Nanoimprint Lithography

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Introduction

Nanoimprint Lithography (NIL) is an emerging nanoreplication technology with the potential for high throughput and low cost for a huge variety of applications. The basic idea is to have a stamp which contains a (nano-) pattern. This pattern may be binary but can also contain different height levels, curved or sloped featured (e.g. microlenses) etc. In a typical nanoimprint process this stamp is then pressed into a soft material which is coated on a substrate. This soft material can be a UV-curable material but also a thermoplastic one. After UV-curing or cooling down below the glass transition temperature the stamp is removed from the now hardened material, which then features the reverse topography of the stamp. Postprocessing steps like reactive ion etching may follow, however the polymer can also already be the finished device. Since the first proposal by Richard Feynman in his famous lecture “There is plenty of room at the bottom” (1959) and the first publications of S. Y. Chou [1], [2], Haisma [3] and Xia [4] in the mid 1990ies a lot of progress has been made as far as equipment, processes and materials are concerned. Hot embossing or thermal NIL (using a thermoplastic polymer), UV-NIL (utilizing a UV-curing polymer) and micro- or nano-contact printing (µ/n-CP), where an ink is transferred from the stamp to the substrate) are 3 basic variants of the same nanoimprint idea.

Each of these 3 processes appears in a different form in the literature. There is roller NIL [5], reversal NIL [6], combined photo- and nanoimprint lithography [7] etc. The imprint polymer can be droplet dispensed [8] or spin coated [9]. Typically hot embossing processes require higher pressures than UV-NIL processes [10] with µ-CP processes using the lowest pressure [11].

Advantages

The main advantages of NIL are the following:

a) high resolution in a fast process: Due to the stamping nature of the process, NIL is inherently parallel and therefore fast. It may take hours, days or weeks to fabricate the master stamp, but to replicate the patterns only takes seconds or minutes. Soon after the first publications it was shown, that sub 10 nm features can be replicated (see e.g. [12] or [13]).

b) direct 2.5D patterning: If the stamp exhibits several different height levels or curved features, this can be replicated as well (see e.g. [14] or [16]).

c) direct structuring of functional materials: After the imprinting step it is not mandatory that an etching step follows to transfer the pattern into the substrate. In many cases the structured polymer is already the final device (see e.g. [17]).

These advantages make NIL very interesting for industrial but also research applications. Nanoimprint Lithography has also been included in the ITRS roadmap [15] and in technology review’s list of “10 Emerging Technologies That Will Change the World” [19].

Challenges

The Stamp

The stamp is a central part in the imprinting process. The result of the imprint process usually can only be as good as the stamp. Stamps are commonly fabricated by electron beam (e-beam) lithography. The e-beam lithography is followed by reactive ion etching (RIE). For stamps with 2.5dimensional structures, i.e. features that contain multiple height levels or curved and inclined surface features (but no undercut features!) grey-scale lithography (either optical or e-beam is used). Also the use of two-photon polymerization for stamp fabrication has been reported [20]. A promising technology is also PMLP (projection maskless patterning) by IMS Nanofabrication AG [18], that allows the use of several thousand of beams in parallel combined with direct patterning of the substrate [21], [22].

Soft stamps e.g. from PDMS (Poly-dimethylsiloxane) are made from nanostructured masters by casting the liquid PDMS on the master and removing it after the PDMS has been hardened (see e.g. [23]).

The stamps have to be compatible with the imprint material, i.e. they must be easy to remove from the hardened polymer and they must not undergo a (chemical) reaction with the imprinting material. To reduce the sticking of the stamp to the imprint polymer, usually an anti-adhesion layer is applied to the stamp. Such a layer is typically a self-assembled monolayer of fluorinated silanes [24]. There is however a debate going on regarding the durability and therefore also the suitability of such layer for the production process, and diamond-like carbon layers have been suggested and tested [25], [26].

To reduce the risk to damage the stamp during the imprint process it is advantageous to use working stamps instead of the original master. These stamps are replicated from the master and then used for imprinting. Materials for such working stamps can be Ormocer-based materials like Ormostamp [27], [28] or polymeric materials like PFPE (perfluoropolyether) [29] – [31], but also PDMS.

The Materials

The following parameters have to be considered when designing or choosing a suitable polymer for a certain process:

a) Adhesion to the substrate. The polymer has to stick to the substrate and it has to wet the substrate. Adhesion promoters like Ti-Prime [32] or HMDS (Hexamethyldisilazane) can be used.

b) Non-adhesion to the stamp. When stamp and substrate are separated from each other the cured polymer has to remain on the substrate and not on the stamp. Should for some reason the polymer stick on the stamp, it must be easy to remove from the stamp, without the danger of changing the features on the stamp during the cleaning procedure.

c) Functionality. The imprinting polymer has to fulfill certain tasks after having been patterned, e.g. serve as an etching mask. In this case the etching selectivity has to be high enough with respect to the substrate (see e.g. [33], [34]). The polymer can also serve as an optical element, in that case the optical parameters and the durability for the desired application are important [35], [36].

d) Process compatibility. The imprint polymer must not interact with the stamp material. Any swelling of soft stamps has to be avoided.

e) nCP inks. Similar considerations are valid for the inks used in nCP. Again they must not destroy the stamp, wet the substrate but also the stamp to allow for a homogeneous distribution on the stamp surface. A high vapor pressure of the ink molecules has to be avoided to reduce the risk of material deposition in areas where not deposition is wanted. Diffusion on the substrate surface has to be minimized [37], [38]. For the stamp material similar considerations are valid.

The Process

Contact

The first challenge is to bring the stamp in close and homogeneous contact with the substrates. Both stamp and substrate are not perfectly flat. There are several approaches regarding this topic, which basically all make it possible for the substrate of the stamp (or both) to bend during the imprinting process: a compliant layer [39], flexible stages [40] or air cushions [41] are used to name a few examples. When bringing the stamp into contact one has to take care not to trap too much air in the cavities of the stamp. In many cases small air bubbles dissolve in the imprint material, larger bubbles however remain for a long time and therefore the process time is significantly increased. It is obvious that the inclusion of particles between stamp and substrate has to be avoided.

Residual Layer

The residual layer is the layer of imprinting polymer that remains in the areas where the material has been pressed down. This layer can usually not be avoided, since either too much time or too much force would have to be exerted to reduce it almost completely (see e.g. [42] p. 53ff). It is also not completely unwanted since it prevents the stamp from getting into direct hard contact with the substrate, which is especially advantageous if hard stamps are used. To enable further processing like reactive ion etching this layer has to be removed (by oxygen plasma etching). If the residual layer is homogeneous and thin this breakthrough etch can be performed without degrading the overall pattern quality. To optimize the residual layer thickness, knowing the filling factor of the stamp is critical, i.e. the ratio of cavities on the stamp to the total stamp area, as it determines the necessary amount of material to fill all cavities and still produce a homogeneous film, without any unfilled features. To achieve a homogeneously thin residual layer, the filling factor should be constant on the stamp (which can not always be achieved) and the pressure distribution during the imprinting process has to be as homogeneous as possible, which is mainly a quality criterion for the imprinting setup. Another parameter that enters the equation is the viscosity of the imprinting polymer. For imprint polymers with higher viscosity as used e.g. in hot embossing often a compromise has to be made between imprinting time and imprinting pressure on the one hand and residual layer thickness on the other hand. Time and pressure should be kept small, which increases the residual layer thickness. Residual layer thicknesses below several 10 nm can be achieved routinely and are very well suited for post-processing.

Alignment

To bring stamp and substrate very close to each other, do the alignment and then press the stamp into the imprinting polymer, without misaligning is difficult to achieve. Often in-liquid alignment is performed, i.e. alignment when the stamp is already pressed into the imprinting polymer (with less pressure than needed for the actual imprinting step). For the often necessary sub 100 nm alignment accuracy optical microscopes have been used, implementing Moiré-alignment markers and sub-pixel image processing [43] diffraction techniques [44] or interferometric setups [45]. Also dual focus x-ray alignment microscopes have been used for alignment in NIL [46]. Stamp and substrate distortions influence the alignment accuracies over larger areas so that again the imprinting pressure homogeneity is crucial for good results [47].

Demolding

After the imprinting process the stamp has to be removed from the substrate. Here the structure can be damaged in various ways, either by being deformed or ripped off. If the adhesion of the imprint polymer to the substrate is not high enough it can happen that large areas of the polymer are removed from the substrate and stick to the stamp, which then requires careful cleaning.

Depending on the kind of stamp and equipment used either parallel demolding or peeling off can be used. Flexible stamps are often advantageous for easy demolding, since they can deform and the forces acting on the imprint polymer are reduced.

Inspection

It is an unsolved issue how a fast inspection of nanoscale features on a large area can work, especially if the geometry of the features is complex and has many height levels. Many investigations concerning this topic have been performed by Molecular Imprints Inc. [48], e.g. [49].

Examples

Examples for the successful use of nanoimprint lithography stem from a wide range of very different applications. Most of them are still to be found in a research environment, but there are also industrial applications, where NIL is already used as a production tool or where it is planned to be used. Many examples can be found in the field of optics or photonics, like the fabrication of metamaterials [50], [51], polarizers [52], [53] and for the fabrication of photonic crystal structures [54], [55]. Nanoimprint lithography is also used for the replication of diffractive optical elements and microlenses [16] also for mass production e.g. [56] performed on equipment of EVG [57], [58]. It has been used to structure the donor-acceptor interface in organic solar cells [59]. The replication of multi-level features has been published e.g. in [60] or [61]. In the field of biology NIL has been used for example to pattern substrates for cell growth [62], [63] to fabricate Gold nanoislands [64] and to prepare chemical gradients on surfaces [65]. One of the most demanding but also interesting applications will be the preparation of next generation hard disks, so called bit patterned media. Here nanoimprint lithography will most probably find a real high volume industrial application (see e.g. [66], [67]). The list of applications could be extended significantly.

Conclusions

Nanoimprint Lithography has been shown to be able of high resolution and high throughput patterning making it highly interesting for a number of applications, in a research environment as well as for industrial applications. The challenge is to improve materials and processes and also the equipment even further to meet the demands of the industry. Nevertheless nanoimprint lithography is already today a very powerful tool for nanopatterning.

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