Chapter 3

Fabrication Technologies and Instruments

3.1 Introduction

The available fabrication technologies and instruments for fabricating the sub-wavelength grating will be described in this chapter. Among the fabrication parameters, the period of the sub-wavelength grating is the most essential one. Generally speaking, the shorter period of sub-wavelength grating is, the higher polarization efficiency will be. Consequently, the pattern definition processes should be well-considered. Electron beam lithography technology can be utilized to fabricate nano-structure; however, the area of sub-wavelength grating is restricted due to that fabricating a large size sub-wavelength grating, say 1 cm x 1cm, is costly and time-consuming. On the other hand, interferometric lithography can produce nano-structure more efficiently, but the feature size is limited by the wavelength of the interference light. In this chapter, we will elucidate above pattern definition processes along with the replication process, which is UV-nanoimprint lithography technology, in detail.

3.2 Electron Beam Lithography (EBL) Technology

Electron beam lithography technology, employing high energy electron beams, is a technique for creating the extremely fine patterns. Derived from the early scanning electron microscopes, the technique in brief consists of a scanning beam of electrons across a surface covered with a resist film sensitive to those electrons, thus depositing energy into the desired pattern on the resist film. The process of forming the beam of electrons and scanning it across a surface is very similar to the CRT display mechanism; however, EBL typically has three orders of magnitude higher in resolution. The main characteristics of EBL are

(1) It is capable of very high resolution, almost to the atomic level.

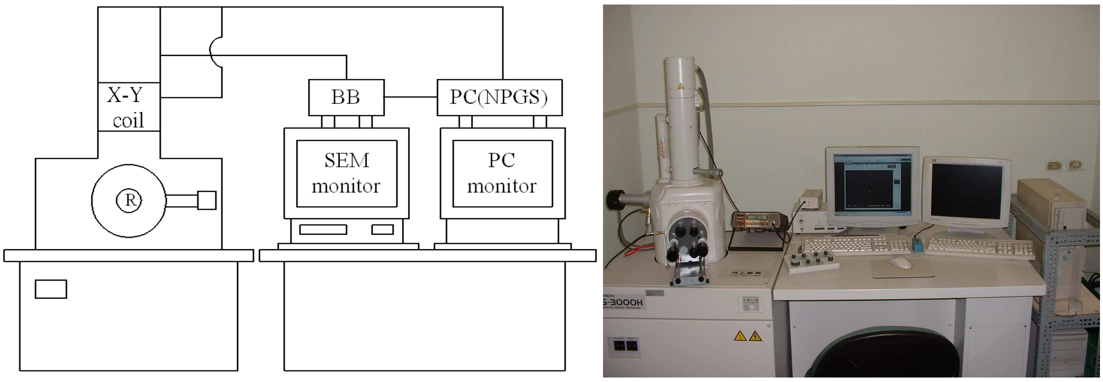
(2) It is a flexible technique that can work with a variety of materials and almost infinite number of patterns.

(3) It is slow, being one or more orders of magnitude slower than optical lithography.

(4) It is expensive and complicated. Electron beam lithography tools can cost several millions of dollars and requires frequent maintenance works to be operated in good conditions.

The electron beam writer used in the experiment consists of a scanning electron microscope (SEM) and a SEM conversion system Nanometer Pattern Generator Systems (NPGS) which is used to design the patterns and to control the electron beam, as shown in Fig. 3.1. In addition, polmermethyl methacrylate (PMMA) is one candidate for EBL resist. PMMA possesses following characteristics

- Positive tone
- Very high resolution, low contrast
- Poor dry etch resistance
- Several dilutions available, allowing a wide range of resist thickness
- No shelf life or film life issues
- Not sensitive to white light
- Developer mixtures can be adjusted to control contrast and profile



(a) (b)

Fig. 3.1 (a) Schematics, and (b) photograph of an electron beam writer.

PMMA is usually purchased in two high molecular weight forms (496 K or 950 K) in a casting solvent such as chlorobenzene or anisole. Electron beam exposure breaks the polymer into fragments that are dissolved preferentially by a developer such as MIBK. MIBK alone is too strong a developer and removes some of the unexposed resist. Therefore, the developer is usually diluted by mixing in a weaker developer such as IPA. A mixture of 1 part MIBK to 3 parts IPA produces very high contrast but low sensitivity. By making the developer stronger, say, 1:1 MIBK：IPA, the sensitivity is improved significantly with only a small loss of contrast.

3.3 Interferometric Lithography

Interferometric lithography provides a universal method to generate high reslution periodic features over a large area. The basic principle of interferometric lithography is two beams interference. After interference, the periodic fringes are than generated. The periodic fringes can be transferred to the photoresist by exposure to fabricate the periodic grating structure on the resist.

Referring to Fig. 3.2, the resultant electric field of two s-polarized plane waves incident on a wafer at angles of θ_1 and θ_2 with respect to the normal plane is given by

$$E(x)=\left(u_1 e^{-i\frac{2\pi}{\lambda}x\sin\theta_1}+u_2 e^{i\frac{2\pi}{\lambda}x\sin\theta_2}\right) \qquad 3.2.1$$

where u_1, u_2 are the amplitudes of the two electric fields.

Hence the light intensity distribution at the wafer plane is

$$\begin{aligned} I(x) &= E(x)E^*(x) \\ &= {u_1}^2+{u_2}^2+2u_1u_2\cos\left[\frac{2\pi}{\lambda}x(\sin\theta_1+\sin\theta_2)\right] \qquad 3.2.2 \end{aligned}$$

In the special case when the intensities of two beams are equal (i.e. $I_0={u_1}^2={u_2}^2$)

$$I(x)=2I_0\left(1+\cos\left[\frac{2\pi}{\lambda}x(\sin\theta_1+\sin\theta_2)\right]\right) \qquad 3.2.3$$

The nonlinear response of photoresist can then transform this aerial image into a binary grating pattern of lines and spaces. The grating period can be expressed as

$$\Lambda=\frac{\lambda}{(\sin\theta_1+\sin\theta_2)} \qquad 3.2.4$$

When two coherent laser beams interfere within the coherent length, the generated period of interference can be defined as $\Lambda=\lambda/2\sin\theta$; where Λ is the generated period, λ is the wavelength of incidence, and θ is the angle of incidence. From the period definition, the smaller fringe period can be obtained by interference with shorter incident wavelength λ or larger incident angle θ [20].

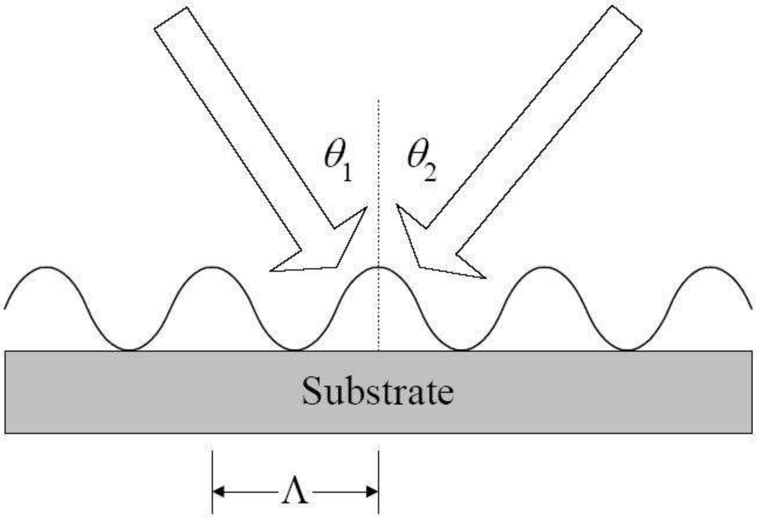


Fig. 3.2 Schematic diagram of interferometric lithography

3.4 UV-nanoimprint Lithography Technology

UV-nanoimprint lithography, which is also called step and flash imprint lithography (SFIL), is a technology to form nano-scale structure with UV-curing under the room temperature. The technology developed by Prof. C. G. Willson in 1999 was proposed to improve the deformed situation during hot embossing imprint lithography.

In UV-nanoimprint lithography, photo-sensitive polymer is utilized to substitute thermal plasticity polymer. Besides, a mold with high transmittance for UV-light is used to carry out the imprint processes [21]. The schematic diagram of UV-nanoimprint lithography which includes six steps is shown in Fig. 3.3:

(1) Substrate coating：First step is spin coating a layer of substrate on the wafer. The thickness is about several hundred nanometers.

(2) Photo-sensitive polymer coating：Next, the liquid photo-sensitive polymer with low viscosity is coated on the substrate. The thickness is around 100nm and the viscosity is usually below 1 Pa-s.

(3) Imprinting：Then, the transparent mold with nano-scale pattern is put on the top surface of the substrate to proceed with the imprint process.

(4) UV-curing：In consolidation, the liquid photo-sensitive polymer is then formed and solidified with appropriate UV-curing.

(5) Mold releasing：After mold releasing, the nano-scale pattern is transferred to the photo-sensitive polymer.

(6) Reactive Ion Etching (RIE)：The nano-scale pattern of the photo-sensitive polymer is then transferred to the substrate by RIE.

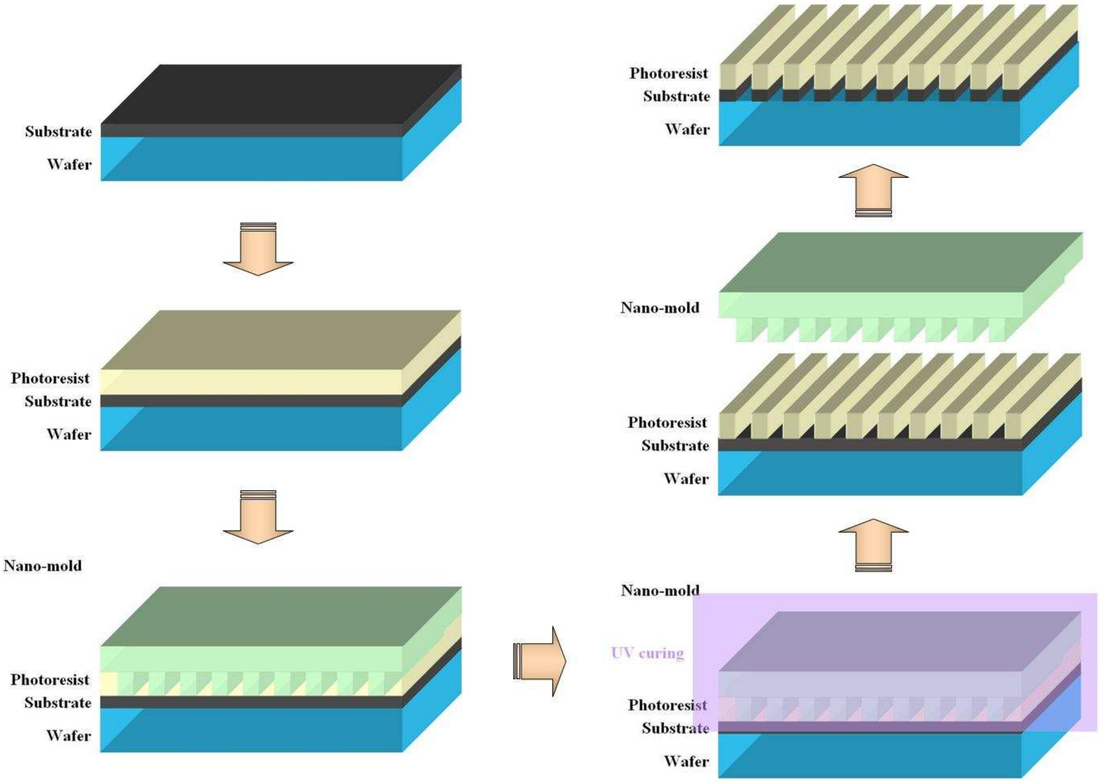


Fig. 3.3 Schematic diagram of UV-nanoimprint lithography

Owing to the liquid photo-sensitive polymer is low viscosity, the pressure utilized during UV-curing process is around 0.01-1 bar, which is smaller than it used in hot embossing imprint lithography. Besides, UV-nanoimprint lithography can be carried out under room temperature, which is far lower than the temperature of the embossing imprint lithography. For avoiding the formed polymer adhering to the mold, the release agent is usually coated on the top surface of the mold about several nanometers and added in the liquid photo-sensitive polymer.

Furthermore, C. G. Willson combines UV-nanoimprint lithography with step and flash imprinting, which utilized small-sized mold to proceed with imprinting step by step. As a result, the imprinting uniformity is not only better than that wide-area imprinting directly, the small-sized mold also can reduce the production cost and raise the yield.

3.5 Fabrication Process of Sub-wavelength Grating

In this section, the fabrication processes of sub-wavelength grating which combining pattern definition technology (e-beam lithography or interferometric lithography) and UV-nanoimprint lithography technology will be demonstrated. In the nanoimprint lithography, the mold with nano-scale feature is the most important component. Thus, the fabrication of the mold with the nano-structure (the pattern definition process) becomes essential. Briefly speaking, the fabrication processes can be divided into three parts. First, master molds with nano-scale feature are fabricated by e-beam lithography and interferometric lithography individually. Next, the fabricated master molds will be reproduced with PDMS（Poly Dimethyisiloxane）. After the mold fabrication, the PDMS mold will be used for the nanoimprint processes.

3.5.1 Fabrication Process of Master Mold (I) --- by E-beam Lithography

In the experiments, quartz wafer was adopted to be the substrate. The details of steps to produce sub-wavelength grating with quartz by EBL were listed below：

(1) Wafer cleaning：The first step was initial-clean. It removed particles, which would cause defects in the final structure, from the wafer surface.

(2) Aluminum deposition：Because the quartz wafer was not a conductor, electrons would accumulate on its surface during exposure. Such a phenomenon was so called *charge-up*. In order to avoid charge-up, a quite thin aluminum layer (about 50Å) was evaporated on the quartz as a conductive layer.

(3) Resist coating：The coating of electron resist, which was PMMA in our experiment, was then applied. Substrates were placed on a vacuum chuck in the coater and the PMMA was dropped onto the wafer. A uniform and thin electron resist layer was coated on the wafer surface when the wafer was spun by the coater. The coated thickness of PMMA depends on both the concentration of PMMA solution and the speed of coater. For example, a 3% PMMA solution is able to produce a thickness of 100-1000 *nm* at the speed of coater of 1000-5000 rpm for 60 seconds.

(4) Baking：The coated resist was baked on a hotplate at 160°C for 15 minutes. The condition of baking was less critical, but the temperature must be between 150℃ and 200℃ for at least 10 minutes. Otherwise, the resist may be over-baked.

(5) Exposure：The wafers were put into an E-beam system after baking. The desired patterns, gratings with a period of 0.4 ~ 0.6 um in the experiments, were drawn by the Nanometer Pattern Generator Systems (NPGS) before exposure. The focusing electron beam was then controlled by the NPGS to scan patterns on PMMA with certain amount of dosage.

(6) Development and Rinse：The exposed resist was developed for 75 seconds in 1:3 MIBK：IPA, rinsed for 25 seconds in IPA, and then dried with nitrogen gas.

(7) RIE：Because there was a thin aluminum layer on the quartz substrate, RIE with BCl_3 gas was then used to remove the remnant aluminum layer.

The flowchart of fabricating sub-wavelength grating on quartz is shown in Fig. 3.4.

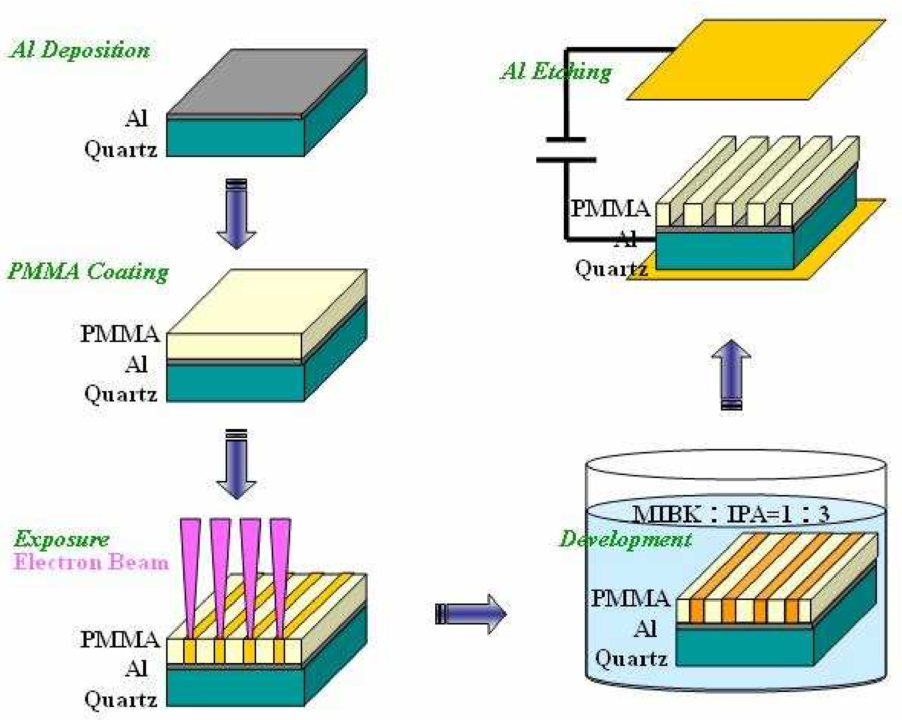


Fig. 3.4 Flowchart of fabricating sub-wavelength grating on quartz.

3.5.2 Fabrication Process of Master Mold (II) --- by Interferometric Lithography

The first step in this process is PR spin-coating. The thickness and uniformity control of photoresist will affect final result. Therefore, we prefer thin PR to minimize the influence due to the variation of intensity distribution.

Here we choose interferometric lithography to get the periodic grating pattern. Argon Laser with long coherent length（>1 m）is utilized as the source of exposure, and we use the wavelength of 244nm. From $\Lambda = \lambda / 2\sin\theta$, we can vary the angle of incidence to fabricate the different gratings. Taking the grating we made as example, the incident angle in interferometric lithography is 37.6° to generate the grating with 200 nm period.

The experimental layout is shown in Fig. 3.5. A PBS is used to separate the polarization of light, and only pure TE-mode light is used. A pinhole and a lens are used to produce the collimated light. The location of the mirrors, M_1 and M_2, can be tuned to control the angle of incidence.

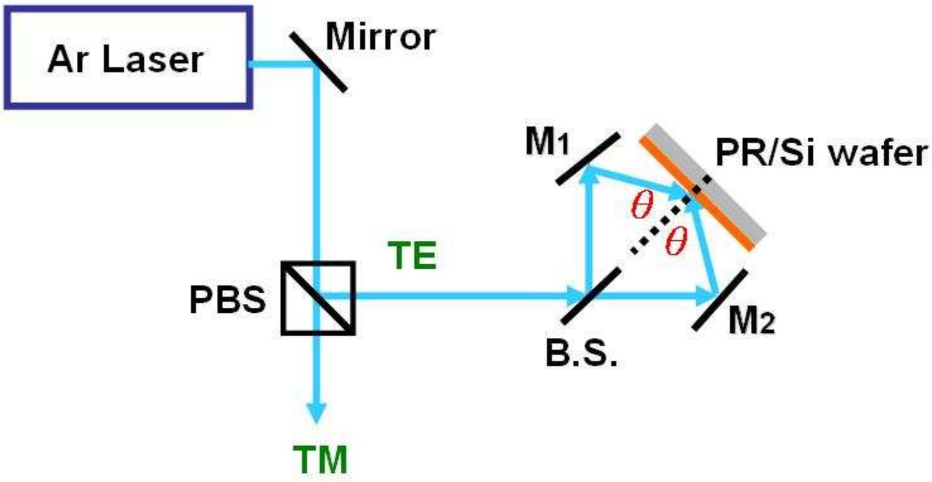


Fig. 3.5 Interferometric lithography exposure setup

From the setup mentioned above, we can fabricate uniform gratings within 1 cm^2. The main constraint in area size comes from the size of optics, especially the beam size expanded by objective lens. In order to produce larger size parallel beams, we use a pinhole and objective lens as a beam expander and it will enlarge the beam size to 1.5 ㎝ diameter round area. Then, using aperture confine the uniform region with 1 ㎝ diameter for exposure.

After two beams interference, the sample with photoresist is then treated as post-exposure-bake（PEB）at 110 ℃ for 60 seconds to harden and increase the adhesion of the photoresist, as shown in Fig. 3.6. Then, the resist is developed by using standard developer（Tetramethylammonium hydroxide, TMAH, 2.38％）with appropriate development time. After that, the mold with nano-scale feature is defined. Then, the mold is rinsed in de-ionized（D.I.）water to cease the development process and subsequent nitrogen purge to dry the sample. Finally, the mold is hard baked at 120 ℃ and the fabricated mold will be utilized to proceed with the following fabrications of sub-wavelength grating.

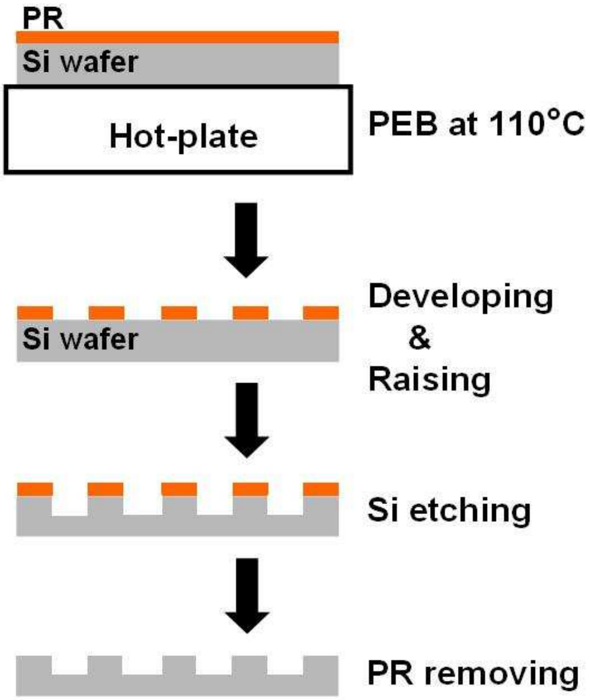


Fig. 3.6 Processing flow chart of master mold fabrication

3.5.3 Fabrication Process of Replicated PDMS Mold

Before nanoimprint process, the fabricated master mold needs to be reproduced with PDMS. For UV-nanoimprint lithography is selected here, the mold must have high transmittance for UV light. Besides, PDMS is flexible and easy to replicate the nano-scale structure to other nonplanar surface. The operation of PDMS is to add the curing agent into PDMS colloid, and heat the mixture to make the PDMS solidfied. Since PDMS is a fluid colloid before solidifing, PDMS is usually utilized to fabricate various micro-elements by casting. The detail steps to produce PDMS mold are listed below：

(1) Materials mixing：The materials of this fabrication are PDMS colloid and a curing agent with Pt catalyst. PDMS colloid and the curing agent are well mixed to the ratio

10：1.

(2) Casting：Next, the mixed PDMS colloid is poured onto the top surface of the case mold with nano-scale feature fabricated by interferometric lithography.

(3) Vacuum：Because the structure of the case mold is very subtle, it is difficult to permeate the structure for the colloid. The bubbles in the gap would cause the structure defect of the PDMS after PDMS solidified. Besides, the bubbles generated during mixing would also affect the result of PDMS. Therefore, pumping a vacuum could eliminate the bubbles in the colloid to improve the quality of the PDMS mold.

(4) Solidifying：PDMS is baked on a hot plate at 75 °C for 60 minutes for PDMS solidifying. Otherwise, PDMS can be placed at room temperature about 24 hours and the colloid also solidified.

(5) Mold releasing：After PDMS solidifying, the case mold and the PDMS mold are separated and the nano-scale pattern of the case mold is transferred to PDMS. The appearance of PDMS mold is transparent and elastic.

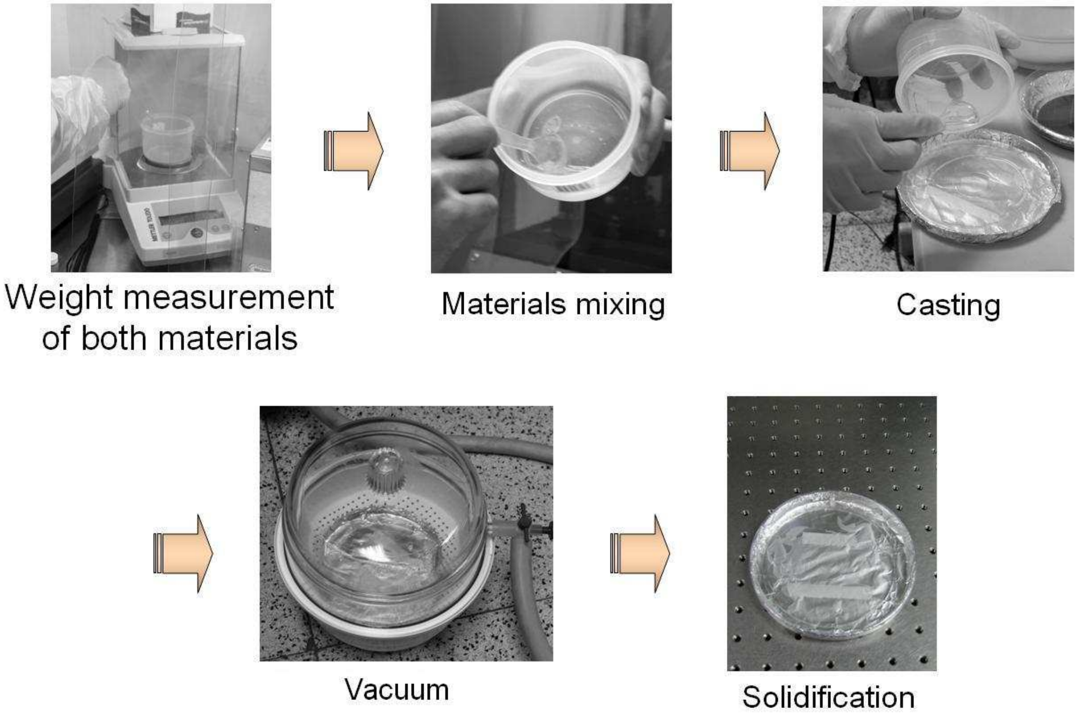


Fig. 3.7 Flow chart of the PDMS mold fabrication

3.5.4 Fabrication Process of Sub-Wavelength Grating by Using UV-nanoimprint Lithography Technology

The flow of fabricating sub-wavelength grating by using UV-nanoimprint lithography is shown in Fig. 3.8. We choose mr-L 6000.5 to be the photoresist here. The physical and chemical properties of mr-L 6000.5 are summarized in the following：

Dynamic Viscosity (25℃, 1000 rpm)	6.0 ± 2 mPas
Density	1.016 g/cm^3
Colour	clear, colourless
Film thickness at 3000 rpm	0.5 ± 0.05 μm

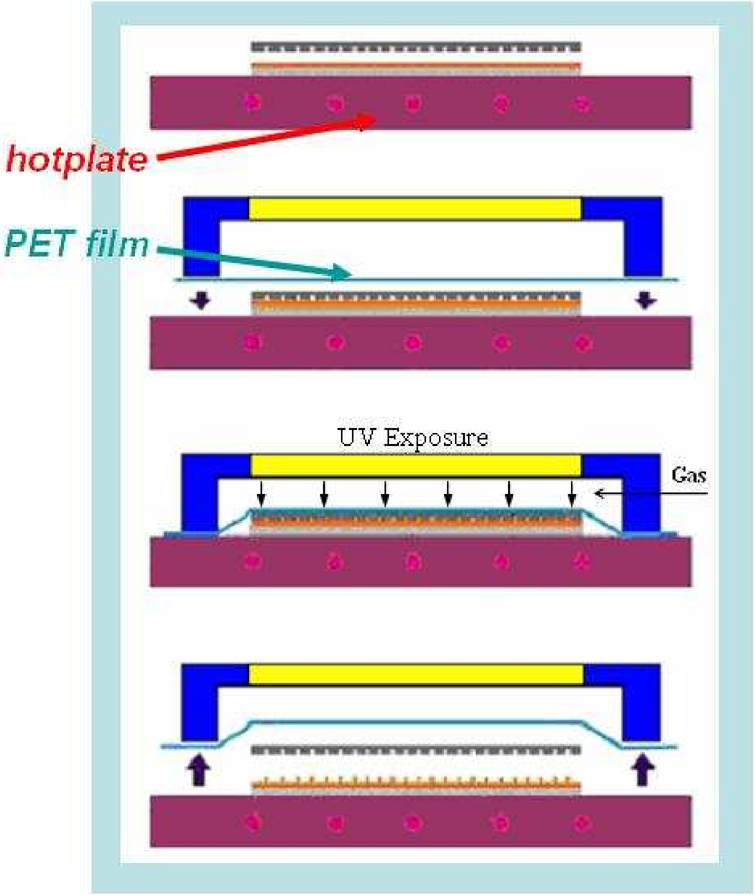


Fig. 3.8 Flow of sub-wavelength grating fabrication with UV-nanoimprint lithography

In the experiments, quartz wafer is adopted to be the major substrate we would like to fabricate on. The detail steps to produce sub-wavelength grating with metal layer only on quartz by UV-nanoimprint lithography are listed below：

(1) Wafer cleaning：The first step is initially clean to remove particles from the wafer surface, which will affect the ultimately fabricated structure and its efficiency.

(2) Resist coating：The coating of photoresist is applied. Substrates are placed on a vacuum chuck in the coater and the mr-L 6000.5 is dropped on to the wafer. A uniform and thin resist layer can be coated on the wafer surface after the wafer is spun by the coater. Thickness of mr-L 6000.5 depends on both concentration of mr-L 6000.5 solution and speed of coater. For example, a 3% mr-L 6000.5 solution is able to produce thickness of 400-900 nm at speed of coater of 1000-6000 rpm for 30 seconds.

(3) Baking：The coated resist is baked on a hot plate at 150 °C for 2-5 minutes.

(4) Imprinting：The baked wafer is located in an imprinting chamber. The PDMS mold with the nano-scale sturcture is pressed on the top surface of photoresist. A PET film is covered on the top surface and the chamber is locked. The function of the PET film is to make imprint pressure uniform. Then, the gas (nitrogen) is applied to pressurize the PDMS. The imprint temperature is between 80 and 120 °C.

(5) Exposure：The resist becomes solid after UV curing. The exposure quantity depends on the thickness of the resist film. It is 200-400 mJ/cm^2 at a film thickness of 0.5 μm and intensity of the lamp of 13 mW/cm^2 at 365 nm.

(6) PEB：Immediate after the exposure a baking step is enclosed. The irradiated resist film is baked 10 min at 100 °C on a contact-hotplate.

(7) Mold releasing：Decompress and demold after the PDMS mold cools down under T_g (35 °C). After mold releasing, the nano-scale pattern is transferred to the mr-L 6000.5.

(8) Etching：Dry etching is then applied sequentially to etch the residual resist and form the resist profile. The negative tone photoresist mr-L 6000.5 exhibits high resistance

to acidic and alkaline etching solutions and plating bathes (pH 1 – 13) and high dry etch stability.

(9) Metal evaporation：Because the aluminum grating is desired, the aluminum film is evaporated onto the sample by oblique e-beam evaporation, which will be described in the next section.

3.5.5 Oblique E-beam Evaporation

After UV-nanoimprint, aluminum grating is expected to be fabricated directly from the deposition process. Then, the deposition of Al shall have good directionality. Typical thin film deposition techniques used in semiconductor manufacturing includes thermal evaporation, e-beam evaporation, sputtering, and chemical vapor deposition (CVD). Among the above deposition techniques, E-beam evaporation has good directionality, but has poor sidewall coverage.

When the standard E-beam evaporation is applied, the direction of beam source is normal to the sample. As a result, the sample can not be structured as the desired Al-grating, as shown in Fig. 3.9. To produce the desired grating (coating aluminum on one sidewall only), the oblique E-beam evaporation is applied, as shown in Fig. 3.10. By tilting the sample with a certain angle and fixing it on a metal post, only one sidewall and the protruding part of resist are coated with aluminum, while other parts remains uncoated.

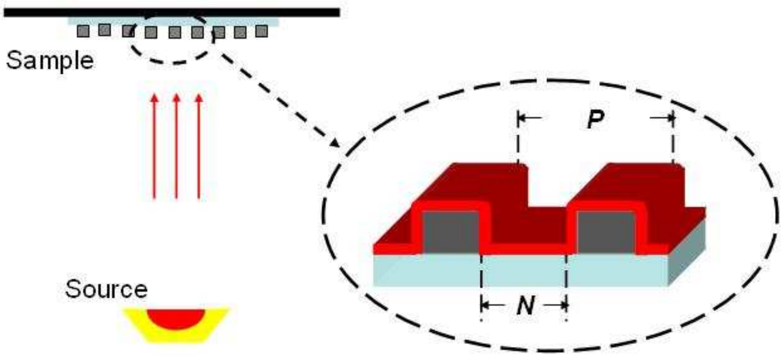


Fig. 3.9 Process setup and results of standard evaporation

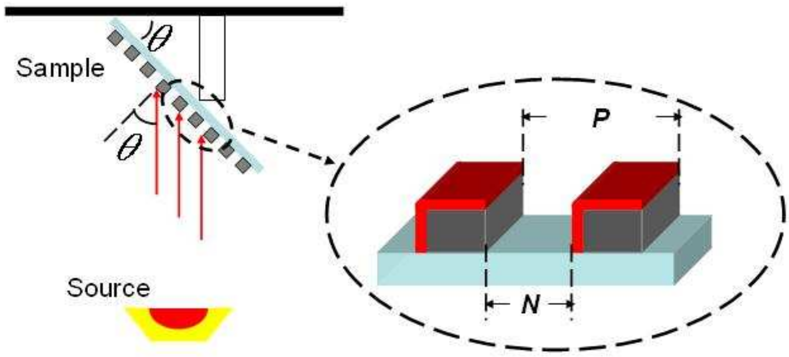


Fig. 3.10 Process setup and results of oblique evaporation

3.6 Measurement System

After the fabrication of sub-wavelength grating, the inspection will be performed to make sure that the fabricated nanostructures agree with the original design. First, SEM and AFM will be introduced sequentially. Besides, the experimental setup used to evaluate efficiencies of light separation will also be demonstrated.

3.6.1 Scanning Electron Microscope (SEM)

Scanning electron microscope (SEM) is an essential instrument to measure the accuracy and fidelity of the fabricated nanostructures. Using a series of electromagnetic lenses to focus the accelerated electron beam, the diameter of electron beam can be converged to the dimension of $10^{-3}\mu m$. The secondary electrons are generated where the focused accelerated electrons bombard the sample. Detecting the secondary electrons can determine the location of bombardment. Simultaneously, the focusing electron beam scans the surface of sample, with the aid of scanning coil, to map the feature of measured area, as shown in Fig. 3.11. Using SEM, the feature variation of a few angstroms can be observed. In our work, a JOEL JSM 7000F SEM was used to measure the quality of the fabricated nanostructures. The line width, etching depth, and each layer can be accurately measured.

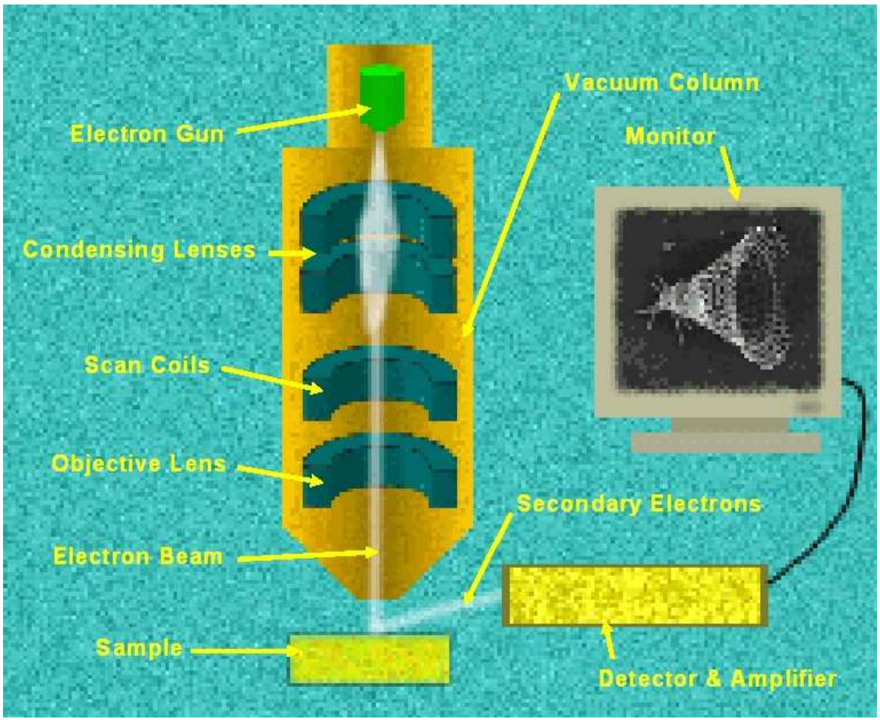


Fig. 3.11 Schematic diagram of scanning electron microscope

3.6.2 Atomic Force Microscope (AFM)

AFM consists of a scanning sharp tip at the end of a flexible cantilever across a sample surface while maintaining a small, constant force. The tips typically have an end radius of 2 nm to 20 nm, depending on tip type. The scanning motion is conducted by a piezoelectric tube scanner which scans the tip in a raster pattern with respect to the sample (or scans to the sample with respect to the tip). The tip-sample interaction is monitored by reflecting a laser off the back of the cantilever into a split photodiode detector. By detecting the difference in the photodetector output voltages, changes in the cantilever deflection or oscillation amplitude are determined. A schematic diagram of this mechanism is depicted in Fig. 3.12.

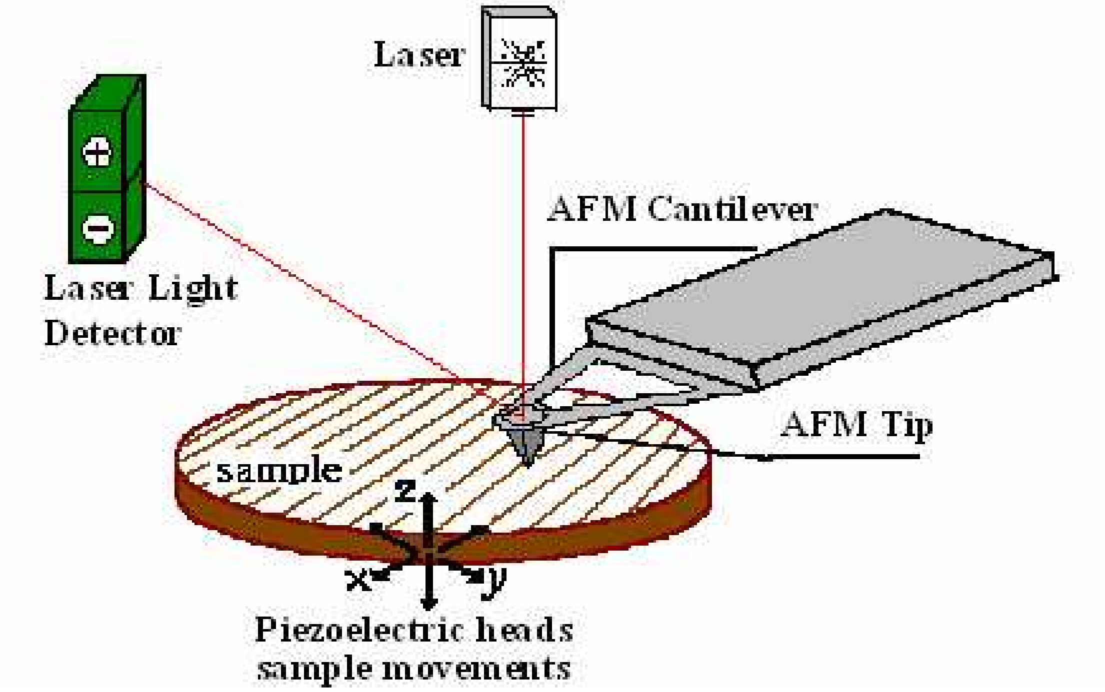


Fig. 3.12 Concept of AFM and the optical lever

The two most commonly used modes of operation are contact mode AFM and TappingMode^{TM} AFM, which are conducted in air or liquid environments. Contact mode AFM consists of scanning the probe across a sample surface while monitoring the change in cantilever deflection with the split photodiode detector. A feedback loop maintains a constant cantilever deflection by vertically moving the scanner to maintain a constant photodetector difference signal. The distance the scanner moves vertically at each x, y data point is stored by the computer to form the topographic image of the sample surface. This feedback loop maintains a constant force during imaging, which typically ranges between 0.1 and 100 nN .

TappingMode AFM consists of oscillating the cantilever at its resonance frequency (typically ~300 kHz) and lightly "tapping" on the surface during scanning. The laser deflection method is used to detect the root-mean-square (RMS) amplitude of cantilever oscillation. A feedback loop maintains a constant oscillation amplitude by moving the scanner vertically at every x, y data point. Recording this movement forms the topographical image. The advantage of TappingMode over contact mode is that it eliminates the lateral, shear forces present in contact mode, enabling TappingMode to image soft, fragile, and adhesive surfaces without damaging them, which can be a drawback of contact mode AFM.

3.6.3 Optical Efficiency Measurement Setup

The sample size is about 1 cm × 1 cm limited by the size of the optics, we then need to design an experimental setup to measure the efficiency of both TM-mode transmittance and TE-mode reflectance. The fabricated sub-wavelength grating is evaluated by means of a setup shown schematically in Fig. 3.13.

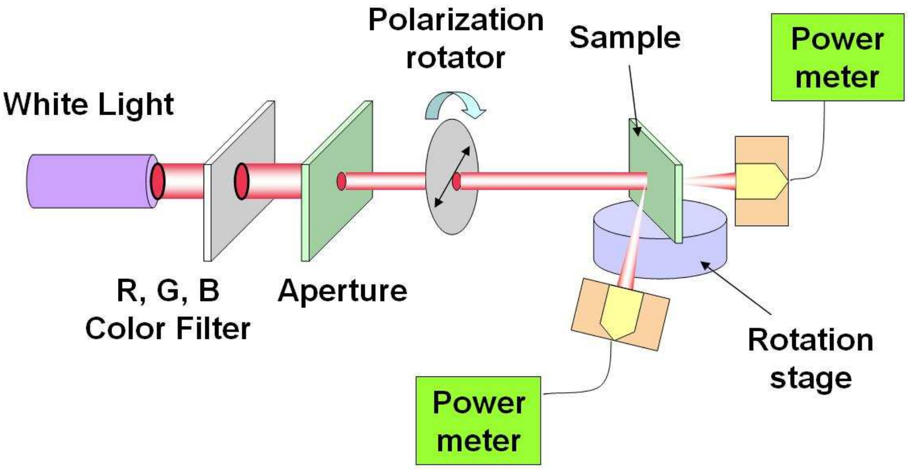


Fig. 3.13 Schematic diagram of the efficiency measurement setup

A white light with red, green, and blue three color filters is used as our light source. The light is focused onto the 1 cm^2 fabricated structure. Besides, we can control the input polarization by a polarization rotator. Two photodetectors are used to measure the transmittance and the reflectance simultaneously.