CHAPTER 3 EXPERIMENT AND METHODOLOGY

This chapter will present experiment methods to deposit aluminium titanium nitride thin film at different currents and deposition times. The properties of the thin film such as crystalline structure, surface morphology, thickness and microstructure 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 Equipments and Materials

The experiments for this work were divided into 3 main parts as following: 1) coating system and materials, 2) aluminium titanium nitride thin films preparation and 3) characterization of aluminium titanium nitride thin films.

3.1.1 Coating System and Materials for Aluminium Titanium Nitride Thin Film

1. Vacuum coater is a custom designed and constructed dc magnetron sputtering system by The Vacuum and Thin Film Technology Laboratory (VTTF) at the department of Physics, faculty of Science of Burapha University.
2. Materials
   a. The 99.97 % purity of titanium target
   b. The 99.999 % purity of aluminium target
   c. Two types of substrate are glass slide and silicon (100) wafer. Glass slide substrates are being used to study pressure conditions and the lowest current in which glow discharge is occurring if cathode is titanium target. It is also used in the studying of optimum conditions for aluminium titanium nitride thin film deposition. While silicon wafers are used in studying crystalline structure of $AlTi_3N$ thin film for optimizing deposition parameters.
   d. Two types of gas are argon (99.999%) and nitrogen (99.999%) which acting as sputtering and reactive gasses respectively.

3.1.2 Preparing of Aluminium Titanium Nitride Thin Film

Aluminium Titanium nitride thin film were deposited by the vacuum coater as in section 3.1.1, however in this part three types of substrate i.e. glass slides, silicon(100) wafer and carbon coated copper transmission electron microscopy (TEM) grid are used. The optical properties and roughness of the deposited $AlTi_3N$ thin films on glass slide substrates were studied while the crystalline structure, surface morphology and the thickness of the deposited films on silicon wafer substrate were studied and finally the phase and nanostructure of the films on TEM grid substrate were studied.

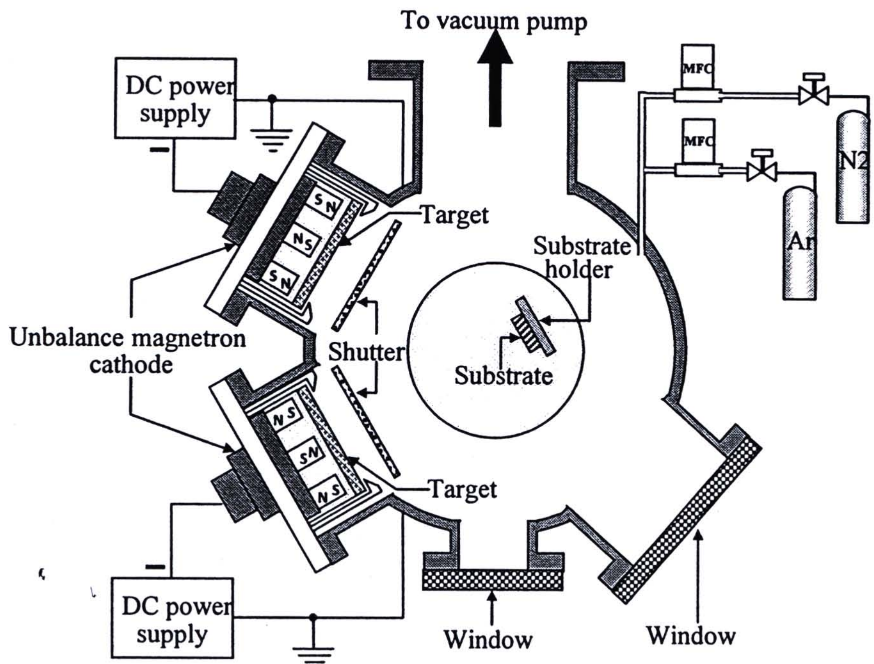
3.1.3 Characterization of Aluminium Titanium Nitride Thin Film

1. Microstructure and phase of aluminium titanium nitride were studied by X-ray diffractrometer Rint 2000 (Rigaku Corporation) at the Department of Metallurgical Engineering of Chulalongkorn University.
2. Surface morphology and thickness of aluminium titanium nitride thin film were evaluated by Atomic Force Microscope (Digital Instruments, Nanoscope III) in a tapping mode at the Scientific and Technological Research Equipment Centre of Chulalongkorn University.
3. Crystallinity structure and orientation of the aluminium titanium nitride thin film were studied by Transmission Electron Microscopy (Jeol, JEM-2100) working at 160 kV at the Scientific and Technological Research Equipment Centre of Chulalongkorn University.
4. The microstructure and thickness of aluminium titanium nitride thin film was obtained by FE-SEM (Hitachi, S4700) at the Thai Microelectronics Center.

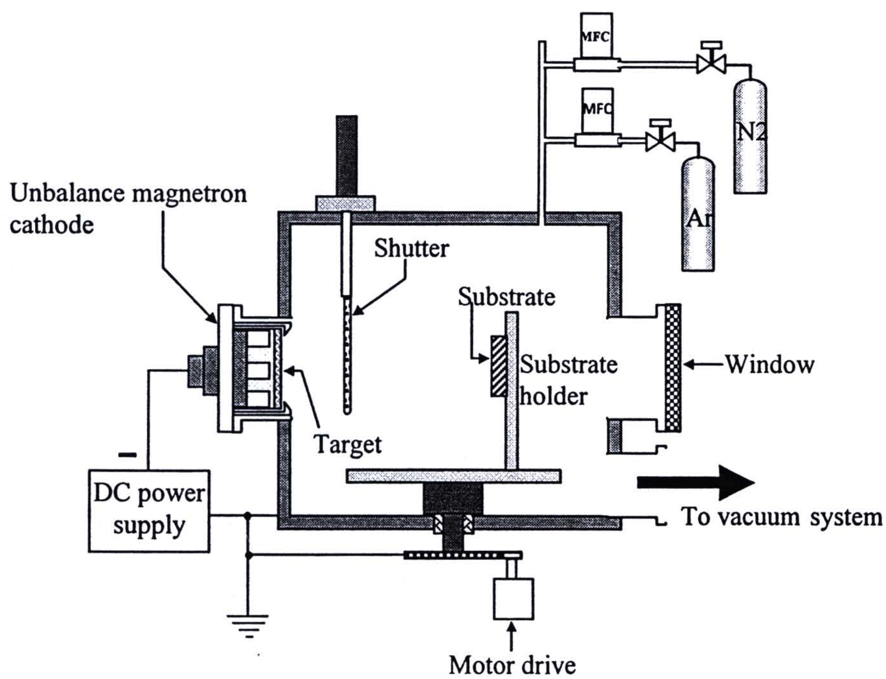
3.2 Reactive DC Sputtering Coater System [55]

Aluminium titanium nitride thin films were prepared by a dc unbalance magnetron sputtering coater system as shown in Figure 3.1-3.2 by reactive sputtering technique under vacuum condition. In order to obtain films of good properties, it is necessary to reduce the pressure inside the chamber to 10^{-6} mbar. The sputtering coater system is consisting of 2 parts, one is the vacuum system and another is the coating system.

1. The vacuum system is responsible for creating vacuum condition for the sputtering system. This part is consisting of the cylindrical chamber of the magnetron, the vacuum pump system and the pressure gauges. The cylindrical chamber of the magnetron is designed built and has the diameter by height of 31x37 cm. The vacuum pump system is includes of diffusion pump which responsible for high vacuum pumping and a rotary pump which act as backing pump. The pressure gauges are PFEIFFER which consist of display (TPG300) and two sensors (cold cathode gauge, IKR050 and pirani gauge, TPR010).
2. The coating system is a thin film deposition part and is consisting of two magnetron cathodes (releasing heat by water) with the diameter of 120 mm. The target are titanium,76 mm in diameter and 3 mm in thickness (purity of 99.97%), aluminium,76 mm in diameter and 3 mm in thickness (purity of 99.999%) installed at the cathode which connected to a high power direct current power supply. Mass flow controllers (MKS type 247D) were used to control the flow rates of ultra high purity of both sputter gas (Argon 99.999%) and reactive gas (nitrogen 99.99%).



(a) Top view



(b) Side view

Figure 3.1 Diagram showing main parts of coater system: (a) top view (b) side view [55]

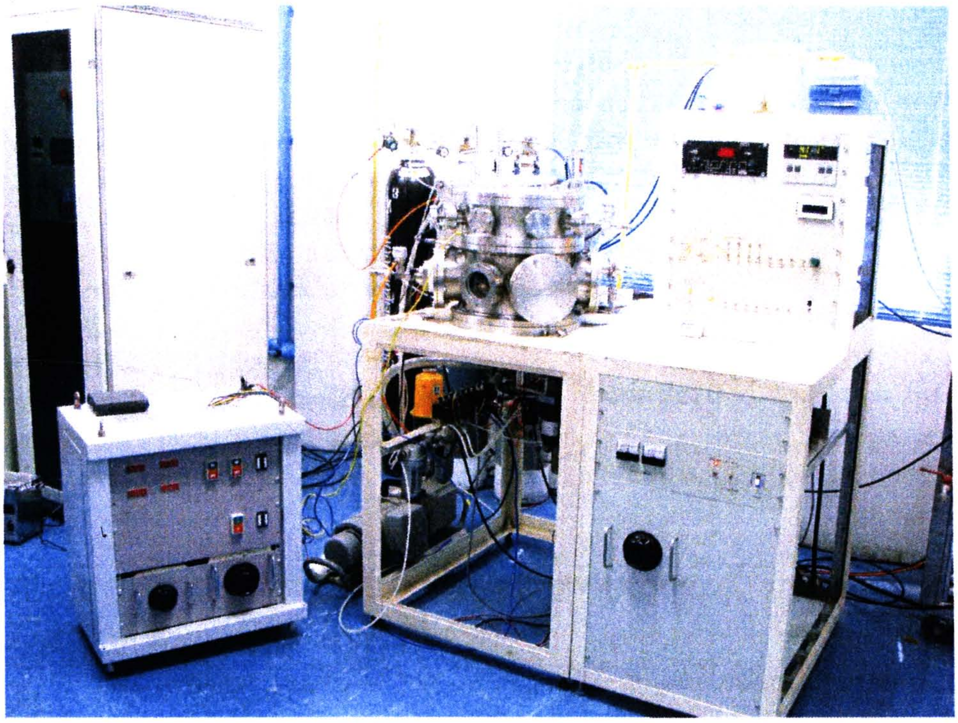


Figure 3.2 The Vacuum coater at Burapha University which has been used in this work [55]

3.2.1 Vacuum Preparation

Prior to deposition of thin films by sputtering method it is crucial that the pressure in chamber is reduced to high vacuum state, this to reduce contamination in thin film due to residual gasses. The appropriate pressure for depositing aluminium titanium nitride thin films is considered to be in the range of 10^{-3} – 10^{-7}mbar. The vacuum system as described previously consists of diffusion pump which supported by rotary pump. These pumps are connected to vacuum chamber by pipes and on-off valves as shown in Figure 3.3. Warming up of the pumps every time is essential before start pumping. First, the rotary pump is used to reduce the chamber's pressure from atmospheric pressure to lower level of around 10^{-2} mbar. Afterward begin pumping by applying diffusion to reduce pressure from 10^{-2} mbar until the pressure of 10^{-5} – 10^{-7} mbar is attained.

The processes of vacuum creation

1. Checking that roughing valve, backing valve and high vacuum valve is in close state.
2. Turn on main switch to allow the power supply to the system.
3. Turn on rotary switch to activate rotary pump.
4. Open backing valve to pump air to depart from diffusion pump until the pressure reading from pirani gauge(connecting to backing valve) is lower than 10^{-2} mbar; the pressure that is appropriate for diffusion pump to operate, switch on diffusion pump to activate heater and boiling the diffusion oil's for approx. 20 minutes.

5. Place the substrates to the substrate holder inside the chamber. To open the chamber, the operator must check whether the chamber is at vacuum state. If it is at vacuum, then open the air admittance valve to allow air into chamber until the inlet and outlet pressure is equal. Open the top plate to place the substrates, when finish placing the substrate, close the top plate and air admittance valve.
6. Create vacuum chamber. Preliminary vacuum condition in chamber is created by rotary pump. First, close the backing valve and then open the roughing valve to let the rotary pump to pump air out of chamber until the pressure reading from pirani gauge at backing connection is lower than 10^{-2} mbar. Consecutively, before beginning to create high vacuum chamber by diffusion pump, the roughing valve must be closed and the backing valve and the high vacuum valve are opened. Let the diffusion pump to operate until high vacuum level inside the chamber is reach i.e. in the range of $10^{-5} - 10^{-6}$ mbar.
7. When the base pressure inside the chamber is about $5x10^{-5}$ mbar starts aluminium titanium nitride deposition process.

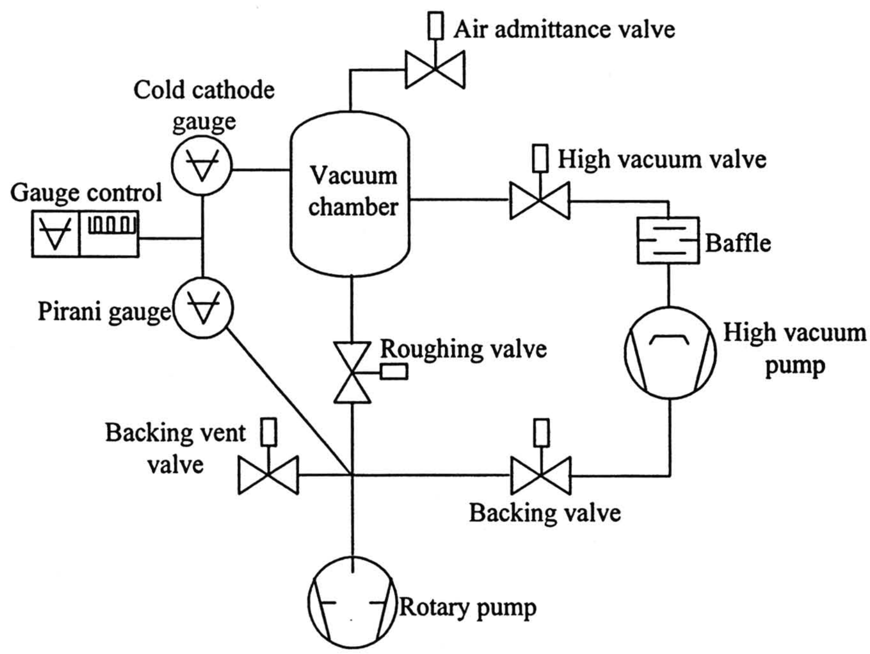


Figure 3.3 Pumping system diagram of sputtering coating system [55]

3.3 Substrate Preparation Process for Thin Film Deposition

The characteristics of $AlTi_3N$ studied in this work were deposited on 3 types of substrates; glass slide, silicon wafer and carbon coated copper transmission electron microscopy (TEM) grids. Contamination such as organic materials on the substrates can severely deteriorate the quality of the film deposited and obviously prevent the film to tightly attach on the substrate surface. For substrate cleaning, the substrates were ultrasonic cleaned in solutions of trichloroethylene, acetone and isopropyl alcohol sequentially and cleaning for 10 minutes in each solution. Use clean forceps to pinch substrates and dry with hot air. Finally, the substrates were placed on the holder inside the chamber for deposition.

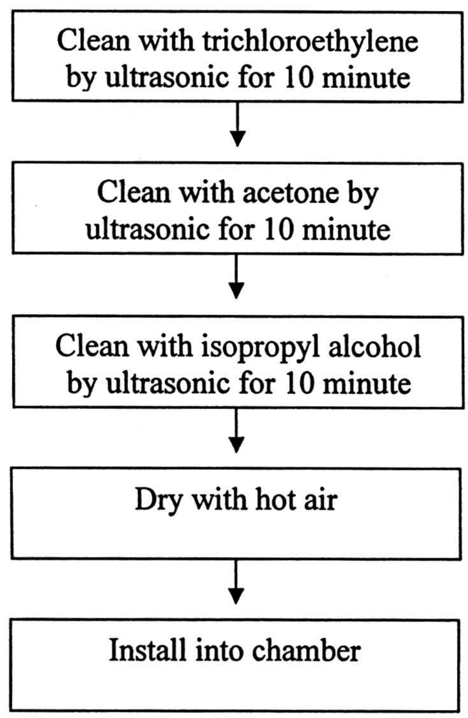


Figure 3.4 Substrate cleaning process

3.4 Preparing of Aluminium Titanium Nitride Thin Film

This section present of deposition at various Ti sputtering current by varying deposition time for part 1. Part 2 show the deposition at different Al sputtering current with fixed Ti sputtering current and deposition time as follow

3.4.1 Deposition of $AlTi_3N$ at Different Ti Sputtering Current and Deposition Time

The steps for preparing aluminium titanium nitride thin film for the nanostructure study on unheated substrates at different sputtering currents and deposition times by the coating system are outline as below:

1. Provide cleaned substrates; glass slide which is previously dropped with correction pen liquid on it, silicon wafer and TEM grid and place the substrates on substrate holder and set the target-substrate distance to 13cm and then close the lid of vacuum chamber.
2. Create vacuum condition in the chamber until pressure is approx. 5×10^{-5} mbar and record the pressure reading as base pressure of the system.
3. Release fixed flow rate of argon gas at 8 sccm into the chamber such that operate pressure is about 5×10^{-3} mbar.
4. Apply the sputtering current of 0.6 A to cathode of titanium and aluminium sputtering targets for glow discharge process to begin while the shutter remains in position to separate between cathode and substrates. Let pre-sputtering runs for 3 minutes to clean the targets.
5. Release fixed flow rate of nitrogen gas at 4 sccm into chamber allowing mixing time with argon in chamber for a minute.
6. Open shutter of both sputtering targets to begin deposition titanium aluminium nitride on substrates and record voltage (V), current (I) of each sputtering target and total pressure (P_t) reading during deposition. Make deposition for Ti sputtering current of 0.6 A with fixed Al sputtering current at 0.6 A and deposition for 15 minutes.
7. Terminate the thin film deposition process by turning off power supply, argon and nitrogen gases. Vent air into the chamber before removing substrates that deposited $AlTi_3N$ film out of the chamber.
8. Rerun process No.1- No.7 in this section on each new set of the substrates for deposition times of 30, 45 and 60 minutes respectively.
9. Rerun process No.1 – No.8 for different Ti sputtering currents of 0.7, 0.8, 1.0 and 1.2 A. and analyze coated $AlTi_3N$ thin films on every substrates.

Summarized of the experimental settings for depositing aluminium titanium nitride thin films at different sputtering currents and deposition times are shown in table 3.1.

Table 3.1 Experimental conditions setting for deposition of aluminium titanium nitride thin films at different the sputtering currents and deposition times

Condition	Specification
Target	Titanium (99.97%), Al (99.999%)
Substrate	Glass slide, Silicon wafer, TEM grid
Substrate temperature	Room temperature
Base pressure (mbar)	$5.0x10^{-5}$
Total pressure (mbar)	$5.0x10^{-3}$
Ar flow rate (sccm)	8
N_2 flow rate (sccm)	4
Ti current (A)	0.6, 0.7, 0.8, 1.0 and 1.2
voltage (V)	400, 450, 500, 550, and 600
Al current (mA)	0.6
voltage (V)	280
Distance from target to substrate (cm)	13
Time (min)	15, 30, 45 and 60

3.4.1 Deposition of $AlTi_3N$ at Different Al sputtering current and Deposition Time

The steps for preparing aluminium titanium nitride thin film for the nanostructure study on unheated substrates at different Al sputtering currents with Ti sputtering current and deposition time were kept constant by the coating system are outline as below:

1. Provide cleaned substrates; glass slide which is previously dropped with correction pen liquid on it and silicon wafers and place the substrates on substrate holder and set the target-substrate distance to 13 cm and then close the lid of vacuum chamber.
2. Create vacuum condition in the chamber until pressure is approx. 5×10^{-5} mbar and record the pressure reading as base pressure of the system.
3. Release fixed flow rate of argon gas at 8 sccm into the chamber such that operate pressure is about 5×10^{-3} mbar.
4. Apply the sputtering current of 0.6 A to cathode of titanium and aluminium sputtering targets for glow discharge process to begin while the shutter remains in position to separate between cathode and substrates. Let pre-sputtering runs for 3 minutes to clean the targets.
5. Release fixed flow rate of nitrogen gas at 4 sccm into chamber allowing mixing time with argon in chamber for a minute.
6. Open shutter of both sputtering targets to begin deposition titanium aluminium nitride on substrates and record voltage (V), current (I) of each sputtering target and total pressure (P_t) reading during deposition. Make deposition for Al sputtering current of 0.2 A with fixed Ti sputtering current at 0.6 A and deposition for 60 minutes.
7. Terminate the thin film deposition process by turning off power supply, argon and nitrogen gases. Vent air into the chamber before removing substrates that deposited $AlTi_3N$ film out of the chamber.
8. Rerun process No.1- No.7 in this section on each new set of the substrates for Al sputtering current of 0.4 and 0.6 A, respectively, and analyze coated TiAlN thin films on every substrates.

Summarized of the experimental settings for depositing aluminium titanium nitride thin films at different sputtering currents and deposition times are shown in table 3.2.

Table 3.2 Experimental conditions setting for deposition of aluminium titanium nitride thin films at different the Al sputtering currents

Condition	Specification
Target	Titanium (99.97%), Al (99.999%)
Substrate	Glass slide, Silicon wafer
Substrate temperature	Room temperature
Base pressure (mbar)	$5.0x10^{-5}$
Total pressure (mbar)	$5.0x10^{-3}$
Ar flow rate (sccm)	8
N_2 flow rate (sccm)	4
Al current (A)	0.2, 0.4 and 0.6
voltage (V)	256, 250 and 245
Ti current (A)	0.6
voltage (V)	300
Distance from target to substrate (cm)	13
Time (min)	60

3.5 The Study of Aluminium Titanium Nitride Thin Film Properties

The study of aluminium titanium nitride thin film properties such as crystalline structure and surface morphology of the deposited films are described in this section.

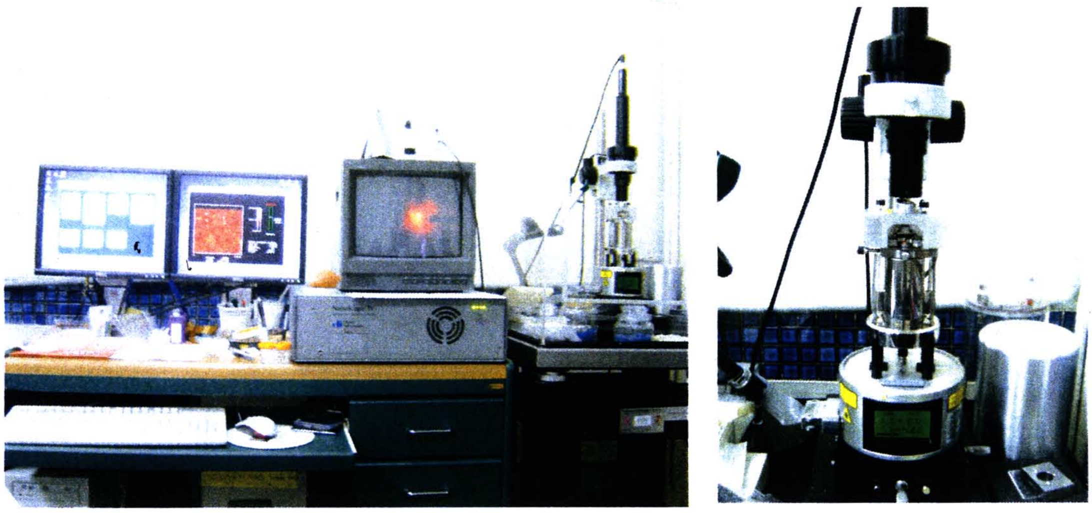
3.5.1 Characterization of Aluminium Titanium Nitride Thin Film

Crystalline structure of the films deposited on silicon wafers are investigated by X-Ray diffractrometer technique using Cu-k_α as x-ray source and take measurements in low angle mode. The 2θ scan angle range is between 20^O and 65^O and the spectrums obtained are stored as x-ray diffraction pattern and compared with the highest intensity position of 2θ of the JCPDS files for determining the crystalline structure of the films. Figure 3.5 shows the XRD used in this work.

Figure 3.5 The X-Ray Diffractrometer (XRD)

3.5.2 The Study of Surface Morphology of Aluminium Titanium Nitride Thin Film

Surface morphology of the $AlTi_3N$ thin films deposited on glass slide substrates were analyzed by the AFM technique as RMS (root mean square) roughness. Figure 3.6 shows the AFM used and the measurement is done tapping mode with high resolution in nano-scale. The thickness and surface roughness measurement are carried out over the scanning area of 1x1 μm^2 of the thin films.



(a) (b)

Figure 3.6 The Atomic Force Microscope (AFM) in a tapping mode, by Digital Instruments, Nanoscope III (a) AFM and display part (b) AFM [55]

3.5.3 The Study of Crystalline Structure and Orientation of Aluminium Titanium Nitride Thin Film

Transmission Electron Microscopy (TEM) as shown in Figure 3.7 is used for analyzing the crystalline structure and orientation of the $AlTi_3N$ thin films deposited on TEM grid. The TEM working potential for this study is at 160 kV operating in high resolution mode TEM(HRTEM) for analysis of d-spacing and Selected Area Electron Diffraction (SAED) for analysis of phase and structure of the deposited $AlTi_3N$ thin films.

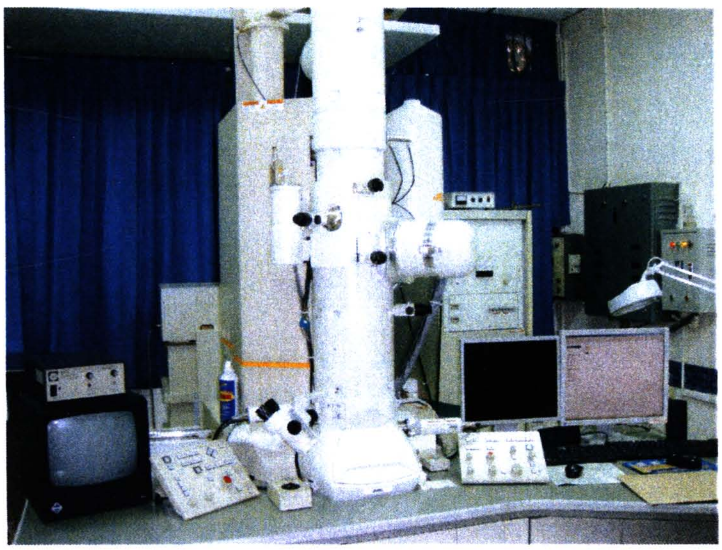


Figure 3.7 The Transmission Electron Microscopy (TEM) working at 160 kV, by Jeol, JEM-2100 [55]

3.5.4 The Study of Cross-Section Images of Aluminium Titanium Nitride Thin Film

For cross-section and thickness investigation of the $AlTi_3N$ thin films deposited on silicon substrates are analyzed by Field Emission Scanning Electron Microscopy (FE-SEM) (Hitachi, S-4700) as shown in Figure 3.8.

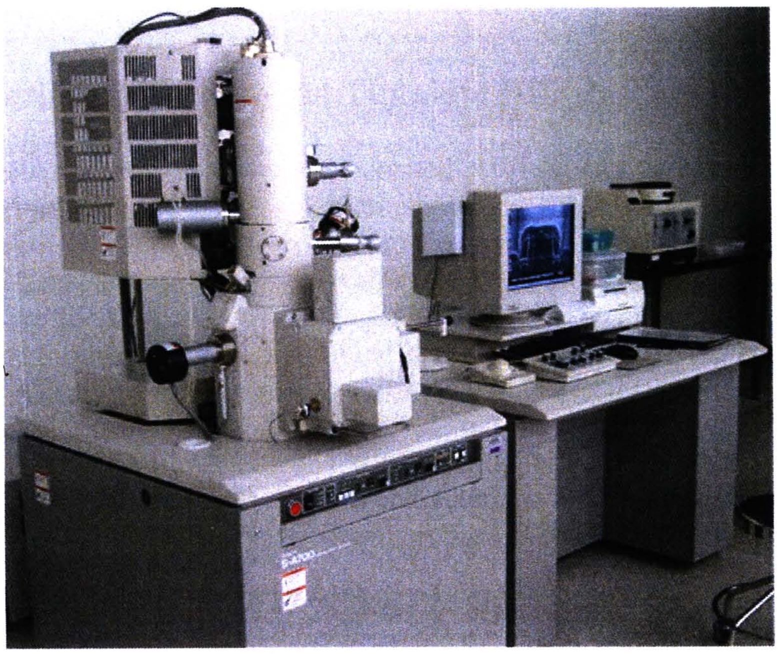


Figure3.8 The Field Emission Scanning Electron Microscopy (FE- SEM), by Hitachi, S-4700 [55]