Nanoimprint Technology
Nanotransfer for Thermoplastic and Photocurable Polymers

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Nanoimprint Technology
Nanotransfer for Thermoplastic and Photocurable Polymers

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The Microsystem and Nanotechnology book series provides a thorough contextual summary of the current methods used in micro- and nanotechnology research and how these advances are influencing many scientific fields of study and practical application. Readers of these books are guided to learn the fundamental principles necessary for the topic, while finding many examples that are representative of the application of these fundamental principles. This approach ensures that the books are appropriate for readers with varied backgrounds and useful for self-study or as classroom materials.

Micro- and nanoscale materials, fabrication techniques, and metrology methods are the basis for many modern technologies. Several books in this series, including *Introduction to Microsystem Technology* by Gerlach and Dotzel, *Microfluidic Technology and Applications* edited by Koch, Evans, and Brunnschweiler, and *Fluid Properties at Nano/Meso Scale* by Dyson, Ransing, P. Williams, and R. Williams, provide a resource for building a scientific understanding of the field. Multiscale modeling, an important aspect of microsystem design, is extensively reviewed in *Multiscale Analysis of Deformation and Failure of Materials* by Jinghong Fan. Modern topics in mechanics are covered in *Nano and Cell Mechanics: Fundamentals and Frontiers* edited by Espinosa and Bao. Specific implementations and applications are presented in *AC Electrokinetics: Colloids and Nanoparticles* by Morgan and Green, *Digital Holography for MEMS and Microsystem Metrology* edited by Asundi.
This book, edited by Jun Taniguchi, presents the fundamental methods of nanoimprint technologies and the principles of fabrication and materials selection that are essential for their successful implementation. Included in this work are examples of theoretical modeling of the physical phenomena that govern micro- and nanofabrication and the invaluable insight they provide for informing process design and parameters.

Horacio D. Espinosa
Ron Pethig
Preface

The technique of nanoscale pattern transfer technology using a mold has attracted attention because this technology makes nanotechnology industries and applications possible. This field of technology has evolved rapidly, year by year. However, because of these rapid advances, it is difficult to keep up with the technological trends and the latest cutting-edge methods. In order to fully understand these pioneering technologies, comprehension of the basic science and an overview of the techniques is required. In this book, the latest nanotransfer science – based on polymer behavior and polymer fluid dynamics – is described in detailed but easy-to-understand language. Based on their physical science, injection molding and nanoimprint lithography are explored. These exemplifications of concrete methods will help the reader to create an accurate picture of nanofabrication. Furthermore, the newest cutting-edge nanotransfer technologies and applications are also described. We hope the reader will benefit from knowledge of these new technologies and be left with a basic comprehension of nanotransfer mechanisms and methods.

Jun Taniguchi
1

What is a Nanoimprint?

Jun Taniguchi

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The technical term “nanoimprint” first appeared in “nanoimprint lithography,” as used by Professor S.Y. Chou in 1995 [1]. “Nano” means $10^{-9}$, and usually refers to nanometer (nm) scale objects and structures. “Imprint” means to press and make engraved marks, and so has almost the same meaning as pressing, embossing, and printing. However, lithography has a special meaning, and is the main technique for fabricating nanopatterns in the semiconductor process. The lithography process is shown in Figure 1.1.

First, a photoresist is coated on a silicon (Si) substrate. A photoresist is a material whose solubility changes when exposed to light (photons). The photomask is made of quartz and chromium (Cr), producing a light contrast—the quartz area is transparent whereas the Cr area does not transmit light. Thus, the photomask defines the area of the photoresist that will be exposed to light. An excimer laser (KrF: wavelength 248 nm, ArF: wavelength 193 nm) is used as the light source. The photomask is placed over the photoresist on Si, then light is exposed through the photomask (Figure 1.1(a)) to produce the exposed areas of the photoresist (Figure 1.1(b)). The exposed areas are changed into two types by liquid immersion. This liquid is called the developer, and the liquid immersion process is called development. After development, the photoresist where the exposed areas...
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Light source (ArF, KrF) → Quartz → Cr → Photomask

(a) Lithography set-up

Si wafer → Resist

(b) After light exposure

Si wafer → Exposed area

(c) After development

Si wafer → Positive tone

Si wafer → Negative tone

Figure 1.1 Lithography process

were removed is called positive type whereas the photoresist where the exposed areas remain is called negative type. These two types form the resist pattern on the silicon wafer. Using the resist patterns, successive semiconductor processes such as dry etching, ion implantation, and metal wiring are carried out. Dry etching is the process of removing silicon substrate using the developed resist for an etching mask. Dry etching uses an active gas such as CF₄, SF₆, or CHF₃ for the silicon substrate, by creating a plasma at low pressure. The activated species (ions or radicals) also etch the development resist, hence the term “photoresist.” The ion implantation process is the process of doping donors and acceptors to create p- and n-type regions. Metal wiring is performed by the lift-off process, as follows: after development, metal is deposited by sputtering or evaporation, then the resist is removed by the remover, which dissolves the resist polymer. After removal of the resist, metal wiring remains on the silicon substrate and this area acts as an electrode and power supply. Therefore, the resolution of the resist
pattern is very important for all processes because lithography determines the design rule of silicon devices such as ultra-large-scale integrated circuits (ULSIs). The design rule is the gate length or half pitch of line and space, and this index measures how small the transistor is. A small design rule enables many transistors to be formed per unit area, enabling a densely integrated electronic circuit which can be used to create high value-added devices such as large memory devices and high-performance central processing units (CPUs).

The following photolithography equation determines the resolution and hence the design rule for lithography [2]:

\[ R = k_1 \times (\lambda/\text{NA}) \]  
\[ \text{(1.1)} \]

where \( R \) is the resolution, \( k_1 \) is a process factor depending on the optical system of the stepper or scanner, \( \lambda \) is the wavelength of the light source, and \( \text{NA} \) is the numerical aperture of the lens, given by

\[ \text{NA} = n \times \sin \theta \]  
\[ \text{(1.2)} \]

where \( n \) is the refractive index of the light path and \( \theta \) is the angle of aperture, thus \( 0^\circ < \theta < 90^\circ \). The photolithography exposure system includes a stepper and scanner, which can reduce the exposed pattern area to \( 1/4 \) of the mask pattern by reduced-projection optical lenses. Here, “stepper” means the “step and repeat” motion of the Si wafer stage during light exposure and “scanner” means the continuous motion of the Si wafer stage during light exposure. This system has precise stage and optical elements, and so the cost of the system is extremely high. According to eqs (1.1) and (1.2), a fine pattern can be obtained by a small wavelength (\( \lambda \)) and a large NA. Thus, photolithography has a limit to miniaturization; various techniques are required to exceed this limit, which are usually expensive.

In contrast, nanoimprint lithography (NIL) can exceed this limit because the patterning mechanism is merely physical pressing. The NIL process is shown in Figure 1.2.

First, a nanoscale patterned mold is prepared. A silicon wafer with resist layer is also prepared (Figure 1.2(a)). Two types of resist layer are mainly used: thermoplastic polymer and photocurable polymer. The thermoplastic polymer is solid at room temperature, but begins to flow (liquefies) upon applying heat. Thus, the shape of the thermoplastic polymer is deformed by heating and pressing of the mold. Meanwhile, the photocurable polymer is liquid at room temperature and so is easily deformed by mold pressing [3]. However, to solidify this resin, exposure to ultraviolet (UV) light is required, for which a mercury lamp i-line (365 nm) is usually used. UV light does
not transmit through the silicon wafer, so the mold must be UV-transparent. Quartz or sapphire is transparent to UV light, and so these materials are used for the mold. After preparing the pattern transfer, the mold presses the resist layer on the silicon wafer (Figure 1.2(b)). After solidification of the resist layer, the mold is released from it (Figure 1.2(c)). At this time, the convex part of the mold engraves the concave part of the resist layer, but the convex part of the mold does not contact the silicon wafer. Usually, a residual layer remains above the silicon wafer. This residual layer is unnecessary and is removed by oxygen plasma ashing and so on (Figure 1.2(d)). After these processes, the silicon wafer has a mask pattern as shown in Figure 1.1(c), therefore NIL can act as a lithography process.

The advantages of NIL are as follows. It is a simple process and thus cost-effective; once a nanoscale mold has been prepared, nanoresolution patterns
What is a Nanoimprint?

can be obtained at low cost. Furthermore, sub-10 nm feature patterns by NIL were reported in 1997 [4], which is a major step in the semiconductor field because NIL is a simple, cost-effective, and high-resolution process. The potential of NIL is well known worldwide, and many companies and researchers are currently conducting semiconductor research [5]. In addition, NIL is very useful for other fields such as three-dimensional (3D) pattern transfer. When NIL is used for the semiconductor process, the residual layer must be removed, but in other fields it is not necessary to remove it. When the residual layer is removed, a mask pattern for silicon is obtained, but this is a two-dimensional pattern. That is, the silicon surface is painted with or without the resist mask. In contrast, by using a mold with a 3D pattern, the nanoimprint process creates a 3D replica. This kind of 3D fabrication is difficult to achieve by photolithography. Furthermore, 3D replica patterns are widely used for optical elements and surface-modified uses. For example, a moth-eye structure (which is a kind of anti-reflective structure), diffractive optical elements, gratings, Fresnel lenses, polarizers, sub-wavelength plates, and wire-grid polarizers are all optical devices. Surface-modified devices include cell culture plates, hydrophobic surfaces (lotus-effect surfaces), and adhesive surfaces such as gecko finger structures. Therefore, NIL is widely used for 3D nanofabrication, and this versatile process is called “nanoimprint technology.” Therefore, NIL now means not only lithography but also 3D fabrication. This book mainly describes nanoimprint technology for 3D fabrication.

Many preparations are required to perform nanoimprint technology, such as the transfer polymer, mold fabrication process, transfer machine, and measurement system. The main transfer polymers are thermoplastic polymer and photocurable polymer, but their transfer processes are different. In addition, different transfer machines are also required for each polymer. Thus, in this book, thermoplastic and photocurable polymers are dealt with in separate chapters.

The pattern transfer of thermoplastic polymer is described in Chapters 2 and 3. First, Chapter 2 describes the history of polymer processing and the principle of the transfer method. Then, Chapter 3 describes the characteristics of thermoplastic polymer and the transfer method, and also simulation results. These simulations are very helpful for identifying thermoplastic behavior and how deformation develops over time. Nanoimprint technology using thermoplastic polymer requires a thermal cycle, so this kind of NIL is called “thermal cycle NIL” or simply “thermal NIL.” The technical terms “thermoplastic polymer,” “thermoplastic resin,” and “thermoplastic” have almost the same meaning.
Mold fabrication processes are described in Chapter 4. The mold is the key component of nanoimprint technology, and so it is very important to be able to make a fine and precise mold. The mechanical cutting process and electron beam lithography and dry etching process required to obtain a nanoscale 3D shape mold are described in detail. Machine tools and accurate machine positioning and control have been developed, enabling sub-micrometer order 3D cutting shapes to be fabricated. The merit of using cutting tools is rapid fabrication. Electron beam lithography (EBL) involves exposure to an electron beam instead of excimer laser light. An electron beam can be focused to less than several nanometers, so a finer pattern (less than 10 nm) can be delineated. Electron beam lithography is usually used for the photomask in the semiconductor process, but by using EBL and successive dry etching technologies, nanoimprint molds can be fabricated. This book also describes various mold materials. The technical terms “mold,” “stamp,” and “template” have almost the same meaning.

Nanoimprint technology using photocurable polymer is described in Chapter 5. In this case, ultraviolet light is used to harden the photocurable polymer, so this kind of NIL is called “ultraviolet NIL,” or UV-NIL. This chapter describes the UV-NIL mechanism, photocurable polymer science, UV-NIL machine, release agents, and measurement methods. Usually, nanoscale patterns are observed with a scanning electron microscope (SEM) and atomic force microscope (AFM), but these methods are for microscale local observation. In this chapter, a macroscale non-uniform measurement system is described. The release agent is the coating material on the mold surface, which prevents the photocurable polymer from sticking. The technical terms “photocurable polymer,” “photocurable resin,” “UV-curable polymer,” and “resin” have almost the same meaning.

Chapter 6 outlines the latest nanoimprint technologies, as well as actual applications and some devices made by nanoimprint technology.

This book outlines nanoimprint technology using thermoplastic and photocurable polymers, and describes in detail nanoscale transfer technology, materials, machines, know-how, and trends.

References