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Development of a novel, low-viscosity UV-curable polymer system for UV-nanoimprint lithography

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Abstract

There are two basic types of nanoimprint lithography: hot embossing using thermoplastic or thermosetting polymers and UV-based nanoimprint lithography (UV-NIL) using UV-curable polymer systems. Since the interest in UV-NIL has been constantly increasing within the last years, the need of suitable low-viscosity resists has increased, too. The availability of such materials is one key element of the UV-NIL technology. In this contribution a novel, spin-coatable polymer system for UV-NIL is presented. Suitable polymer components were evaluated using photoDSC analysis. Their ratio was adjusted in such a way that the overall dynamic viscosity of the mixture remained low which was beneficial for the flow behaviour. Film thicknesses in the range of 150–500 nm could be obtained by spin-coating. The new polymer system was characterised in UV-NIL processes and in plasma etching investigations. Imprinted micrometer as well as nanometer scale patterns with feature sizes in the range of 30 nm to several microns are shown.

Keywords: UV-nanoimprint lithography; Resist; UV curing; Spin-coating

Nanoimprint lithography (NIL) is regarded as a promising candidate for a next-generation lithography. According to the ITRS roadmap 2005 industrial mass production using NIL will be employed at the 32 nm and 22 nm node within the next decade. Its progress is closely linked to the availability of suitable resists and polymers which meet all the requirements of this technology. In principle, there are two types of nanoimprint lithography: hot embossing using thermoplastic or thermosetting polymers [1] and UV-based nanoimprint lithography (UV-NIL) using UV-curable polymer systems [2]. One key feature of UV-based nanoimprint lithography is that the imprint step takes place at room temperature and that no annealing steps are necessary. Pattern shift due to different coefficients of thermal expansion of mould and substrate do not occur. Since time-consuming heating and cooling phases are not needed, the cycle times of UV-nanoimprinting processes are much shorter compared to hot embossing. Another advantage is that one can combine low imprint pressures with low residual layer thicknesses by choosing a low viscosity polymer system. The interest in UV-NIL has been constantly increasing within the last years, and the need of suitable low-viscosity resists has increased, too. But there are few publications dealing with UV-curable polymer systems for UV-NIL [2,3]. The availability of such materials allowing short cycle times in industrial mass production is one key element of the UV-NIL technology.

One can differentiate two strategies of UV-nanoimprinting which differ in various aspects. The UV-NIL approach, first described in 1996 [2], comprises resist deposition by spin-coating and wafer-scale or step and repeat processing. In contrast, in the S-FIL approach the liquid resist is dispensed on the substrate giving an array of droplets and

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cured stepwise [4]. Each method of deposition requires different polymer properties regarding viscosity, adhesion, dry etching behaviour and other physical parameters. As a consequence, one needs a tailor-made liquid polymer system, so that the user can fully exploit the whole technological potentials of UV-NIL or S-FIL. These considerations led to completely different approaches in the development of suitable resists for each technology.

In this contribution the development of a novel, low-viscous and spin-coatable polymer system for UV-NIL, mr-UVCur06, is reported. This work was carried out in a project for the development of a complete process technology to produce three-dimensional nanostructures with ultra high precision [5]. Fig. 1 shows the general scheme of an UV-NIL process for the generation of nanostructures. Each step sets specific requirements, which have to be fulfilled by a suitable polymer material. The most important are low viscosity, high resolution, fast UV curing, low shrinkage, high dry etch selectivity, and sufficient stability in subsequent processes, e.g. pattern transfer. In order to achieve low film thicknesses in the range of 100–300 nm by spin-coating the viscosity of the liquid has to be sufficiently low, preferably below 15 mPa s. But the viscosity has various other effects on the imprint performance of a UV-NIL polymer. Generally, defect-free films with high quality and high thickness uniformity after spin-coating are more difficult to attain with decreasing viscosity. Its major effect relates to the flow behaviour and the imprint performance, which can be derived from the following general formula describing the imprint step [6] (t_f imprint time, η_0 viscosity of the polymer, s width of stamp protrusions, p imprint pressure, h_f final residual layer thickness, h_0 initial film thickness).

$$t_f = \frac{\eta_0 s^2}{2p}\left(\frac{1}{h_f^2} - \frac{1}{h_0^2}\right)$$

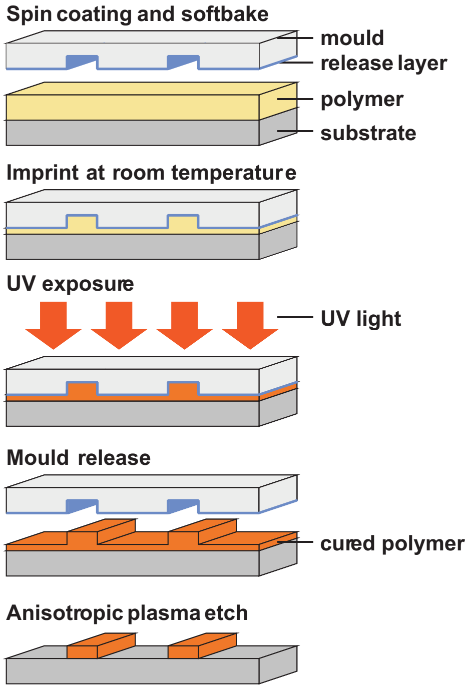

Fig. 1. UV-NIL process.

The mould cavities are filled up faster with decreasing viscosity η_0 under a certain imprint pressure, as the flow of the polymer material proceeds easier. Imprint pressures can be reduced and lower residual layer thicknesses are possible under constant imprint conditions. Of course, the minimum residual layer h_f attained by a fully inserted stamp depends on the initial film thickness and the pattern geometry [7]. But the time necessary to achieve this minimum value h_f is lower. This is beneficial for the implementation of UV-NIL in industrial processes where cycle times have to be minimised. Other important parameters in the materials design are shrinkage and dry etching behaviour. The volumetric shrinkage caused by the photopolymerisation reaction should be low to guarantee high pattern transfer fidelity during the imprint step. The etch resistance of the cured polymer was tuned by the selection of components containing particularly cyclic or aromatic moieties. We used purely organic compounds without silicon-containing components. This allows the user to remove the polymer completely by oxygen plasma. A contaminated mould could be cleaned in the same way without any polymeric residues.

Our goal was to formulate a liquid mixture of reactive components with a viscosity as low as possible without diluting it with organic solvents. There are two main polymer classes, which may be considered for such a photocurable system: acrylates (free-radical polymerisation) and epoxy compounds (cationic polymerisation). Since (meth)acrylates generally show higher polymerisation reactivity and faster curing rates than epoxy systems, we focussed on this polymer class. Their photochemical characteristics are well-known and the effects of individual compounds on the curing behaviour, reactivity or adhesion are described manifold in the literature. Numerous acrylate raw compounds, monomers as well as oligomers, are commercially available, so that adjustments of the polymer properties should be possible. Fig. 2 shows schematically the curing reaction of acrylates initiated by UV light. Various UV-curable compounds and photoinitiators were investigated concerning their effects on viscosity, UV-curing, adhesion, film quality and nanoimprint performance. Suitable polymer components were selected and evaluated using photoDSC (differential scanning calorimetry) measurements, spin-coating and UV-imprinting tests.

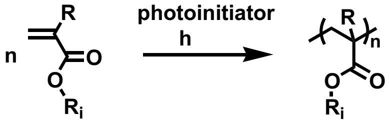

Fig. 2. Free-radical polymerisation of (meth)acrylates initiated by UV exposure (acrylates R=H, methacrylates R=CH_3, R_i various functional groups).

The curing rate of the photocurable polymer had to be increased by variation of its components, as the UV dose