Nanotechnology Science and Technology

# NANOIMPRINT LITHOGRAPHY

## Principles, Processes and Materials

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NANOTECHNOLOGY SCIENCE AND TECHNOLOGY

# NANOIMPRINT LITHOGRAPHY: PRINCIPLES, PROCESSES AND MATERIALS

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Nova Science Publishers, Inc.
*New York*

**LIBRARY OF CONGRESS CATALOGING-IN-PUBLICATION DATA**

Lan, Hongbo, 1970-
Nanoimprint lithography : principles, processes, and materials / authors, Hongbo Lan, Yucheng Ding, and Hongzhong Liu.
p. cm.
Includes bibliographical references and index.
ISBN 978-1-61122-501-3 (softcover)
1. Nanoelectronics. 2. Microlithography. 3. Nanostructures. I. Ding, Yucheng, 1961- II. Liu, Hongzhong, 1971- III. Title.
TK7874.84.L36 2010
621.3815'31--dc22 2010038653

*Published by Nova Science Publishers, Inc. † New York*

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# NANOTECHNOLOGY SCIENCE AND TECHNOLOGY

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# PREFACE

Nanoimprint lithography (NIL) has now been considered a promising method with low-cost, high throughput and high resolution to produce micro/nanometer-scale patterns, especially for fabricating the complex 3-D and large-area micro/nano structures. It was accepted by the International Technology Roadmap for Semiconductors (ITRS) in 2009 for the 16 and 11 nm nodes, scheduled for industrial manufacturing in 2013. Toshiba has validated nanoimprint lithography for 22 nm and beyond. The resolution potential has been demonstrated by the replication of 2.4-nm features.

NIL was first invented by Prof. Stephen Chou and his students in 1995 as a low-cost and high throughput alternative to photolithography and E-beam lithography (EBL) for researchers who needed high resolution patterning, motivated by the high expense and limited resolution of optical lithography. In the past 15 years, scientists and researchers from academia and industry have made significant contributions for the advances in NIL and its practical applications. Prof. Grant Willson's group pioneered UV-based nanoimprint lithography (UV-NIL), and developed Step and Flash Imprint Lithography (SFIL) process. Prof. Heinrich Kurz's group proposed soft UV-NIL. Prof. Lars Montelius's group and Obducat developed STU® (Simultaneous Thermal and UV) technology. Furthermore, Prof. Clivia M. Sotomayor Torres's group, Prof. Yoshihiko. Prof. L Jay Guo's group, Hirai's group, Prof. H.Schmid's group, Prof.Jouni Ahopelto's group, Prof.Yong Chen's group, etc., are dedicated to the investigations on NIL and its applications. Many accomplishments achieved and efforts conducted by these researchers all over the world have pushed the rapid developments of NIL, as well as their applications across multiple disciplines. More and more researchers and engineering technicians are being attracted by the non-conventional patterning technologies due to its prominent advantages and potential new applications.

In addition, there are five leading suppliers for the NIL tool and process in the world which include Molecular Imprints, Obducat, EVG, Süss, Nanonex. They have now developed and held their own proprietary NIL processes or patents respectively, for instance, Simultaneous Thermal and UV (STU®) technology and Intermediate Polymer Stamp (IPS®) technology from Obducat; Jet and Flash™ (former S-FIL®) and IntelliJet™ from Molecular Imprints, Soft UV-NIL and Step and Repeat Process for EVG from AMO, Substrate Conformal Imprint Lithography (SCIL) and for Süss from Philips patent; and Air Cushion Press from Nanonex. The resists used in NIL have been provided by commercial suppliers (e.g., NanoNex, Microresist technologies GmbH or Sumitomo Ltd.). NIL Technology ApS (NILT) is a special provider for NIL molds and nanopatterning using NIL. Actually, the driving force of NIL advances comes from a variety of new NIL applications. NIL techniques have demonstrated great commercial prospects in several market segments, hard disk drives (HDDs), high-brightness light-emitting diodes (HB-LEDs), flat panel displays, flexible macro-electronics devices, and polymer and functional imprint materials.

NIL technology involves two fundamental aspects: the basic research and the application research. The basic research consists of the principle, process, template (mold), material (resist, functional material, etc), and tool, which aims to meet the different application requirements, namely the fabrication of micro/nano structures or devices. NIL applications mainly cover nanoelectronics, optoelectronics, nanophotonics, nano-biology, optical components, etc. The book primarily focuses on three key issues of NIL: principle, process and materials. Latest progresses and innovations in this area provided a pool of focused research efforts, relevant to a wide readership from academic researchers to practicing engineers. The goal of the book is to present the basic principle, process and materials for the NIL, and to discuss prospects and challenges for the NIL which can offer some references for researchers further conducting the NIL investigation and for engineering technicians to better understand and utilize the new technique.

*Hongbo Lan*

# CONTENTS

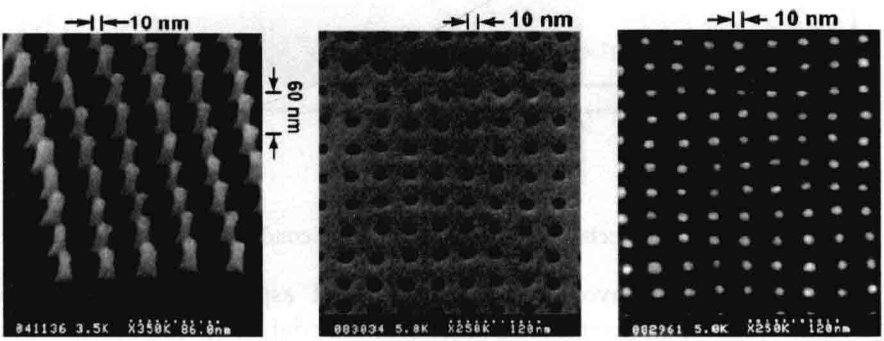
*Chapter 1*

# INTRODUCTION

Lithography, the fundamental fabrication process of semiconductor devices, has been playing a critical role in micro-nanofabrication technologies and manufacturing of Integrated Circuits (IC). Optical lithography (photolithography) was the first and the earliest microfabrication technology used in semiconductor IC manufacturing. It is still the main tool of lithography in today's VLSI (Very Large Scale Integrated Circuit) and MEMS. Traditional optical lithography, including contact and project photolithography, has contributed significantly to the semiconductor device advancements. As of 2009, the most advanced form of photolithography is immersion lithography, in which water is used as an immersion medium for the final lens. It is being applied to the 45 nm and 32 nm nodes. Several companies, including IBM, Intel and TSMC, have prepared for the continued use of current lithography, using double patterning, for the 22 nm and 16 nm nodes, and extending double patterning beyond 11 nm. However, as the resolution requirement increases for fabrication of finer and smaller components and devices, the technological dependence on photolithography becomes a serious problem since the photolithography resolution is restricted by the diffraction limitation of optics [1, 2]. Currently, maintaining the rapid pace of half-pitch reduction requires overcoming the challenge of improving and extending the incumbent optical projection lithography technology while simultaneously developing alternative, next generation lithography (NGL) technologies to be used when optical projection lithography is no longer more economical than the alternatives [2]. Candidates for next generation lithography include: extreme ultraviolet lithography (EUV-lithography), electron beam lithography (EBL), focused ion beam lithography (FIB), X-ray lithography, maskless lithography

(ML2), interference lithography, and nanoimprint lithography, etc. Among NGL candidates and emerging nanopatterning techniques, nanoimprint lithography (NIL) has several important advantages over conventional optical lithography and other NGLs; it is non-optical by design, and the resolution appears to be limited only by the resolution of structures that can be generated in the template or mold. It is neither limited by diffraction nor scattering effects nor secondary electrons, and does not require any sophisticated radiation chemistry. In particular, the prominent advantage of NIL compared to other lithography techniques, NGL and micro/nanomanufacturing technologies, is the prominent ability to create 3-D and large-area micro/nano structures with low cost and high throughput. In addition, due to the parallel nature of NIL, it has a very high production rate which is well suitable for mass production. It has been considered as one of the most promising NGLs due to its unique principle and outstanding advantages. Furthermore, NIL is also one of the most promising low-cost, high-throughput technologies for manufacturing nanostructures [3,4,5].

Nanoimprint lithography (NIL) was initially proposed and developed by Stephen Chou in 1995 [5]. It is a novel method of making micro/nanometer scale patterns with low cost, high throughput and high resolution. Unlike traditionally optical lithographic approaches, which create pattern through the use of photons or electrons to modify the chemical and physical properties of the resist, NIL relies on direct mechanical deformation of the resist and can therefore achieve resolutions beyond the limitations set by light diffraction or beam scattering that are encountered in conventional lithographic techniques [6]. At present, structures with feature sizes down to 5 nm have been realized. Compared with optical lithography and next generation lithography (NGL), the difference in principles makes NIL capable of producing sub-10 nm features over a large area with a high throughput and low cost [7]. Fig1.(a), (b) and (c) show the scanning electron micrographs (SEMs) of a mold 10-nm-diameter pillar array and imprinted 10 nm hole arrays in poly(methymethacrylate) (PMMA) as well as 10 nm metal dots after transfer (lift-off) [7]. Due to its prominent advantages and great potential, MIT's Technology Review listed NIL as one of 10 emerging technologies that will strongly impact the world [8], and it was accepted by International Technology Roadmap for Semiconductors (ITRS) for the 32 node and beyond, scheduled for industrial manufacturing in 2013. Toshiba has validated nanoimprint lithography for 22 nm and beyond. What is more significant is that NIL is the first sub-30 nm lithography to be validated by an industrial user [9]. Moreover, NIL has been used to fabricate various micro/nanostructures and devices for nanoelectronics, optoelectronics, nanophotonics, optical components, biological applications, etc. The patterns can take many forms, from simple rectilinear patterns for nanowire development to complex diffractive optical elements for LED general lighting applications. According to current reports, NIL current applications mainly involve the following fields: magnetic storage media (hard disk media, NAND flash memory), optical storage media (HD-DVD, Blu-Ray), photonic (opto) electronics (high brightness LEDs, OLED, LCD, field emission display, flat panel display, organic light emitting display , flexible macro-electronic, ), optical elements (microlens, diffractive grating, waveguide, tunable optical filters, nano wire grid polarizer), biological devices (biosensors, Nanofluidic devices, microarrays for genomics, proteomics and tissue engineering, nanoscale protein patterning), nanoelectronics (molecular electronics, AFM tips,), high-end semiconductors and high density interconnects, other NEMS/MEMS applications (solar cell, fuse cell, CNT sensor, etc), etc. In particular, NIL techniques currently have demonstrated great commercial prospects in several market segments, hard disk drives (HDDs), high-brightness light-emitting diodes (HB-LEDs), flat panel displays, flexible macro-electronics devices, optical components and functional polymer devices. In addition, a recent investigation was performed in order to assess the process capabilities of NIL, based on a study of published research and to identify the application areas where NIL has the greatest potential. The results suggest NIL is most suited to producing photonic, microfluidic and patterned media applications, with photonic applications the closest to market [10].




(a) (b) (c)

Figure 1. SEM micrographs demonstrated by S. Y. Chou in 1997 [7]. (a) a $SiO_2$ mold with 10 nm diameter pillars with a 40nm period arrays which are 60nm tall, (b) imprinted hole arrays in PMMA, (c) 10 nm metal dots after pattern transfer using lift-off process.

NIL has, over the last decade, gone from being a new and exciting research topic to be a technology used in the most advanced parts of various industries. NIL has now been considered as an enabling, cost-effective, simple pattern transfer process for various micro/nano devices and structures fabrications. The progress made in the recent years enabled NIL not only to be a serious NGL candidate but also to be a platform for one of the ten technologies in MIT Technology Review being evaluated to change the world. It has now been added to the ITRS in 2009 [11] for the 16 and 11 nm nodes, as shown in Figure 2. The resolution potential has been demonstrated by the replication of 2.4-nm features, shown in Figure 3 [12].

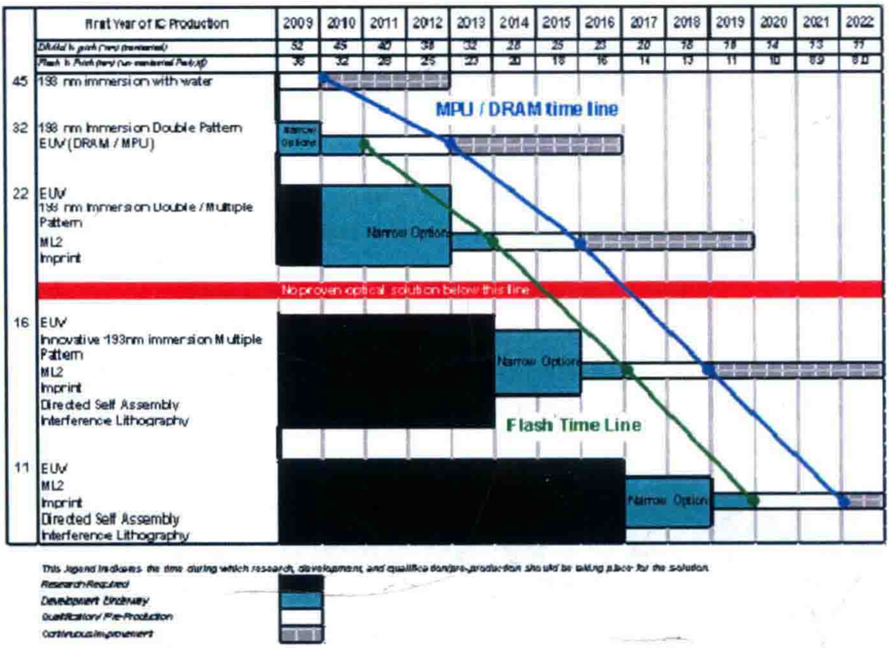



Figure 2. International Technology Roadmap for Semiconductors (ITRS, 2009) [11].

NIL technique involves following several aspects: principle, process, template (mold), material (resist, functional material, etc), tool, and its various applications. This book mainly focuses on three key issues of NIL: principle, process and materials. Following the introduction, the principle and fundamental process for NIL are presented in Section 2. Some variations of NIL and its recent progresses regarding NIL processes are addressed in Section 3. NIL materials including imprint materials (resists and functional materials) and mold materials are discussed in Section 4. In addition, prospects and challenges in NIL are elaborated in Section 5. Finally, Section 6 concludes and summaries the chapter. As a result, the significant contribution of this book is to present the basic principle, process and materials for the NIL, and to discuss prospects and challenges for the NIL which can offer some references for researchers further conducting the NIL investigation, and for engineering technicians to better understand and utilize the new technique.

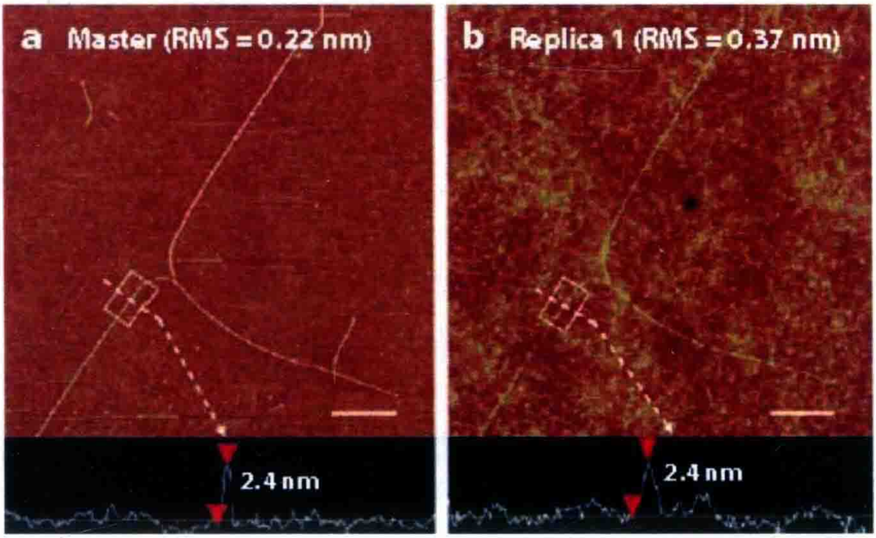



Figure 3. AFM images of (*a*) a master template and (*b*) the faithfully imprinted replica of the 2.4-nm-diameter single-wall nanotube (SWNT) structures on the template. The white scale bars are 1 μm [12].

*Chapter 2*

# PRINCIPLE AND FUNDAMENTAL PROCESS FOR NIL

## 2.1. PRINCIPLE OF NIL

NIL is based on the principle of mechanically modifying a thin polymer film (mechanical deformation of the resist) using a template (mold, stamp) containing the micro/nanopattern, in a thermo-mechanical or UV curing process. In other words, NIL uses the direct contact between the mold (template) and the thermoplastic or UV-curable resist to imprint (or replicate) the pattern, unlike optical lithography, does not require expensive and complex optics and light sources for creating images. The switch from using light to using contact to pattern brings some advantages. For instance, it can achieve resolutions beyond the limitations set by light diffraction or beam scattering that are encountered in conventional techniques, simplifies process and largely reduces cost. The resolution of NIL mainly depends on the minimum template feature size that can be fabricated. However, that also simultaneously produces new challenges and issues, the most important of which are alignment and the 1x mask/template fabrication. Since NIL can be considered as such a process based on squeeze flow of a sandwiched viscoelastic material between a mold and a substrate, the property of interface between the two materials has to be considered throughout the entire process, both from topographical, chemical, and mechanical points of view. Furthermore, the characteristics of the interface and surface have a great impact on the demolding capability and filling behavior which can strongly influence pattern quality and throughput [13-15].

The patterned polymer can even act as a functional device, e.g. lens for imaging sensors, micro fluidic chip, biomedical array etc. It can also be used as a high resolution mask for subsequent steps of the process (metal deposition, electroplating, etching and lift-off process). Moreover, various substrates, including silicon wafers, glass plates, flexible polymer films, polyethyleneterephtalate (PET) polymer film, and even nonplanar substrates can be utilized for NIL [16]. The ultimate resolution of the patterns fabricated by NIL is primarily determined by the resolution of the features on the surface of the mold. Because of the 1X nature of NIL compared with 4 X for photolithography, the 1X template must be more accurate than conventional masks.

As a result, distinct features for NIL involve four points:

1) The contact nature of the process;
2) Direct mechanical deformation of the resist;
3) The 1X nature of NIL compared with 4 X for photolithography;
4) Parallel patterning.

Two crucial steps, namely the resist filling rheology behavior and demold capabilities, have decisive influence on transferred pattern quality and throughput for NIL. The surface and interface properties among mold, resist and substrate have to be investigated fully in order to better understand the nature and mechanism of NIL. The prominent advantage of NIL compared to other lithography techniques and NGL is the outstanding ability to fabricate large-area and complex three-dimensional (3D) micro/nanostructures with low cost and high throughput.

## 2.2. Theoretical Analysis for NIL

NIL generally includes two basic steps: pattern replication (or imprint) and pattern transfer. For the imprint procedure, it can be further divided into four stages: approaching between mold and substrate, filling resist into cavities of the mold, squeezing and compressing resist (thinning resist film), as well as the separation between the mold and the imprinted pattern on the substrate (demolding). The behaviors of the resist thin-film squeeze flow (including the resist flow, filling, rheology, and the thickness reduction of the residual layer) and the characteristic of the demolding have decisive influence on transferred pattern quality and throughput. Moreover, they play a central role in understanding the principle process of NIL. In order to better understand the NIL mechanism and achieve the suitable imprint conditions (e.g., pressure, temperature, pattern layout of the mold, and time), it is necessary and important to explore and investigate the behaviors of resist thin-film squeeze flow, filling and rheology, as well as the interface properties between template and resist.

Prior to the theoretical analysis and modeling, the following conditions are assumed for the NIL system.

1) Vertical motion between the mold and the substrate without relative sliding;
2) Parallel between the mold and the substrate.

And the resist is presumed below.

1) Resist is considered as incompressible Newtonian liquid during imprinting;
2) Compared with viscosity force, gravity force can be ignored;
3) Compared with viscosity force, inertia force can be neglected during resist flow;
4) Both surface tension and capillary attraction of the resist are neglected;
5) Resist has no sliding on the interface;
6) Viscosity and density of the resist keep constant.

Figure 4 shows the schematic diagram of patterns replication. The feature patterns of the mold are the rectangular cavities. The initial state of the mold, resist and substrate is shown in Figure 4 (a). Where $h_0$ is the initial height of the resist, $h_r$ is the depth of the cavity, $h_f$ is the residual layer thickness, $S_i$ is the distance of from $i$th cavity to $i$+1th cavity, $W_i$ is the width of $i$th cavity, $S$ is the length of the mold, $L$ is the width of the mold, $\eta$ is the viscosity of the resist. Figure 4 (b) illustrates the imprinted patterns after demolding.

When these cavities of the mold are completed filled with resists, the mold can be assumed a plane plate during the thinning resist film process. Figure 5 shows the schematic diagram of the analysis model for the mold deformation. Where $p$ represents uniform load, $h(t)$ denotes a given displacing amount of resist of height, $u(z)$ is velocity value along $x$ direction, $v(z)$ and $w(z)$ represent velocity value along $y$ and $z$ direction respectively, $\delta_x$ and $\delta_z$ denote the distortion unit body along $x$ and $z$ direction, $\tau_{ij}$ represents shearing stress rate,