Chapter 2

Experimental Procedures

2.1 Introduction

First of all, we used several metals as interlayer of the multilayer catalysts for CNT synthesis and found the most fitting ones for CNT growth at low temperature. Then we fabricated triode structure on silicon substrate and diode structure on glass substrate to prove the superiority of novel multilayer catalysts in CNT-FED. Finally, we accomplished many kinds of analysis for the above mentioned. The scheme of the whole experimental procedures was shown in Fig. 2-1.

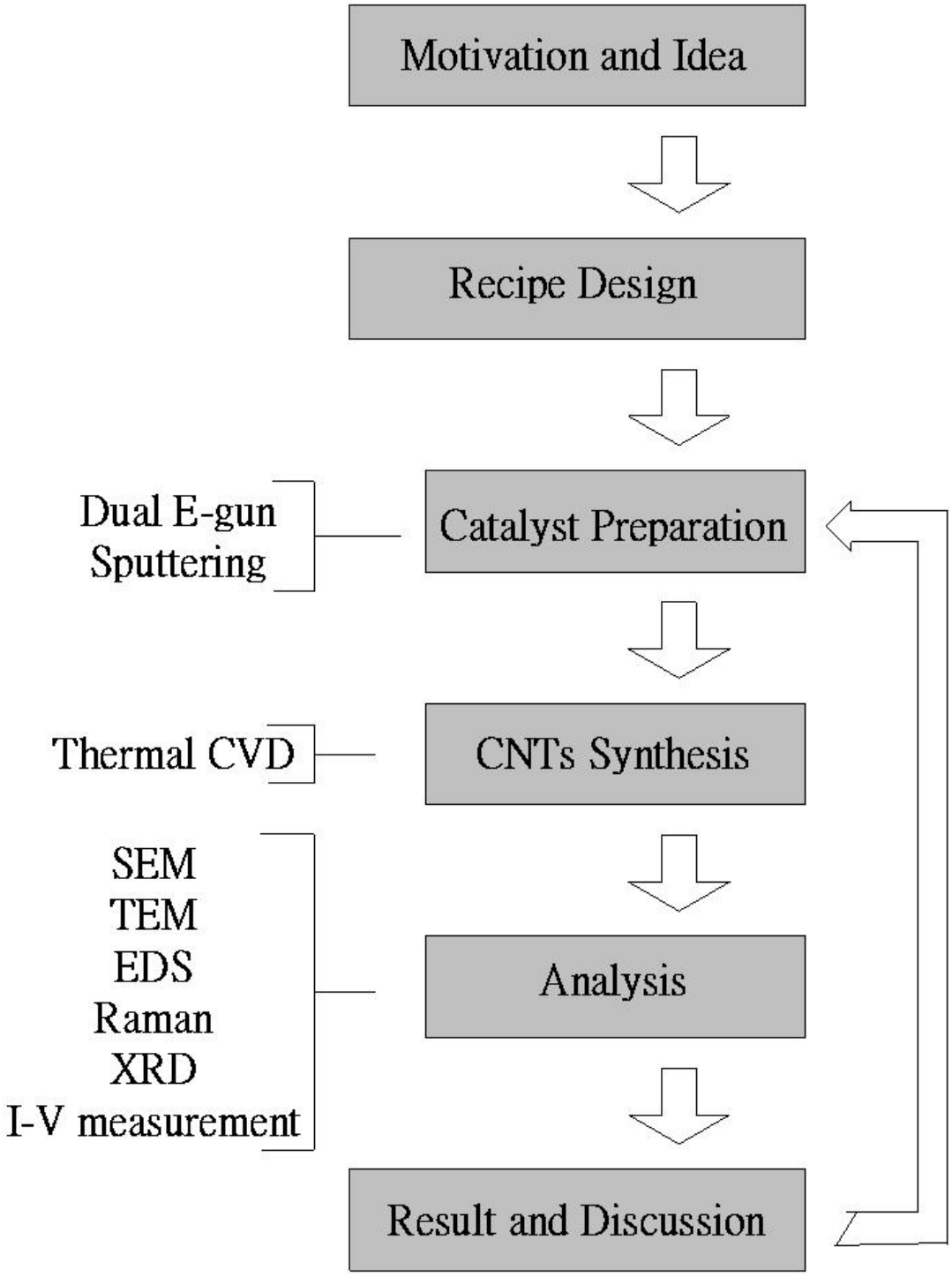


Fig. 2-1 Schematic experimental procedures

2.2 CNTs Grown using Multilayer Catalyst Films at Low Temperature

2.2.1 Forward Arrangement

A (100) n-type silicon wafer was prepared for the substrate. After the RCA clean and lithography processes, we defined three kinds of patterns in 1 mm*1 mm area (squares of 1000*1000、100*100、10*10 um^2) for CNT field emission arrays. A 2000Å Cr layer was deposited by dual E-gun evaporation (JAPAN ULVAC EBX-10C) as the cathode between the substrate and catalysts. We investigated nine materials as interlayer of multilayer catalyst films, including Cu, W, Mo, Cr, Pt , Ta, Hf, Ti and Cr metal films. From table 2-1, it was seen that the surface energies of above referred to Reference-45.

Table 2-1 work functions and surface energies for (a) monovalent, divalent, and trivalent nontransition metals, (b) 3d metals,(c) 4d metals, (d) 5d metals. [45]

Metal	Surface	Work function			Surface energy			
		Jellium[a]	Present	Expt.[b]	Jellium[a]	Present		Expt.[c]
		(eV)	(eV)	(eV)	(J/m^2)	(eV)	(J/m^2)	(J/m^2)
Li	bcc (110)	3.09	3.33	(2.9)	0.326	0.247	0.458	0.525
	bcc (100)	2.92	3.15		0.371	0.332	0.436	
Na	bcc (110)	2.75	2.94	(2.75)	0.190	0.242	0.307	0.260
	bcc (100)	2.58	2.76		0.216	0.263	0.236	
K	bcc (110)	2.37	2.38	(2.30)	0.111	0.139	0.116	0.130
	bcc (100)	2.21	2.34		0.115	0.220	0.129	
	fcc (111)		2.41			0.132	0.112	
Rb	bcc (110)	2.28	2.32	(2.16)	0.086	0.127	0.092	0.110
	bcc (100)	2.12	2.22		0.098	0.207	0.107	
	fcc (111)		2.29			0.120	0.089	
Cs	bcc (110)	2.17	2.09	(2.14)	0.069	0.117	0.072	0.095
	bcc (100)	2.01	2.03		0.079	0.210	0.092	
	fcc (111)		2.10			0.111	0.070	
Be	hcp (001)		5.62	(4.98)		0.583	2.122	2.70
Mg	hcp (001)	3.44	3.86	(3.66)	0.554	0.356	0.642	0.76
Ca	fcc (111)	3.10	2.86	(2.87)	0.325	0.296	0.352	0.49
	bcc (110)		2.84			0.293	0.339	
Sr	fcc (111)	2.94	2.42	(2.59)	0.256	0.287	0.287	0.41
	bcc (110)		2.39			0.291	0.282	
Ba	bcc (110)	2.83	2.28	(2.7)	0.233	0.286	0.260	0.37
	fcc (111)		2.23			0.277	0.258	
Ra	bcc (110)		2.25			0.288	0.247	
Eu	bcc (110)		2.42	(2.5)		0.317	0.342	0.45
Yb	fcc (111)		2.51			0.318	0.391	0.50
	bcc (110)		2.45			0.328	0.391	
Al	fcc (111)	3.72	4.54	4.24	0.921	0.56	1.27	1.16

(a)

Table 2-1 work functions and surface energies for (a) monovalent, divalent, and trivalent nontransition metals, (b) 3d metals,(c) 4d metals, (d) 5d metals. [2-1]

Metal	Surface	Work function		Surface energy		
		Theory	Expt.[a]	Theory		Expt.[b]
		(eV)	(eV)	(eV)	(J/m^2)	(J/m^2)
Sc	hcp (001)	3.74	(3.5)	0.48	0.82	1.28
	fcc (111)	3.84		0.44	0.76	
Ti	hcp (001)	4.59	(4.33)	0.90	1.95	2.10
	fcc (111)	4.63		0.72	1.56	
V	bcc (110)	5.12	(4.3)	0.82	2.02	2.55
	fcc (111)	4.88		0.99	2.55	
Cr	bcc (110)	5.45	(4.5)	1.33	3.63	2.30
	fcc (111)	5.27		1.10	3.09	
Mn	fcc (111)	5.45	(4.1)	1.17	3.24	1.60
Fe	bcc (110)F^c	5.16	(4.5)	0.96	2.66	2.48
	bcc (110)	5.78		1.12	3.09	2.48
	fcc (111)	5.54		1.15	3.28	
Co	hcp (001)F^c	5.48	(5.0)	0.94	2.74	2.55
	hcp (001)	5.81		1.08	3.18	2.55
	fcc (111)	5.76		1.10	3.23	
Ni	fcc (111)F^c	5.68	5.35	0.90	2.69	2.45
	fcc (111)	5.77	5.35	0.88	2.63	2.45
Cu	fcc (111)	5.30	4.94	0.69	1.96	1.83
	fcc (100)	5.26	4.59	0.85	2.09	
	fcc (110)	4.48	4.48	1.33	2.31	

(b)

Metal	Surface	Work function			Surface energy			
		Slab[a]	Present	Expt.[b]	Slab[a]	Present		Expt.[c]
		(eV)	(eV)	(eV)	(J/m^2)	(eV)	(J/m^2)	(J/m^2)
Y	hcp (001)		3.38	(3.1)		0.48	0.68	1.13
	fcc (111)	3.46	3.42		1.15	0.45	0.65	
Zr	hcp (001)		4.15	(4.05)		0.85	1.53	2.00
	fcc (111)	4.38	4.35		1.75	0.68	1.22	
Nb	bcc (110)	4.66	4.80	4.87	2.36	0.79	1.64	2.70
	fcc (111)	4.63	4.69	(4.3)	2.20	0.96	2.06	
Mo	bcc (110)	4.94	5.34	4.95	3.14	1.38	3.18	3.00
	fcc (111)	4.98	5.09	(4.6)	2.64	1.06	2.50	
Tc	hcp (001)		5.36			1.12	2.80	3.15
	fcc (111)	5.15	5.42		2.63	1.06	2.69	
Ru	hcp (001)		5.84	(4.71)		1.28	3.32	3.05
	fcc (111)	5.33	5.73		2.99	1.12	2.90	
Rh	fcc (111)	5.44	5.91	(4.98)	2.53	1.09	2.78	2.70
	fcc (100)	5.25	6.14		2.81	1.31	2.90	
Pd	fcc (111)	5.53	5.90	5.6	1.64	0.77	1.88	2.05
	fcc (100)	5.30	5.96		1.86	0.90	1.90	
Ag	fcc (111)	4.67	5.01	4.74	1.21	0.50	1.12	1.25
	fcc (100)	4.43	5.02	4.64	1.21	0.62	1.20	
	fcc (110)	4.23	4.40	4.52	1.26	0.94	1.29	

Table 2-1 work functions and surface energies for (a) monovalent, divalent, and trivalent nontransition metals, (b) 3d metals,(c) 4d metals, (d) 5d metals. [2-1]

(c)

Metal	Surface	Work function		Surface energy		
		Theory	Expt.[a]	Theory		Expt.[b]
		(eV)	(eV)	(eV)	(J/m^2)	(J/m^2)
La	hcp (001)	3.21	(3.5)	0.43	0.57	1.02
	fcc (111)	3.30		0.43	0.57	
Lu	hcp (001)	3.57	(3.3)	0.50	0.77	1.23
	fcc (111)	3.65		0.47	0.72	
Hf	hcp (001)	4.26	(3.9)	0.94	1.75	2.15
	fcc (111)	4.54		0.75	1.39	
Ta	bcc (110)	5.08	4.80	0.86	1.79	3.15
	fcc (111)	4.86	(4.25)	1.06	2.27	
W	bcc (110)	5.62	5.25	1.70	3.84	3.68
	fcc (111)	5.09	(4.55)	1.06	2.50	
Re	hcp (001)	5.71	5.75[c]	1.34	3.27	3.60
	fcc (111)	5.88		1.34	3.28	
Os	hcp (001)	6.42	(4.83)	1.60	4.04	3.45
	fcc (111)	6.25		1.37	3.46	
Ir	fcc (111)	6.63	5.76	1.36	3.41	3.00
	fcc (100)	7.05	5.67	1.75	3.81	
Pt	fcc (111)	6.74	5.7[d]	0.98	2.35	2.48
	fcc (100)	6.97		1.19	2.48	
Au	fcc (111)	6.01	5.31	0.72	1.61	1.50
	fcc (100)	6.16	5.47	0.88	1.71	
	fcc (110)	5.40	5.40	1.31	1.79	

(d)

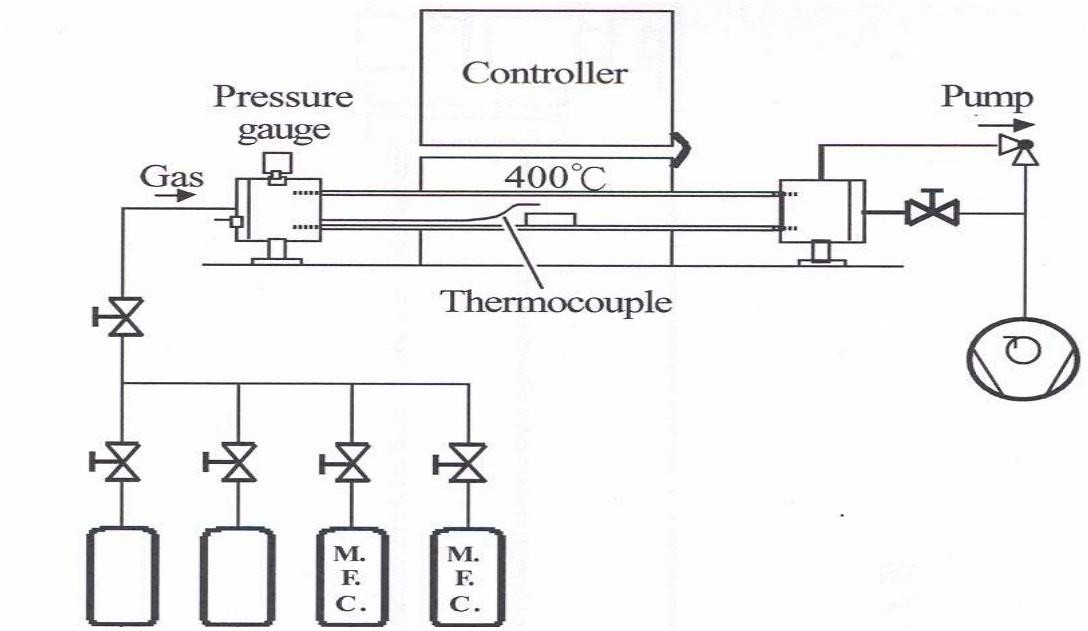
100A Al, 20A interlayer, and 20A Co were deposited on the patterned Cr cathode by sputtering, each of the three multilayer catalyst films was deposited layer by layer at 0.1A/s (deposition rate) using sputtering system (ENGLAND Ion Tech Microvac 450CB). After the deposition of the catalysts into the patterns as described above, the photoresist was lifted off in acetone solution. At last, the samples were already accomplished for CNT growth.

2.2.2 CNT Synthesis

The samples with different catalysts were transferred into a thermal CVD chamber (Fig. 2-2). First, the catalyst film must be pretreated to form nano-particles with H_2. It is more difficult for catalyst film to become particles without plasma treatment. Then, the hydrocarbon gas source was added to synthesize CNTs. In this instrument, there were two types of hydrocarbon gases: CH_4 (**methane**) and C_2H_4 (**ethylene**). According to researches by Siegal et al.,[46]the chemical reactivity of these compound is related to their heats of formation, obtained from the CRC Handbook of physics and Chemistry, and shown in Fig.2-3.In general, the greater bond numbers are, the more reactive energies will be. Therefore, Because of the differences of chemical reactivity, we applied C_2H_4 (**ethylene**) (more reactive) to synthesize CNTs in general. The whole experimental process was presented schematically in Fig. 2-4.

(a)

Fig. 2-2 A (a) photo and (b) schematic picture of thermal CVD



(b)

Fig. 2-2 A (a) photo and (b) schematic picture of thermal CVD

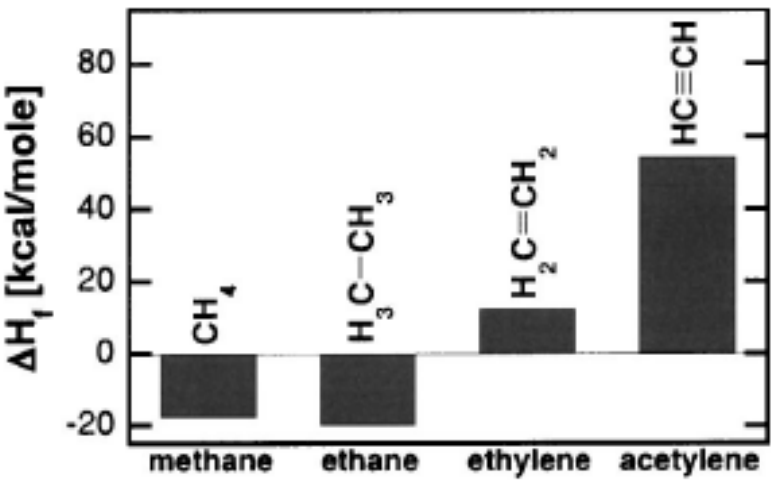


Fig. 2-3 Heat of formation of various hydrocarbon gases. [46]

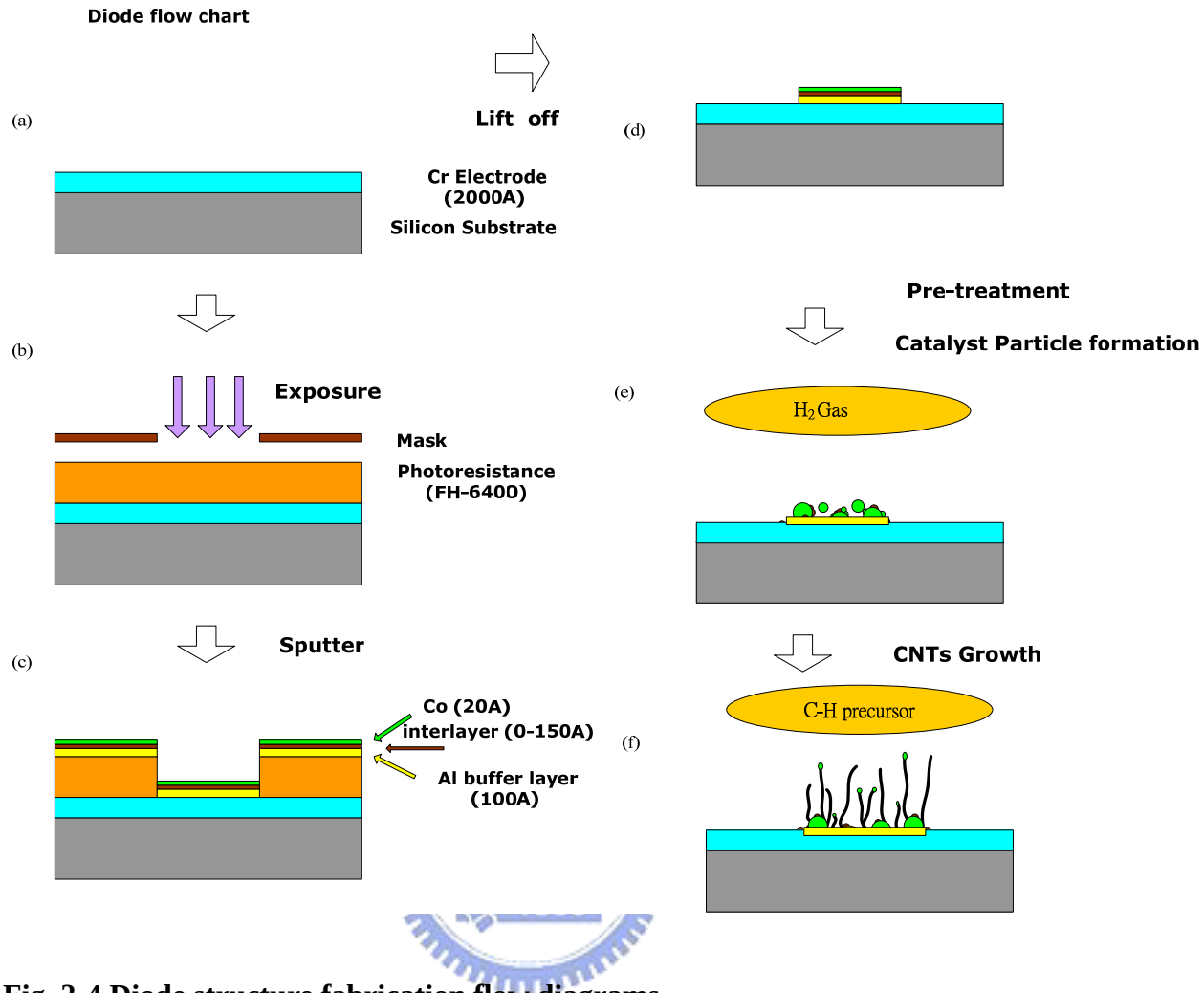


Fig. 2-4 Diode structure fabrication flow diagrams

(a) 2000A Cr cathode deposition by Egun, (b) Lithography procedure (c) Multilayer catalysts deposition, (d) Lift photoresist off, (e) Pretreatment, and (f) CNT growth.

To synthesize CNTs, several experiments were proceeded. In experiment A, we grew CNTs with a different interlayer at 550 ℃ and there will be an exhaustive investigation in the following section of results and discussions. In experiment B, we compared different composition proportion of Co/Cr, Co/Ti, and tried to find out the limit of thickness of interlayer. In particular, it is generally believed that the formation of catalyst nanoparticles is necessary before CNT growth-pretreatment. The

pretreatment method is classified by the surface energy of interlayer as shown in Fig.2-5. We chose Ta, Hf, Ti, Cr to be investigated in experiment C, respectively. Experiment D was investigated at 500℃. From Exp.C, we also find some roles about heat of formation carbide in catalyst growth CNTs (Fig.2-6).

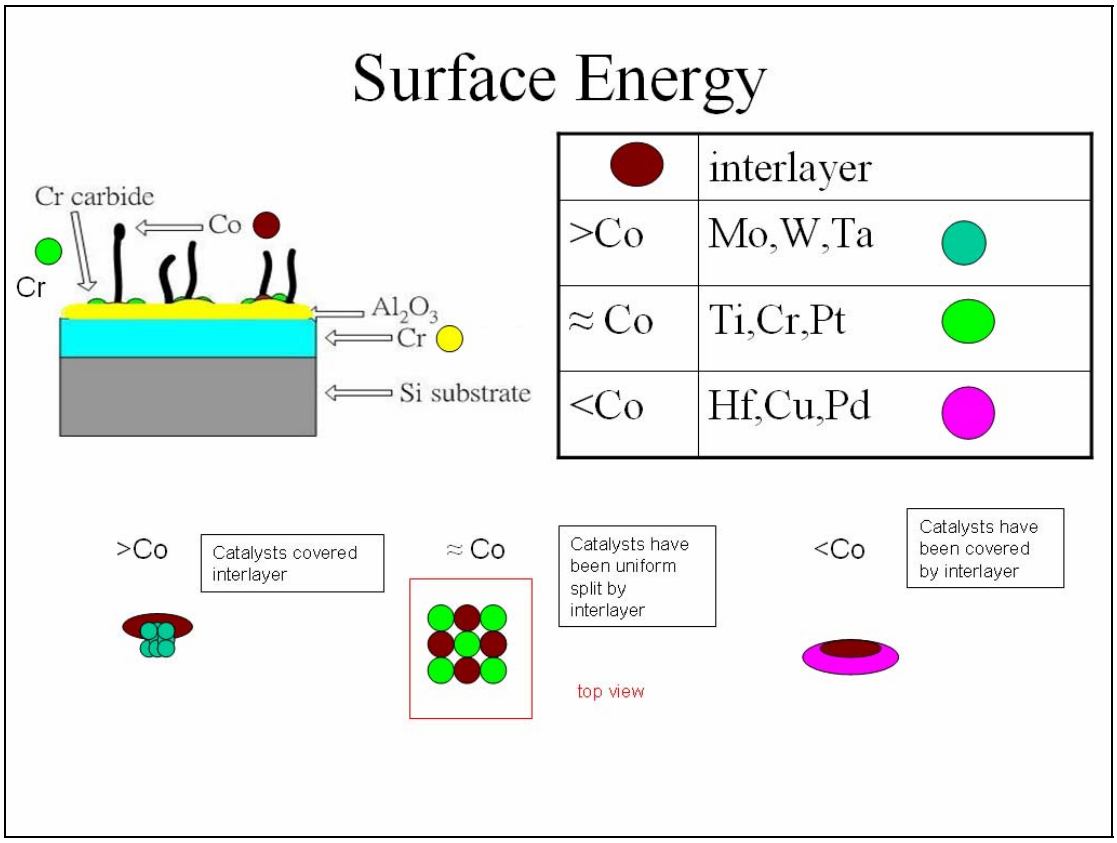


Fig. 2-5 Surface Energy with catalyst interface reaction diagrams [this work]

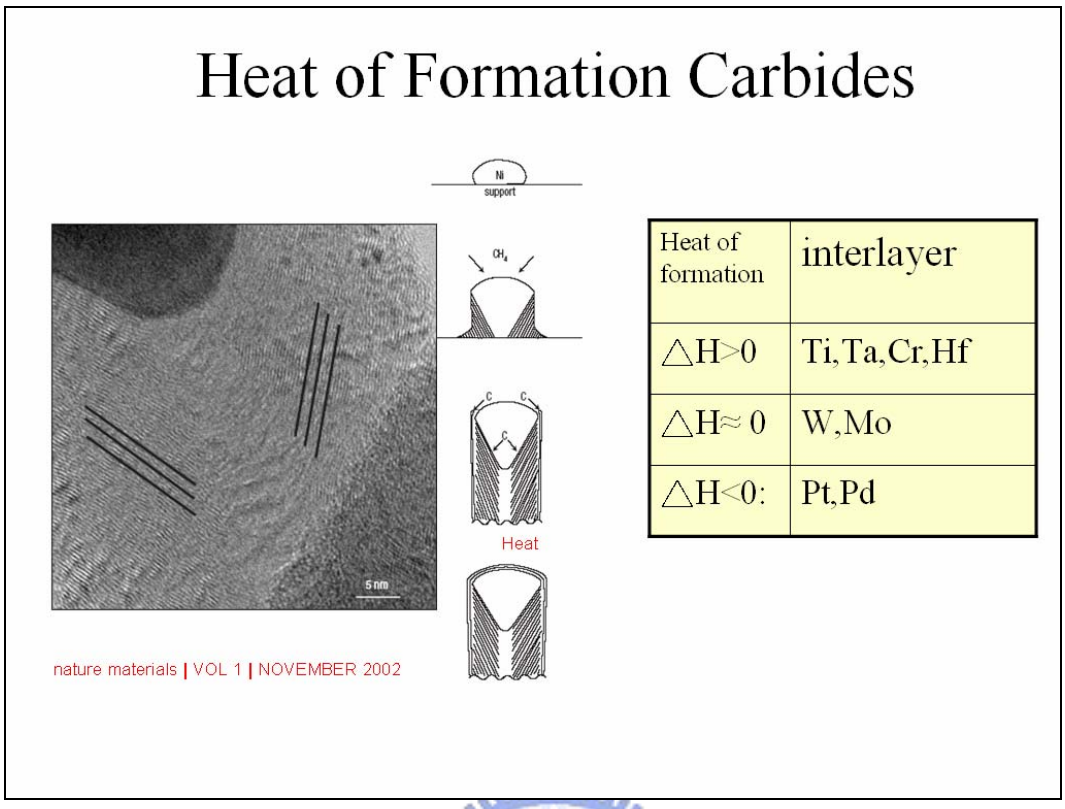
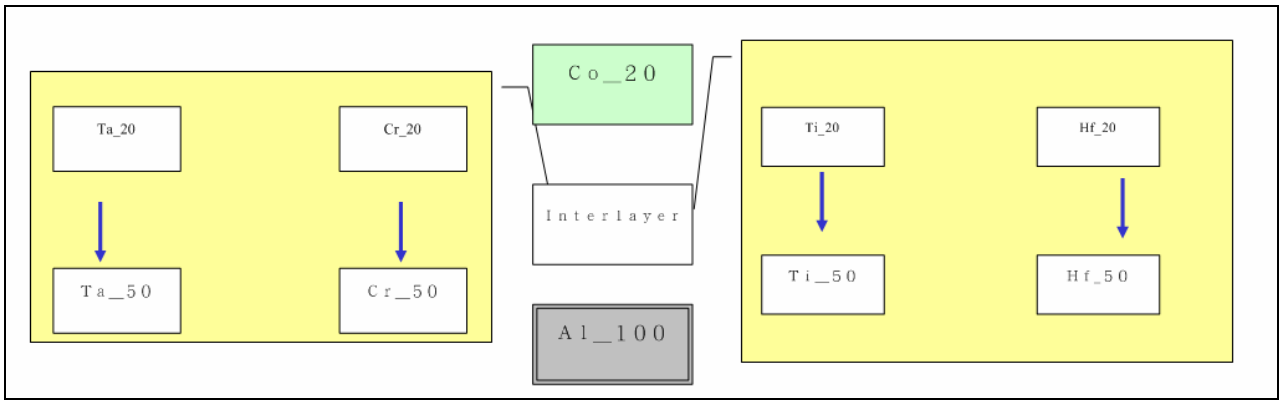


Fig. 2-6 Heat of Formation Carbides diagrams [this work]

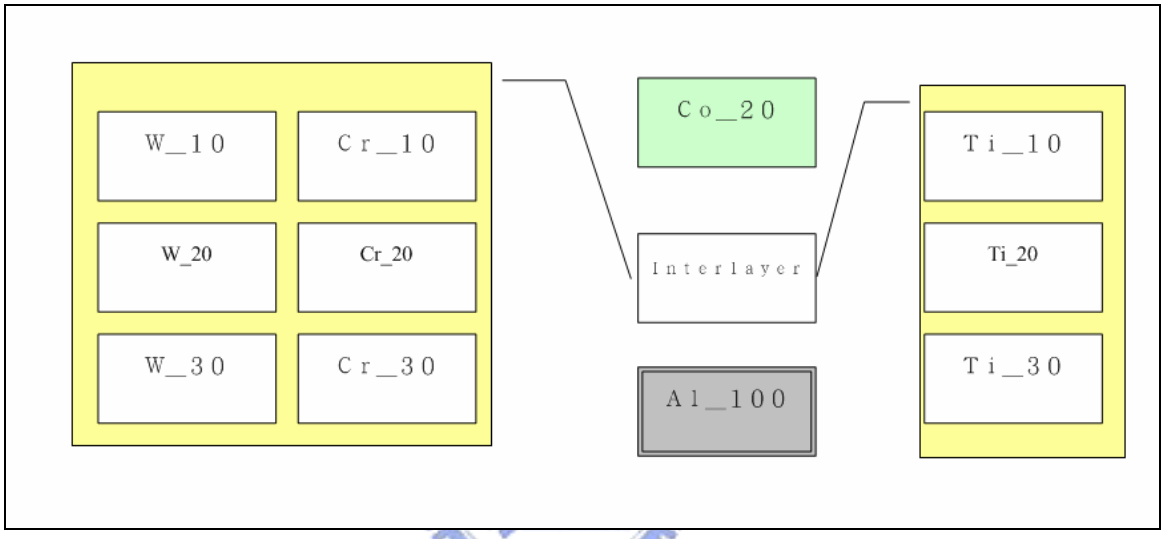
Finally, the stress test experiment is holed on to find out the suitable thickness of interlayer. The experimental parameters of CNT synthesis were described as follows.

Experiment A

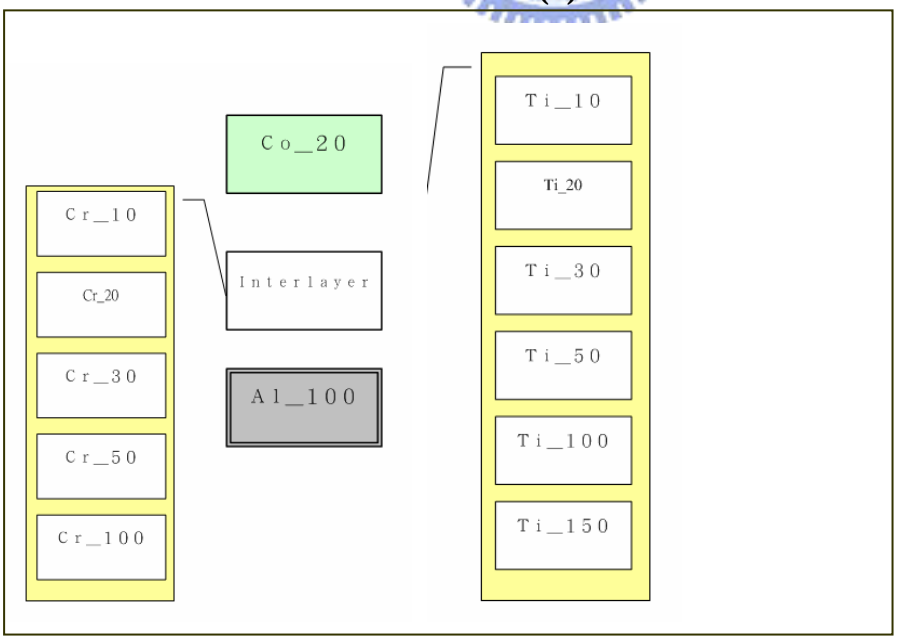
The thickness of nine interlayer was deposited at 20 A, we took the process variation into consideration, and also did some sample tests in 10 A ,30 A and 50 A. Finally, the catalysts' nano-films were pretreated at 550℃ for 5 minutes with 50 sccm H_2, and for 5 minutes with 1000sccm N_2, respectively. Then 75 sccm C_2H_4 (**ethylene**)and 1000 sccm N_2 was added to grow CNTs at 550℃ for 30 minutes, as shown in Fig.2-7 (a) & (b)



(a)



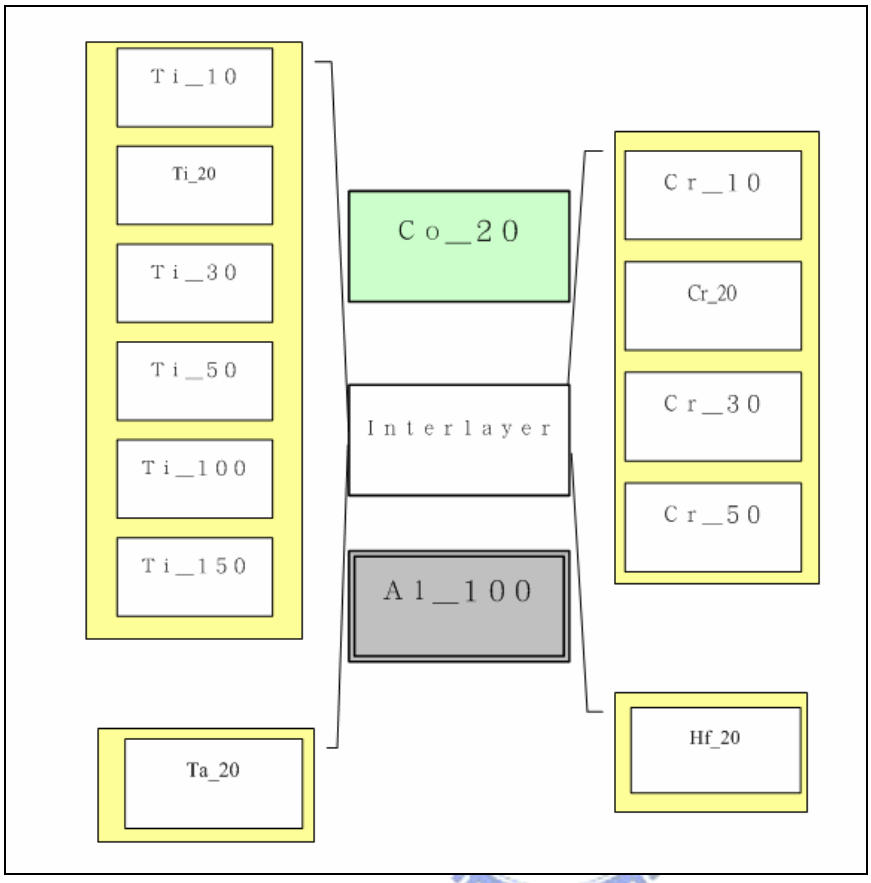
(b)



(c)

Fig. 2-7 Experiments A-D diagrams (a) thickness increased to 50 A (b) thickness from 10 A to 30 A (c) Cr : thickness added to 100 A ,and Ti : added to

150 A (d) growth temperature lowed down to 500℃, repeat the experiment.



(d)

Fig. 2-7 Experiments A-D diagrams (a) thickness increased to 50 A (b) thickness from 10 A to 30 A (c) Cr : thickness added to 100 A ,and Ti : added to 150 A (d) growth temperature lowed down to 500℃, repeat the experiment.

Experiment B

Using the Experiment A results, we compared different composition proportion of Co/ Cr, Co/Ti, and tried to find out the limit of thickness of interlayer. The growth recipe is the same as experiment A, as shown in Fig.2-7 (c)

Experiment C

The catalysts' nano-films were pretreated at 550℃ for 5 minutes with 50 sccm H_2, and for 5 minutes with 1000sccm N_2, respectively. Pretreatment before CNT growth was investigated.

Experiment D

The growth recipe is the same as experiment A, except the growth temperature. Temperature was lowed down to 500℃, and we reinvestigated the interlayer which showed the excellent field emission properties in Exp.A, as shown in Fig.2-7 (d)

Finally, both samples were grown in 550℃ and 500℃ by each. The electric characteristics were measured by Keithley 237 in a 10^{-6} torr chamber for stress test by 1 hr. We also applied an ITO glass with phosphor coating on it as the anode to observe the luminescent image.

2.3 MIM Triode Structure on Si Substrate

2.3.1 Structure Fabrication

The fabrication procedures of the triode structure for CNT-FED were shown in Fig. 2-8. A (100) n-type silicon wafer as the substrate was cleaned by RCA- Clean. As shown in Fig. 2-8(a), 2000A Cr as the cathode, 1 um SiO_2, and 2000A Cr as the gate were deposited layer by layer using the E Gun, Plasma Enhanced Chemical Vapor Deposition(PECVD), and E Gun, respectively. Then there are two masks in the lithography process as Fig. 2-8(b). One whose shape is stripe defines the gate region and isolate the neighbor devices. The other one whose shape is square defines the catalyst metal deposition region. As described in Fig. 2-8(c), the gate and SiO_2 were

etched in the wet etching, respectively. With the previously patterned photoresist layer as the shadow mask, 100A Al, 30A Cr, and 20A Co ,another condition 100A Al, 30A Ti, and 20A Co were deposited on the patterned Cr cathode by Sputter (Fig. 2-8(d)). Finally, the Al and catalyst layers on photoresist were removed by the lift-off method as presented in Fig. 2-8(e), and transferred into the thermal CVD chamber for CNT growth immediately.

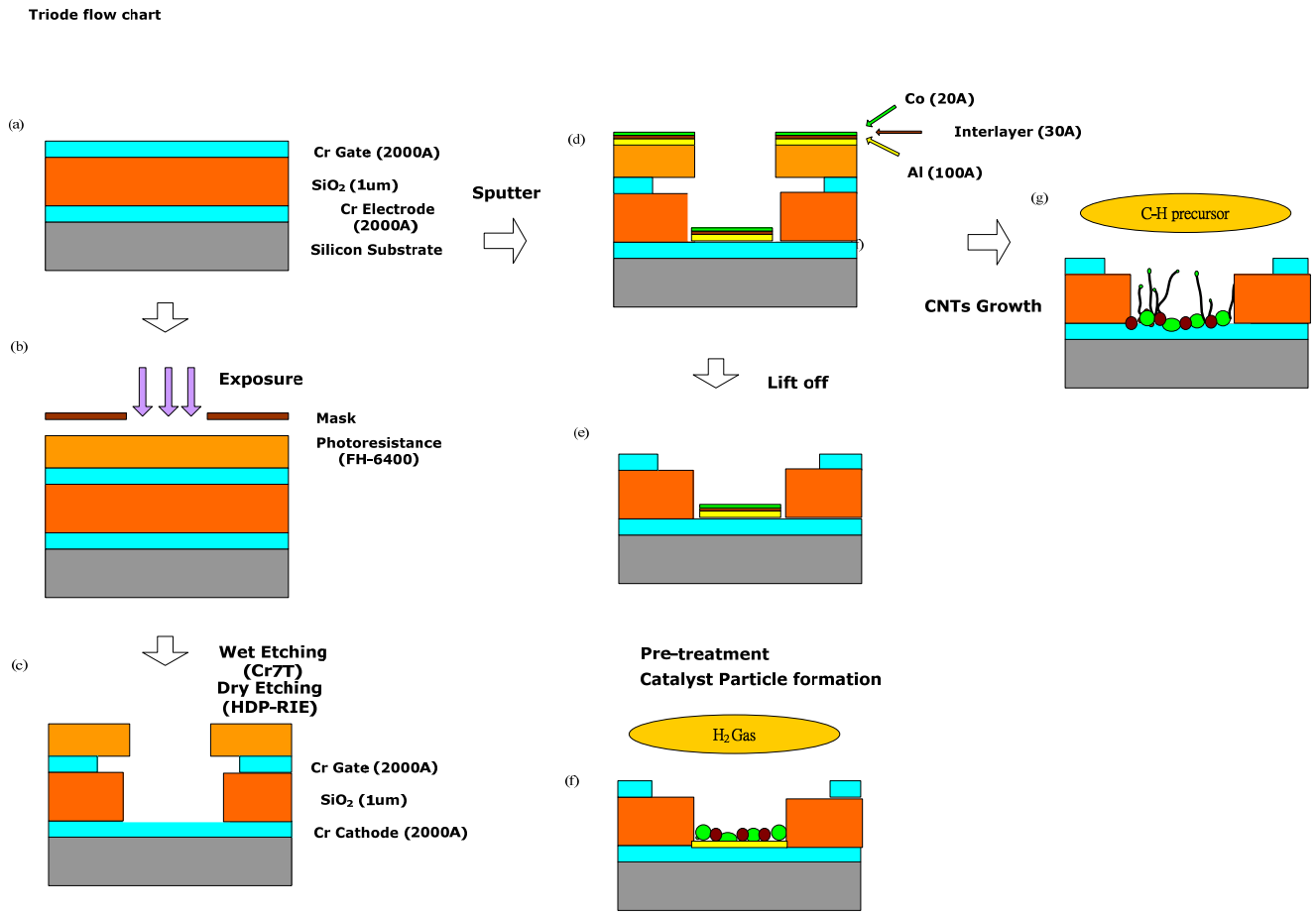


Fig. 2-8 Triode structure fabrication flow diagrams

(a) 2000A Cr cathode, 1um SiO_2, and 2000A Cr gate deposition by Egun, PECVD, and Egun, respectively. (b) Lithography procedure, (c) Define the gate and spacer by wet etching, (d) Multilayer catalysts deposition, (e) Lift photoresist off, (f) Pretreatment, and (g) CNT growth.

We chose growth-time at 30, 45, and 60minutes, controlled CNTs length for gained optimum field efficiency and anode current density.

2.3.2 CNT Synthesis

Since the triode structure had been fabricated, we synthesized CNTs in thermal CVD chamber with Co/Cr/Al and Co/Ti/Al as the catalysts were at relatively low temperature (550℃). By means of changing the growth time, we tried to increase more active carbon radicals for catalyst particles and synthesized CNTs at 500℃. The experimental parameters were described as follows.

Experiment E:

The growth recipe is the same as experiment A at 550℃. Beside, the growth-time was added to 45, and 60 minutes.

Experiment F:

The growth recipe is the same as experiment E at 550℃.However, the growth temperature was changed to 500℃.

2.4 CNTs Grown on Glass Substrate

2.4.1 Sample Preparation

A glass substrate, soda-lime glass, was prepared for Diode structure. The continuous process was shown completely in the Fig. 2-9. A 2000A Cr was deposited as a cathode electrode by sputtering system (Fig. 2-9(a)). We dined the catalyst film region in the lithography process as shown in Fig. 2-9b). The 20A Co / 30A Cr/ 100A Al, or 20A Co / 30A Ti/ 100A Al were deposited by sputter system (Fig. 2-9(c)).

Finally, the photoresist was removed and the diode structure on glass substrate was transferred to thermal CVD chamber for CNT growth.

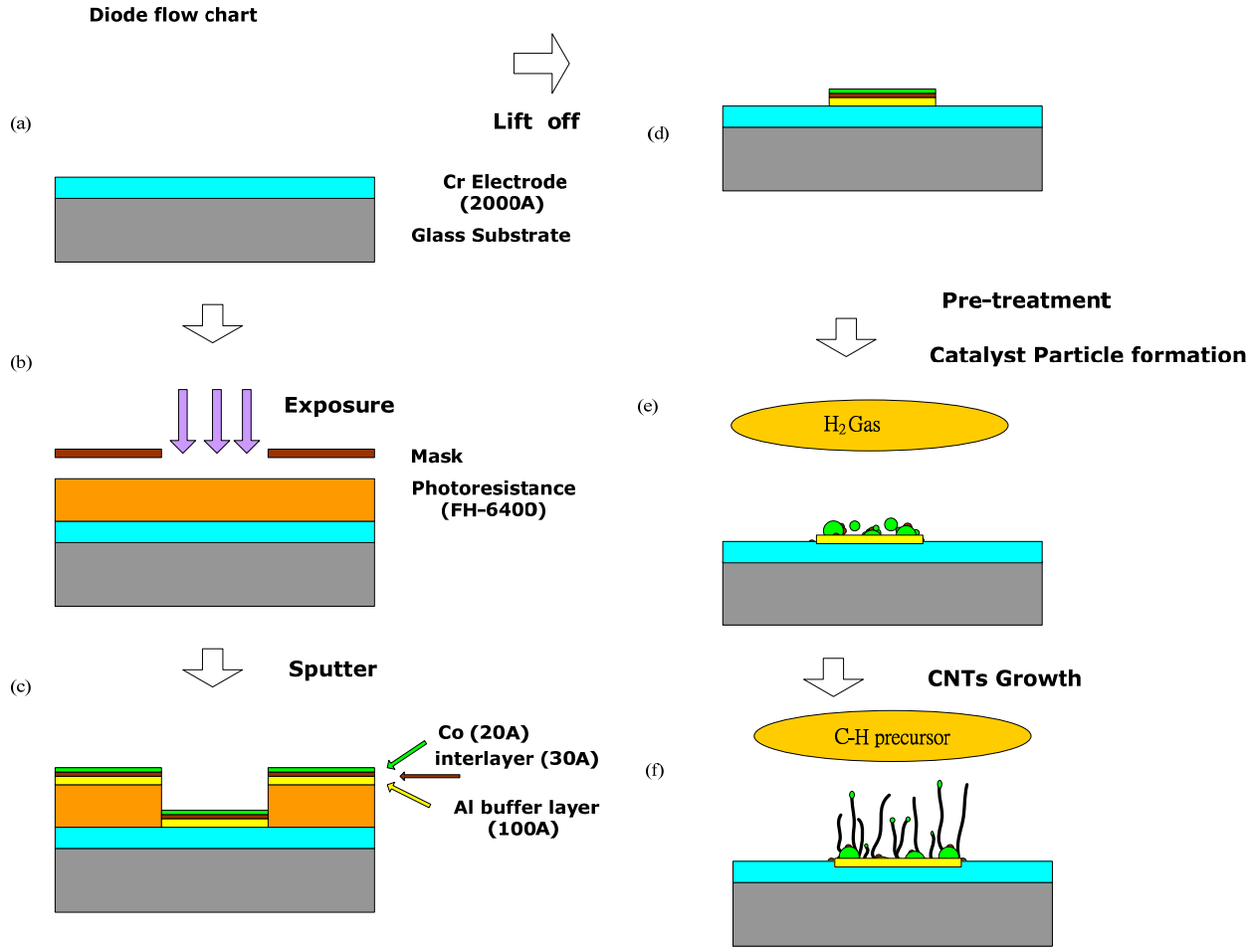


Fig. 2-9 Diode structure of CNT-FED on glass substrate
(a) 2000A Cr cathode deposition by Egun, (b) Lithography procedure (c) Multilayer catalysts deposition, (d) Lift photoresist off, (e) Pretreatment, and (f) CNT growth.

2.4.2 CNT Synthesis

The sample of patterned catalyst film on glass substrate was loaded into the thermal CVD chamber for CNT growth. In order to avoid the melting of soda-lime glass and contamination of the chamber, we set a silicon wafer under the glass

substrate, then we synthesized CNTs as described in the following.

Experiment G:

Prior to CNT growth, the catalysts' nano-films were pretreated at 550℃ for 5 minutes with 50 sccm H_2 and 1000sccm N_2, respectively. Then 75 sccm C_2H_4 and 1000sccm N_2 was added to grow CNTs at 550℃ for 60 minutes.

2.5 Analysis

Surface morphology and internal structure of CNTs synthesized in our experiments were characterized by a Hitachi S-4700I high-resolution field-emission scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HR-TEM) respectively. Simultaneously, the Energy Dispersive X-Ray (EDS) detected the types of the elements. In addition, Raman spectra revealed the two peaks of CNTs (graphite and defect) and XRD analysis revealed which elements were around the CNT bottom. X-ray photoemission spectra (XPS) analysis revealed which chemical bonding of elements formation after sputtering. The electric characteristics were measured by Keithley 237 (Fig. 2-10) in a 10^{-6} torr chamber. We also applied an ITO glass with phosphor coating on it as the anode observed the luminescent image.

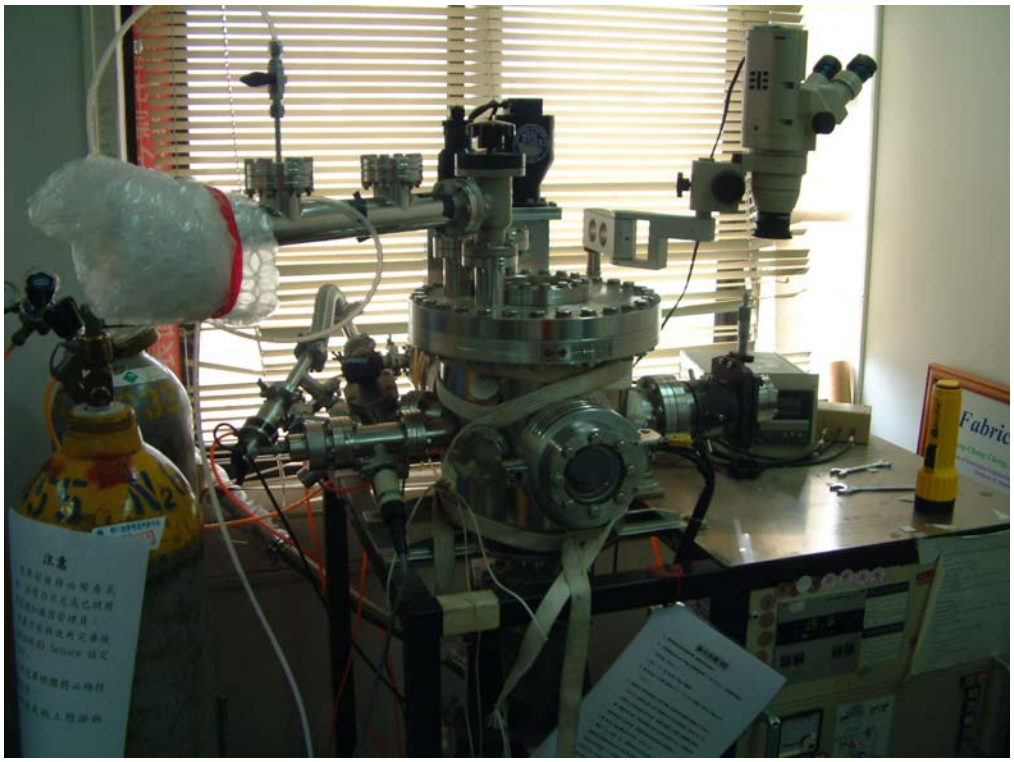
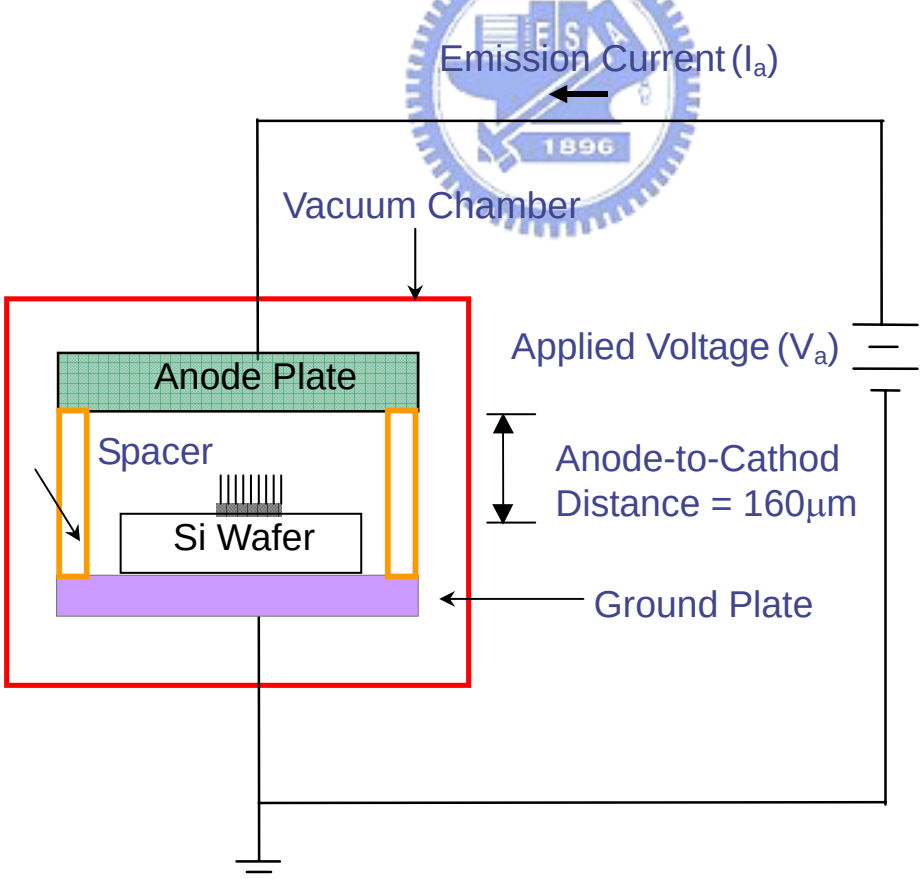


Fig. 2-10 High vacuum measurement system



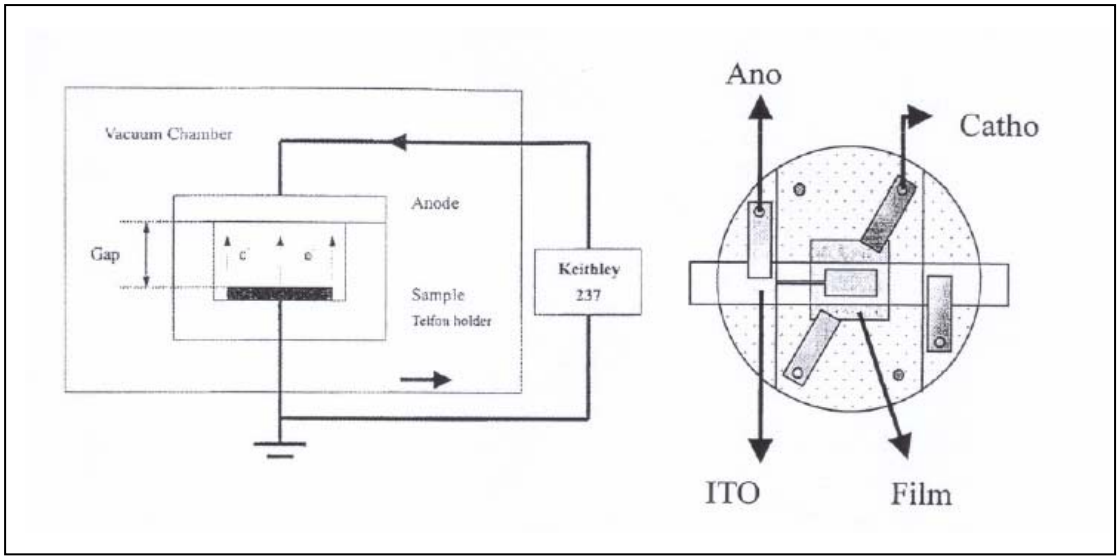


Fig. 2-10 High vacuum measurement system