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Technical note

IMPRINT LITHOGRAPHY ON POLY(2-HYDROXYETHYL METHACRYLATE), (PHEMA), AND EPOXYDISED NOVOLAC, (EPN) POLYMERS

F. A. Zacharatos[a,b], A. Olziersky[a], I. Raptis[a], E. Hristoforou[*b]

[a]NCSR "Demokritos", Institute of Microelectronics, Agia Paraskevi, Athens 15310, Greece
[b]Laboratory of Physical Metallurgy, National Technical University of Athens, Zografu Campus, Athens 15780, Greece

Nanoimprint lithography (NIL) is a very effective, non-conventional lithographic method, which takes advantage of the mechanical and thermal properties of polymeric materials and structures them with application of pressure and high temperature. An imprint process that presses a mold into a thin polymeric film of poly(2-hydroxyethyl methacrylate), PHEMA, and epoxydised novolac, (EPN), cast on a silicon substrate, has been developed and demonstrated. For the fulfillment of the experiments, a home-made apparatus was designed and implemented. The printed structures had a feature size of 1μm and their depth didn't exceed 50 nm in some cases.

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1. Introduction

The demand of dimension shrinkage in the microelectronic devices increases as the time passes, because this is the only way to achieve greater integration density. According to the International Technology Roadmap of Semiconductors, (ITRS)[1], the forthcoming generations of integrated circuits (ICs) with critical dimension of 65 and 45nm will be achieved by 193 nm and 193 nm-immersion optical lithography. However, as far as it concerns smaller critical dimensions, the future is ambiguous. Optical lithography confronts severe obstacles in the sub 65nm patterning. The most prevalent lithographic technologies for sub-65 nm patterns are considered to be EUV (extreme UV lithography), electron projection and nanoimprint lithography (NIL). In addition to the above dimension limitation, photolithographies cannot be used with many organic and biological materials due to their chemical incompatibility with typical photoresists and developers. Consequently, the need of utilizing alternative lithographic methods has become more intense.

One of the most promising non-conventional lithographic methods is nanoimprint lithography [2]. Imprint technology, using compression molding of thermoplastic polymers, is a low cost mass manufacturing technology and has been around for several years. Features with dimensions on the order of 1μm have been routinely imprinted in polymeric films. Compact disks that are based on imprinting of polycarbonate compose the most well known example[3]. Other examples are imprinted poly(methylmethacrylate), (PMMA) films, with a feature size on the order of 10 nm [4] and magnetic recording media comprising monodisperse high-anisotropy nanoparticles in a self-organized patterning [5,6].

In the present work we will demonstrate that NIL is able of producing lines and trenches with 1 μm minimum feature size and 50 nm depth on the surface of thin polymeric films of poly(2-hydroxyethyl methacrylate), (PHEMA), and epoxydised novolac, (EPN), in a very low-cost way, by using a home-made apparatus. This research aims to study the behaviour of these two novel materials and to define the optimum conditions for their utilization as NIL-resists.

[*] Corresponding author: eh@metal.ntua.gr

Nanoimprint lithography has 3 basic steps as shown in Fig. 1. The first step consists of the process of spin coating a polymeric resist, usually PMMA, on a suitable substrate (usually Si wafer), baking it in order to remove the solvent and finally heating it above its glass transition temperature (T_g), (a). The second step is the imprint step, in which a mold with structures on its surface is pressed into the thin resist cast on the substrate, followed by quenching and finally removal of the mold. This step duplicates the microstructures on the mold in the resist film (b). In other words, the imprint step creates a thickness contrast pattern in the resist. During the imprint step, the resist is heated to a temperature above its T_g. At that temperature, the resist, which is thermoplastic, becomes a viscous liquid that can flow and, therefore, can be readily deformed into the shape of the mold. The resist's viscosity decreases as the temperature increases. The third step is considered to be the pattern transfer where an anisotropic etching process, such as reactive ion etching, (RIE), is used to remove the residual resist in the compressed area. This step transfers the thickness contrast pattern into the entire resist (c).

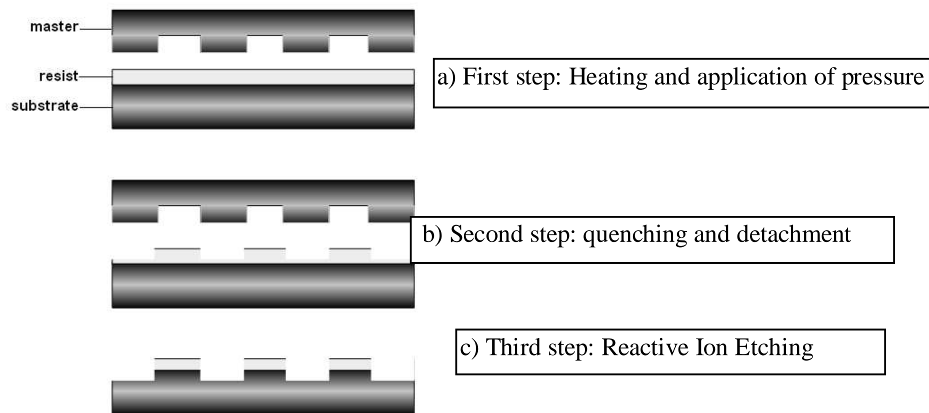


Fig. 1. NIL procedure flow chart.

Unlike conventional lithography methods, imprint lithography itself does not use any energetic beams. Therefore, nanoimprint lithography's resolution is not limited by the effects of wave diffraction, scattering and interference in a resist, and backscattering from a substrate. Furthermore, imprint lithography is fundamentally different from stamping using a monolayer of self-assembled molecules. Imprint lithography is more of a physical process than a chemical process. It is conceivable that in the future, the mold used in imprint lithography can be made using a high-resolution but low-throughput lithography, and then imprint lithography can be used for low-cost mass production of nanostructures.

An alternative technology, very similar to NIL, is photo-curable nanoimprint lithography[7]. The difference between the preceding technique and UV-NIL is that the latter utilizes UV radiation to achieve resist curing and therefore, requires the fabrication of a UV transparent master. The UV-NIL procedure consists of the following steps:

1. A photocurable prepolymer is applied to a substrate such as silicon, quartz and glass.
2. The master is imprinted on the substrate.
3. Ultra-violet light is irradiated to the prepolymer to harden.
4. The master is removed from the substrate.

The greatest advantage of this technology is that heating above T_g is not demanded and therefore defects that are caused due to phase transitions (glass-viscosoelastic etc) are avoided.

2. Experimental

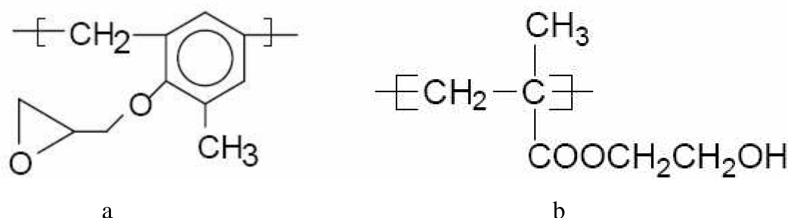
2.1 Si Masters

Within the framework of the present study, the masters were fabricated by means of optical lithography. A glass/Cr mask that consists of lines whose width varies from 1.5 – 40.0 μm and their

length is much greater (1 cm), was designed and fabricated in a commercial mask shop. The pattern of the mask was transferred to the substrate with a conventional lithographic and dry etching process as described below: At first, Si (100) 3′′ wafers are spin-coated with positive resin (AZ 5214) and heated up to 95 ^{o}C for 10 min. Next, the mask is placed in the mask aligner (Karl Suss MJB 3) where it is brought into contact with the wafer and both are exposed to UV radiation for 15 s. Then, the wafer is submerged in the AZ 726 developer for 1 min. During this step, the areas of the positive resin that have been exposed to the radiation are dissolved, whereas the others remain on the surface of the wafer. The final step of the process is no other than plasma etching. The wafer is placed into the chamber of the reactive ion etcher that is supplied with SF_6 gas. An RF AC voltage is applied at 400 W power. The process takes place in 10^{-5}bars vacuum. The exact pattern of the mask is replicated on the Si surface during the etching. In these conditions the etching rate is 350 nm/min, and the wafers are etched for about 30 sec in order not to have a depth greater than 200 nm, to avoid detachment problems and pattern deformations.

2.2 Polymeric materials

A thermoplastic polymer is required for a successful imprint experiment. Thermoplastic polymers, when heated a few degrees above their glass transition temperature, present viscose-elastic behaviour. They can be easily deformed and their elongation limits are multiplied. If they are cooled below T_g the deformation they have undergone is almost totally reversed. Both PHEMA[8] and EPN[9] are thermoplastic materials. They exhibit excellent properties for the specific experiment. Their glass transition temperature is low, 87 ^{o}C and 53 ^{o}C correspondingly and they present a very small value of thermal (<1%) and pressure shrinkage (<0.1%) for the experimental conditions range. Poly(2-hydroxyethyl methacrylate) with MW 300,000 was purchased from Aldrich Co. As far as it concerns epoxydised novolac, the specific polymer was prepared in our laboratory. Epikote 164, a cresol epoxy novolac polymer from Shell chemical company, has been used as the raw polymeric material. This polymer is fractionated before use following the procedure, which is described below: Firstly, a certain quantity of Epikote 164 is dissolved into Methyl Isobutyl Ketone, MIBK in 1:4 ratio. Afterwards, the head of the polymer (high MW fraction) is omitted. Next the tail of the polymer (low MW fraction) is removed. The remaining medium MW fraction is heated to 60 ^{o}C until the solvent evaporates completely. Finally the medium fraction is weighted and usually consists half of the initial quantity. A solvent is used to adjust the viscosity of the resist. In our study the medium fraction has been used. Its mean MW is 3,900. The chemical structure of both materials (PHEMA, EPN) is shown in the figures below (Fig. 2a, 2b).



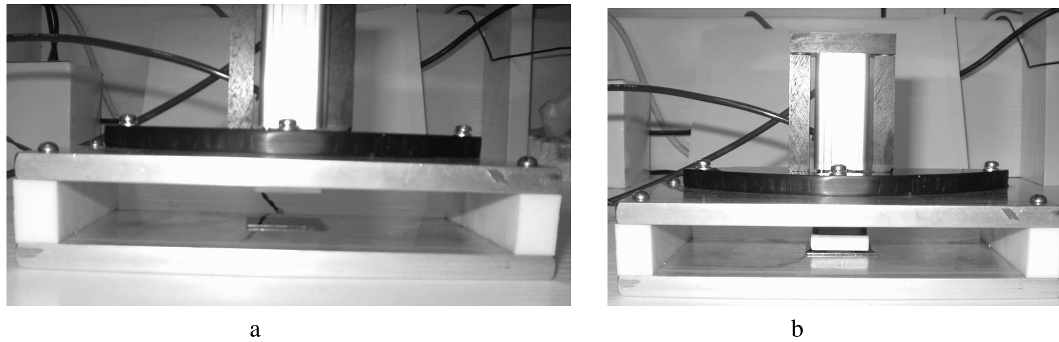
a b

Fig. 2. a) Chemical structure of epoxydised novolac polymer. b) Chemical structure of 2-hydroxyethyl methacrylate.

2.3 Apparatus

In case of imprinting thermoplastic polymers a precise temperature control during the process is needed. For the fulfillment of the experiments the necessity of the design and the implementation of a specialized apparatus emerged. The setup that contributed in the success of the NIL experiments is illustrated in the figures below (Fig. 3a, 3b). It is composed of an appropriate holder on which a piston may move up and down when it is supplied with gas. A nitrogen supply is connected to the apparatus and provides the necessary pressure (3 bars at most). The pressure is

changed with the pressure controller and the temperature is adjusted by using a hot plate. A thermocouple is embedded in the bottom of the metallic plate of the apparatus exactly above the area where the specimen is placed. Using this simple approach it is possible to have continuous control of both molding pressure and sample's temperature.



a b

Fig. 3. Photographs of NIL setup: a) No pressure is applied; b) The master is pressed against the substrate.

2.4 Nil process

The process flow chart is illustrated in Fig. 4. Firstly, the substrate is spin-coated with either PHEMA 4% w/w solution or EPN 16% w/w solution in ethyl-(s)-lactate (a). The solutions had sustained overnight stirring and were cleaned with 0.2μm filters. The thickness of the polymeric film varied from 200-500 nm depending on the desired minimum feature size. After post apply baking, the wafer is placed on the base of the apparatus and is heated up to 120 ^{o}C using a hot plate (b). This value exceeds the T_g of both materials. Afterwards, the Si master is brought into contact with the polymer film and is pressed against it with application of 3 bars pressure (c). Simultaneously, the imprint setup is removed from the hot plate, while pressure is continuously applied, and the following quenching allows the thermoplastic polymer to return to the solid state. When the system reaches the room temperature the master is easily detached from the substrate, which is now formed with the contrast mask pattern (d).

Tests with several values of pressure and temperature have been made. Pressure and temperature increase were followed by more exact pattern replication The greater pressure value that was tested (3 bars) lead to optimum results as long as it was applied when the temperature had reached 120 ^{o}C. Greater temperature values did not have noticeable effects, whereas smaller values were considered to be inadequate, concerning viscosity reduction.

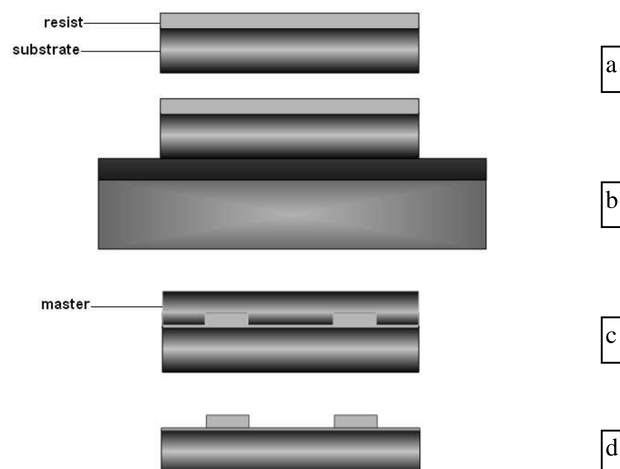


Fig. 4. Schematic representation of NIL process.

3. Results and discussion

3.1 Characterization

To compare the imprinted resist profile and the profile of the master features, the masters were examined using a scanning electron microscope SEM in order to have a clear image of the surface structure of the masters. Typical results of the transferred pattern on the Si master surface are shown in the figures (Fig. 5a-d) below.The first two pictures are top view micrographs of trenches with feature size 2 and 5 μm. The other two are cross section photos of the same trenches, which indicate that the etching depth is not greater than 200 nm.

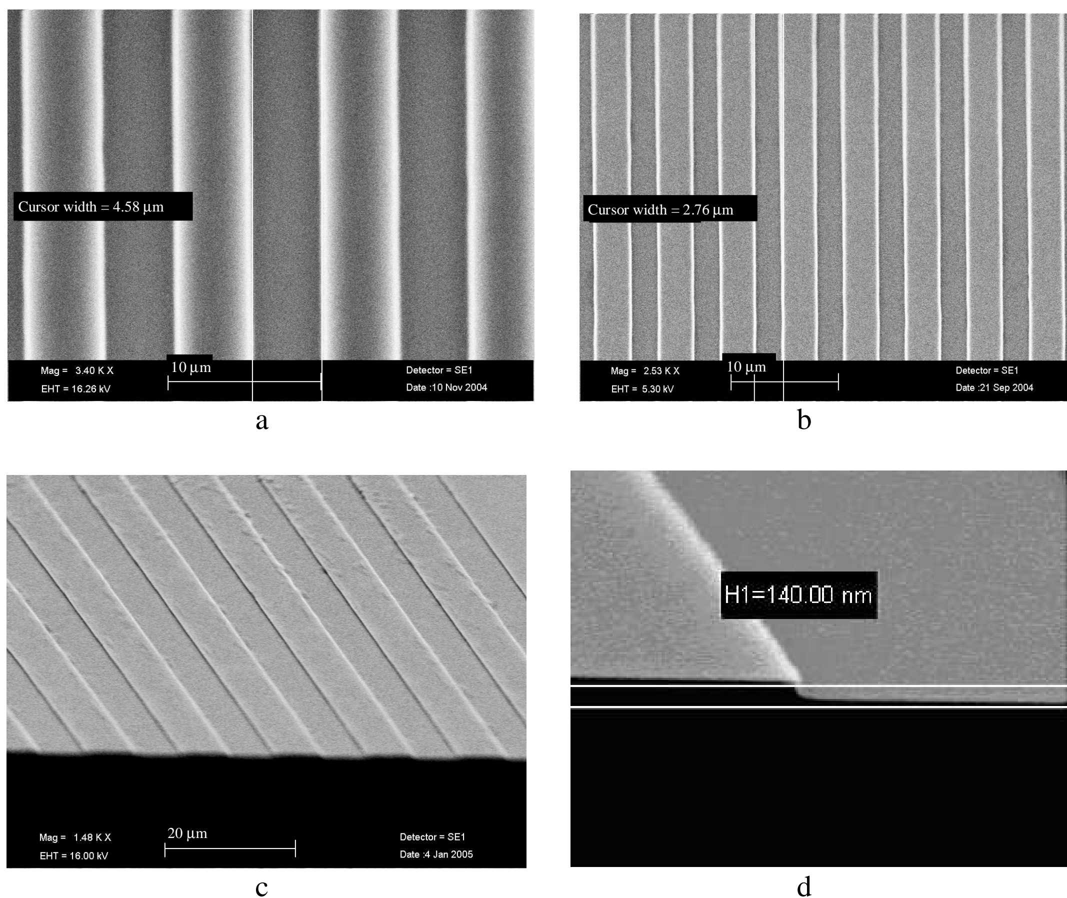


Fig. 5. SEM micrographs of the master's morphology: a) Top view 2.0 μm; b) Top view 5.0 μm; c) Cross section 2.0 μm; d) Cross section 5.0 μm.

The resist profile shown in the Figs. 6,7 comes from the closed end of the mold fingers; therefore, a precise comparison between the mold shape and the resist profile is not feasible. However, comparison of the general features, such as the linewidth heights, and slight bending at the end of each line, indicated that the polymeric profile conformed to the mold.

For the characterization of the imprinted samples SEM was considered to be the most appropriate tool. The first group of pictures (Fig. 6a-d) consists of top view and cross-section micrographs of trenches with feature size varying from 2 - 3μm imprinted on EPN. It is obvious that the width of the trenches has not sustained any changes during the imprint process. The formation of trenches with depth smaller than 50 nm has been achieved.

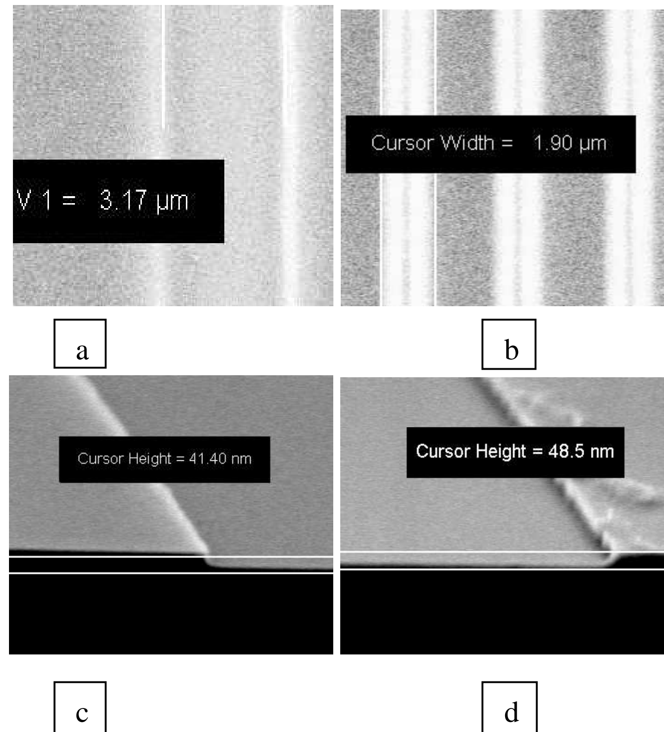


Fig. 6. SEM micrographs of imprinted structures on EPN: a) Top view 3.0 μm; b) Top view 2.0 μm; c) Cross section 3.0 μm; d) Cross section 2.0 μm;

The second group of pictures (Fig. 7a-d) consists of top view and cross section SEM micrographs from the PHEMA tests. The photos contain areas printed with trenches with feature size 1.5-2.0 μm and printed depth of 50-70 nm.

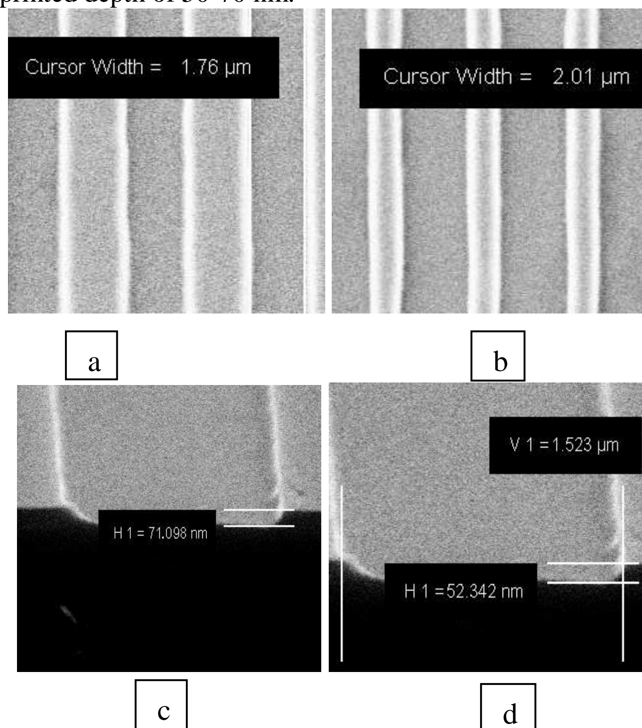


Fig. 7. SEM micrographs of imprinted structures on PHEMA: a) Top view 1.5 μm; b) Top

view 2.0 μm; c) Cross section 1.5 μm; d) Cross section 2.0 μm.

3.2 Repeatability

NIL process repeatability and master durability are two key issues in making imprint lithography a manufacturing technology. The same master was used to imprint PHEMA and EPN over 20 times and both the mold and the resist profile were examined every time. No noticeable changes or cracks were observed in either the resist profile or the master. Although over 20 times imprinting can hardly be considered a repeatability and durability test, we should expect the process to have a good repeatability and mold durability. This is because mold release agents are very effective, the resist held above glass-transition temperatures is very soft, and the mold intrusion does not touch the substrate.

4. Conclusions

The results shown in the presented work lead to the following conclusions: First of all we managed with a very low cost apparatus to acquire a satisfactory resolution (1 μm width 50 nm depth), limited only by the master's feature sizes (1μm – 40μm). Second, NIL can structure a large area (several square microns) at once, hence offering high troughput. We also succeeded in using other thermoplastic materials, apart from PMMA, as resists for the imprint test. Their behaviour was excellent and allowed us to create structures with size limited only by the minimum feature size of the glass/Cr mask, since the depth of the printed pattern did not exceed 50 nm in some cases. PHEMA, due to its lower viscosity contributed in obtaining more exact structures and leaded in successful results at most of the tests. As far as it concerns EPN although its T_g has a very small value (53 ^oC), we observed that it created structures with many defects, whose dimensions were often comparable with the trenches' ones.

We believe that with a proper selection of the polymer and mold materials and an optimization of the pressing conditions, the sticking and defect problems associated with the traditional contact printing can be avoided making NIL a reliable manufacturing technology.

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