Chapter 3

Fabrication Technologies and Instruments

3.1 Introduction

The fabrication technology and instruments available to fabricate the sub-wavelength grating will be described in this chapter. Because the sub-wavelength grating interested in this thesis is mainly applied in display technologies, period of the sub-wavelength grating which is smaller than wavelength of visible spectrum, i.e. 0.4 μm to 0.8 μm, is then essential. Generally speaking, the smaller the period of sub-wavelength grating is, the higher the efficiency of light separation is. It is difficult to fabricate fine structure by utilizing general semiconductor process. High resolution electron beam lithography technology is therefore adopted for the easiness of fabricating sub-wavelength grating with fine structure.

3.2 Electron Beam Lithography (EBL) Technology

Electron beam lithography technology, employs high energy electron beams, is a specialized technique for creating the extremely fine patterns required by the modern electronics industry for integrated circuits, the academic research of physical and chemical properties of nanostructures, and the fabrication of mask used in semiconductor devices. Derived from the early scanning electron microscopes, the technique in brief consists of scanning a beam of electrons across a surface covered with a resist film sensitive to those electrons, thus depositing energy in the desired pattern in the resist film. The process of forming the beam of electrons and scanning it across a surface is very similar to CRT display mechanism, but EBL typically has three orders of magnitude higher in resolution. The main attributes of the technology 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 require frequent service to be in good operating conditions.

The electron beam writer used in experiment consists of a scanning electron microscope (SEM) and 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 of the first materials developed 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

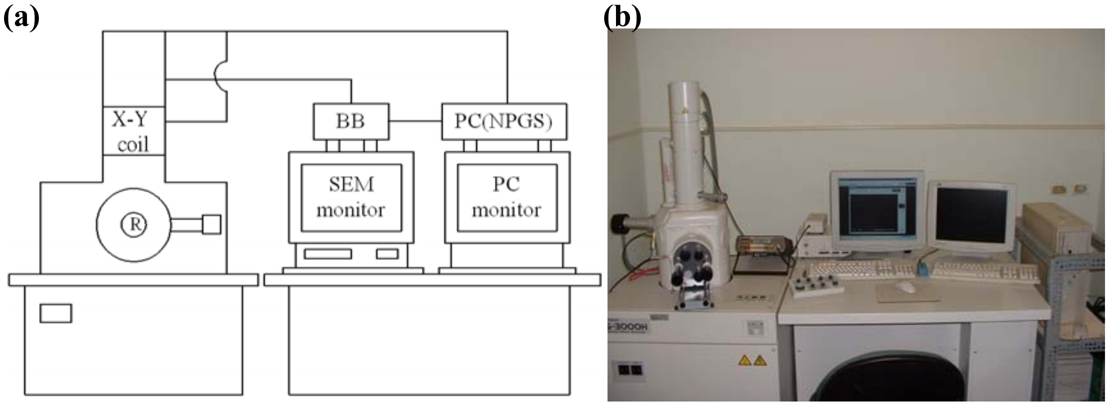

Fig. 3.1 (a) Schematics, and (b) photograph of an electron beam writer.

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.

Although EBL tools are capable of forming extremely fine probes, things become more complex when the electrons penetrate into the substrate. As the electrons penetrate the resist, they experience many small angle scattering events (forward scattering), which tend to broaden the initial beam diameter. As the electrons penetrate through the resist into the substrate, they occasionally undergo large angle scattering events (backscattering). The backscattered electrons cause additional resist exposure which is called the electron beam proximity effect. The most common technique of proximity correction is dose modulation. If the proximity effect is properly corrected, under-cut, as shown in Fig. 3.2, which is helpful to lift-off can be formed.

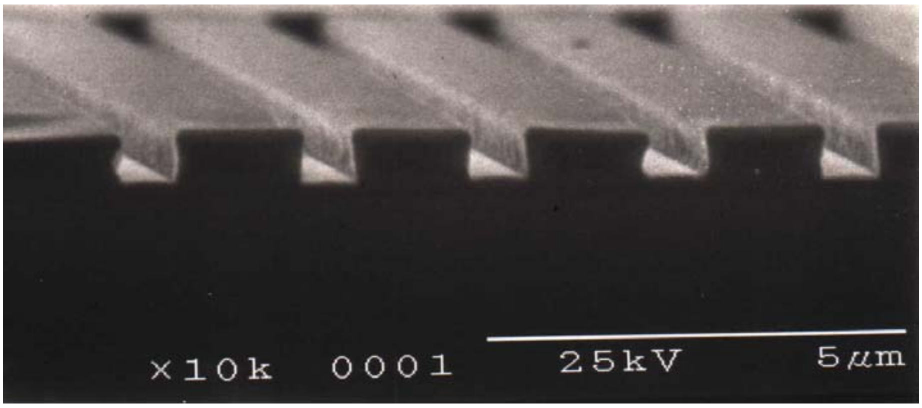

Fig. 3.2 Under-cut of PMMA.

Furthermore, the optical mask, which usually restrains the linewidth of structure in optical lithography, is unnecessary in electron beam lithography because the electron beam directly defines patterns on electron resist. The process is then simplified. In the next section, three different fabrication processes of EBL for fabricating sub-wavelength grating will be demonstrated. Besides, measurement systems used to evaluate the fabricated sub-wavelength grating will be also introduced in the last sections of this chapter.

3.3 Fabrication Process of Electron Beam Lithography

The basic fabrication process of e-beam lithography is different for varied requirements. Process like lift off, reactive ion etching (RIE), etc. could be involved owing to different needs. There are three fabrication processes to fabricate sub-wavelength grating with single and double layer. It is easier to fabricate sub-wavelength grating with single-layer than that with multi-layer. Therefore, we will start with the fabrication of sub-wavelength grating with single layer, grating with double layer will be followed.

3.3.1 Fabrication Process of Grating with Metallic Layer Only

In the experiments, both quartz and silicon wafers were adopted. Quartz wafer was the major substrate we would like to fabricate on. However, it is more suitable to inspect the cross-sectional view of fabricated nanostructure by means of the silicon wafer. The detail steps to produce sub-wavelength grating with metal layer only on quartz by EBL were listed below：

(1) Wafer cleaning：First step was initially clean. It removed particles, which would affect the ultimately fabricated structure and its efficiency, from the wafer surface.

(2) Germanium deposition：Because 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 germanium layer (about 50Å) was evaporated on quartz as a conductive layer. The reason for choosing germanium was that it could be easily etched with CF_4 gas.

(3) Resist coating：The coating of electron resist was applied. Substrates were placed on a vacuum chuck in the coater and the PMMA was dropped on to the wafer. A uniform and thin electron resist layer can be coated on the wafer surface after the wafer was spun by the coater. Thickness of PMMA depended on both concentration of PMMA solution and speed of coater. For example, a 3% PMMA solution was able to produce thickness of 100-1000 nm at 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 non-critical, but it must be baked at 150℃ < T < 200℃ for at least 10 minutes or may also be over baked at 160℃ for 1-2 hours.

(5) Exposure：The wafers were put into E-beam system after baking. The desired patterns, line array with center-to-center distance of 0.2 μm in the experiments, were drawn by NPGS before exposure. Focusing electron beam was then controlled by interface of NPGS to scan the corresponding patterns on PMMA with certain of dosage.

(6) Development and Rinse：The exposed resist was developed for 75 seconds in 1:3 MIBK：IPA and rinse for 25 seconds in IPA. Then, blow dry with nitrogen.

(7) RIE：Because there was a thin germanium layer on quartz, RIE with CF_4 gas was then used to remove germanium layer.

(8) Metal evaporation：Because aluminum structure was expected to be produced, aluminum film was evaporated onto the sample by thermal evaporator.

(9) Lift-off：The samples were immersed into acetone for 15 minutes after removing from evaporator. Then we agitated substrates and acetone with an ultrasonic cleaner to dissolve the unexposed PMMA with its cover lift-off, and the desired metallic nanostructure remained on the substrate.

The flow of fabricating single-layered sub-wavelength grating was shown in Fig. 3.3.

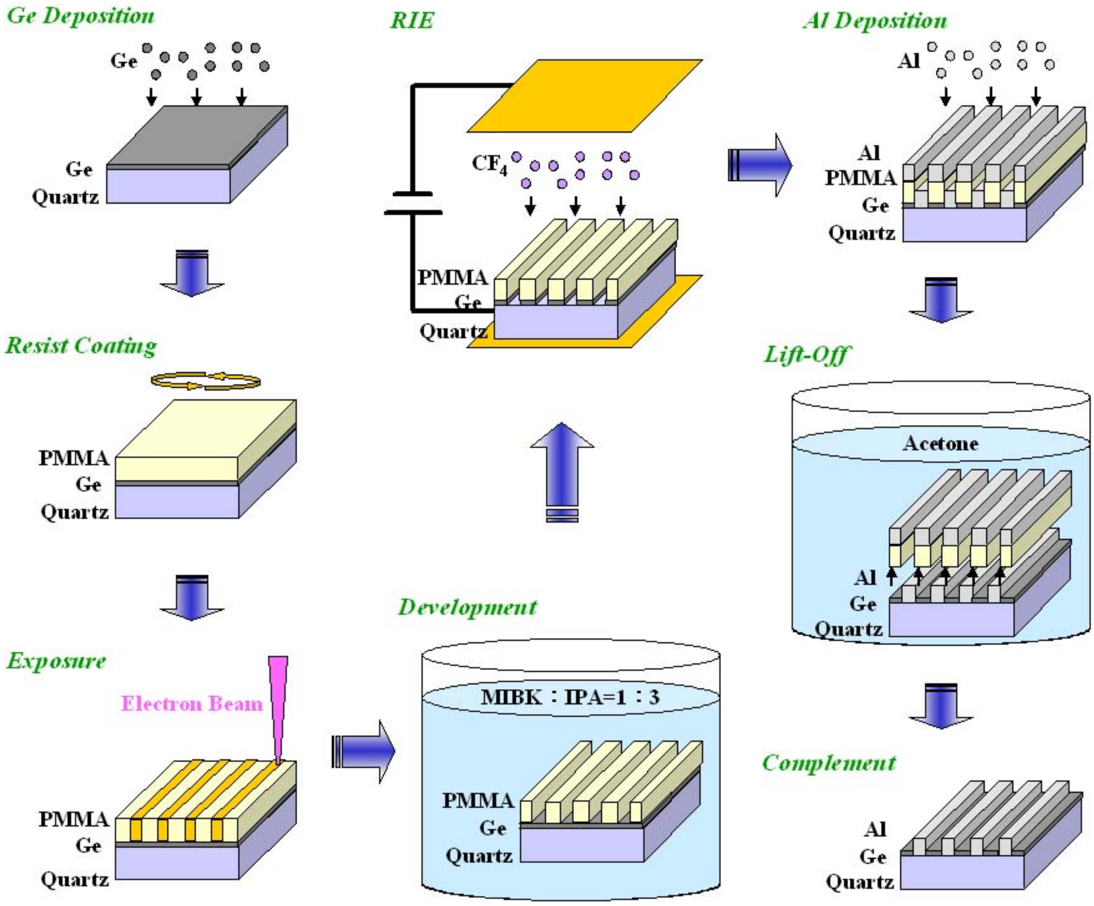

Fig. 3.3 Flow of fabricating single-layered sub-wavelength grating.

3.3.2 Fabrication Process of Sub-Wavelength Grating with Double-Layered Structure by Using Tri-Level Resist System

To fabricate a thicker or multi-layered sub-wavelength grating, we could just increase the thickness of PMMA. However, the thicker the PMMA was, the easier it would collapse due to under-cut phenomenon. For this reason, the process mentioned above was modified by transferring wet dissolution to dry etching. A tri-level resists system was then introduced to fabricate sub-wavelength grating with thicker or multi-layered structure. Two polymers could be combined in a multilayer if they were separated by a barrier such as SiO_2, aluminum, titanium, or germanium, forming a so-called tri-level resist. The detail steps for forming tri-level resist system and fabricating nanostructures were listed below：

(1) Wafer cleaning：First step was initially clean as before.

(2) PMMA/MMA coating：PMMA/MMA which was another kind of electron resist usually applied in tri-layer resist system was spin coated on quartz. Such material could be easily etched by RIE with oxygen.

(3) Baking：The coated PMMA/MMA was baked on a hotplate at 160℃ for 15 minutes.

(4) Interlayer deposition：Germanium was chosen as interlayer in the experiments. Besides being a conductive layer, it also served as an excellent mask for RIE in oxygen.

(5) Resist coating：The PMMA was spin coated on interlayer after interlayer was deposited.

(6) Baking：The coated PMMA was also baked on a hotplate at 160℃ for 15 minutes. Then, the tri-level resist system was formed.

(7) Exposure：The wafers were then put into E-beam system to expose PMMA.

(8) Development and Rinse：The exposed PMMA was developed for 75 seconds in 1:3 MIBK：IPA and rinse for 25 seconds in IPA. Then blow dry with nitrogen.

(9) RIE：RIE with CF_4 and oxygen was then applied sequentially to form a high aspect ratio resist profile.

(8) Materials evaporation：The desired structure was aluminum plus SiO_2. Thus, SiO_2 and aluminum were evaporated onto the sample sequentially by thermal evaporator.

(9) Lift-off：The samples were immersed into acetone for 15 minutes after removing from evaporator. Then we agitated substrates and acetone with an ultrasonic cleaner to dissolve the PMMA/MMA with its cover lift-off, and

the desired nanostructure remained on the substrate.

The flow of fabricating sub-wavelength grating with double layer structure by using tri-level resist system was shown in Fig. 3.4.

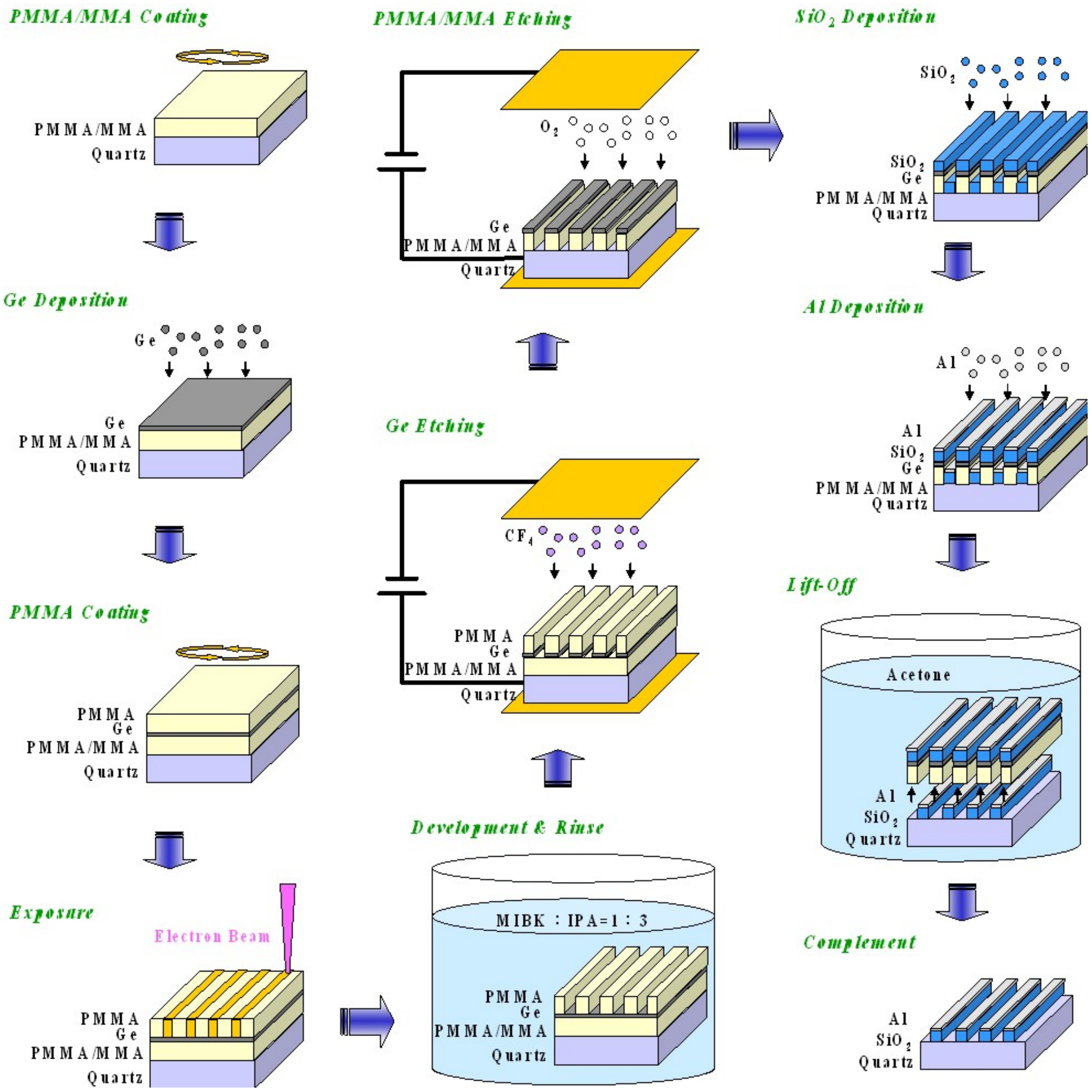

Fig. 3.4 Flow of fabricating sub-wavelength grating with double-layer structure by using tri-level resist system.

3.3.3 Fabrication Process of Sub-Wavelength Grating with Double-Layered Structure by Using Inductive Coupled Plasma-Reactive Ion Etching (ICP-RIE)

ICP-RIE process, instead of tri-level resist system, could also fabricate the sub-wavelength grating with multi-layer. The basic structure of RIE was shown in Fig. 3.5. Two electrode plates were connected with RF generator. The molecules in the electric field were accelerated and excited the bound electrons which generated plasma. The ion densities were not high enough $\left(\sim 10^{9} cm^{-3}\right)$ due to a high operation pressure. Thus, a structure with low aspect ratio was then etched.

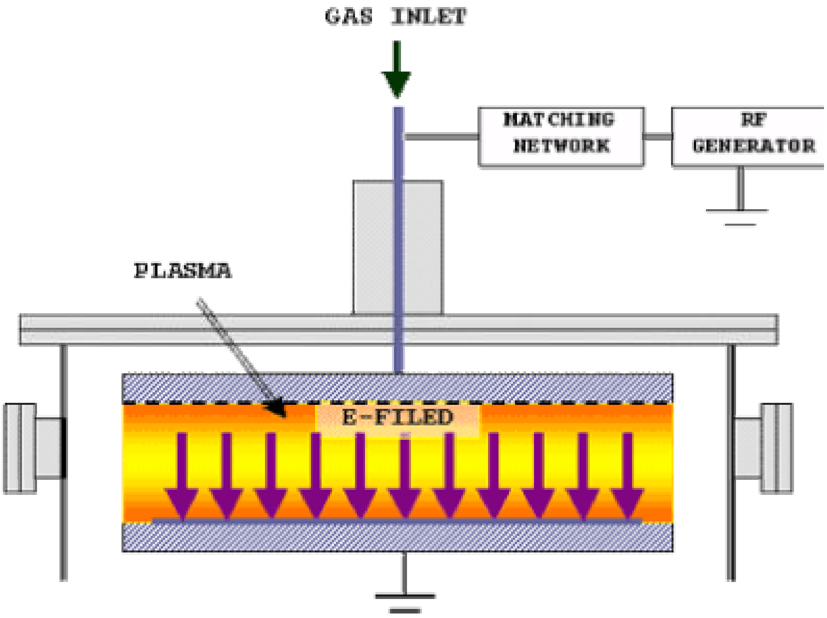

Fig. 3.5 Schematic diagram of conventional RIE system.

The basic structure of ICP-RIE was shown in Fig. 3.6. A current was applied on the coil, which would induce a magnetic field to generate a secondary inductive current by means of certain media like air, vacuum or a ferromagnetic core. The secondary inductive current then released its energy through plasma. Therefore, ICP-RIE was a high-density-plasma system which used magnetic confinement of electrons to generate very high ion densities $\left(> 5\times10^{11}cm^{-3}\right)$. The structure with high aspect ratio was able to be etched by such a high ion densities. ICP-RIE was introduced into the experiment to go deep etching process with the advantage of etching structure of high aspect ratio.

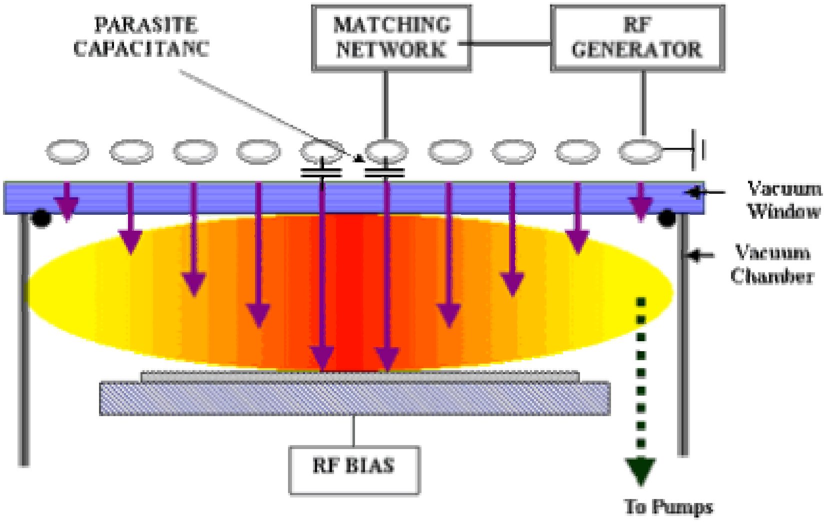

Fig. 3.6 Schematic diagram of high-density-plasma ICP-RIE system.

On the other hand, the lift-off process of a structure with high aspect ratio was not very easy to achieve. A new fabrication process by means of ICP-RIE, which was simpler than using tri-level resist system, was therefore proposed to fabricate sub-wavelength grating with double-layered structure. The detail steps were listed below：

(1) Wafer cleaning：First step was initially clean as before.

(2) Materials deposition：The desired materials were deposited on quartz first. In the experiment, SiO_2 and aluminum were applied.

(3) Resist coating：The PMMA was spin coated on aluminum after SiO_2 and

aluminum were deposited.

(4) Baking：The coated PMMA was baked on a hotplate at 160°C for 15 minutes.

(5) Exposure：The wafers were then put into E-beam system to expose PMMA.

(6) Development and Rinse：The exposed PMMA was developed for 75 seconds in 1:3 MIBK：IPA and rinse for 25 seconds in IPA. Then blow dry with nitrogen.

(7) Mask deposition：The etching mask was formed on aluminum after development. The material and thickness of etching mask needed to be selected properly in order to etch structure with high aspect ratio. Here, gold was chosen due to its high etching selectivity ratio compared with aluminum and SiO_2.

(8) Lift-off：The samples were immersed into acetone for 15 minutes. Then we agitated substrates and acetone with an ultrasonic cleaner to dissolve the unexposed PMMA with its cover lift-off, and the titanium mask remained on the substrates.

(9) ICP-RIE：Then ICP-RIE with Cl_2 and CF_4 was then applied sequentially to etch Al and SiO_2 respectively and form a high aspect ratio nanostructure.

The flow of fabricating sub-wavelength grating with double layer structure by using ICP-RIE process was shown in Fig. 3.7.

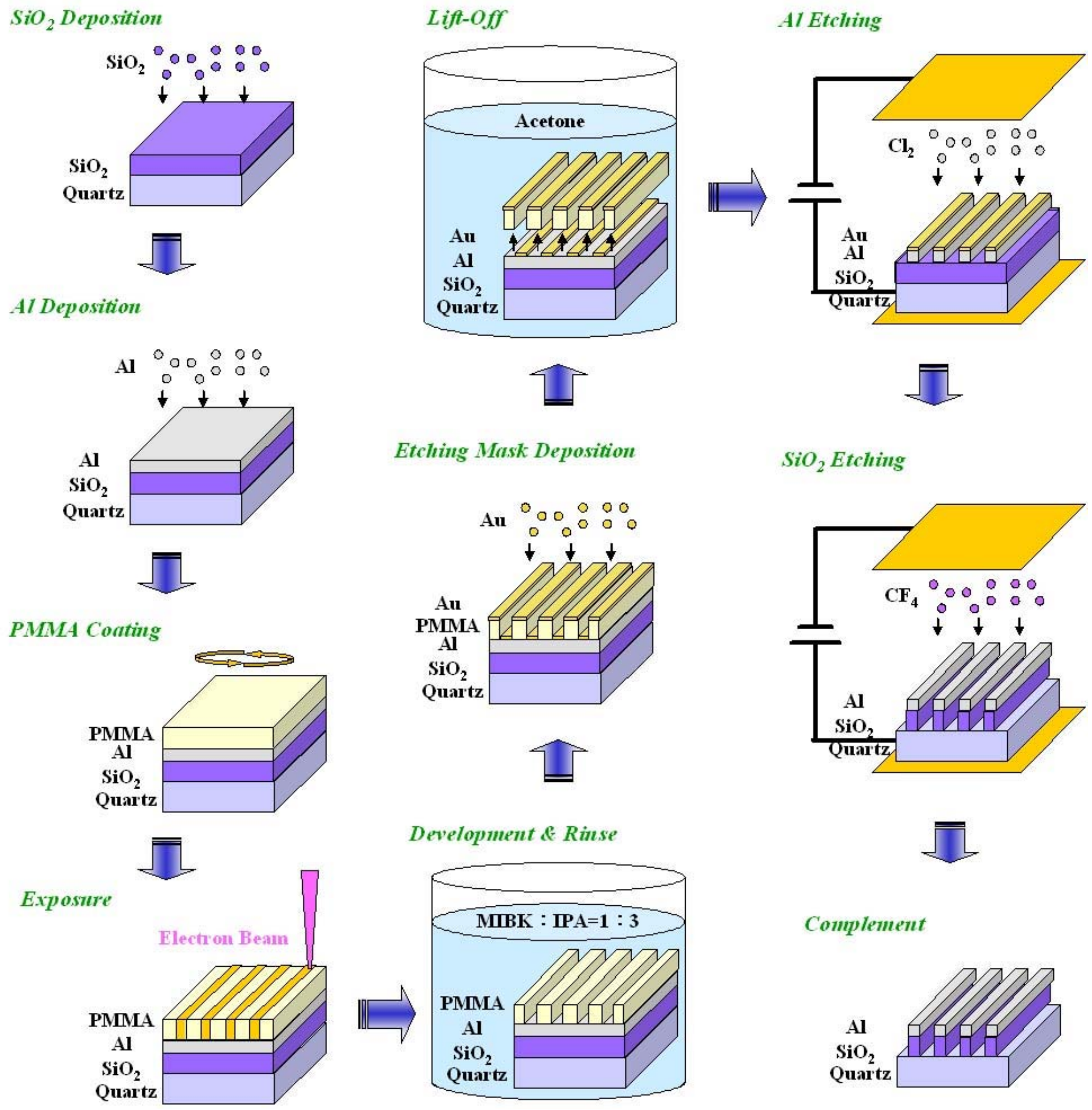

Fig. 3.7 Flow of fabricating sub-wavelength grating with double layer by using ICP-RIE process.

3.4 Measurement System

After the fabrication of sub-wavelength grating, the inspection will be performed to make sure that the fabricated nanostructures are in keep 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.

3.4.1 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. 3.8. Using SEM, the feature variation of a few angstroms can be observed. In our work, a HITACHI S-3000H SEM was used to measure the quality of the fabricated nanostructures. The line width, etching depth, and each layer can be accurately measured.

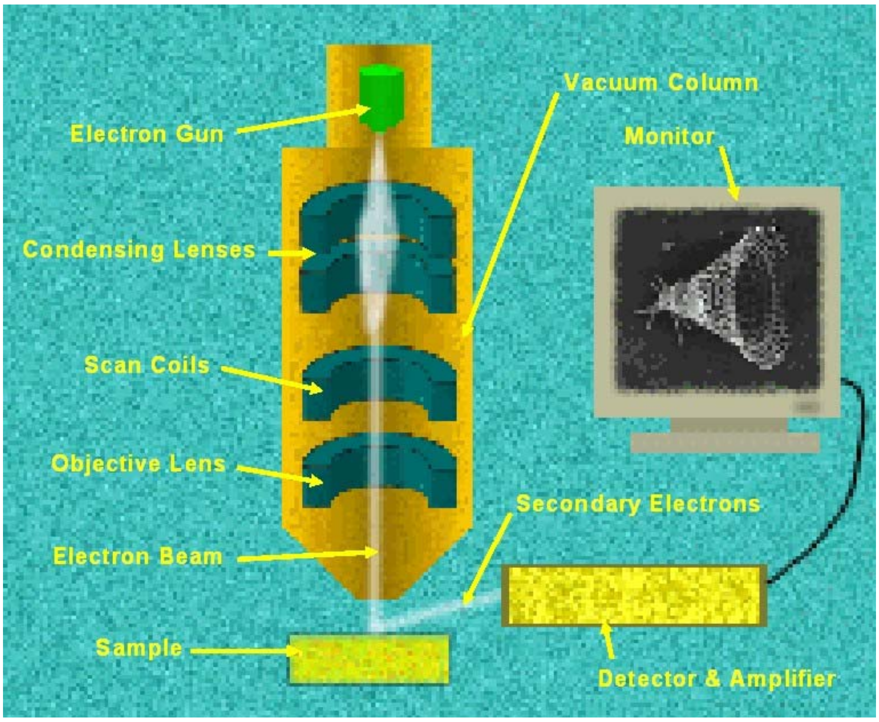

Fig. 3.8 Schematic diagram of scanning electron microscope.

3.4.2 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. 3.9.

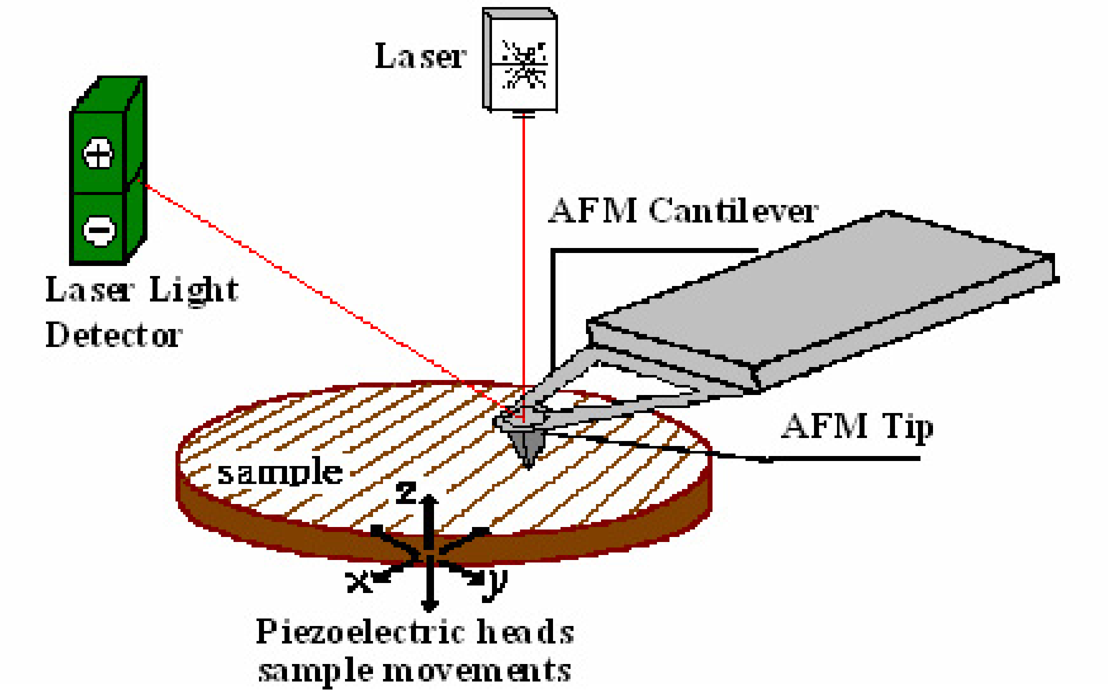

Fig. 3.9 Concept of AFM and the optical lever.

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 to $100\,nN$.

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.

3.4.3 Efficiency Measurement Setup

Because the sample size was only 80 μm × 80 μm, limited by the e-beam writer used, we therefore needed to design an experimental setup to measure the efficiency of both P rays transmittance and S rays reflectance. The fabricated sub-wavelength grating was evaluated by means of a setup shown schematically in Fig. 3.10.

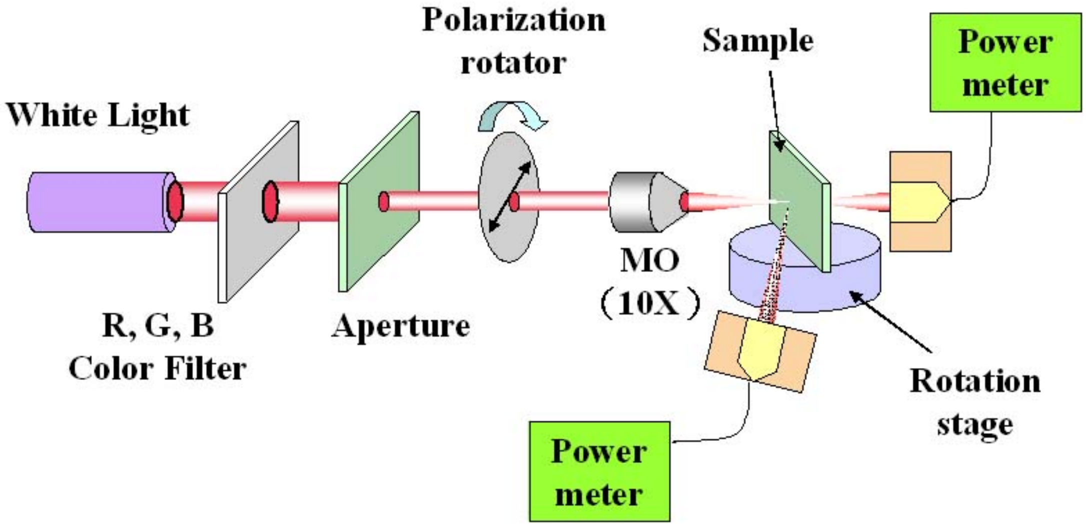

Fig. 3.10 Schematic diagram of the experimental setup for the characterization of the fabricated sub-wavelength grating.

A white light with red, green, and blue three color filters was used as our light source. The light was focused onto the 80 μm × 80 μm aperture of the fabricated structure with a microscope objective lens. In addition, we could control the input polarization by a polarization rotator. Two photodetectors were used to measure the transmittance and the reflectance simultaneously.