Chapter 3 Experimental Detals

In this chapter, all the samples in my work are grown by AIXTRON HT-400 low-pressure metalorganic chemical vapor phase epitaxy (LP-MOCVD) system. The growth procedure for hexagonal GaN, Si-doped GaN, Mg-doped GaN, and In isoelectronic doped GaN:Mg would be described in detail later.

The films property characterization systems for determining these grown epilayers qualities such as Deep-level transient spectroscopy (DLTS), Hall measurement, Raman scattering, and photoluminescence (PL) spectroscopy will be described in the later sections.

3.1 Sample preparations

The III-nitrides and related materials are grown by low pressure MOCVD system. The main element of the system consists a horizontal reactor which is made of quartz. In order to avoid any pre-reactions in the gas stream, the group-III and group-V sources were separately introduced through different gas inlets into the deposition zone of the reactor. A high purity SiC-coated graphite was used as the susceptors. In order to achieve a growth temperature of higher than 1,000℃ for the nitride, a 20 KW radio frequency (RF) generator was used as the heater. The growth temperature was measured by a *S*-type thermocouple which is feedback-controlled through the temperature controller. To avoid oxygen contamination, the glove box, behind the reactor is constantly primed with N_2 gas. Electronic-grade trimethyl-indium (TMIn), trimethylgallium (TMGa), and high-purity ammonia (NH_3, 5N5) were used as the

precursor sources of In, Ga, and N, respectively. Biscyclo-pentadienyl-magnesium (Cp_2Mg) was used as the *p*-type dopant source in the nitride compound growth. Purified nitrogen (N_2) was used as the main carrier gas, which is through a getter purifier. Nonetheless, the bubbling gas for MO sources is purified hydrogen (H_2). The mass flow controllers (MFC) were used to regulate precise source molar flow rates during the deposition. The schematic diagram of piping system is drawed in Fig. 3-1. The source line details in this system for group-III nitride growth are summarized in Table 3-1.

Table 3-1 The source equipment details of MOVPE system for group-III nitrides growth.

	Source Name	Bubbling Temp. (℃)	MFC (sccm)	Vapor Pressure (torr)
MO Source	TMIn	10	500	0.75
	TMGa	-12	10	35.39
Hydride Source	NH_3	--	2000	--
Dopant Source	Cp_2Mg	20	500	0.03

For group-III nitride deposition, (0001) *c*-face sapphire (Al_2O_3) with the size of 2″ was used as a substrate. Prior to epitaxial film growth, the Al_2O_3 substrate was deployed at 1,200℃ (10 min) in a H_2 ambient for thermal cleaning, then nitridated at 1,050℃ in a NH_3 and H_2 mixed ambient. a typical sample structure and temperature-to-time curve of GaN growth procedure are depicted in Figs. 3-2(a) and 3-2(b). Due to the high lattice mismatch (~14%) between GaN epilayer and sapphire substrate, the nucleation layer was usually grown between them to minimize the strain

and reduce the defect density. Therefore, we grew a set of GaN samples with varying nucleation layer thickness and another set of samples with varying recrystallization temperatures to study the optimization of nucleation layer growth condition. Since the growth temperature is very sensitive in high quality GaN growth, another series of samples change the grown temperatures to find the best growth temperature parameter. Other important growth parameters such as growth rate r_g, V/III ratio and mixed carrier gas effect (N_2/H_2 ratio) were employed in preparing different series of samples aiming at the electrical property optimization. Under the same growth conditions, we grew a series of Si-modulation doped GaN films with varying a periods of doping layers from 0 ~ 40 pairs to investigate the modulation doping effect. Finally, high-quality GaN with low background and high mobility was able to be obtained from an optimized set of growth parameters. Using the same set of growth conditions, we grew another series of Mg doped GaN samples with varying Cp_2Mg flow rate from 0.118 to 0.585 μmol/min (*i.e.* from 100 to 500 sccm) during the epilayer growth to investigate the Mg doping effect. Two series of isoelectronic In-doped p-GaN samples were grown at 1110 ℃ with 300 Å buffer layers. The growth process is similar to the GaN growth. The respective flow rates for TMGa and NH_3 were 10.3 μmol/min and 0.7 standard liter per minute. For CP_2Mg flow rate, the constant TMIn flow rate was 25.5μmol/min. For TMIn flow rate series, TMIn diluted with hydrogen was used at four different flow rates of 0.22, 0.44, 1.1, and 2.12 μmol/min.

3.2 Characterization Sysytems

Raman spectroscopy is a powerful tool for assessing crystalline quality. The linewidths and shifts of Raman peaks also indicate macroscopic strains of crystal

subject related to compressive (blue shift) or tensile (red shift) stresses on a microscopic scale.

As shown in Fig. 3.3, the block diagram of our Raman scattering system consists of a double-grating monochromator and a multichannel Si photodiode array detector. There were neutral density (ND) filters, interference filter, focusing lenses, and reflecting mirrors in the optical path. A pair of polarizer and analyzer was inserted in the incident and scattered optical path for analyzing the polarized Raman scattering. The incident laser beam was ~50º oblique to the sample normal and was focused by a f = 4 cm converging lens to a small spot size (~30-50 μm in diameter). The average power on GaN film was 50 mW (power density about 2.5 ~7 kW/cm^2). The interference filter was used to remove plasma lines from the gas discharge and the notch filter was placed in front of the entrance slit to further reduce the strong elastic Rayleigh scattering. The scattered light was collected by a f / 1.4 camera lens and imaged into the entrance slit of the double monochromator (Jobin Yvon U-1000). This monochromator served as the dispersion element, which consists of a cosecant-driver and two 10 × 10 cm^2 size holographic gratings of 1800 grooves/mm. The dispersed Raman signals were accumulated by a multi-channel detector (Princeton Instruments IRY-1024G) with the ST-100 controller. This image intensi…ed silicon photodiode (ISPD) consists of a proximity-focused microchannel plate (MCP) intensifier and a linear photodiode array (EG&G Reticon RL-1024SAF). They are coupled by an optical fiber to eliminate window-to-target reflection and image distortion, and to enhance signal to noise ratio (S/N). Several advantages of this multichannel detector are the high speed data acquisition and capability to monitor simultaneously a wide spectrum in which we are interested. It is almost lag-free, each diode is fully recharged in < 1 μsec. The device contains 1024 discrete pixels with 25

μm center separation, and 2.5 mm height.

The pumping light source includes a mixed Ar^+ / Kr^+ ion laser (Coherent Innova 70 Spectrum) with different emission lines covering the range from violet-blue (457.9 nm) to red (647.1 nm). As the excitation source, it is used in conjunction with individual interference filters for Raman measurements. It is worth noting that each excitation wavelength has its own penetration depth that helps probe different depth in the multilayer structures.

The Raman spectrum is obtained by subtracting the ”dark” from the ”signal” response. The dark spectrum is measured by attenuating the laser light with a typical 1% ND filter. Therefore, we can have a background-free spectrum with only 1 % signal loss. A personal computer receives the Raman signal for data processing. The typical spectral resolution for Raman data was about 2-3 cm^{-1}

The luminescence property of epilayers was examined by PL measurement. The schematic drawing of the PL measurement system is shown in Fig. 3-4. For the PL experiments, we utilized a single-grating monochromators (ARC Spectro PRO-500), a photomultiplier tube (Hamamatsu R955), and He-Cd laser (Kimmon IK5552R-F). The laser operates at the 325 nm with an output power of 22 mW in providing the UV excitation for our wide bandgap epifilms. The spectral resolution of the PL data was better than 0.2 nm. For low-temperature PL measurements, the samples were situated in a 20 K closed cycle cryogenic system (APD HC-2D) with temperature controlled by a Lakeshare 330 temperature controller. The lowest temperature of samples can be cooled down to ~14 K.

The electrical property of samples was probed by a Hall measurement system. The schematic drawing of the Hall system is shown in Fig. 3-5. The system contains a current source (Keithley, Model 220), a voltage meter (Keithley, Model 196), a current meter (DMM, Model 485), and a scanner (Keithley, Model 705). The magnetic field used in the measurement is about 10^4 Gauss. For Hall experiments, indium (In) balls and Ni/Au bilayer were mostly used as the metal contact for *n*-type and *p*-type nitride films, respectively. To assure good ohmic metal-contacting characteristics of *n*-type and *p*-type samples, the In and Ni/Au metal contacts in N_2 ambient were annealed with 700℃ thermal annealing (TA) for 30 minutes.

Either a scanning electron microscopy (SEM) was used to examine the morphology of the sample's surface. The film thickness is probed by either the SEM or the α-step profilometer. The impurity concentrations in the sample were measured by secondary ion mass spectroscopy (SIMS).

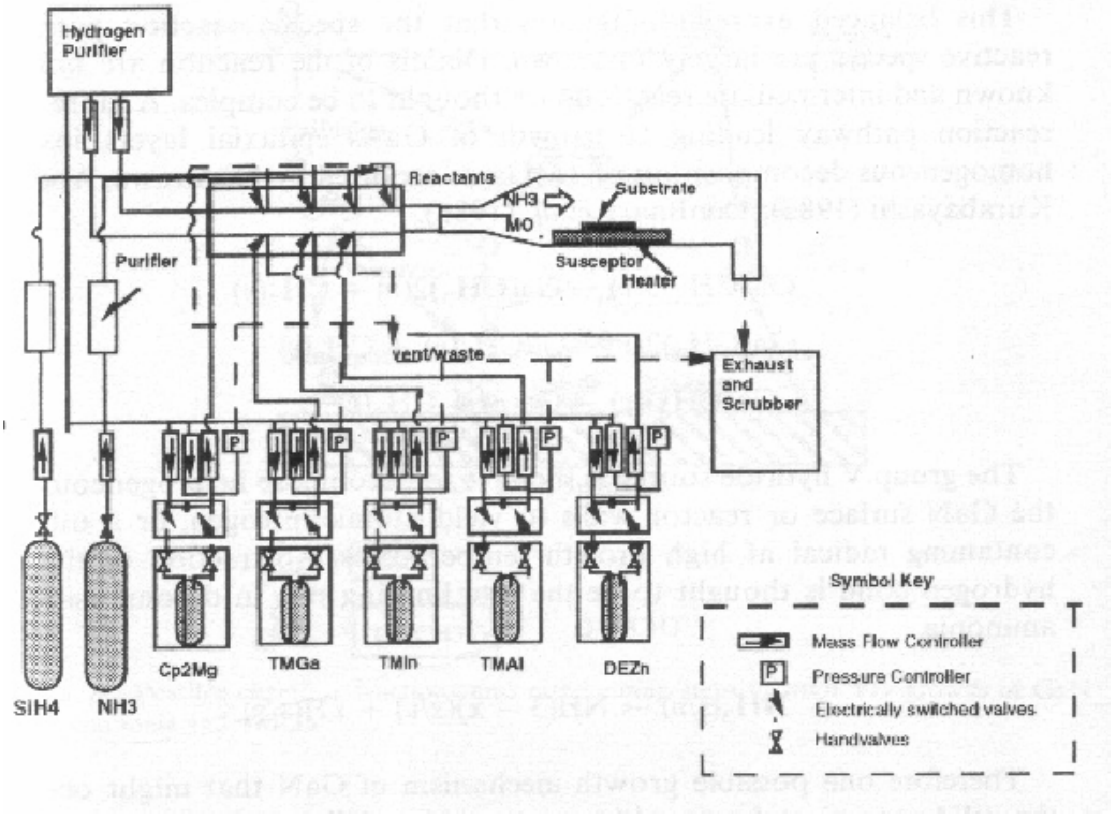
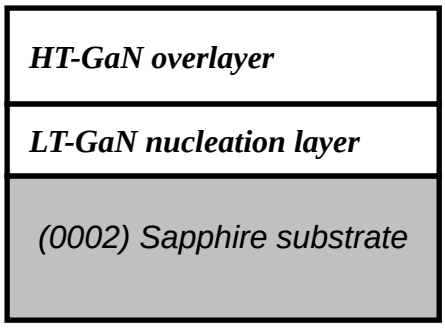
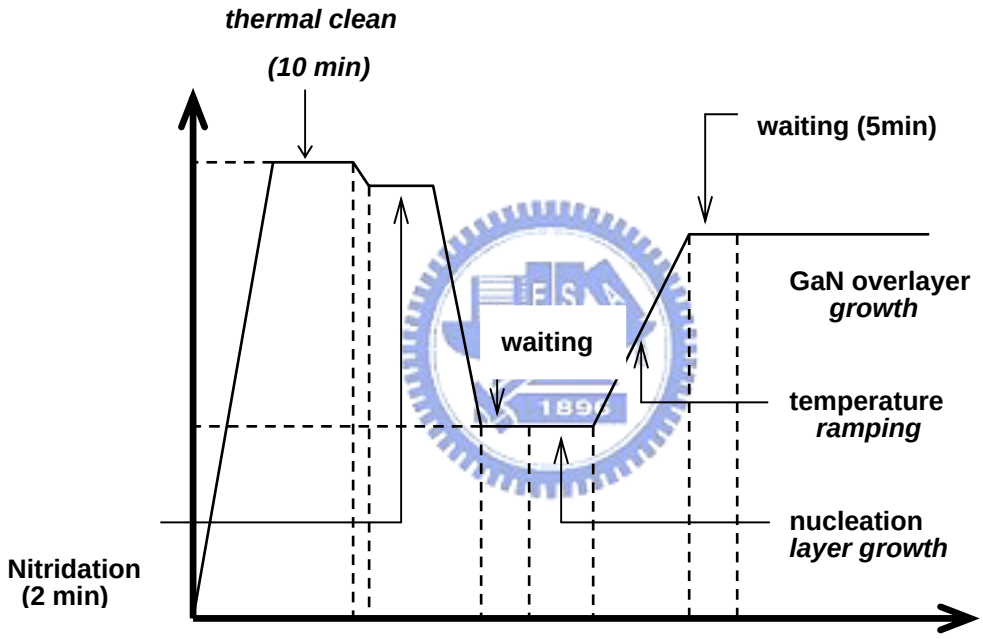


Fig 3.1 Schematic of horizontal type GaN MOCVD system



(a)



(b)

Fig. 3-2 The schematic diagrams of (a) GaN sample structure and (b) the corresponding growth procedure.

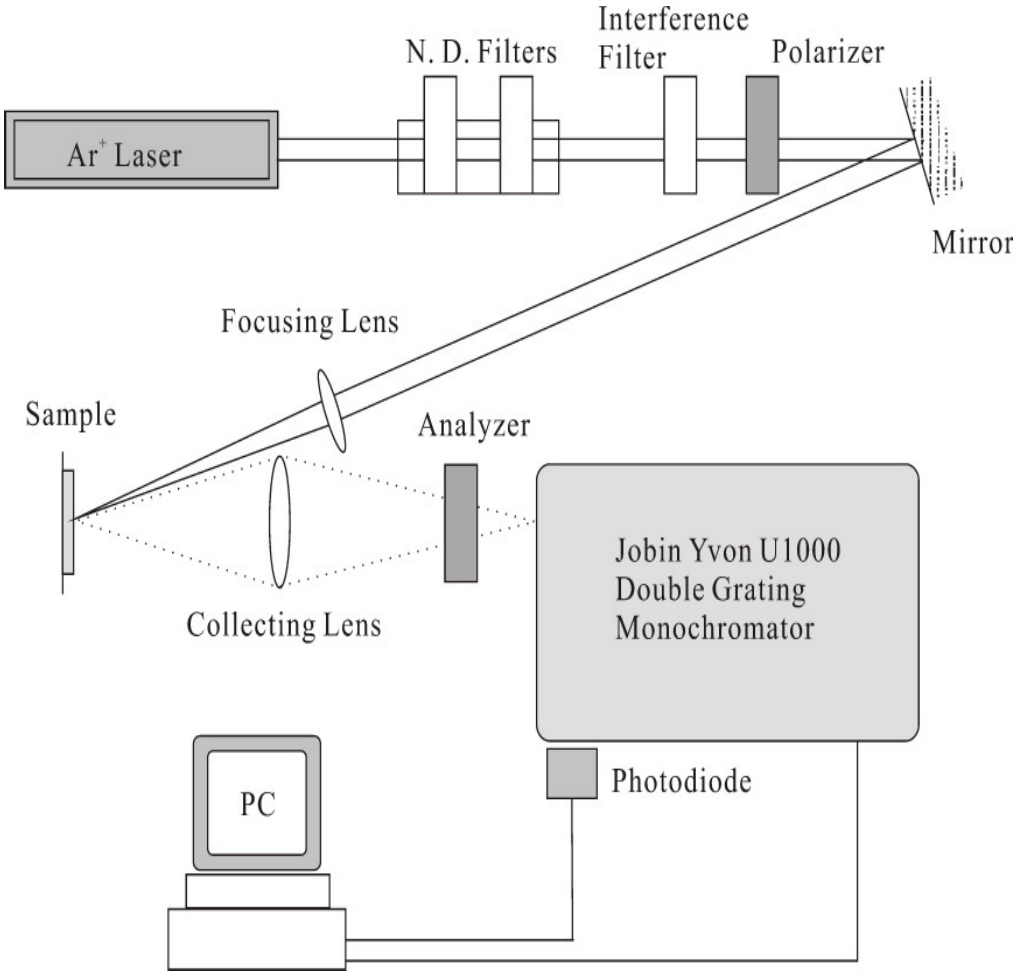


Fig 3.3 Raman scattering system block diagram.

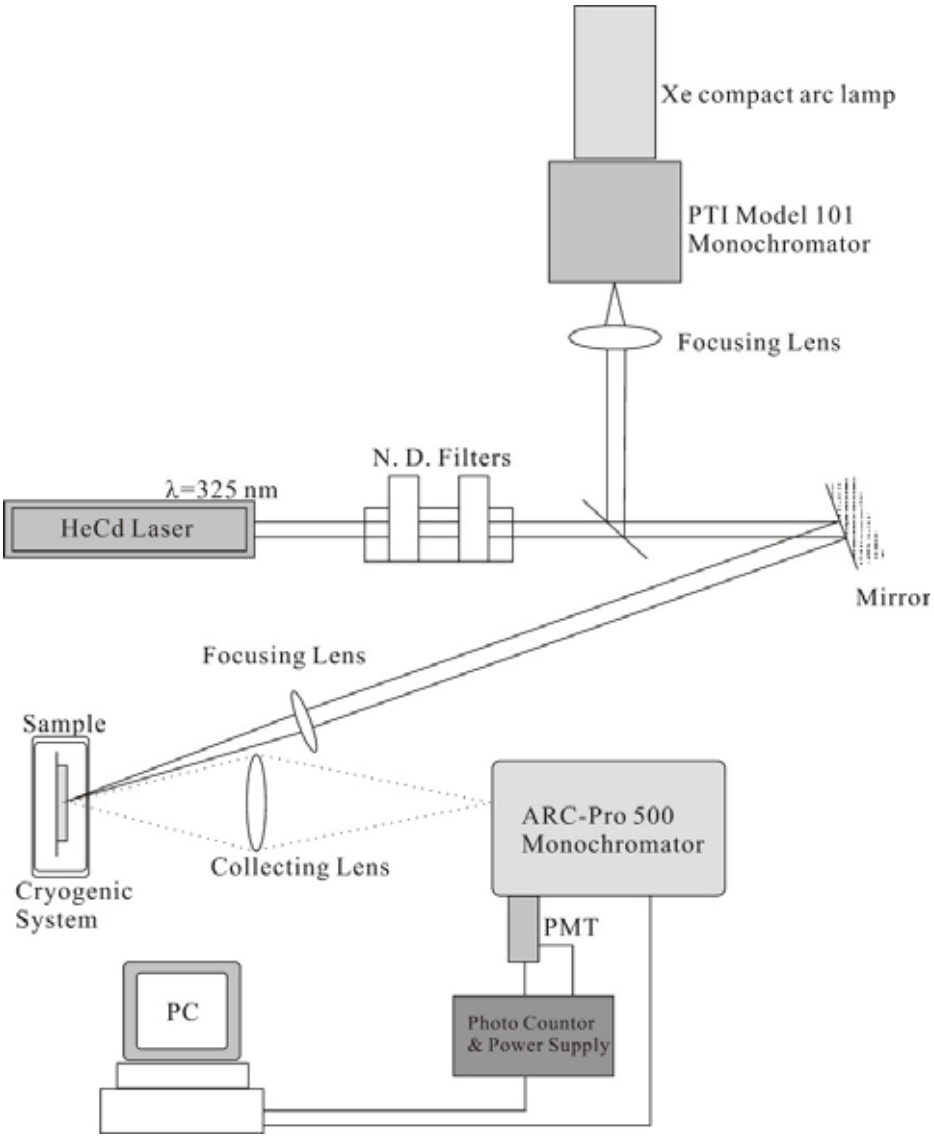


Fig 3.4 Photoluminescence and Photoluminescence excitation detection system block diagram

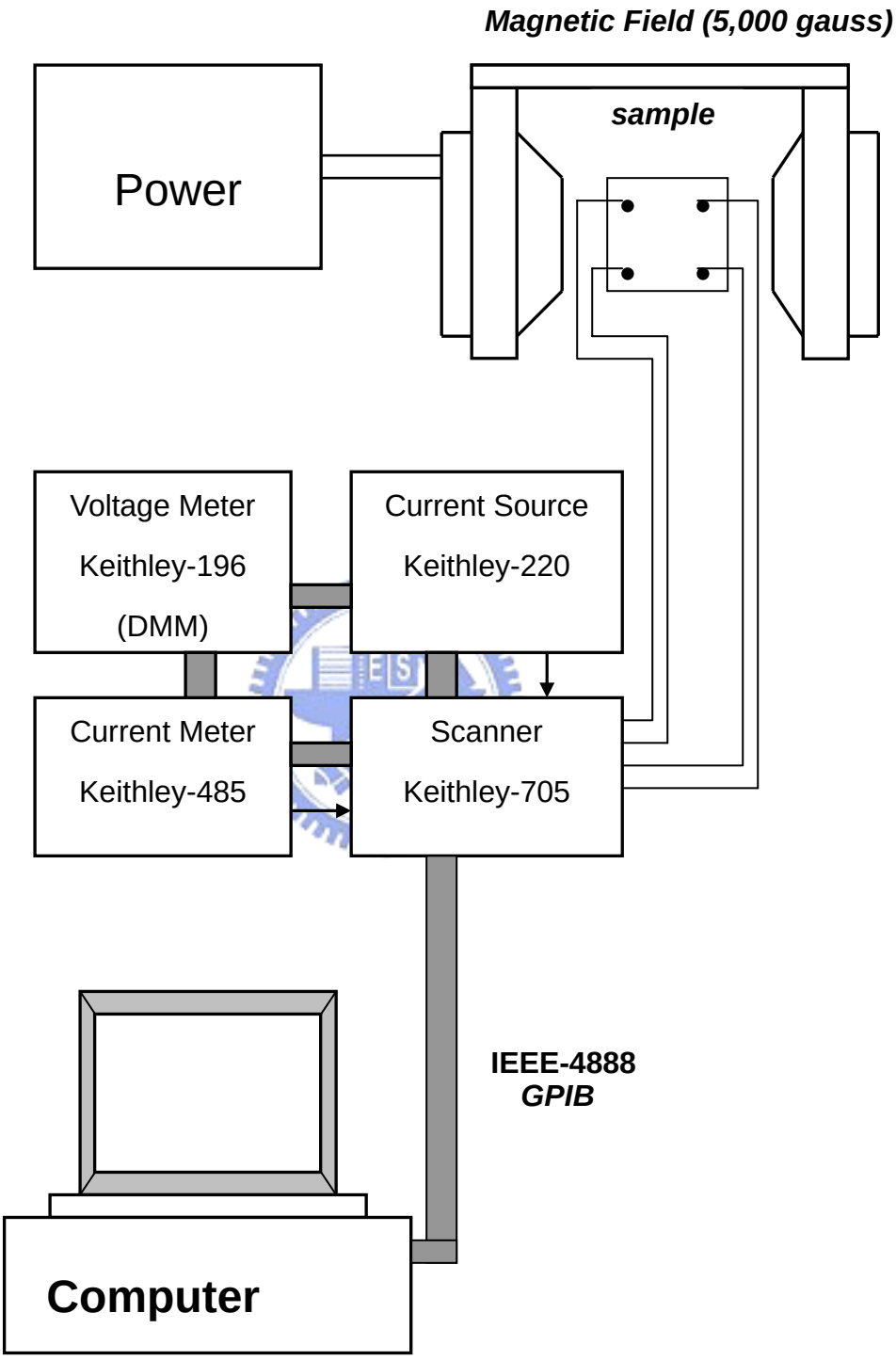


Fig 3.5 The schematic diagrams of the Hall measurement system.