Photo-polymerisation kinetic study of UV-NIL dedicated resists

P.Voisin[1,2,3], M. Zelsmann[1], H. Ridaoui[1]; C. Gourgon[1], J. Boussey[1], K. Zahouily[4]
[1]*LTM-CNRS &* [2]*CEA-LETI, 17 rue des Martyrs, F-38054 Grenoble Cedex 9, France*
[3] *STMicroelectronics, rue Jean Monnet, F-38926 Crolles, France*
[4] *Photo'nPolymers, 66 rue Général de Gaulle, F-68460 Lutterbach, France*

Thanks to its high potential in terms of throughput, alignment capability and high resolution, UV curing NanoImprint Lithography (UV-NIL) is nowadays considered as a promising next generation lithography technique.
This paper reports on the properties of UV-NIL dedicated imprinting materials. Studied solutions are composed of an epoxy-acrylate based monomer and a variable amount (1, 2 and 4 % in weight) of three different photoinitiators (PI) called α, β and γ. The corresponding viscosity, measured with an Anton Paar Physica MCR 300 rheometer, was found to be around 740 mPa.s. Various dilutions were prepared in order to address initial film thicknesses in the 100 -500 nm range.
These materials were then spun on silicon wafers and exposed using a broad band mercury lamp (365 - 435 nm wavelength range) with a power density of 13 mW / cm². UV sensitivity was studied by FTIR spectroscopy which allows us to monitor the polymerisation rate by observing the disappearance of the acrylate function versus the exposure time (Fig. 1). Fig.2 shows the deducted photo-polymerisation kinetic curves for a monomer solution containing 1 % of the three PI under inert atmosphere. For the β-type PI, a 95 % conversion is observed with a dose as less as 20 mJ / cm^2.
Besides, the impact of the PI concentration is analysed. Under inert atmosphere (Fig. 3), we observed that, the lower the PI amount is, the higher the cure rate and polymerisation ratio are. This is certainly because a too high content of PI reduces the mobility of the polymer chains, thus slowing down the polymerisation mechanism. Presence of oxygen (Fig. 4) is shown to slow down the UV curing reaction and reduces the polymerization ratio. This effect is attributed to an inhibiting mechanism: free radicals formed by the photolysis of the PI are quickly captured by O_2 molecules to form peroxyl radicals and can therefore not initiate or participate in any polymerization reaction.
Finally, the lithographic properties of these high sensitivity resists were characterized by conducting step and repeat imprinting experiments. Measured shrinkage ratios and residual layer thickness and uniformity are in excellent agreement with the requirements of this advanced patterning technique and first etching resistance results for these materials were shown to be comparable to standard 193 nm optical lithography resists.[1] A detailed study of the relation between the cure rate and plasma etching resistance is now under progress.

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[1] P. Voisin et al., Characterisation of UV-NIL dedicated resists, MNE 2006

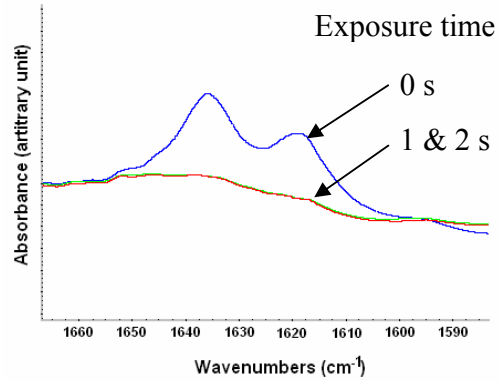

Fig. 1: Acrylate FTIR spectroscopy signature of the monomer solution containing 1 % of γ-type PI after different exposure times and under inert atmosphere

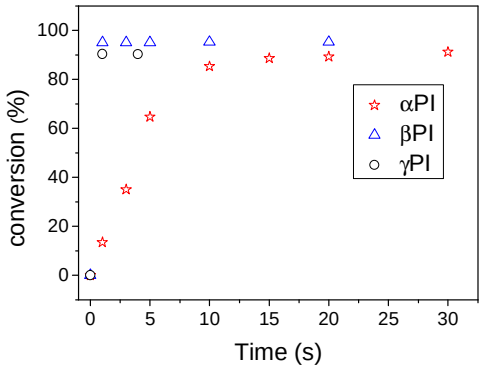

Fig. 2: Photo-polymerisation kinetic curves of the monomer solution containing 1 % of the three different photoinitiators under inert atmosphere

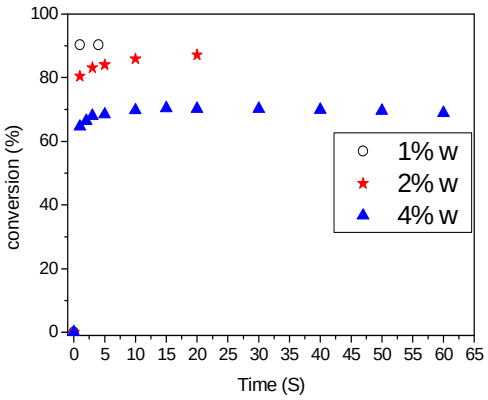

Fig. 3: Photo-polymerisation kinetic curves of the monomer solution containing three different concentrations of γ-type PI under inert atmosphere

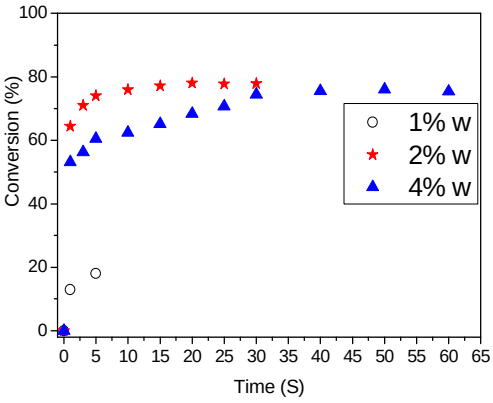

Fig. 4: Photo-polymerisation kinetic curves of the monomer solution containing three different concentrations of γ-type PI under ambient air