polyhedral silsesquioxane (SSQ) functionalized with photo-polymerizable aliphatic epoxy groups [2, 3]. These materials are very attractive because they present a high thermal and mechanical resistance as well as a reduced dielectric constant (low-*k*). They have an interest in nanoimprinting as etch masks (the high silicon content ensuring a high plasma etch resistance) or to fabricate mould replicates, but the more attractive application seems to be the fabrication of interconnects in microelectronics. Direct imprinting of multi-tier moulds into low-k materials is expected to reduce the complexity of the dual damascene fabrication process.
By varying the length of the alkyl spacer between the SSQ cages and the epoxy groups, the final properties of the polymer can be modulated. We have synthesized a series of fully substituted monomers (8 functions per cage) with increasing alkyl chain length from 4 up to 10 methylenes named C4 to C10 (Figure 1). The polymerization proceeds under UV light exposure in an EVG770 NIL stepper equipment and with the help of a photoinitiator combined with a sensitizer. Optimization of the photo-curable formulation allows us to maximize the conversion rate and the cross-linking of the polymer as evidenced by FTIR spectroscopy. Furthermore, an original in-situ UV ellipsometric setup allows us to measure directly photo-polymerization kinetic curves (Figure 2).
Macroscopic properties of the polymer are directly correlated to the material structure: we found that the dielectric constant of the polymer was reduced from 3.7 to 3 when the alkyl spacer is increased, i.e. when the free space between the SSQ cages is maximized. Nevertheless, a balance has to be found because a too large increase of the alkyl chain length reduces the mechanical and thermal properties as evidenced by thermogravimetric analysis.
With the aim of further lowering the dielectric constant and improving the thermal properties, work is currently under progress on partially grafted SSQ cages and on the grafting of different kinds of molecules such as fluorinated or aromatic groups.

[1] A. Sellinger, R. M. Laine, Chem. Mater. **8**, 1592 (1996).
[2] J. V. Crivello, R. Malik, J. Polym. Sci. Part A **35**, 407 (1997).

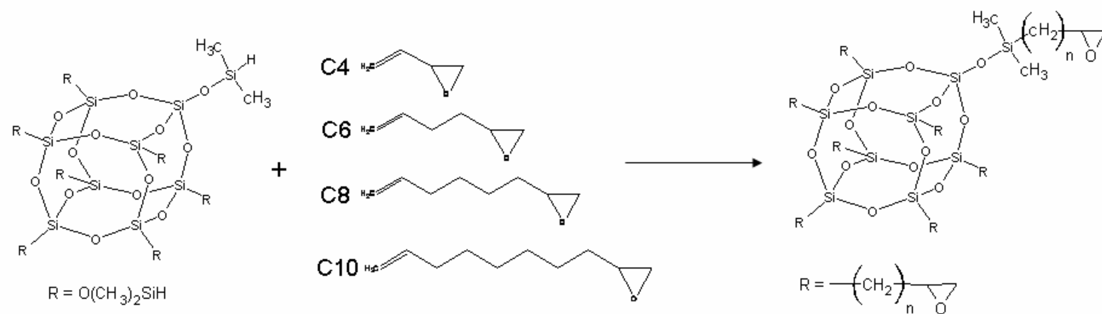

Figure 1: Preparation of liquid photo-polymerizable aliphatic epoxy silsesquioxane resists

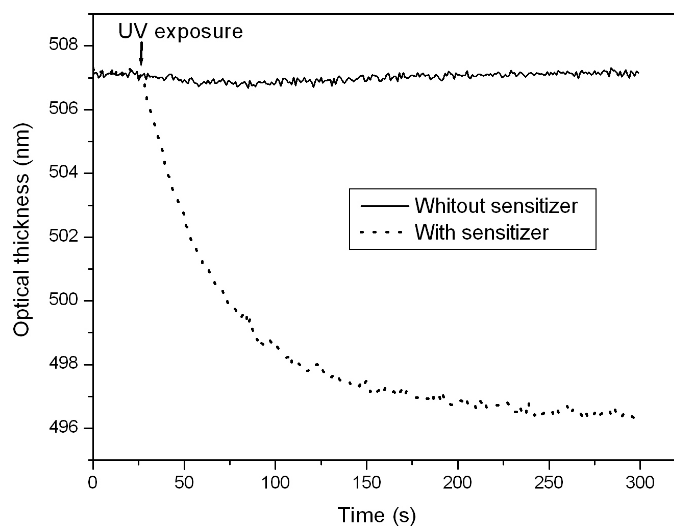

Figure 2: Photo-polymerization kinetic curves mesured by in-situ UV-ellipsometry in the case of the C6 material with (dotted line) and without (solid line) sensitizer