

Chapter 3

Materials and Methods

This chapter presents the experimental set-up for this work. It will be started with the materials and chemicals had been used in this study. Then, the electrodes preparation techniques will be introduced, it composes of substrate pretreatment, metal-organic chemical vapor deposition of Ir, IrO₂ and SnO₂ over various substrates. The electrochemical oxidation of model solution and restaurant effluent from Chulalongkorn University Student Canteen are presented. Finally, the materials characterization methods are also introduced in this chapter.

3.1 Chemicals

(Methylecyclopentadienyl) (1,5-cyclooctadiene) iridium (I), 99 %w/w was supplied by Strem Chemicals, Inc., Iridium (III) acetylacetonate, 98 %w/w and Tetraethyltin 97 %w/w were supplied by Aldrich Chemical Co., Inc. The other chemicals used in this research work are analytical grade.

The effluent from Chulalongkorn University Student Canteen was used in this study. The effluent was collected from the wastewater collection system of Chulalongkorn University after passed the grease trap.

3.2 Substrate pretreatment

To improve the surface roughness of substrates and the adhesion of deposited films, the substrates need to be cleaned by the appropriating solvent and/or etched by specific acid. In this part, the several treatment techniques for some substrates are presented.

3.2.1 Stainless steel 316L

To remove some impurities stainless steel SUS 316L sheets (25.4 mm x 16.2 mm x 10 mm) were polished by sand paper. Degreased in acetone with sonication for 15 minute, rinsed with deionized water and dried by compressed air.

3.2.2 Borosilicate glass

The borosilicate glass sheets (25.4 mm x 16.2 mm x 10 mm) were carefully degreased in acetone with sonication for 15 minute, rinsed with deionized water and dried by compressed air

3.2.3 Silicone wafer

The Si wafers (8 mm x 10 mm) were degreased in hot acetone, rinsed with deionized water and dried by compressed air.

3.2.4 Titanium

Ti sheets (8 mm x 30 mm) were etched in hot 35% HCl for 1 hr, rinsed by deionized water and dried by compressed air.

3.2.5 Tantalum

Ta substrates (8 mm x 30 mm) were etched in 40% HF from 1 min to 24 hr, rinsed by deionized water and dried by compressed air.

3.2.6 Tantalum carbide over tantalum

TaC/Ta sheets were brushed by stainless steel rotating brush and etched in 40% HF for 1 hr to remove free carbon on the surface.

3.3 Deposition of TiO₂ by spray coating

When TiO₂ is illuminated with light, its electron is promoted from the valence band to the conduction band of the semiconducting oxide to give an electron/hole pair. The valence band potential is positive enough to generate hydroxyl radicals at the surface [53]. However, the quantum yield of photocatalysis is very low [54]. The electrochemical-assisted hydroxyl radical production on TiO₂ surface is very attractive for wastewater [54].

The deposition of TiO₂ coated electrode was the following [50].

1. 1 g of TiO₂ was suspended in 100 ml of methanol, the suspension was homogenized by sonication
2. The cleaned SUS 316L was heated to 80 °C
3. The precursor solution in (1) was sprayed to heated substrate using simple atomizer
4. The procedure was repeated until a uniform coating of TiO₂ was visible on the substrates.

5. The coated substrates were annealed in air at 700 °C. After 1 h the substrates were removed from the furnace and allowed to cool at room temperature

3.4 Deposition SnO₂ by spray pyrolysis

The most common procedure to apply a thin layer of SnO₂ is a spraying of tin precursor solution onto a hot substrate surface. To improve the conductivity of SnO₂ film, it can be doped with other metal ions such as Sb³⁺. The procedure of SnO₂ coating by spray pyrolysis was the following [27].

1. Dissolve 10 g SnCl₄·5H₂O and 0.1 g SbCl₃ in 100 ml of methanol
2. The cleaned borosilicate glass sheet was heated to 500 °C.
3. The precursor solution in (1) was sprayed on the hot borosilicate glass surface by using a simple atomizer
4. The procedure was repeated until a uniform coating of Sb₂O₅ doped SnO₂ was visible on the substrates

3.5 Metal-organic chemical vapor deposition

From some attractive advantages for the growth of thin film, MOCVD was adapted to the deposition for electrode preparation in this research work. The metal-organic chemical vapor deposition of IrO₂, Ir and SnO₂ films were studied with the CVD apparatus presented in Figure 3-1.

The deposition was studied in horizontal hot-wall CVD reactor with 1.2 cm diameter and 15 cm isothermal zone. The organometallic precursors were contained in a thermostated bubbler at desired temperature. Helium was used as the carrier and oxygen was as co-reactive gas. The gas flow rate was monitored and controlled by mass-flow controller and the total pressure was automatically controlled by using an absolute pressure gauge coupled to the throttle valve system.

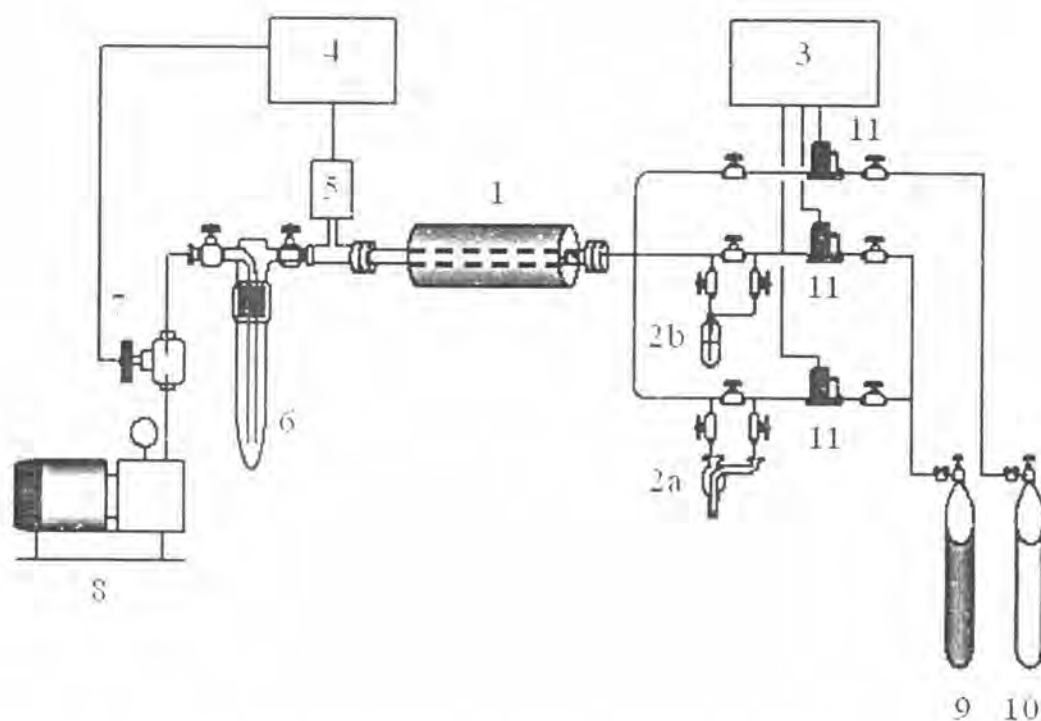


Figure 3-1 MOCVD apparatus; 1) Hot-wall CVD reactor, 2a) 1st bubbler for Ir(acac)₃ or (MeCp)Ir(COD), 2b) 2nd bubbler for TET, 3) Gas flow controller, 4) Pressure controller, 5) Pressure regulator, 6) Cold trap, 7) Throttle valve, 8) Vacuum pump, 9) He tank, 10) O₂ tank and 11) Mass-flow controller

3.5.1 Choice of precursor

There are several iridium source precursors were used in deposition of Ir and IrO₂ by metal-organic chemical vapor deposition [44-52]. Due to its excellent air stability, Ir(acac)₃ was used as precursor for IrO₂ deposition. However, its high melting point, low volatility of Ir(acac)₃ and difficulty control of mass transport has limited Ir(acac)₃ in this work. For better volatility and vapor phase transport properties, the other iridium source, (MeCp)Ir(COD) was used in this study.

There is some organo-tin which can be used as precursors for preparation of SnO₂ in MOCVD process [42]. However, the best tin precursor is tetraethyl tin because its molecular size is most appropriate for forming of regularly arranged Sn-O bonds leading to the prepared SnO₂ film with good crystallinity [42]. Due to its good properties, tetraethyl tin was used as tin source precursor in this work.

3.5.2 Choice of substrate

The various types of substrates were used in this study. The silicone wafer was as substrate for the calibration of MOCVD. Titanium was used as substrate for Ir and IrO₂ deposition by MOCVD. Titanium, iridium coated titanium, tantalum and tantalum carbide over tantalum were used as substrates for SnO₂ deposition.

3.5.3 Substrate placement

To study the growth rate profile of coatings in the reactor, Si wafer substrate was used in the calibration of the reactor. The cleaned Si wafer (8 x 10 cm) was placed in each 2.5 cm from the entrance of the reactor. In case of IrO₂ deposition, Si wafer at 5.0-7.5 cm were substituted by Ti

substrate. For Ir and SnO₂ deposition, the Si wafer was substituted by actual substrate at 10.0-12.5 cm and 17.5-20.0 cm, respectively. The placement of Si wafer and actual substrates is presented in Figure 3-2.

3.5.4 Deposition condition

The deposition conditions for IrO₂, Ir and SnO₂ are presented in Table 3-1.

Table 3-1 Deposition conditions for IrO₂, Ir and SnO₂

Parameter	Operating condition
MOCVD of IrO₂	
Deposition temperature	400 °C
Total pressure	25 Torr
Molar ratio of O ₂ /Ir(acac) ₃	11,000-17,000
MOCVD of Ir	
Deposition temperature	300-350 °C
Total pressure	12 Torr
Molar ratio of O ₂ /(MeCp)Ir(COD)	125-1,545
MOCVD of SnO₂	
Deposition temperature	380 °C
Total pressure	15 Torr
Molar ratio of O ₂ /TET	300-1,200

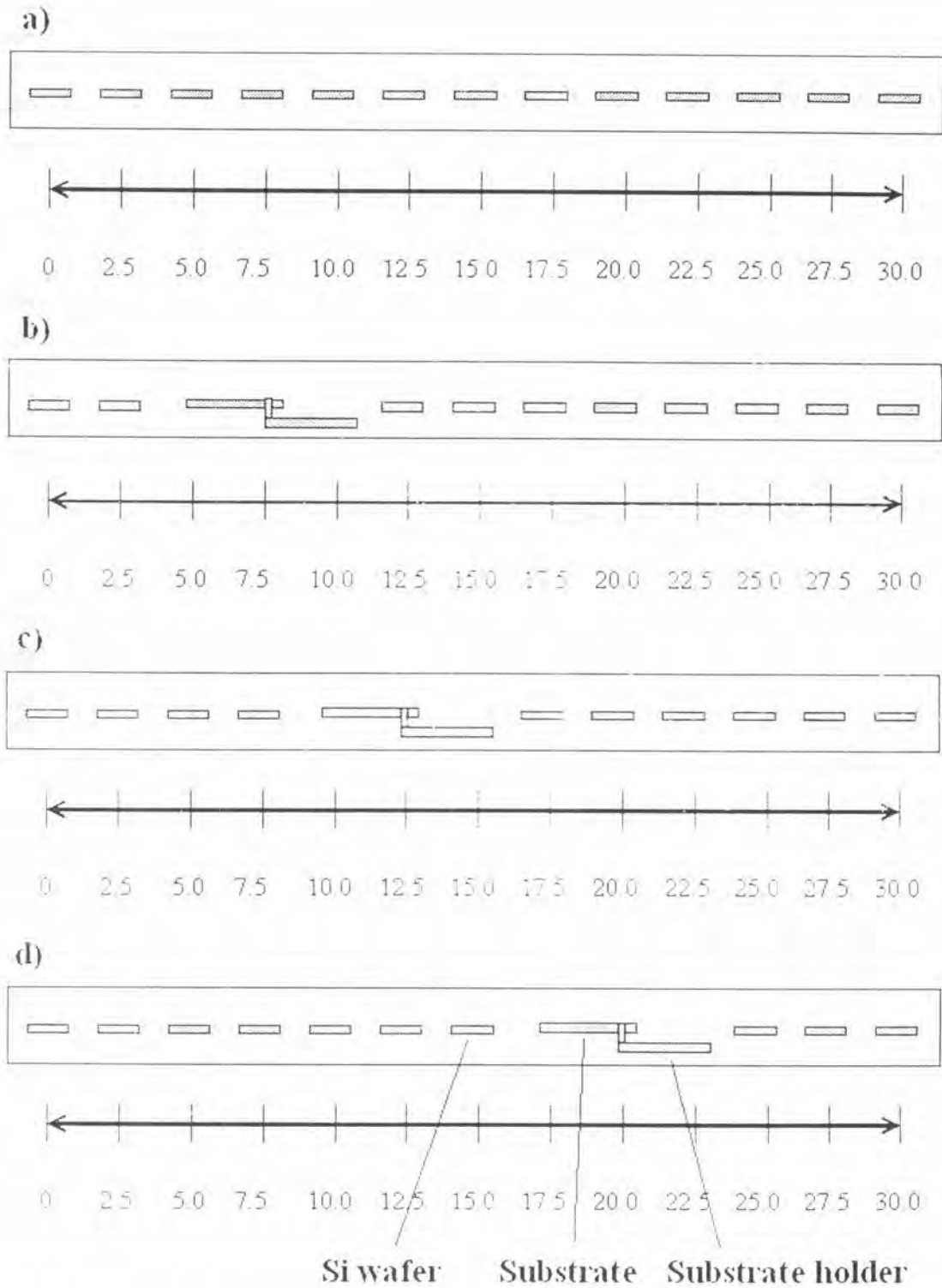


Figure 3-2 Schematic diagram of silicon wafer and actual substrates placement in MOCVD reactor; a) Reactor calibration, b) IrO_2 deposition, c) Ir deposition and d) SnO_2 deposition

3.5.5 Deposition characterization

The surface morphology and microstructure of the coatings were characterized by X-ray diffraction (XRD, Cu K α), scanning electron microscope (SEM) and profilometer for roughness measurement. The relative average deposited films growth rate was determined by weight measurement.

3.6 Electrochemical Characterization

The electrochemical oxidation of organic pollutants was studied in the two parts of experiments. Firstly, the experiments were operated in batch condition. Then, the experiments were operated in continuous condition. The electrochemical oxidation was studied constant at applied current.

3.6.1 Batch electrochemical oxidation

The electrochemical characterization was performed in a three-electrode electrochemical reactor with 18 ml capacity. The prepared electrodes were used as anode, the 316L stainless steel was used as cathode and the saturated calomel was used as reference electrode. The apparatus is presented in Figure 3-3. The characteristic of model solution and operating condition was presented in Tables 3-2 and 3-3, respectively.

Table 3-2 Characteristics of model solution

Parameter	Amount
Oxalic acid (mg/L)	756
Sulfuric acid (mg/L)	14.7
Total organic carbon (mg/L)	160

Table 3-3 Operating condition for batch electrochemical oxidation of model solution

Parameter	Operating condition
Current density	5-10 mA/cm ²
SnO ₂ film thickness	1.8-3.6 micron
Residence time	0-6 hr
Stirring	300 rpm

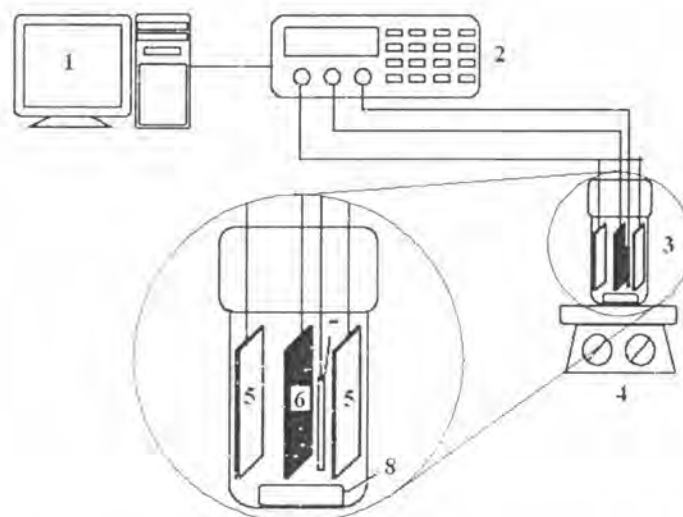


Figure 3-3 Schematic diagram of batch electrochemical oxidation apparatus; 1) PC with control software, 2) Potentiostat, 3) Electrochemical reactor set, 4) Magnetic stirrer, 5) SUS 316L cathodes, 6) Anode, 7) Reference electrode and 8) Magnetic bar

3.6.2 Continuous electrochemical oxidation

The continuous electrochemical oxidation was also performed in a three-electrode electrochemical reactor with 18 ml capacity. The prepared electrodes were used as anode, the 316L stainless steel was used as cathode. The feed solution was fed to the reactor by peristaltic pump and the effluent was collected at sample trap. The apparatus is presented in Figure 3-4. The operating conditions were represented in Table 3-4.

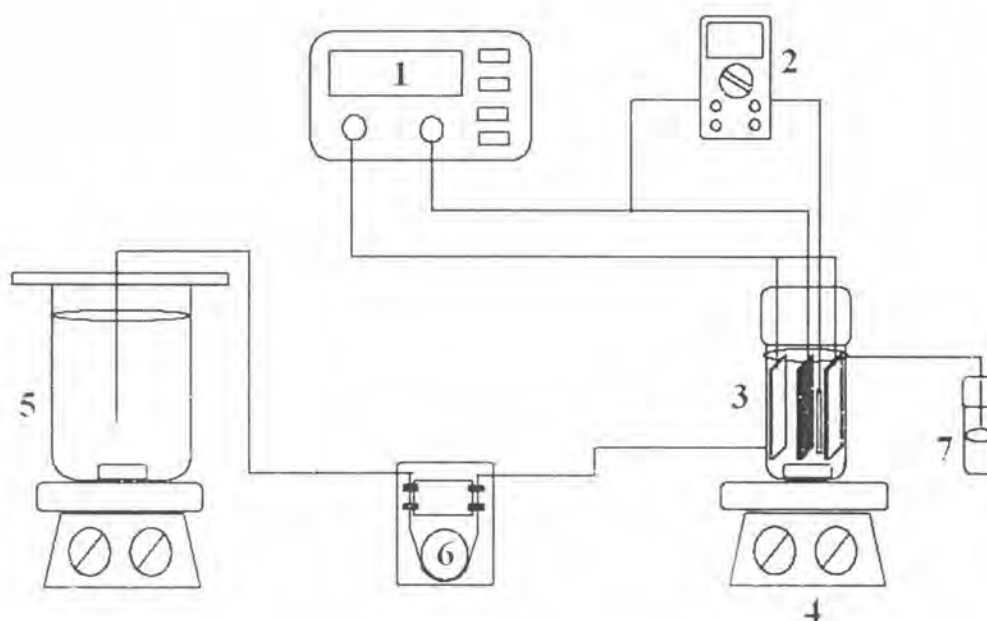


Figure 3-4 Schematic diagram of continuous electrochemical oxidation apparatus; 1) Power supply, 2) Volt meter, 3) Electrochemical reactor set, 4) Magnetic stirrer, 5) Feed reservoir, 6) Peristaltic pump , 7) Sample trap

Table 3-4 Operating condition for continuous electrochemical oxidation

Parameter	Operating condition
Current density	5-10 mA/cm ²
SnO ₂ film thickness	1.8-3.6 micron
Residence time	2-3 hr
Stirring	300 rpm

3.6.3 Pollutant removal efficiency

The pollutant removal efficiency was investigated by using oxalic acid and effluent from Chulalongkorn University Student Canteen as model solution. The total organic carbon (TOC) was determined by Shimadzu TOC-5050A analyzer. The instrument is presented in Figure 3-5. The chemical oxygen demand (COD) was determined by closed reflux-titration method. Both total organic carbon and chemical oxygen demand were followed standard methods for the examination of water and wastewater [55].



Figure 3-5 Shimadzu TOC-5050A TOC analyzer