# Chapter 3 Experimental and Methodology

This chapter will present experiment methods to deposit DLC/a-Si thin films at different thickness stack ratio as monitoring by in-situ ellipsometry on tantalum wafer substrate. The properties of the thin film such as surface morphology, chemical bonding structure, chemical composition, thickness, optical property and mechanical properties are carefully studied and analyzed. The equipments, tools and materials used in this work will be described in detail along with the processes or experimental methods underlying each section.

## 3.1 Equipment and Material

The experimentation for this work are divided into 3 main parts as following: 1) Optimum condition of the coating system for DLC/a-Si thin film stack ratio 2) DLC/a-Si thin film stack ratio preparation and 3) Characterization of DLC/a-Si thin film stack ratio.

### 3.1.1 Optimum Condition for DLC/a-Si Thin Film Coating System

1. DLC/a-Si coater is a commercial custom designed and constructed RF ion source, PVD dc magnetron sputtering and pulse filtered cathodic arcs (PFCA) model NEXUS DLC-X system by Veeco Company Inc.

2. Materials
   a. The 99.999 % and 99.999 % purity of silicon and graphite target for seed and DLC layer respectively.
   b. Three types of substrate are germanium (100), tantalum and silicon (100) wafer substrate. Tantalum wafer substrates are being used to monitoring films growth thickness by in-situ ellipsometry. It is also used in the studying of of DLC/a-Si thin film stack ratio deposition. While germanium and silicon wafers substrate are used in studying of DLC/a-Si thin film stack ratio deposition.
   c. One type of gas is argon 99.999 % which acts as etching and sputtering.

3. The optimum recipe DLC overcoat process deposition consists of three steps following;
   a. The substrates are pre-clean with low energy Ar ion plasma etching and incident angle 60 degree respect to substrates with 60 seconds.
   b. The a-Si seed layer is deposit on the cleaned wafer substrates using DC magnetron with a power of 150 W, incident angle 44 degree respect to substrate and Ar gas flow rate of 40 sccm.
   c. DLC layer is deposit using PFCA with a pulse frequency of 1 Hz, normal incident angle respect to substrate, arc voltage of 950V and coil voltage of 900 V.

### 3.1.2 Preparing of DLC/a-Si Thin Film Stack Ratio

DLC/a-Si thin films were deposited by the NEXUS DLC-X system coater as in section 3.1.1, however in this part three types of substrate i.e. tantalum wafer, silicon (100) wafer and germanium (100) wafer as substrate is used. The film thickness was monitored using *in-situ* ellipsometry with Ta wafer as a thickness monitor. The growth rate also compare with silicon (100) wafer. The properties of the thin film such as surface morphology, chemical bonding structure, chemical composition, thickness, optical property and mechanical properties were studied on germanium wafer substrate.

### 3.1.3 Characterization of DLC/a-Si Thin Film

1. Chemical bonding of the DLC/a-Si thin films deposited on Ge substrates were studied by Raman spectrometer (A Renishaw Invia Reflex) using visible 514 nm wavelengths from argon ion laser at the Western Digital Thailand.
2. Surface morphology of the DLC/a-Si thin films were evaluated by Atomic Force Microscope (Digital Instruments Veeco, Dimension 5000) in a tapping mode at the Western Digital Thailand.
3. Chemical composition of the DLC/a-Si thin film were studied by X-ray photoelectron spectroscopic (PHI Quantera SXM Scanning X-ray) in depth profile mode at the data storage institute (DSI) Singapore.
4. The thickness of the DLC/a-Si thin films was obtained by Transmission Electron Microscopy (FEI, Tenai $G^2$) working at 200 kV at the Western Digital Thailand.
5. The TEM sample preparation of the DLC/a-Si thin films was obtained by Focus Ion Beam (FEI, Strata 400 STEM) working at 2-30 kV at the Western Digital Thailand.
6. Optical properties and thickness of the film were studied by Spectroscopic Ellipsometry (J.A. Woolam) with the incident angle at 75 degree and the wavelength of 280 to 800 nm at the Western Digital Thailand.
7. Mechanical properties of the DLC/a-Si thin films were evaluated by Nanoindentation (Hysitron Inc. Triboindenter®) in a scratch and wear mode at the Western Digital Thailand.

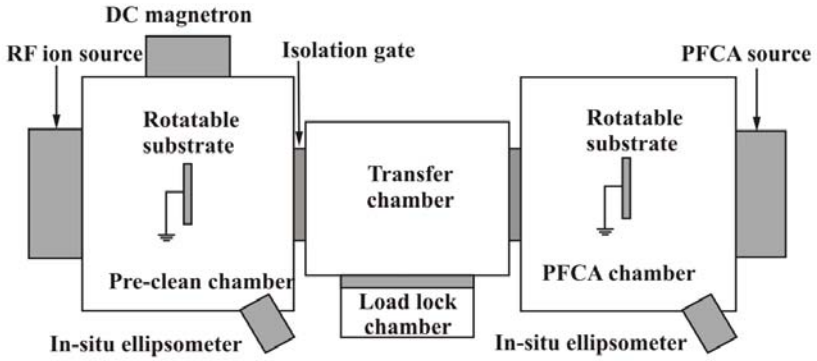
## 3.2 Pulsed Filtered Cathodic Arc (PFCA) System

### 3.2.1 Continuous Versus Pulsed

From a commercial point of view, the overwhelming majority of cathodic arc system operates in continuous direct current (DC) mode. The reason is the high deposition rate that can be obtained this way. This is true for non-filtered and filtered systems. The typical arc current is between 40 A and 100 A, with the lower limit determined by arc chopping (i.e. spontaneous extinguishing of the arc discharge), and the upper limit determined by power considerations as well as enhanced macroparticle production. In principle, the arc current can be much higher, leading to proportionally higher plasma production and deposition rate but with constrains due to the power supply as well as cooling of plasma source and substrate. For some applications, deposition with pulsed arcs can have advantages over DC operation. The power consumption can be easily regulated via the arc duty cycle (on/off ratio) rather than the arc current. Spot steering is not an issue since the arc spots travel only a limited distance from the point of ignition. Ignition can be designed to occur in the center of disk cathode with the arc spot “repelling” each other; the pulse is conveniently chosen to end when the spots arrive at

the cathode rim. Pulsed arcs can be operated with very high currents, sometimes matching the average plasma production of DC arcs.

(a)




(b)

**Figure 3.1** Pulsed filtered cathodic arc (PFCA) system Veeco company Inc, model, Nexus DLC-X (a), schematic diagram of PFCA system (b).

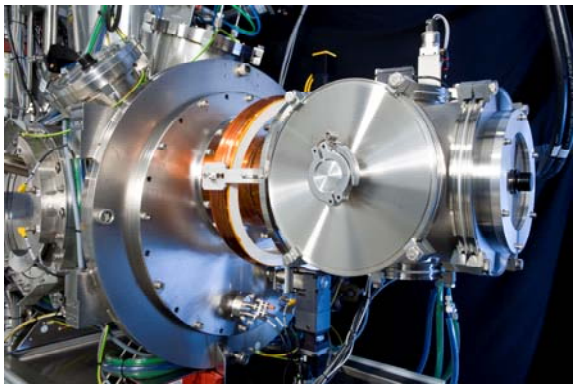
Figure 3.1(a) shows the pulsed filtered cathodic arc (PFCA) system used in this work (Veeco company Inc, model Nexus DLC-X) is shown by a schematic diagram in Figure 3.1(b)[82]. The system consists of four vacuum chambers, i.e. one load lock chamber, transfer chamber, pre-clean chamber and pulsed filtered cathodic arc (PFCA) chamber. All chambers were attached together by isolation gate valve. Each chamber has its own turbo molecular pump to evacuate the chamber individually. In addition, the ionization gauges were used to measure the pressure in all four chambers. Prior to the deposition processing of the DLC films, all chambers were evacuated to a base pressure of about $5.0 \times 10^{-7}$ torr.

The transfer chamber was equipped with an automated robot arm system for transferring the substrate from load lock chamber to pre-clean and PFCA chambers. The load lock chamber was used to load-in substrates manually (during the chamber was under atmospheric pressure). The load lock chamber was then evacuated by a turbo molecular pump. After the pressure in the load lock chamber reach a pressure of $5.0 \times 10^{-5}$ torr, the isolation gate valve between transfer chamber and load lock chamber opened. Then, the robot arm will pick up the substrate and transfer to substrate fixture in the pre-clean chamber.

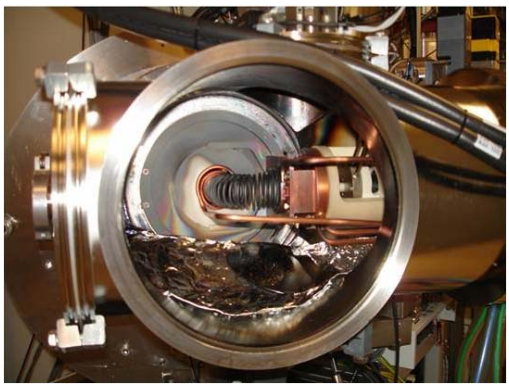
The pre-clean chamber was equipped with RF ion source, 16 inch in diameter, and DC magnetron sputtering source with a target of 4 inch in diameter. The ion source was

used for pre-cleaning of the substrate whereas the DC magnetron source was used for the deposition of amorphous silicon (a-Si) as a seed layer. The substrate with deposited silicon layer was then transferred to substrate fixture in the PFCA chamber by robot arm. The PFCA chamber is equipped with a cathodic arc for the deposition of DLC film.

The substrate fixtures in pre-clean and PFCA chambers are capable of tilt and rotation. Therefore, the a-Si seed layer and DLC film can be deposited onto the substrate at any required incident angle. Furthermore, pre-clean and PFCA chambers were installed with a multi-wavelength ellipsometry (J.A. Woollam, model M-2000) for in-situ monitoring of the film thickness of a-Si layer and DLC film, respectively.



(a)



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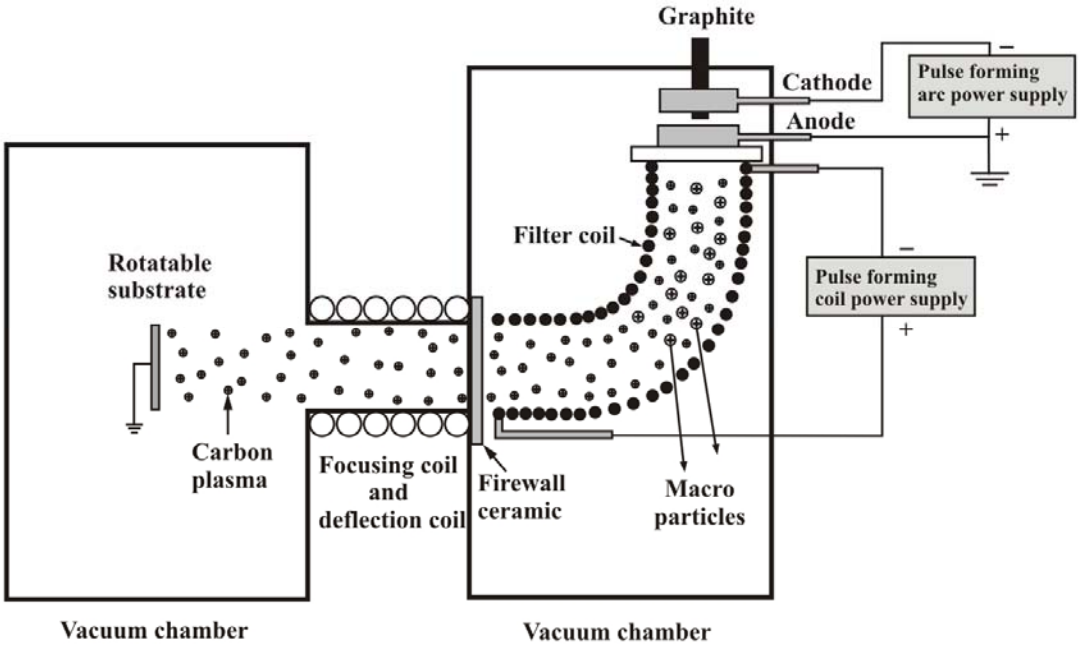



(c)

**Figure 3.2** PFCA chamber and cathodic arc source (a-b), schematic diagram of PFCA chamber and cathodic arc source (c).

Figure 3.2 (a-c) shows the cathodic arc source includes a high purity graphite cathode of 0.25 inch in diameter and 8 inch in length. The arc power supply is operated in pulsed mode. The positive potential of power supply is connected with anode and ground. The voltage between anode and cathode, called arc voltage, can be varied from 0-1000 V with pulse frequency in a range from 1-5 Hz. Since the distance between anode and graphite cathode is about 2mm, it is high enough to create current discharge between anode and cathode. Then, graphite is vaporized at the cathode. All charge particles are fed into a curved 90 degree filter coil. Electrons are moved in spiral along magnetic field generated by filter coil, and ions will be guided due to they are charge particles. In order to improve the film thickness uniformity, a focus coil operates as a magnetic lens to focus or defocus the plasma beam. A deflection coil is used to raster the beam before striking the substrate. The macro particles move in strange trajectory so they may either leave the filter through openings gap between the turns of the coil or stick to the turns. Thus, unwanted macro particles and neutral atoms are filtered out and coating species reaching the substrate are pure carbon plasma.

## 3.3 Film Preparation

Diamond-like carbon (DLC) films were deposited using the pulsed filtered cathodic arc (PFCA) deposition method. Crystalline n-type germanium wafers with (100) orientation, and a dimension of 1 × 1 cm with a thickness of 0.5 mm were used as substrates.

The DLC overcoat process deposition consists of three steps: (1) the substrate was cleaned with low energy $Ar^+$ ion plasma etching and incident angle 60 degree respect to substrate, for 60 seconds, (2) a-Si seed layer was deposited on the cleaned germanium substrate using DC magnetron with a power of 150 W, incident angle 44 degree respect to substrate and $Ar^+$ gas flow rate of 40 sccm, and (3) DLC layer was deposited using pulsed filtered cathodic arc (PFCA) with a pulse frequency of 1 Hz, normal incident angle respect to substrate, arc voltage of 950 V and coil voltage of 900 V. The first two steps were carried out in pre-clean chamber while the third step was done in PFCA chamber. The film thickness was monitored using *in-situ* ellipsometry with Ta wafer as a thickness monitor. Figure 3.3 shows the deposited film layers on germanium substrate. Table 1 shows the details of relative thickness ratio for all DLC/a-Si film stacks.

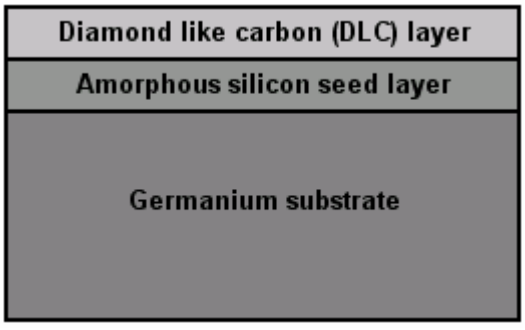



**Figure 3.3** Showing the layers of a-Si and DLC on Ge substrate.

**Table 3.1** DLC and a-Si films thickness for each stack

| DLC (nm) | a-Si (nm) | DLC/a-Si thickness ratio | Total thickness (nm) |
|---|---|---|---|
| 2 | 2 | 2/2 | 4 |
| 2 | 6 | 2/6 | 8 |
| 4 | 4 | 4/4 | 8 |
| 6 | 2 | 6/2 | 8 |
| 9 | 6 | 9/6 | 15 |

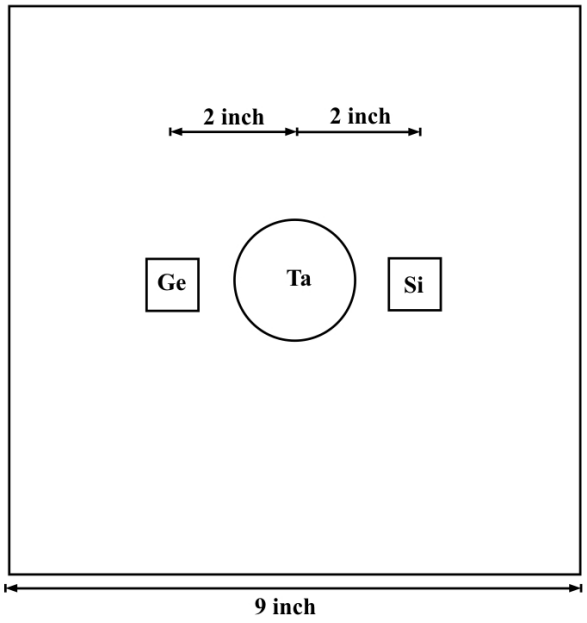



**Figure 3.4** Layout of the samples locked inside the PFCA chamber.

To study effect of surface energy on the growth of DLC/a-Si films on various substrates, the DLC/a-Si film stack 10/7 nm had been coated on Ge and Si substrate simultaneously in the same fixture with Ta monitor wafer. To minimize film coating uniformity, 2 inch of Ta monitor wafer is locked in the center of fixture while 1x1 cm of Ge and Si substrate are locked at left and right hand side with center to center distance 2 inches respectively as shown in Figure 3.4.

Thickness growth control using in-situ ellipsometry, film growth rates can be readily determined from SE data by calculating the change in film thickness over time. Simultaneously, one can also extract the optical constants from SE data. In traditional applications the quality of the analysis depends on optical model accuracy. Unfortunately, modeling errors are often introduced in the underlying layers. The effect is cumulative, making analysis of more than a few layers very difficult unless underlying films are well understood.

'Virtual Interface' models simplify analysis by combining the optical response of underlying layers into a 'pseudo substrate', as shown in Figure 3.5. During analysis, the

layer above the VI is modeled, while the VI itself remains unchanged. Characteristics of the near surface film can be continuously tracked by constantly updating the location of the VI, placing it at some fixed time interval prior to the most recent SE data. The "depth" of the VI is then determined by the time interval and deposition rate.

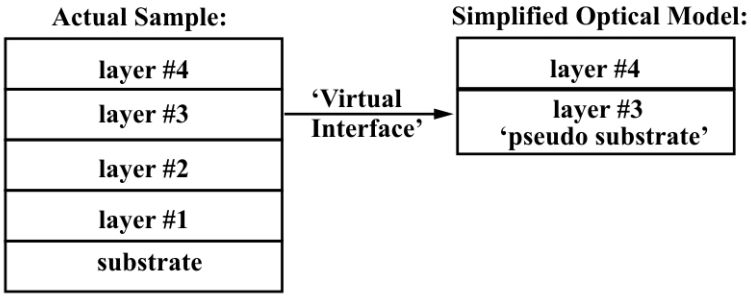



**Figure 3.5** Schematic of a virtual interface model.

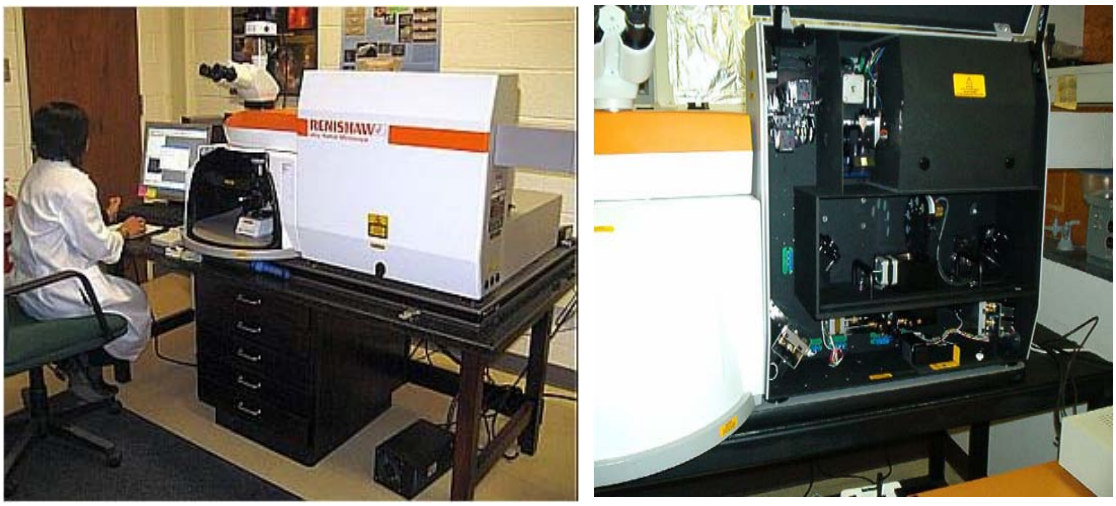
The Woollam Co.'s EASE™ software incorporates the VI concept in two different models, the Growth Rate Optical Constant (GROC) and Generalized Virtual Interface (Gen-VI) layers. The GROC layer utilizes the common pseudo substrate approximation (CPA), which works well for semiconductors, high-index dielectrics, metals, and highly absorbing materials. However, the simplifying assumptions used by theCPAto calculate the VI parameters do not work for dielectric stacks. The Gen-VI layer uses exact thin film equations in the VI calculation, making it valid for semiconductors, metals, or any arbitrary isotropic layer structures, over any time/thickness range. Besides determining the optical properties of the VI, both the GROC and Gen-VI layers calculate the top-most film deposition rate and optical constants n(λ) and k(λ). Both layers assume the film's growth rate and optical constants do not vary throughout the selected time range. In ours films deposition used Generalized Virtual Interface (Gen-VI) layers model.

## 3.4 Study of DLC/a-Si Thin Film Property

The study of DLC/a-Si thin film properties such as surface morphology, chemical bonding structure, chemical composition, thickness, optical property and mechanical properties of the deposited films are described in this section.

### 3.4.1 Study of Chemical Bonding of DLC/a-Si Thin Film

Chemical bonding of the DLC/a-Si films deposited on Ge substrates are analyzed by the Raman technique. Figure 3.6(a) and (b) shows the Raman used and the measurements were performed with a Renishaw inVia Reflex Raman Spectrometer at 514 nm of Ar+ gas laser in back-scattering geometry. The raw spectra were fitted using Gaussian profile to obtain smooth curves. Then, the smooth curves were fitted with two Gaussian-Lorentzian peaks corresponding to the G (graphite) peak and D (disorder) peak.




**(a)** **(b)**

**Figure 3.6** Renishaw inVia Reflex Raman spectrometer using visible 514 nm wavelength from argon ion laser (a) Raman and display part (b).

### 3.4.2 Study of Chemical Composition of DLC/a-Si Thin Film

Surface morphology of the DLC/a-Si films deposited on Ge substrates is analyzed by the AFM technique as roughnes average (Ra) roughness. Figure 3.7 (a) and (b) shows the AFM used and the measurement is done tapping mode with high resolution in nano-scale. The surface roughness measurement are carried out over the scanning area of 1x1 $\mu m^2$ of the thin films.

(a) (b)

**Figure 3.7** Atomic force microscope (AFM) in a tapping mode, Digital Instruments Veeco, Dimension 5000 (a) AFM and display part (b).

### 3.4.3 Study of Chemical Composition of DLC/a-Si Thin Film

The studies of chemical composition of the DLC/a-Si films deposited on Ge substrates are analyzed by the X-ray photoelectron spectroscopic (XPS) depth profiling technique. Figure 3.8 shows the X-ray photoelectron spectroscopic used and the measurements were performed with PHI Quantera SXM Scanning X-ray in depth profile mode with AlKα X-ray source, take of angle 45 degree, spot size 200 μm and sputtering ion gun 1KV.

**Figure 3.8** X-ray photoelectron spectroscopic (PHI Quantera SXM).

### 3.4.4 Study of Thickness of DLC/a-Si Thin Films

Transmission Electron Microscopy (TEM) instrument (FEI, Tenai$^{TM}$ G$^2$ 20) as shown in Figure 3.9 is used for analyzing the thickness of the DLC/a-Si thin films deposited on Ge substrate. The TEM working potential for this study is at 200 kV, Electron source $LaB_6$ or W emitter operating in high resolution mode TEM(HRTEM) for analysis of thickness of the DLC/a-Si thin films deposited on Ge substrate.

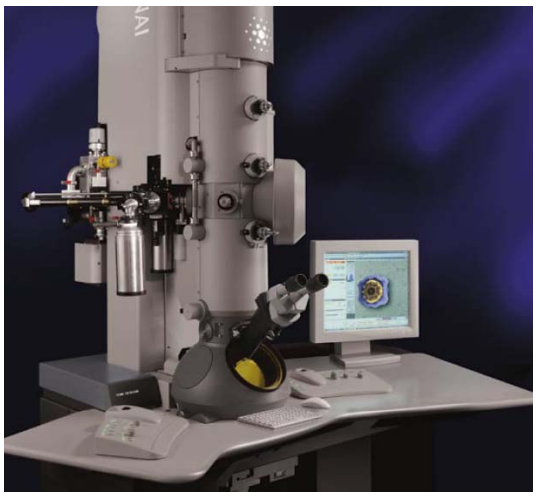


**Figure 3.9** Transmission electron microscopy (TEM) working at 200 kV, FEI, Tenai$^{TM}$ G$^2$ 20.

### 3.4.4.1 TEM Sample Preparation of DLC/a-Si Thin Films

A focused ion beam (FIB) instrument (FEI, Strata$^{TM}$ 400 Dual Beam$^{TM}$) (Figure 3.10) was used for cross-section TEM of the DLC/a-Si thin films deposited on Ge substrate sample preparation.

**Figure 3.10** Focus ion beam(FEI, Strata$^{TM}$ 400 Dual Beam$^{TM}$) working at 2-30 kV.

To conduct the TEM image, the sample must be thin enough to transmit the electrons, typically 0.5 μm or less. As stated in the preceding chapter, FIB instrument was used to mill the sample surface. Prior to inserting the DLC/a-Si film sample into the FIB instrument, the DLC/a-Si film was deposited with Cr layer using an ion beam sputter (Southbaytech, Model IBS/e). The Cr layer, with a thickness of ~30 nm, was used to protect the diffusion of a metal from conducting layer into DLC/a-Si film.

DLC/a-Si film sample deposited with Cr was then inserted into the FIB/SEM dual beam (Strata 400) instrument. In this work, the sample was prepared by an in-situ FIB lift-out technique. The basic principles of this technique have been described in details before by Giannuzzi and Stervie [83]. The FIB cross-sections began by using the ion beam assisted chemical vapor deposition (CVD) process to deposit a 0.5-1 μm thick metal strip on the Cr-coated DLC/a-Si film. In this work, Pt was used as a metal layer for SEM imaging of the FIB-milled surface (Figure 3.11(a)). It was also used to mark the cutting area and to protect the DLC/a-Si film from ion bombardment during an ion milling by the FIB.

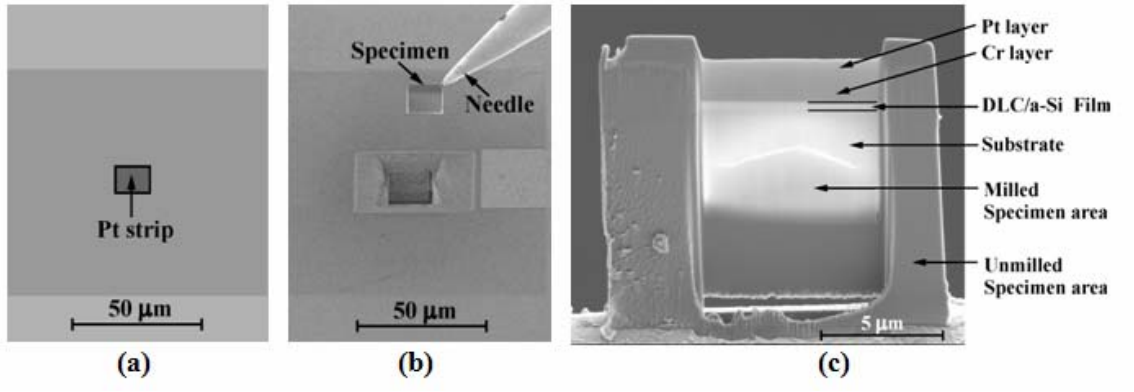



**Figure 3.11** Showing (a) Pt strip, (b) In-situ lift-out of a specimen by means of a nanomanipulator and (c) SEM image of thinned specimen.

Next, high ion beam current of 7 nA was used to cut at a position ~2 µm from Pt strip and parallel to the strip edge. After this step, the sample was tilted by 7° with respect to the ion beam and undercut was made until a specimen with a thickness of approximately 1 µm was obtained. After the undercutting operations, the specimen was tilted back to normal incidence with respect to the ion beam. The specimen was then removed from the FIB instrument using in-situ nanomanipulator mounted inside the FIB chamber. The needle of nanomanipulator was attached and welded onto the top surface of specimen using Pt deposition. Then, the specimen was lifted out of the bulk sample (Figure 3.11(b)). Next step, the needle/specimen assembly was transferred to a 3 mm carbon coated copper TEM grid and the specimen was mounted onto the edge of TEM grid. The needle-Pt junction on the specimen surface was cut by ion milling and finally the needle was separated from the specimen.

In the following step, the specimen was thinned until it became electron transparent (~100 nm) using the 30 kV ion beam and a current of 100 pA. During thinning, the specimen thickness was observed by SEM imaging at low kilovolts. As soon as the Pt top layer started to disappear and the specimen became electron transparent the thinning process was stopped.

(Figure 3.11(c)) shows a typical SEM image of thinned specimen. It should be pointed out that the specimen was partly milled in a rectangular shape. Therefore, the unmilled area of specimen as shown in Figure 11(c) looked like U-shape and acted as a holder of the thinned specimen. Furthermore, the DLC/a-Si film and substrate layers were clearly observed. However, the Cr layer was not clearly distinguished from Pt layer because this SEM image was taken at a low magnification of 8,000x. After the thinning process was finished, the copper grid with a thinned specimen was moved out of the FIB/SEM system. The thinned specimen was further investigated using TEM.

### 3.4.5 Study of Optical Property of DLC/a-Si Thin Films

The refractive index and thickness of the DLC/a-Si thin films stack ratio deposited on germanium substrates are analyzed by variable-angle spectroscopic ellipsometry (SE) (J.A. Woolam) as shown in Figure. 3.12 with measuring wavelength from 290 to 800 nm and at 75° incident angle. The proposed physical model corresponding to each film sample is generated base on appropriate generalized oscillator for the optical dispersion and eventually curve-fitted with the experimental data. The proposed physical model was a double-layer film structure with dense film layer and surface roughness as shown in Figure 3.13.

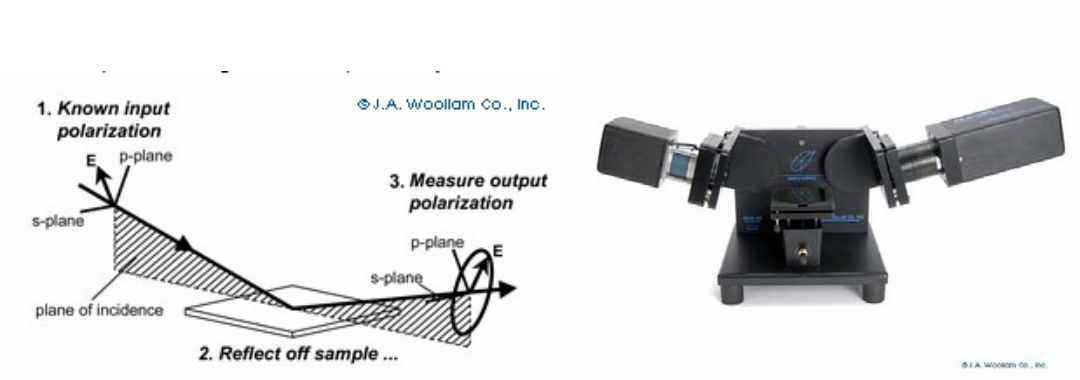



**Figure 3.12** Schematic of ellipsometry technique and ellipsometer system.

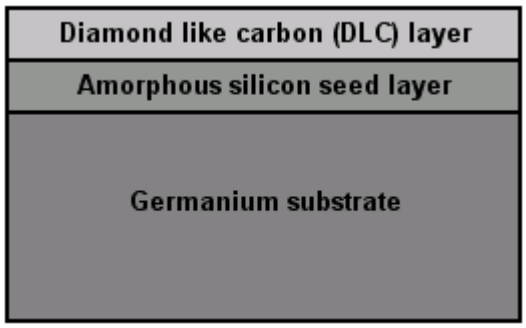



**Figure 3.13** Schematic representation of the double-layer physical models for SE-modeling procedure.