CHAPTER 2

EXPERIMENTAL

2.1 Chemical and equipment

All chemicals used for synthesizing metal (Pt, Au and Ag)-loaded TiO_2 and sensing films were shown in Table 2.1.

Table 2.1 Chemicals, Molecular formula, Molecular weight, Purity and Company

Chemical	**Molecular formula**	**Molecular weight (g/mol)**	**Purity**	**Company/ CAS NO.**
Titanium isopropoxide (TTIP)	$C_{12}H_{28}O_4Ti$	284.2	97%	Sigma-Aldrich/ 546−68−9
Platinum (II) acetyacetonate	$Pt(C_5H_7O_2)_2$	393.29	97%	Sigma-Aldrich/ 15170−57−7
Gold chloride, hydrate	$H(AuCl_4).H_2O$	357.79	49+%	Electron microscopy sciences/ 16961−25−4

Table 2.1 (Cont.) Chemicals, Molecular formula, Molecular weight, Purity and Company

Chemical	**Molecular formula**	**Molecular weight (g/mol)**	**Purity**	**Company/ CAS NO.**
Silver nitrate	$AgNO_3$	169.87	99%	Sigma-Aldrich / 7761−88−8
Xylene	C_8H_{10}	106.16	98.5%	Carlo Erba/ 1330−20−7
Ethanol	C_2H_5OH	46.07	99.9%	Merck/ 64−17−5
Acetonitrile	CH_3CN	41.05	99.5%	Fluka, Germany/ 75−05−8
Ethyl cellulose	−	454.8	48−49.5 %	Sigma-Aldrich/ 9004−57−3
Terpineol	$C_{10}H_{18}O$	154.25	90%	Sigma-Aldrich/ 10482–56–1
Acetone	CH_3COCH_3	58.08	≥99.5%	Sigma-Aldrich/ 67-64-1

Table 2.1 (Cont.) Chemicals, Molecular formula, Molecular weight, Purity and Company

Chemical	Molecular formula	Molecular weight (g/mol)	Purity	Company/ CAS NO.
Al_2O_3 substrates/ interdigitated with Au electrodes (Au/Al_2O_3)	–	101.96	96%	Semiconductor Wafer, Inc/ (NECTEC, THAILAND)

2.2 Instruments

The unloaded TiO_2 and metal-loaded TiO_2 nanoparticles were characterized using the instruments as shown in the Table 2.2.

Table 2.2 Instruments used in the experiments

Instrument	Model/ Company/ Country
X-ray diffractometer (XRD)	Rigaku, TTRAXIII, Japan
Scanning electron microscope (SEM) and energy dispersive X-ray spectroscope (EDS)	JEOL, JSM-6335F, Japan
Transmission electron microscope (TEM, HRTEM)	JEOL, JEM-2010, Japan
Brunauer-Emmett-Teller (BET)	Micromeritics Tristar, 3000, Germany

2.3 Sample preparations of unloaded TiO_2 and metal-loaded TiO_2 nanoparticles synthesized by FSP

Titanium isopropoxide and metal compound were used as precursors. The precursors were dissolved well in organic solvents to obtain a 0.5 M precursor solution. Table 2.3, 2.4 and 2.5 presented the precursors calculation of the flame synthesis of 0–3.0 mol% metal-loaded TiO_2 data. The experimental setup for the synthesis of metal-loaded TiO_2 nanoparticles was shown in Figure 2.1. The loading concentrations of metal were set as 0.25, 0.50, 0.75, 1.0, 2.0 and 3.0 mol%. In a typical run, the precursor is fed into a FSP reactor by a syringe pump with a rate of 5 mL/min while 5 L/min O_2 was being dispersed (5/5 flame). The gas flow rates of methane and O2 supporting flamelet were 1.19, and 2.46 L/min, respectively. The pressure drop at the capillary tip was kept constant at 1.5 bars by adjusting the orifice gap area at the nozzle. The flame height was observed to be approximately 10−12 cm, and was slightly increased by increasing the combustion enthalpy of the solvent. All samples showed a flame as seen in Figure 2.2. After evaporation and combustion of precursor droplets, nanoparticles were formed by nucleation, condensation, coagulation, coalescence and metal deposition on TiO_2 support. Finally, nanoparticles were collected on glass microfibre filters (Whatmann GF/A, 25.7 cm in diameter) with an aid of a vacuum pump.

Table 2.3 Precursors calculation of the flame synthesis of 0–3.0 mol% Pt-loaded TiO_2

Pt-loaded TiO2 - PRECURSOR (mol%)						
Loading						
precursor	**CAS**	**density (g.cm-3)**	**molar weight (g.mol-1)**			**mol% Pt-loaded TiO2**
Ti (IV)isopropoxid 97wt% Ti	546-68-9	0.97	284.26			0.00
Pt(II) acetylacetonate	15170-57-7		393.31			0.25
						0.50
oxide			**molar weight (g.mol-1)**			0.75
Ti			47.867			1.00
O			15.999			2.00
Pt			195.09			3.00
TiO2			79.865			
molarity precursor	0.5	mol/l				
volume	50	ml				
# mol	0.025	mol				

Precursor	Pt (ll) acetylacetonate (g)	Pt (ll) acetylacetonate (mol)	Ti (IV)isopropoxid (ml)	Ti (IV)isopropoxid (mol)	(Organic solvents) Xylene (ml)	Total powder on filter (g)
TiO2	0	0	7.55	0.02500	42.45	0.87
0.25 mol% Pt-loaded TiO2	0.0253	0.000063	7.53	0.02494	42.47	0.89
0.50 mol% Pt-loaded TiO2	0.0507	0.000125	7.52	0.02488	42.48	0.90
0.75 mol% Pt-loaded TiO2	0.0760	0.000188	7.50	0.02481	42.50	0.91
1.0 mol% Pt-loaded TiO2	0.1013	0.000250	7.48	0.02475	42.52	0.92
2.0 mol% Pt-loaded TiO2	0.2026	0.000500	7.40	0.02450	42.60	0.94
3.0 mol% Pt-loaded TiO2	0.3039	0.000750	7.33	0.02425	42.67	0.95

Table 2.4 Precursors calculation of the flame synthesis of 0.25–3.0 mol% Au-loaded TiO_2

Au-loaded TiO2 - PRECURSOR (mol%)					
		Loading			
precursor	**CAS**	**density (g.cm-3)**	**molar weight (g.mol-1)**		**mol% Au-loaded TiO2**
Ti (IV)isopropoxid 97wt% Ti	546-68-9	0.97	284.26		0.25
Gold(III)chloride	16961-25-4		357.79		0.50
					0.75
oxide			**molar weight (g.mol-1)**		1.00
Ti			47.867		2.00
O2			31.998		3.00
Au			196.9666		
TiO2			79.9		
molarity precursor	0.50	mol/l			
volume	50	ml			
# mol	0.025	mol			

Precursor	$HAuCl_4$ (g)	$HAuCl_4$ (mol)	Ti (IV)isopropoxid (ml)	Ti (IV)isopropoxid (mol)	(Organic solvents) Xylene:Ethanol (ml) (70 : 30)	Total powder on filter (g)
0.25 mol% Au-loaded TiO2	0.0456	0.00013	7.5340	0.02487	42.47	0.88
0.50 mol% Au-loaded TiO2	0.0912	0.00025	7.5151	0.02475	42.48	0.89
0.75 mol% Au-loaded TiO2	0.1368	0.00038	7.4963	0.02462	42.50	0.90
1.0 mol% Au-loaded TiO2	0.1824	0.00051	7.4774	0.02449	42.52	0.92
2.0 mol% Au-loaded TiO2	0.3648	0.00102	7.4018	0.02398	42.60	0.93
3.0 mol% Au-loaded TiO2	0.5472	0.00153	7.3263	0.02347	42.67	0.94

Table 2.5 Precursors calculation of the flame synthesis of 0.25–3.0 mol% Ag-loaded TiO_2.

Ag-loaded TiO2 - PRECURSOR (mol%)				
Loading				
precursor	**CAS**	**density (g.cm-3)**	**molar weight (g.mol-1)**	**mol% Ag-loaded TiO2**
Ti (IV)isopropoxid 97wt% Ti	546-68-9	0.97	284.26	0.25
Siver nitrate (AgNO3)	7761−88−8		169.87	0.50
				0.75
oxide			**molar weight (g.mol-1)**	1.00
Ti			47.867	2.00
O2			31.998	3.00
Ag			107.8682	
TiO2			79.865	
molarity precursor	0.5	mol/l		
volume	50	ml		
# mol	0.025	mol		

Precursor	AgNO3 (g)	AgNO3 (mol)	Ti (IV)isopropoxid (ml)	Ti (IV)isopropoxid (mol)	(Organic solvents) Xylene: Acetonitrile (50:50)	Total powder on filter (g)
0.25 mol%_Ag-loaded TiO2	0.010625	0.0000625	7.53	0.0249	42.47	0.81
0.50 mol%_Ag-loaded TiO2	0.021250	0.0001250	7.52	0.0249	42.48	0.82
0.75 mol%_Ag-loaded TiO2	0.031875	0.0001875	7.50	0.0248	42.50	0.82
1.0 mol%_Ag-loaded TiO2	0.042500	0.0002500	7.48	0.0248	42.52	0.83
2.0 mol%_Ag-loaded TiO2	0.085000	0.0005000	7.40	0.0245	42.60	0.85
3.0 mol%_Ag-loaded TiO2	0.127500	0.0007500	7.33	0.0243	42.67	0.86

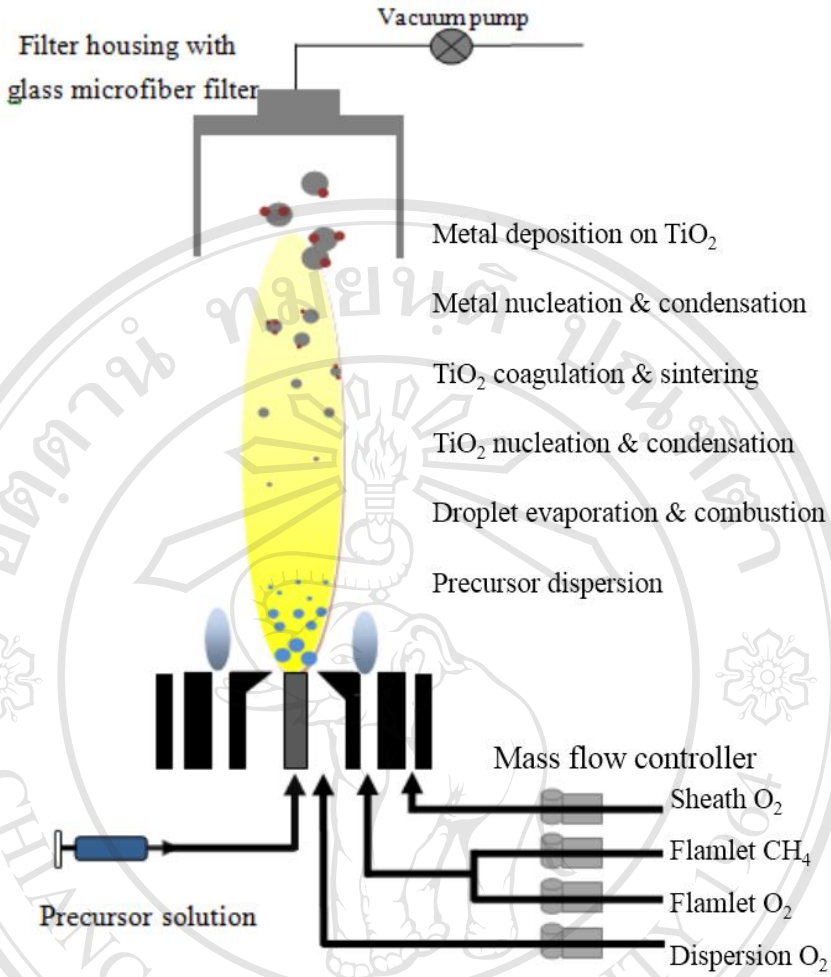

Figure 2.1 Schematic diagram of the experimental setup for the synthesis of metal-loaded TiO_2 nanoparticles by FSP.

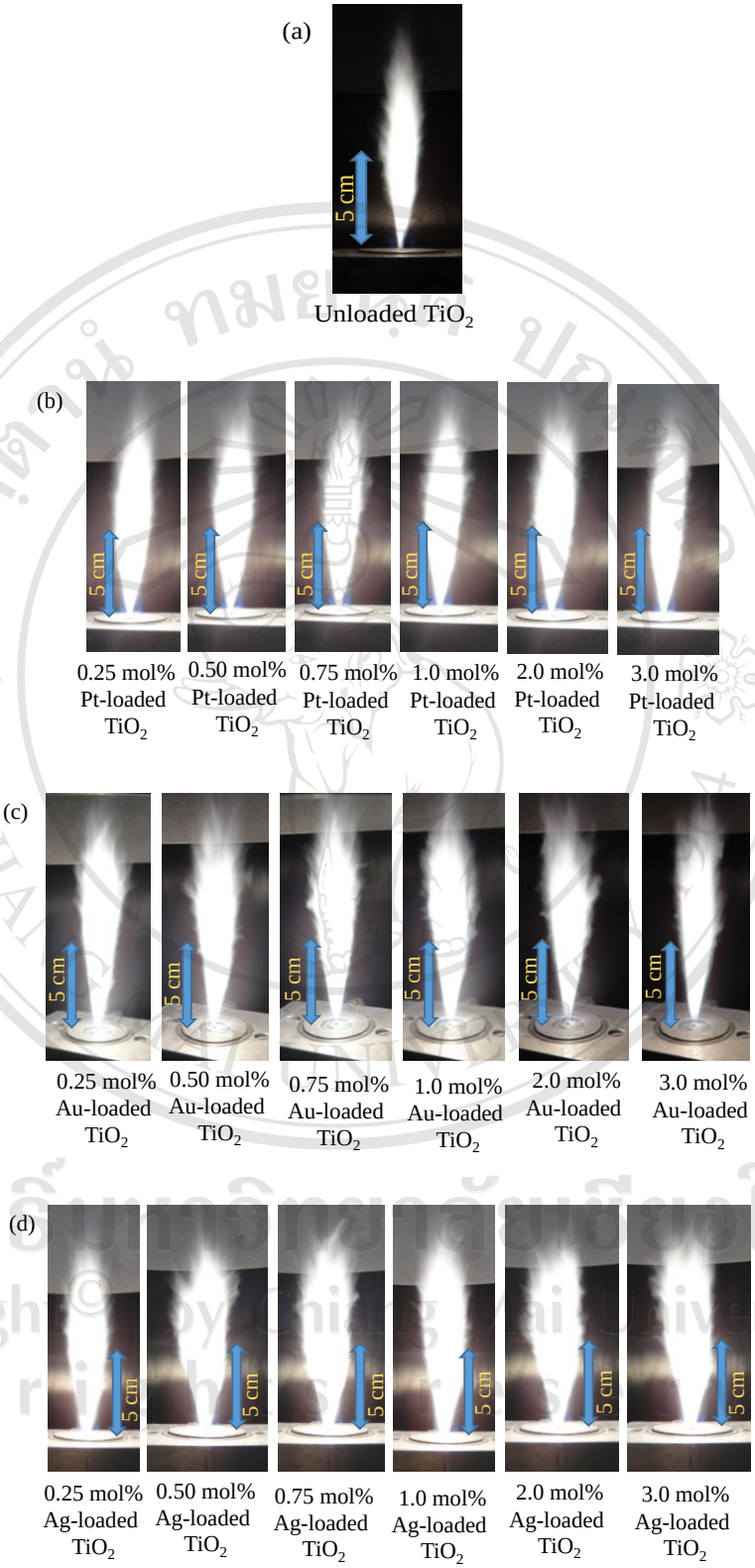

Figure 2.2 Spray flame of (a) unloaded TiO_2, (b) Pt, (c) Au, and (d) Ag-loaded TiO_2 nanoparticles.

2.4 Characterization of nanoparticles

The unloaded TiO_2 nanoparticles and metal-loaded TiO_2 nanoparticles were characterized by using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectrometry (EDS), high resolution transmission electron microscopy (HRTEM) and BET analysis using the equipment as following**:**

The crystalline structure and phase transformation of unloaded TiO_2 and metal-loaded TiO_2 nanoparticles were analyzed by XRD using CuKα radiation. The detection of 2θ values was 20−80° with a step size of 0.06° and a scanning speed of 0.72º/min. Identification of crystalline phases were carried out by comparison of the obtained XRD patterns with JCPDS standards.

The morphology of unloaded TiO_2 and metal-loaded TiO_2 nanopowders were observed and analyzed by SEM and the elemental compositions of the pulp were investigated by EDS. The powders samples were dispersed in absolute ethanol using ultrasonic probe for 20 min. The suspension was dropped onto a gold conductive tape attached to the surface of the SEM brass stub. The stub was then coated with gold by plasma sputtering for 2 min, and an acceleration voltage of 20 kV was used.

The morphology and accurate particle sizes of TiO_2 and metal-loaded TiO_2 nanoparticle were analyzed by HRTEM at an acceleration voltage of 200 kV. The powders samples were dispersed in absolute ethanol using ultrasonic probe for 20 min. The suspension was dropped onto carbon-copper grid. The deposit was dried in air prior to imaging.

The specific surface areas were analyzed from the BET measurements. The specific surface areas (*SSA*) of unloaded TiO_2 and metal-loaded TiO_2 nanoparticles were calculated and the particle sizes (d_{BET}) were determined by 5-point nitrogen

adsorption from the BET measurements at 77 K. All samples were controlled with degassing at 150 °C for 1 h prior to analysis. The particle diameters of unloaded TiO_2 and metal-loaded TiO_2 were calculated from specific surface areas and density of metal and TiO_2 as $d_{BET} = 6/[(\rho_{TiO_2} \times SSA_{TiO_2} \times wt\%_{TiO_2}) + (\rho_{metal} \times SSA_{metal} \times wt\%_{metal})]$ equation, where $\rho_{TiO_2} = 3.84$ g/cm^3 and ρ_{metal} ($\rho_{Pt} = 21.45$ g/cm^3, $\rho_{Au} = 19.3$ g/cm^3 and $\rho_{Ag} = 10.49$ g/cm^3).

2.5 Preparation and characterization of sensors

The sensing films were prepared by mixing nanoparticles into an organic paste composed of ethyl cellulose and terpineol, which acted as a vehicle binder and a solvent, respectively. The resulting paste was spin-coated on Al_2O_3 substrates with interdigitated Au electrodes as shown in Figure 2.4. The films were then annealed at 400 °C using three-zone tube furnace for 2 h with heating rate of 2 °C/min for binder removal. Figure 2.4 (a) shows SEM images of Al_2O_3 substrates interdigitated with Au electrodes. The alumina substrate had a dimension of 0.3 cm × 0.4 cm × 0.04 cm. Interdigit width, interdigit spacing and area of the electrode were 100 μm, 100 μm and 0.24 cm × 0.40 cm, respectively. The electrode pattern was made by DC sputtering of 50 nm-thick Cr and 200 nm-thick Au layers and lift-off process. After TiO_2 thin-film deposition on the interdigitated Au electrodes as shown in Figure 2.4 (b). The morphologies and cross section of sensing films were examined by SEM.

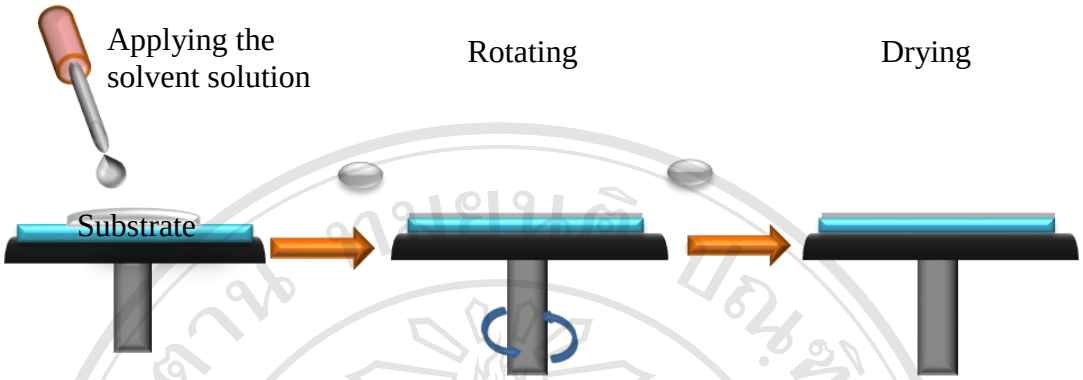

Figure 2.3 The sensors preparation by spin coating technique**.**

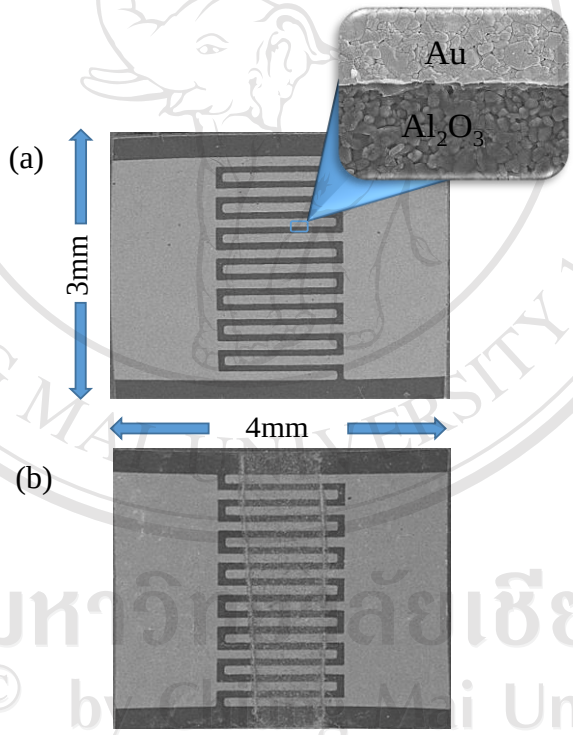

Figure 2.4 SEM images of (a) Al_2O_3 substrates interdigitated with Au electrodes and (b) TiO_2 films sensor on an Al_2O_3 substrate interdigitate with Au electrodes**.**

2.6 Gas sensing characterization

Gas sensing measurements of unloaded TiO_2 and metal-loaded TiO_2 sensors were characterized towards SO_2, C_2H_5OH, CO, CH_3COCH_3 and H_2. The chamber has a cylindrical shape with diameter of ~12 cm and height of ~15 cm. In addition, there was a conical gas distributor with diameter of ~9 cm and height of ~8 cm, spreading gas to all sensors. A standard flow through technique was used to test gas-sensing properties of these sensors. A constant flux of synthetic air of 2 L/min was used as gas carrier into which the desired concentration of pollutants dispersed in synthetic air was mixed. All measurements were conducted in a temperature-stabilized sealed chamber at 20 °C under controlled humidity. The external NiCr heater was heated by a regulated DC power supply to various operating temperatures. The operating temperature was varied ranging from 300 °C to 400 °C. The resistances of various sensors were continuously monitored with a computer-controlled system by voltage-amperometric technique with 50 V dc bias and current measurement through a 6487 Keithley picoammeter. The gas sample exposure time and the clean air restoring time were fixed at 10 min and 25 min, respectively. The target gas concentration was varied from 0.0010 to 0.050 vol% for SO_2, from 0.0050 to 0.10 vol% for C_2H_5OH, from 0.010 to 0.20 vol% for $(CH_3)_2CO$, from 0.0050 to 0.10 vol% for CO and from 0.015 to 1.0 vol% for H_2. The experimental set up for gas testing was shown in Figure 2.5.

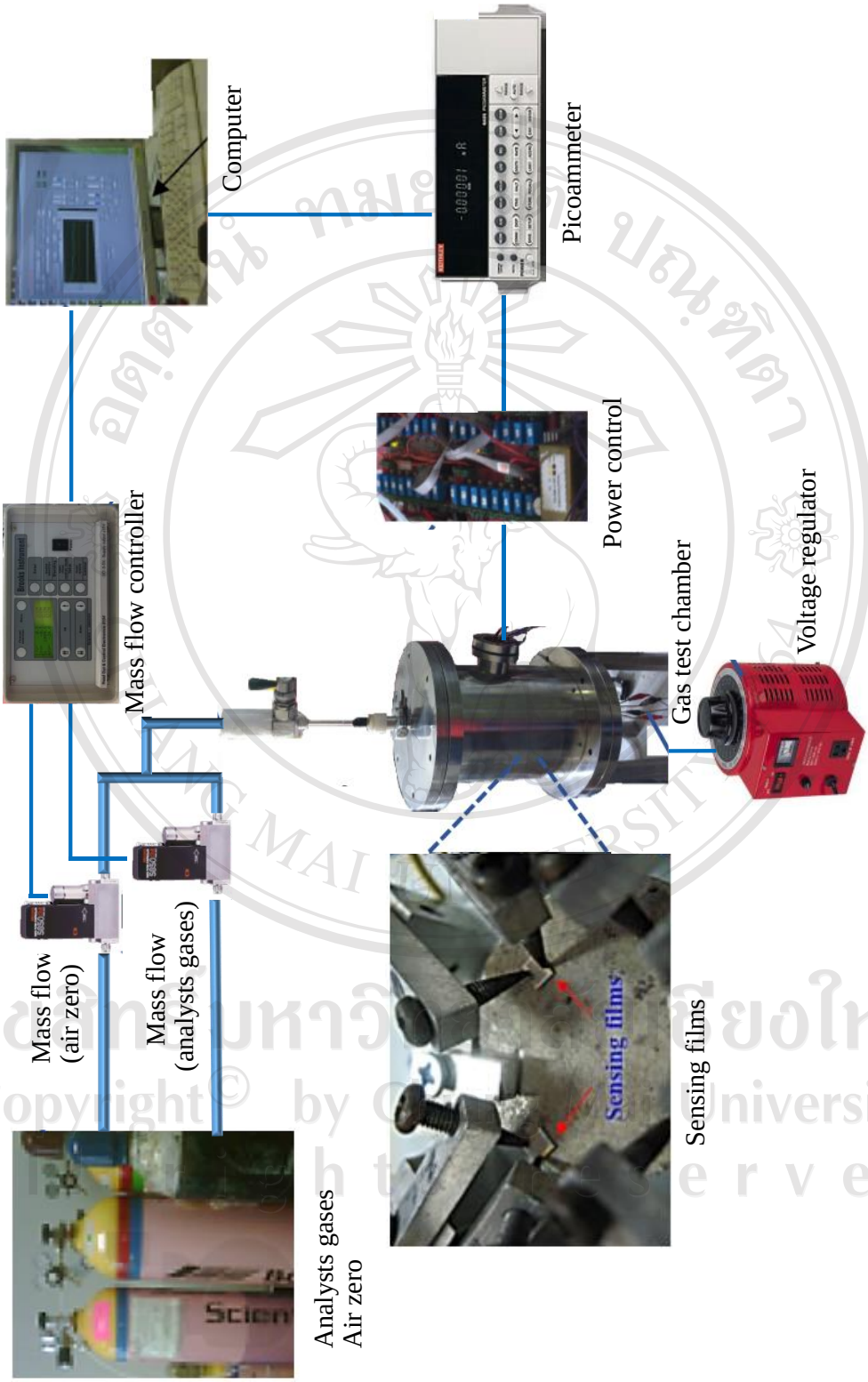

Figure 2.5 The experimental set up of sensing test.