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Efficient Replication of Nanostructured Surfaces

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Abstract: The defined fabrication of nanostructures on surfaces for the nanosciences today largely relies on tools such as scanning probe instruments or electron- and ion beam systems that are serial writing processes. For future production of components and devices, in particular if large nanostructured areas are needed, parallel processes, which are fast and cost-effective, have to be developed. In this paper we review the possibilities for the replication of nanostructures on surfaces using moulding of thermoplastic polymer materials. Using hot embossing, it has been shown that structures below 10 nm can be reproduced reliably and with a high fidelity using laboratory equipment. Mass fabrication of nanostructured components can be achieved using thermal injection moulding with cycle times in the order of 10 sec.

Keywords: Hot embossing · Injection moulding · Nanoimprint · Replication · Thermoplastic

Introduction

Mastering of nanoscale technology is largely possible due to the development of scanning probe microscopy (SPM) based methods. In the nanosciences these methods are widely used for the imaging of surfaces and they also have the capability to carry out manipulations at the atomic scale, making them a useful lithographic tool for researchers. SPMs are therefore perfect tools for generating knowledge and understanding processes on the nanometre scale. For realising defined surface structures above 10 nm, particle beam based tools such as electron-beam pattern generators or focussed ion beam systems are well suited. However, if it comes to applications involving volume manufacturing of nanodevices or large area surface nanostructures, the SPM or particle beam based methods have an inherent disadvantage: due to the serial operation, the processing times become prohibitively long when a large number of devices is required or the areas to be processed are sizeable. Massive parallel use of serial tools, by simply multiplying the number of probes, may ease this problem in the future. The array of SPMs currently under development [1] still requires some progress before it can be made commercially available. Arrays of micromachined e-beam systems, which should significantly speed up the writing process, have also been described in the literature [2] but this approach has not yet been developed into a satisfactory commercial product. The task of massive parallel reproduction has been solved in the semiconductor industry by using a costly serial process just for the fabrication of a master structure (an optical mask with nanostructured absorber patterns) and using the master as a copying tool (by lithographic exposure of the mask pattern on to a photosensitive resist). However, the achievable resolution in optical lithography is strongly dependent on and limited by the wavelength of the light used.

This conventional ‘top-down’ approach taken in semiconductor manufacturing certainly will continue to smaller structures in future, more or less according to Moore’s law. The ITRI roadmap predicts that design features below 50 nm will be in production by 2008 [3], using light with smaller and smaller wavelengths from the UV-range to X-rays. The problem for innovations in nanotechnology using advanced DUV- and future EUV or X-ray steppers lies in the enormous investment cost which can only be economically justified for the production of very high volume nanoproducts such as future memory chips. Consequently there will be a need for a production technology which combines highly reproducible resolution below 100 nm with acceptable processing time and cost, suitable for applications in research and development, as well as small and medium volume products like sensors, micro-optical devices *etc.*

Replication has been known for centuries as a process for mechanical copying of service tools (moulding of pottery) or for reproduction of jewellery or identification tokens (embossing of metal coins). Here the surface relief of a well-engineered hard master-tool is transferred into the soft mould material. Over the past several years, the resolution of replication technology has been extended to the sub-micrometer range with the smallest structures reported below 10 nm. Several methods are used: embossing of thermoplastic polymer materials using hard masters, injection moulding of polymers, shaping of UV-curable or sol–gel materials using hard or soft masters and the so-called soft or micro-contact lithography, where chemicals forming self-assembled monolayers are printed on the substrates with soft elastomeric masters.

In this paper we will summarize our results on sub-micron replication in the area of hot embossing lithography (HEL) on planar surfaces and on some aspects on

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thermal injection moulding of large surface areas containing nanoreliefs. The injection moulding work was carried out in co-operation with the Fachhochschule Aargau (Prof. W. Kaiser, A. D'Amore, D. Simoneta) and the company AWM Werkzeugbau, Muri (M. Gabriel), Switzerland.

General Remarks on Thermoplastic Moulding

The basis of hot embossing and thermal injection moulding is the shaping of thermoplastic polymers by conformal contact of a nanostructured stamp using heat and pressure. The viscosity of the material can be significantly reduced by increasing the temperature of polymer and/or mould, so that pressing a hard master into the polymer at elevated temperatures causes the viscous polymer to flow into the cavities of the mould. The polymer is hardened by cooling and the master can then be separated from the moulded polymer (de-moulding) producing a stable reproduction of the master relief. This process can be repeated reproducibly many times. However, the applications and process conditions can be very different for these two replication techniques: in hot embossing, whole polymer sheets are compressed between the stamps of an embossing press; a prominent modification of this surface patterning process is in-line embossing on polymer foils with a rotating stamper (roll embossing). The thermoplastic material is heated to a temperature above the glass transition temperature T_g (105 °C for PMMA), so that the polymer is sufficiently viscous to flow into the cavities of the mould. In injection moulding, higher temperatures are needed. The polymer melt is injected into a closed cavity and either freezes on direct contact with the cold mould or on subsequent cooling below T_g. This process can be very fast.

For both hot embossing and injection moulding replication processes, it has been shown which process and material parameters must be controlled for optimal moulding. Structures down to 10 nm can be replicated and there is no indication that the replicated size limit has been reached.

Hot Embossing Lithography

Hot embossing offers new possibilities when used on thin polymer films covering a hard substrate (see Fig. 1). In this case the embossed polymer structures can serve as resists for subsequent pattern transfer processes and are thus directly compatible with traditional lithographic processes working reproducibly for structures well below 100 nm with the advantage of a moderate equipment cost, and short process times. In hot embossing lithography (HEL), also referred to as nanoimprint lithography (NIL), the aim is the lithographic structuring of the surface of different hard materials, *e.g.* large area interdigitated electrode structures on silicon chips (see Fig. 2 and [4]) or for the fabrication of nanosieves in membranes [5]. A thin film of a thermoplastic material is coated onto the surface of a chip or hard substrate and structured by pressing a structured stamp into it (Fig. 1). The resulting polymer pattern can then be transferred into a hard material using dry etching or it can be used for a subsequent lift-off process to produce thin metal structures. We have routinely realised HEL structures with feature sizes <100 nm on substrates up to 100 mm diameter using a relatively low cost laboratory press.

To understand the details of the process it is useful to look at the polymer filling of the master's cavities in detail. From AFM investigations of embossing experiments interrupted at various stages we can conclude that the filling of the cavities occurs from the sidewalls towards the centre of the cavities (Fig. 3, Fig. 4). This is particularly the case if the film thickness is of the order of or below the structure size, so that the cavities of the mould have to filled by lateral displacement of the polymer. Interestingly, the air contained in the cavities of the master seems to vanish completely towards the end of the process.

An argument often heard against the use of 'mechanical' lithography for a broad range of applications is the difficulty of precise alignment of the structures on the

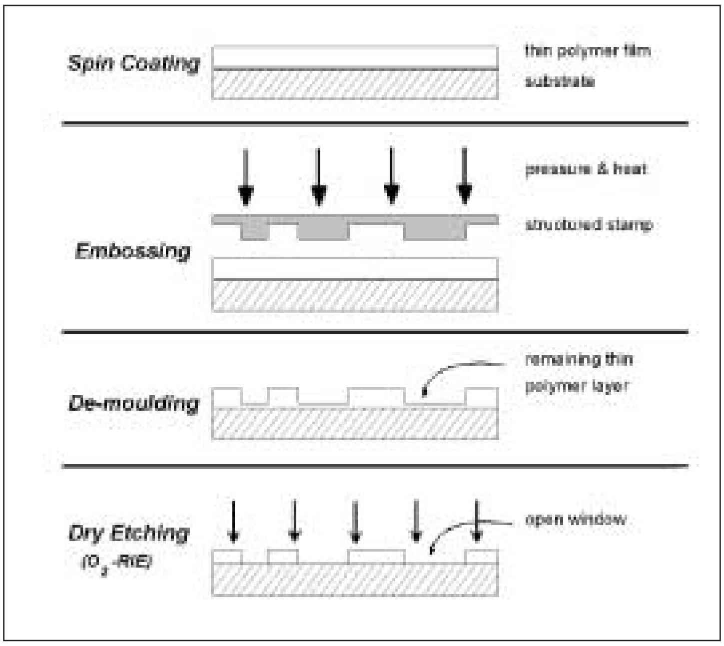

Fig. 1. Process sequence for hot embossing lithography. After de-moulding, an additional process step is needed to open substrate windows. Then the resist can be used for the subsequent pattern transfer processes.

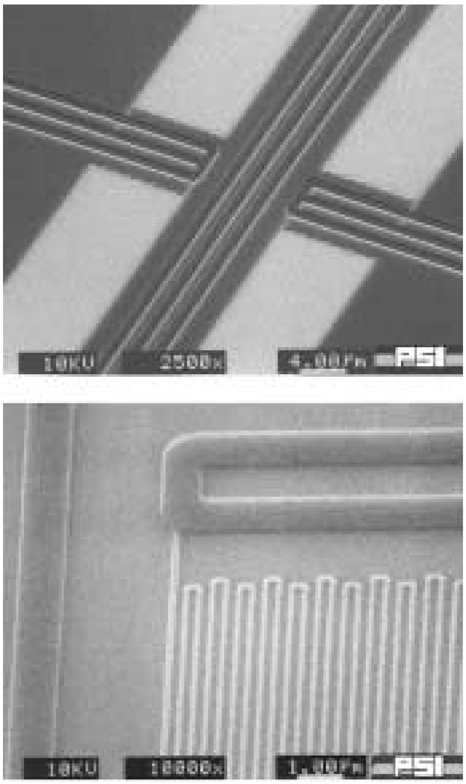

Fig. 2. Above: SEM micrograph of a silicon mould with meander-type cavities for four electrode arrays with length 100 µm, width 10 µm, line period 400 nm and depth 120 nm. Below: SEM micrograph of the moulded PMMA resist. By lift-off (metallization of the substrate areas not covered by resist), interdigitated electrode structures can be generated.

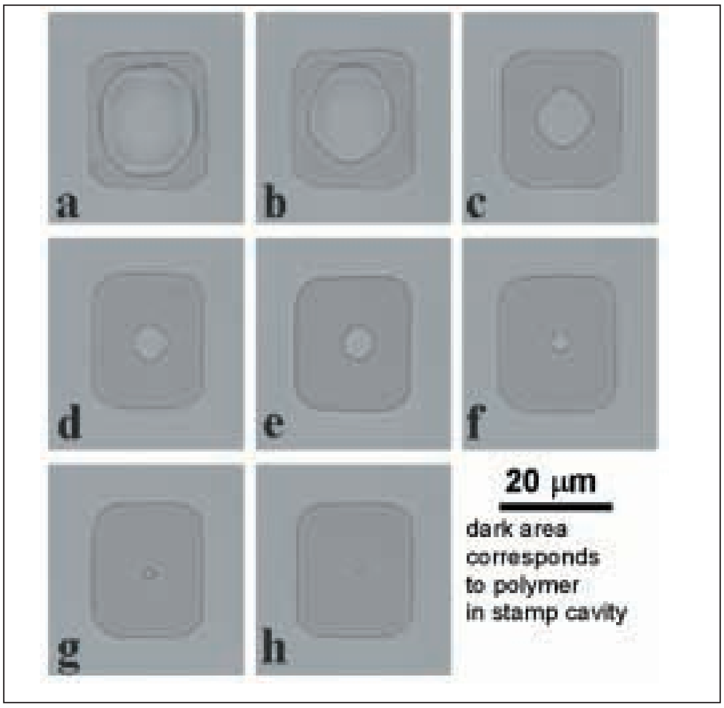

Fig. 3. Thin films are structured by lateral displacement of polymer. The compressed polymer continuously fills the cavity from the borders (a–h). The air is compressed to a fraction of its volume.

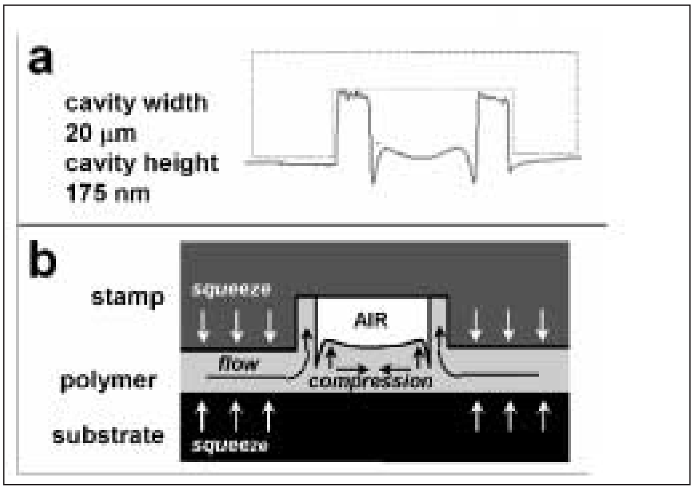

Fig. 4. Filling of a microcavity (a) AFM measurement of a snapshot of partial filling. (b) Schematic view of polymer flow.

substrate. This can indeed be a problem, particularly for applications with several lithography levels requiring alignment with an accuracy of a fraction of the smallest feature size as, for example, in electronic chip production. Some approaches have been taken recently to solve this problem, but the precision achieved is far away from the demands from state-of-the-art steppers. Nevertheless there are many applications where no alignment or at least low alignment precision of the replicated structures on the substrate is necessary. In addition, the process can be applied in a 'mix-and-match' mode together with standard optical lithography and combined optical- and hot embossing lithography tools have become commercially available recently.

For production of hot embossed nanostructures, good moulding results can be achieved with a variety of materials and embossing parameters, particularly with the help of macroscopic flow theory. In addition we observed new phenomena, such as self-assembly due to local electrostatic interaction of polymer and mould, which may lead to new hot embossing lithography techniques [6].

Thermal Injection Moulding

Thermal injection moulding (TIM) is used if structures have to be directly generated on the surface of a large component. A prominent example is the compact disc (CD), where the information is stored as microscopic data-dots (pits) on a transparent disc serving as a mechanical support and optical carrier. We have used a standard CD injection moulding process by inserting a 100 mm diameter silicon wafer with various test-nanostructures as the master (also called stamper) in a modified injection moulding tool (Fig. 5). The nanostructures in the master were written with standard e-beam lithography in PMMA resist and transferred into the silicon surface by reactive ion etching as described in [7]. The thermoplastic polymer used was Makrolon polycarbonate from Bayer. Hundreds of CDs were produced in an AWM moulding tool on a Netstal Discjet injection moulding machine with cycle times as low as 10 sec [8]. An example of the reproduction fidelity of features below 50 nm is given in Fig. 6.

During the moulding and the following cool-down, the moulded parts undergo a shrinkage which must be taken into account for applications where small distances have to be constant and distorsion must be avoided. Examples are optical diffraction devices and calibration gratings [9]. For investigation of the homogeneity of this shrinkage

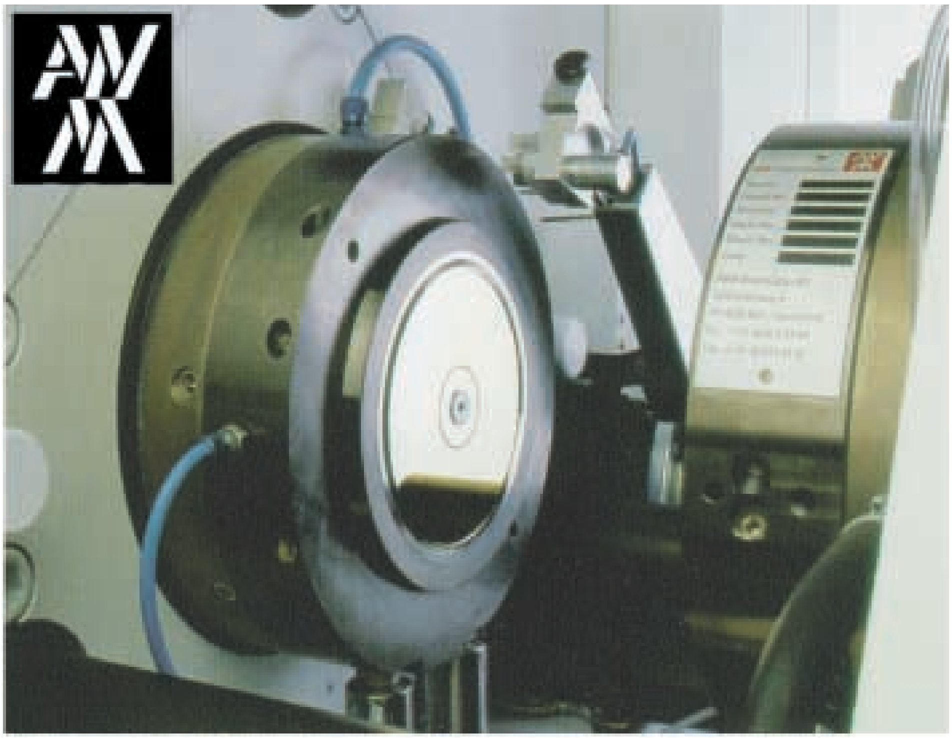

Fig. 5. Compact disc injection moulding tool (AWM Werkzeugbau) installed in a Netstal Discjet injection moulding machine.

Fig. 6. Reproduction of a miniaturized relief featuring a part of the Gutenberg bible on a CD (right side). The facsimile on the left side was reduced by a factor of 10000 by e-beam lithography and etched into a silicon wafer. The line height is about 500 nm and the smallest feature sizes (in the ornamental patterns) are below 50 nm.

over the area of the CD, we made a master with alignment marks distributed over the whole area and measured their distribution on the replicated CD using the interferometrically controlled stage of our e-beam machine. Since the same stage was also used to create the master, systematic errors can be excluded and should be below 0.01%. Fig. 7 shows the relative variation in position of the alignment marks between master and disc and the graph displays the quantitative shrinkage over the radius of the CD [8].

In thermal injection moulding the key factor for a good and fast moulding process is the viscosity of the material, which is largely dependent on the mould temperature. For future high precision applications it is necessary to broaden our understanding of how micro- and nanostructures are moulded and which kind of polymers are best suited for nanostructuring.

Of course, CDs with sub-100 nm datadots will require the development of a reliable and fast read-out mechanism. The development of a suitable read-out system is not trivial, although the appearance of such a system in the consumer market seems to be in sight [1]. Apart from the CD market, a number of other applications may appear for artificially nanostructured polymer surfaces made by injection moulding, for example photonic bandgap materials for optical waveguides, research devices in nanoscience and biomedical research, and templates for what is now called ‘templated self-assembly’ of nanostructures.

Conclusions

The HEL and TIM processes described here provide two robust fabrication technologies for the reproducible generation of polymer surfaces with defined nanostructures in large quantities, and over large areas. HEL in particular is suited for laboratory and small-scale production, and can be easily scaled-up for larger sample sizes. In fact at present, replication appears to be the only feasible process for the fabrication of substantial quantities of defined nanostructures on surfaces with a moderate investment for equipment. Structures <10 nm have been demonstrated and the ultimate resolution seems to be limited only by the availability of appropriate master tools. In addition, the maximum substrate size which can be patterned in a single process step is mostly dependent on tool availability. Currently areas of several cm^2 are routinely handled in several laboratories.

Applications already exist, although mostly as demonstration and research devices [5]. In the future, many more applications in other fields will appear such as the production of photonic materials for optical computing or the creation of biocompatible surfaces for medical implants.

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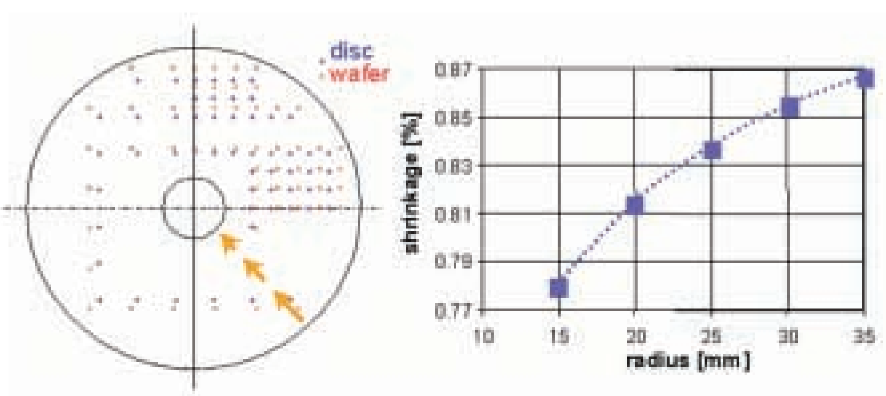

Fig. 7. Positions of the marks on the master (wafer, x) and the replica (disc, +) showing the direction of contraction (the distance of marks between master and CD is enhanced for clarity) and graph showing the radial dependence of shrinkage: the values correspond well with the 0.6 to 0.8 % given for polycarbonate in the data sheets.

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[1] P. Vettiger, M. Despont, U. Drechsler, U. Dürig, W. Häberle, M.I. Lutwyche, H.E. Rothuizen, R. Stutz, R. Widmer, G.K. Binnig, *IBM journal of research and development* **2000**, *44* (Number 3). *http://www.research.ibm.com/journal/rd/443/vettiger.html*

[2] M. Despont, U. Staufer, C. Stebler, H. Gross, P. Vettiger, *Microelectron. Eng.* **1996**, *30*, 69–72. *http://www-samlab.unine.ch/Activities/Projects/MicroColumn/MicroColumn.htm*

[3] ITRS, *http://public.itrs.net/files/1999_SIA_Roadmap/Litho.pdf*

[4] H. Schift, R.W. Jaszewski, C. David, J. Gobrecht, *Microelectronic Eng.* **1999**, *46*, 121–124.

[5] L.J. Heyderman, B. Ketterer, D. Bächle, F. Glaus, B. Haas, H. Schift, K. Vogelsang, J. Gobrecht, L. Tiefenauer, O. Dubochet, P. Surbled, T. Hessler, to be published in *Microelectronic Eng.* (**2003**).

[6] H. Schift, L.J. Heyderman, M. Auf der Maur, J. Gobrecht, *Nanotechnology* **2001**, *12*, 173–177.

[7] H. Schift, A. D’Amore, C. David, M. Gabriel, J. Gobrecht, W. Kaiser, D. Simoneta, *J. of Vac. Sci. Technol. B* **2000**, *18(6)*, 3564–3568.

[8] H. Schift, C. David, M. Gabriel, J. Gobrecht, L.J. Heyderman, W. Kaiser, S. Köppel, L. Scandella, *Microelectronic Eng.* **2000**, *53*, 171–174 .

[9] J. Gobrecht, H. Schift, C. David, W. Kaiser, A. D’Amore, D. Simoneta, L. Scandella, PTB Berichte PTB-F-39 Braunschweig, Germany, **2000**, 1–7.