

## Chapter V

### Synthesis of Tin Alkoxide and Fabrication of Gas Sensors

In this chapter, an attempt to synthesize the sol-gel solution of tin is described. The desired product is a polymeric sol which can be deposited as the uniformed thin films on various substrates such as glass, alumina and Si. By using the advantages of the sol-gel process, a modified substance in a liquid phase can be directly mixed with the sol-gel solution. Thus, the thin film with uniformly dispersed modified substance can be obtained easily.

The desired product should be in the form of tin alkoxide ( $\text{Sn}(\text{OR})_4$ ) or partial alkoxide ( $\text{SnCl}_{4-x}(\text{OR})_x$ ) in which R is the alkyl group ( $\text{R} = \text{C}_n\text{H}_{2n+1}$ ). It may be appropriate at this stage to give the general definition of metal alkoxide. The metal alkoxides have  $\text{M}(\text{OR})_x$  as the general formula and can be considered as derivatives of alcohols ( $\text{ROH}$ ) in which the hydroxylic hydrogen has been replaced by a metal (M)[39,69,70]. Three synthesis routes have been tried to synthesize tin alkoxide, starting from the direct reaction of tin tetrachloride ( $\text{SnCl}_4$ ) with alcohol, the reaction involving alcoholic solution of  $\text{SnCl}_4$  with ammonia, and the reaction involving alcoholic solutions of  $\text{SnCl}_4$  with sodium alkoxides. The third route was classified into two distinctive methods: the simple mixed method and the rigorously controlled method.

At the end of this chapter, the processes for fabricating gas sensors from the sol-gel solutions will be described.

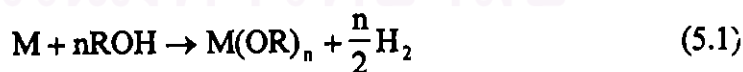
## 5.1 Synthesis of Metal Alkoxides

Metal alkoxides are easily synthesized, for instance, by the direct reaction of metals with alcohols or by the reaction of the corresponding metal chlorides with alcohols. Many metal elements, enclosed in the heavy lined frame in the periodic table (Fig. 5.1), are able to form metal alkoxides. The method required for the synthesis of metal alkoxides generally depends on its electronegativity. The general methods for synthesis of the metal alkoxides are briefly described as follows.

H																	He																												
Li	Be											B	C	N	O	F	Ne																												
Na	Mg											Al	Si	P	S	Cl	Ar																												
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr																												
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe																												
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<table border="1" style="margin-left: auto; margin-right: auto;"> <tbody> <tr> <td>Ce</td><td>Pr</td><td>Nd</td><td>Pm</td><td>Sm</td><td>Eu</td><td>Gd</td><td>Tb</td><td>Dy</td><td>Ho</td><td>Er</td><td>Tm</td><td>Yb</td><td>Lu</td> </tr> <tr> <td>Th</td><td>Pa</td><td>U</td><td>Np</td><td>Pu</td><td>Am</td><td>Cm</td><td>Bk</td><td>Cf</td><td>Es</td><td>Fm</td><td>Md</td><td>No</td><td>Lr</td> </tr> </tbody> </table>																		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu																																
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr																																

Fig. 5.1 Metal elements forming alkoxides.

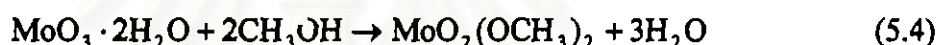
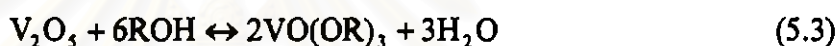
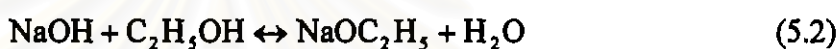
**Reactions of Metals with Alcohols** Highly electropositive elements with valencies up to three (like alkali metals, alkaline earth metals and aluminum), can react directly with alcohols and liberate hydrogen to the metal alkoxides.



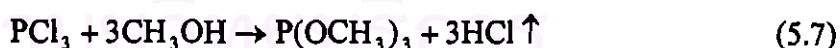
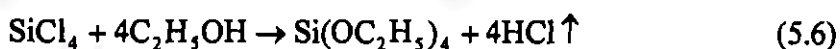
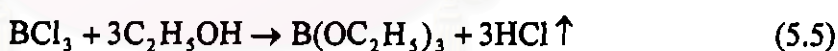
The speed of the reaction depends both on type of the metal and alcohol, which increase with electropositivity and decrease with length and branching of the alkyl chain. Thus sodium reacts strongly with ethanol, but slowly with tertiary butyl alcohol. The reaction with alkali metals such as Na is sometimes carried out in organic solvents such as ether, benzene, or xylene. Alkaline earth metals and

aluminum are often covered with an oxide film which hinders the reaction, thus a catalyst like mercuric chloride is generally required for successful synthesis of alkoxides[69].

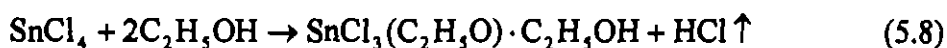
**Reactions of Metal Oxides and Hydroxides with Alcohols** This reaction is usually an equilibrium and extreme susceptibility of the alkoxy derivatives to hydrolysis. Thus, a continuous removal of water, by physical or chemical means, during these reactions is necessary in order to obtain good yields of the final alkoxide products. This has been accomplished using organic solvents (e.g. benzene, toluene, and xylene) in order to extract the by-product water and separate into the another liquid phase.

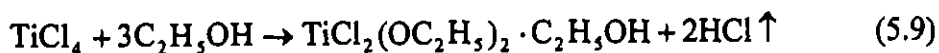


**Reactions of Metal Halides with Alcohols** Metal halides have been used quite extensively as starting materials for the synthesis of a large number of metal alkoxides. This general method is applicable to electronegative elements such as boron, silicon and phosphorus.

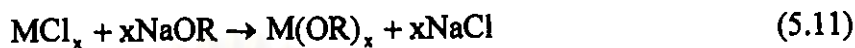
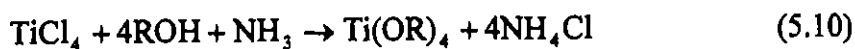


The reactions of chloride of electronegative elements proceed to completion if the hydrogen chloride produced in the reactions is removed by refluxing or even by passage of a current of an inert gas through the reaction mixture. When the central metal atom is comparatively less electronegative, this method employing the anhydrous chloride as a starting material sometimes does not appear to effect complete replacement of halide [71-73].

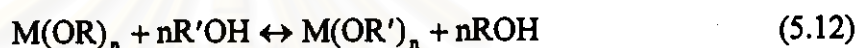




However, in most cases, (e.g. Fe, Ti, Th, Nb etc.) the replacement of halide could be forced to completion by using bases such as pyridine, ammonia, or the alkali metal alkoxides such sodium methoxide.



**Alcoholysis and Transesterification** Metal alkoxides of higher unsaturated, or branched alcohols are difficult to prepare directly and are usually made from lower metal alkoxides by means of alcoholysis.

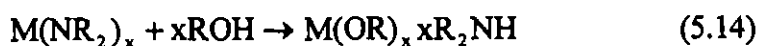


where R' is the alkyl chain. The reaction is driven to completion by distilling the lower boiling alcohol. Metal methoxides are frequently insoluble and cannot be employed as starting materials in this reaction; by the same token, they can be conveniently prepared from solutions of higher alkoxides by precipitation with methanol. Transesterification with carboxylic acid esters is also useful.



where R'' is the alkyl chain.

**Reactions of Metal Dialkylamides with alcohols** This method is particularly successful in the case of those metals which have a greater affinity for oxygen compared to nitrogen. The other advantage of this method is in general higher volatility of dialkylamines which can be volatilised out with greater convenience.

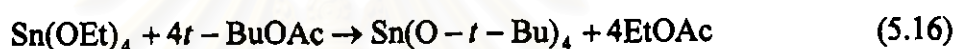


Besides the foregoing methods of synthesis of metal alkoxides, there are also some other methods which will not be mentioned here. These methods have only

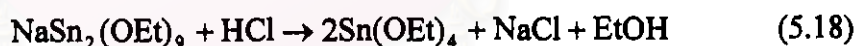
specialized significance[69] such as alcoholysis of organometallic compounds, sulfides and carbides.

Tin (IV) alkoxides are difficult to synthesis[39,71,74-76], comparing with all others in the group IV elements such as C, Si, Ge and Pb, and therefore are not available commercially. From the literature survey[39,71,74-81], we can conclude the possible routes for the synthesis of tin (IV) alkoxides as follows.

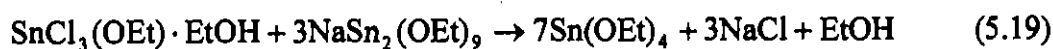
1) *The ammonia method:* The impure tin tetraethoxide is prepared by reacting tin tetrachloride with ethanol in the presence of excess anhydrous ammonia. Treating with *tert*-butyl acetate gives tin tetra-*tert*-butoxide, which could be obtained pure after fractionating off the ethyl acetate.



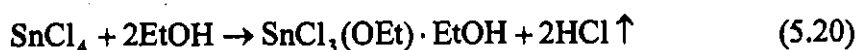
2) *The sodium method:* A bimetallic compound ( $\text{NaSn}_2(\text{OEt})_9$ ) is obtained in the reaction between tin tetrachloride and sodium ethoxide, not tin tetraethoxide ( $\text{Sn}(\text{OEt})_4$ ). The bimetallic compound on further treatment with hydrogen chloride gives tin tetraethoxide.



The tin tetraethoxide produced by reaction in (5.18) is easily to hydrolysis which is probably caused by water. This water is produced by a side reaction involving alcohol and hydrochloric acid. In an attempt to avoid hydrolysis, a reaction with tin trichloride monoethoxide ethanolate ( $\text{SnCl}_3(\text{OEt})\cdot\text{EtOH}$ ) can be used in place of hydrochloric.



The tin trichloride monoethoxide ethanolate is prepared by treating tin tetrachloride with excess alcohol.



An attempt have been tried to synthesis tin (IV) alkoxide by both two mentioned methods. In the ammonia method, it is a complicated and dangerous work to deal with ammonia gas[9,10]. We, therefore, had tried this method with the replace of an ammonia hydroxide solution. The sodium method was also used in our experiments, the details of the experiments will be described in the next section.

## 5.2 An Attempt of Synthesizing Tin (IV) Alkoxide

**Reagents:** All of reagents used in the experiments were analytical grade or equivalence. They were used without any further purification. Table 5.1 lists all reagents used in the experiments.

Table 5.1 List of reagents used in the experiments

No.	Reagents	Purity (%)	Company
1	tin tetrachloride	> 98	Fluka
2	sodium ethoxide	95	Fluka
3	ethanol	100	Riedel-de Haën
4	benzene	100	Carlo Erbra
5	calcium chloride	> 93	Sigma
6	methanol	100	Mallinckrodt
7	sodium methoxide	95	Fluka
8	ammonium hydroxide	30	Carlo Erbra
9	hydrochloric acid	> 37	Riedel-de Haën



### 5.2.1 Preparation of Tin Alkoxide by the Ammonia Method

The chemical reaction in Eq. (5.15) is rewritten here.



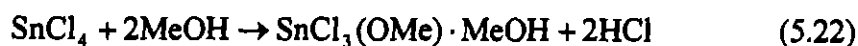
**Procedure:** Special precautions were taken to exclude moisture from all-glass apparatus by heating at 100 °C at least for 2 hours. The synthesis procedures are described as follows.

-SnCl<sub>4</sub> (20ml) was slowly added to ethanol (80 ml) which was externally cooled in an ice bath. The reaction of SnCl<sub>4</sub> with alcohol is a strongly exothermic reaction. Thus, during the addition of SnCl<sub>4</sub>, the whole mixture was rigorously stirred to reduce the elaborated heat. Then, NH<sub>4</sub>OH (90 ml), at least sufficient to react with Cl<sup>-</sup> ions released from the SnCl<sub>4</sub>, was added to the alcoholic solution. The solution was well stirred during addition of the ammonium solution. The NH<sub>4</sub>OH was added until pH of the whole solution became 7.

**Results:** An undesired white solid was precipitated immediately after NH<sub>4</sub>OH solution was added. The white solid did not dissolve in any organic solvent and water. This solid was assumed to be in the form of tin hydroxide (Sn(OH)<sub>x</sub>) which may occur from the hydrolysis of SnCl<sub>4</sub> and H<sub>2</sub>O present in NH<sub>4</sub>OH solution. With this reason, the method failed to synthesize tin alkoxide.

### 5.2.2 Preparation of Tin Alkoxide by the Reaction of Tin Tetrachloride with Alcohol

The chemical reaction is shown in Eq. (5.22).



**Procedure:** Special precautions were taken to exclude moisture from all-glass apparatus by heating at 100 °C at least 2 hours. The synthesis procedures are described as follows.

-SnCl<sub>4</sub> (20ml) was added slowly to methanol (60 ml) which was cooled in an ice bath. During the addition of SnCl<sub>4</sub>, the solution was well agitated with a stirring rod. The HCl produced in the reaction was removed by passing a current of Nitrogen as a source of an inert gas. Even though, the solution was bubbled for more than 2 hours, it still showed a very strong acidic character (pH < 1 measured by bismuth paper). The volume of the solution was reduced to 20 ml by heating, a viscous solution was then obtained.

**Results:** With the following reasons, the obtained solution was not suitable to use as a tin oxide precursor.

1) The solution exhibited a very strong hydrophobic property against the surface of glass and Si substrates. It could not spread over the surface of glass and Si. In other words, it could not wet the surfaces but remained as a drop having a contact angle greater than 90° as shown in Fig. 5.2. This prevented it from using as a spin coating solution. This solution, therefore, did not match our needs. As mentioned above, the desired product is a polymeric sol which must be able to be deposited on various substrates such as glass, alumina and Si substrates to form a uniform thin film.

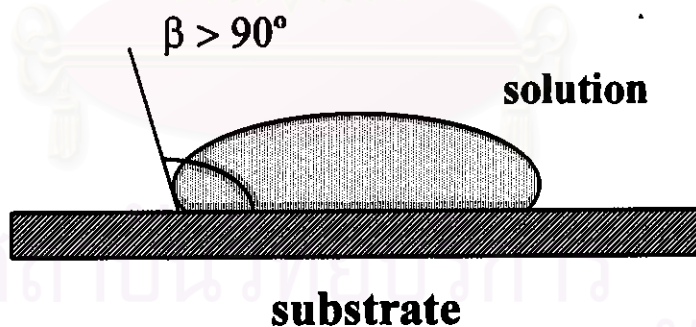


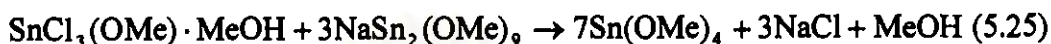
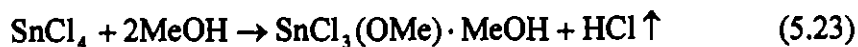
Fig. 5.2 Contact angle between the synthesis solution and glass or Si substrate.

2) The synthesized solution was a strong acid which etched most of metal that came into contact. It could liberate an acidic vapor during heating. This would cause an undesirable damage to the metal part of a equipment during the fabrication process.



### 5.2.3 Preparation of Tin Alkoxide by the Sodium Method with the Simple Mixing Processes

The chemical reaction used in the experiments are shown as follows.



As mentioned above, the chemical reaction in Eq. (5.25) could be replaced by Eq (5.26) by using HCl as an acid instead of  $\text{NaSn}_2(\text{OMe})_9$ . This also had been tried in this thesis, it was found that the final product performed a gellation process during a short storage. This may be due to the added HCl containing a large amount of water. Consequently, it resulted in a hydrolysis of the reaction mixture.

#### ***Procedure:***

##### 1) Preparation of $\text{SnCl}_3(\text{OMe}) \cdot \text{MeOH}$ :

-  $\text{SnCl}_4$  (20 ml) was slowly added to the ice-cooled methanol (60 ml).

The external cooling was performed to reduce the elaborated heat.

##### 2) Preparation of $\text{Sn}(\text{OMe})_4$

- NaOMe (10.54 g) was dissolved in methanol (500 ml). This was done in a 500 ml beaker which was well cooled in an ice bath. The mixture was added dropwise with  $\text{SnCl}_4$  (5 ml). The whole mixture was well stirred and cooled in ice to maintain the temperature below 10 °C. Then, the mixture was further added with the  $\text{SnCl}_3(\text{OMe}) \cdot \text{MeOH}$  (8.3 ml) obtained from the above procedure. During addition, the precipitation of NaCl was observed immediately.

***Results:*** The obtained solution could spread on the surface of glass and Si substrates. Therefore, we had tried to coated the obtained solution on glass and Si substrates by spin coating technique. The spin speed was set at 500 rpm for 5 sec and 3000 rpm for 25 sec for the first and second stage respectively. After sintering at 550 °

C for 1 hour,  $\text{SnO}_2$  thin film was obtained. The complete processes of the film preparation will be described in the section 5.3. The thickness and refractive index of this film were investigated by ellipsometry. The results were  $907 \pm 45 \text{ \AA}$  and  $1.722 \pm 0.167$  for film thickness and refractive index respectively. It was found that the uniformity of the  $\text{SnO}_2$  thin film was very poor observed from the optical microscope as shown in Fig. 5.3. This may result from the further precipitation of the residual NaCl which occurred during the heat treatment processes. In other words, our reaction in Eq. (5.24) or (5.25) did not go to the completion, therefore the solution was still impure too much from the residual NaCl. The attempt had been made to reduce the amount of NaCl in the solution by dialysis of alcohol. This process was shown in Fig. 5.4. However, this process failed to purify the reaction mixture, since the solution became gel during the alcohol exchange. However, the trace of NaCl in the surrounding alcohol could be observed, when it was tested with the  $\text{AgNO}_3$  solution.

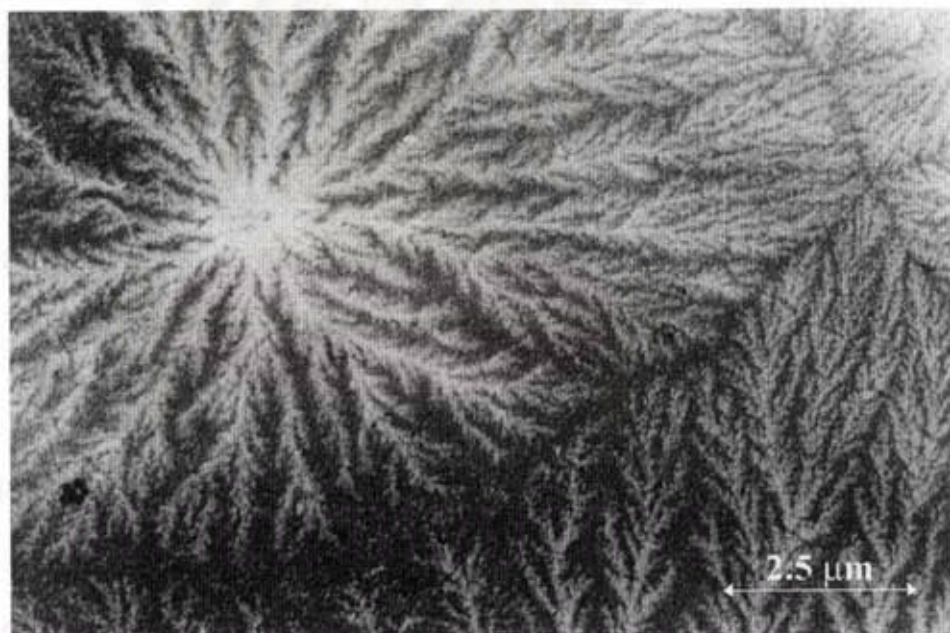


Fig. 5.3 Surface morphology of the  $\text{SnO}_2$  thin film on Si substrate, prepared from the simple method.

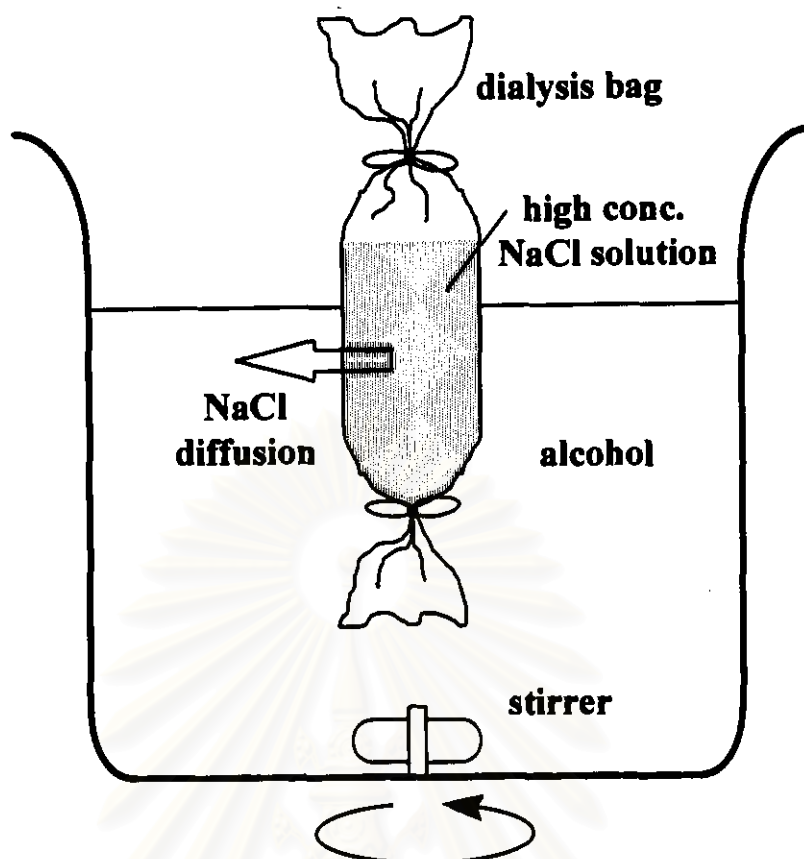


Fig. 5.4 Experimental setup to remove of the residual NaCl by dialysis.

#### 5.2.4 Preparation of Tin Alkoxide by the Sodium Method with the Rigorous Processes.

The chemical reaction used in the experiments are the same as the reactions in the previous section, except, methanol was replaced by ethanol.

**Procedure:** All-glass apparatus fitted with standard interchangeable joint was used and the use of rubber and corks was avoided as much as possible. Special precautions were taken to exclude moisture from all equipment. They were heated at 200 °C at least 2 hours, then left to cool in a desiccator for 30 minutes. The processes could be divided into three main parts. The filter paper was heated at 100 °C at least for 2 hours, and then left to cool in a desiccator for 30 minutes before uses.

### 1) Preparation of $\text{SnCl}_3(\text{OEt})\cdot\text{EtOH}$

- A solution of ethanol (22 ml) in anhydrous benzene (170 ml) was placed in a 1-liter, 3-neck, rounded bottom flask equipped with a dropping funnel, reflux condenser with calcium chloride drying tube, thermometer and gas feeding port. The set up of the equipment is shown in Fig. 5.5. Oxygen free nitrogen (OFN) gas was passed into the solution to exclude moisture from the equipment throughout the experiments. The rounded flask was immersed into an ice bath to lower the temperature to 0-10 °C. At this temperature, the mixture of alcohol and benzene was changed into solid phase. Tin tetrachloride was added dropwise to the solidified mixture via the dropping funnel, while the temperature was maintained below 10 °C. The reaction mixture was heated until the solidified mixture was completely changed to liquid. Further heating was conducted to reflux the reaction mixture for 3 hours. Then, atmospheric distillation of the solvent, i.e. benzene, served to concentrate the product. Finally, the product was dried in vacuum using a desiccator connecting to a rotary pump as shown in Fig. 5.7.

The final product was white crystalline solid with a needle form. The final product weight 46.18 g (*calc.* 54.86, yield 84 %). With different proportions of the reactant mentioned above, the final product could not be crystallized (very slow solidify) and exhibited a strong acidic character.

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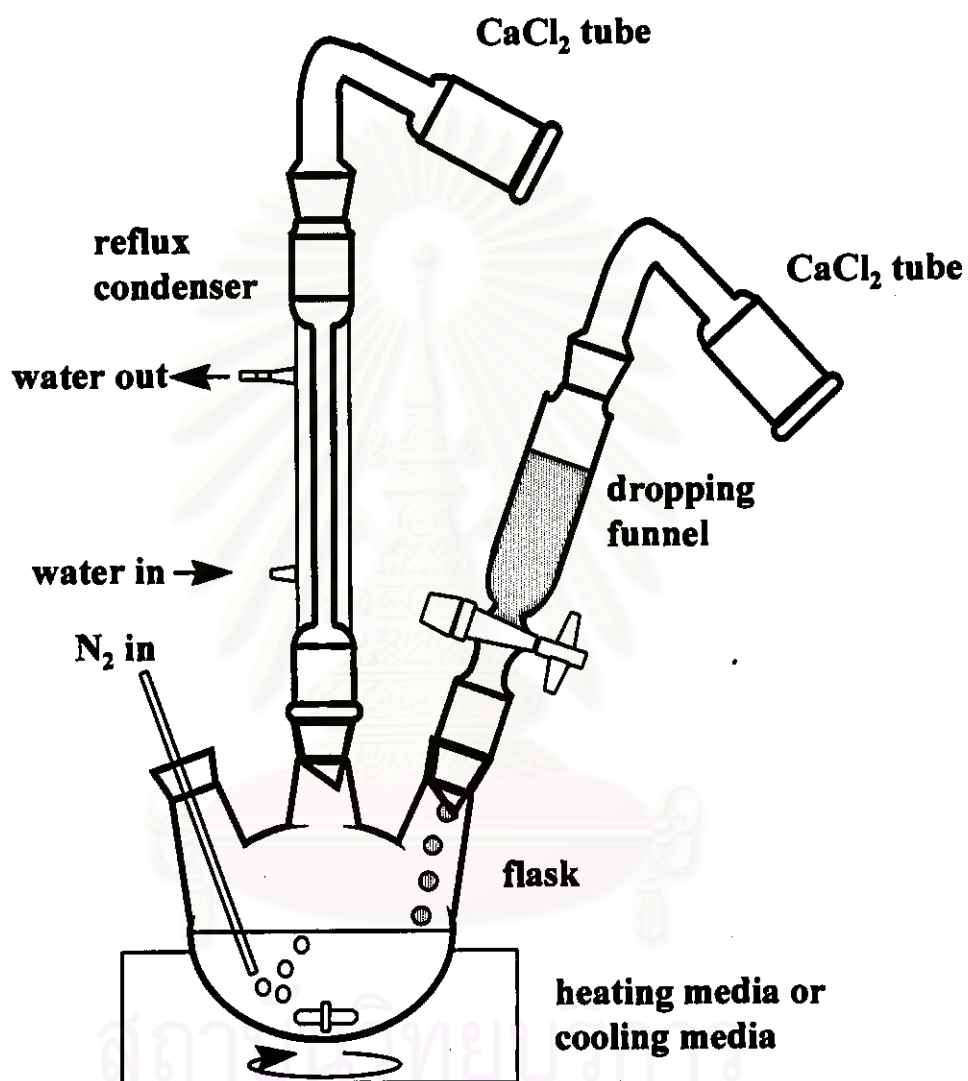


Fig. 5.5 Experimental set up for synthesis of tin alkoxide.



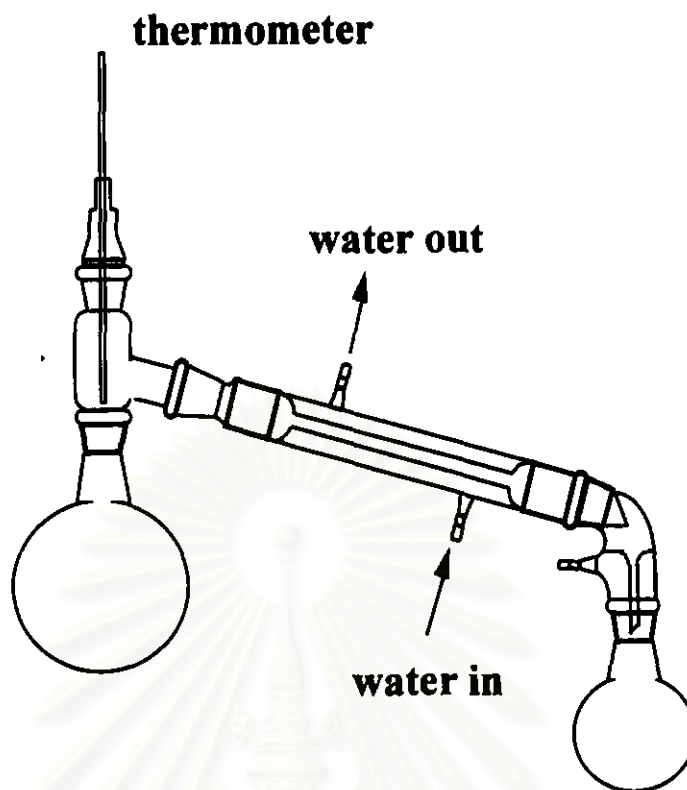


Fig. 5.6. Distillation apparatus.

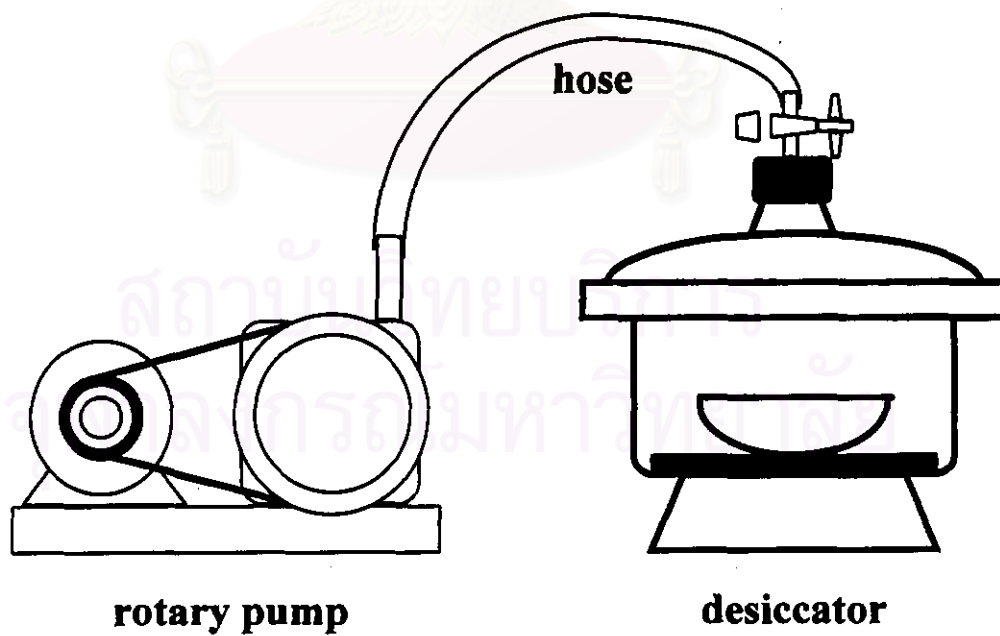
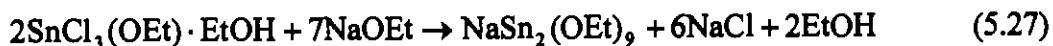


Fig. 5.7 Desiccator connected to a pump, using for drying the reaction product.



## 2) Preparation of $\text{NaSn}_2(\text{OEt})_9$

In this process, the chemical reaction in Eq. (5.24) was modified to the following reaction.



The starting reactant was changed from  $\text{SnCl}_4$  to  $\text{SnCl}_3(\text{OEt}) \cdot \text{EtOH}$ , since the  $\text{SnCl}_3(\text{OEt}) \cdot \text{EtOH}_4$  is white solid, when it is dissolved in alcohol, it is not fuming like  $\text{SnCl}_4$ .

-  $\text{NaOEt}$  (8.27 g) was dissolved in absolute ethanol (220 ml). During dissolving, the solution was well stirred and externally cooled using an ice bath. The solution was put into a 3-neck flask.  $\text{SnCl}_3(\text{OEt}) \cdot \text{EtOH}$  (10.97 g) dissolved in ethanol (50 ml) was added dropwise to the previous mixture, while the reaction mixture was well agitated.  $\text{NaCl}$  precipitated immediately, while the  $\text{SnCl}_3(\text{OEt}) \cdot \text{EtOH}$  was adding. The reaction mixture was refluxed for 3 hours, and, then  $\text{NaCl}$  was filtered off.

## 3) Preparation of $\text{Sn}(\text{OEt})_4$

- The  $\text{NaSn}_2(\text{OEt})_9$  solution obtained from the previous section was place into a 3 neck flask in Fig. 5.5.  $\text{SnCl}_3(\text{OEt}) \cdot \text{EtOH}$  (2 g) dissolved in ethanol (30 ml) was added dropwise via a dropping funnel until the pH of the mixture was 7. Then, the reaction mixture was heated to reflux for 3 hours. The excess  $\text{NaCl}$  was removed by filtration. The solution contained  $\text{Sn}(\text{OR})_4$  (calculation 5.1 %).

**Results:** It was found that  $\text{SnO}_2$  thin film prepared from this solution gave the best uniform film. Fig. 5.8 shows the photograph of surface of  $\text{SnO}_2$  thin film.  $\text{SnO}_2$  films were coated on Si substrate in order to measure film thickness and refractive index. These two parameters were investigated by ellipsometry technique. It was found that the thickness of  $\text{SnO}_2$  thin film could be linearly controlled by varying the number of spin as shown in Fig. 5.8. Fig. 5.9 is also shown refractive index evaluated from ellipsometry technique. The refractive index was almost independent to the film

thickness, this ensured that the prepared  $\text{SnO}_2$  film was highly uniform. The summarized results of tin is schematically demonstrated in Fig. 5.10.

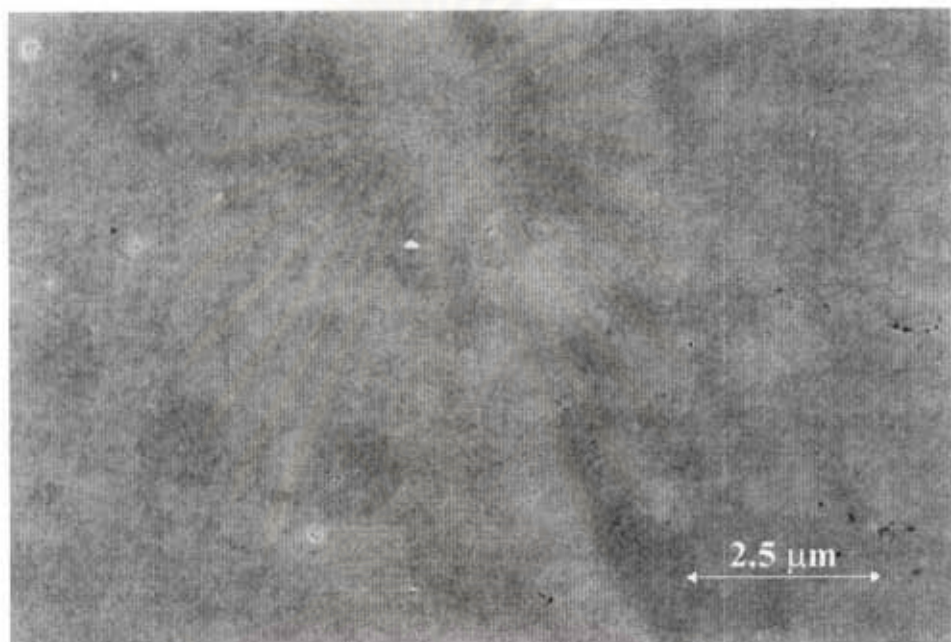


Fig. 5.8 Surface morphology of  $\text{SnO}_2$  thin film prepared from the rigorously controlled method.

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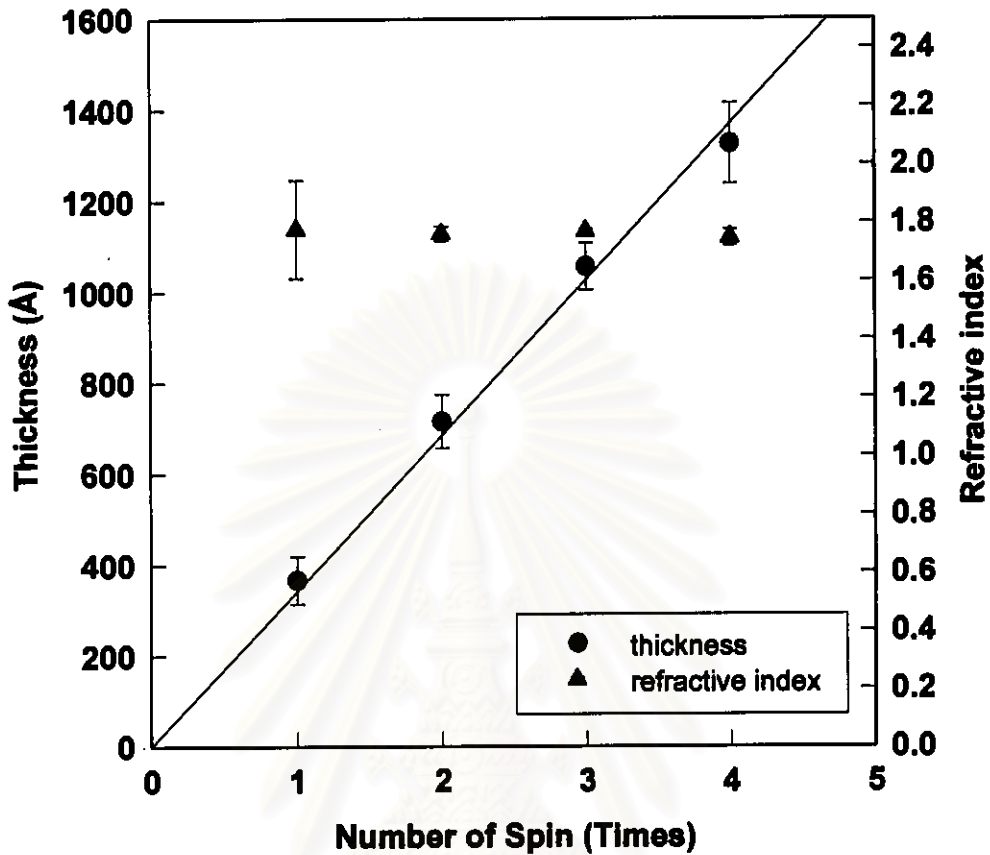


Fig. 5.9 Plot of  $\text{SnO}_2$  film thickness versus the number of spin, refractive index of  $\text{SnO}_2$  thin film is also simultaneously shown.

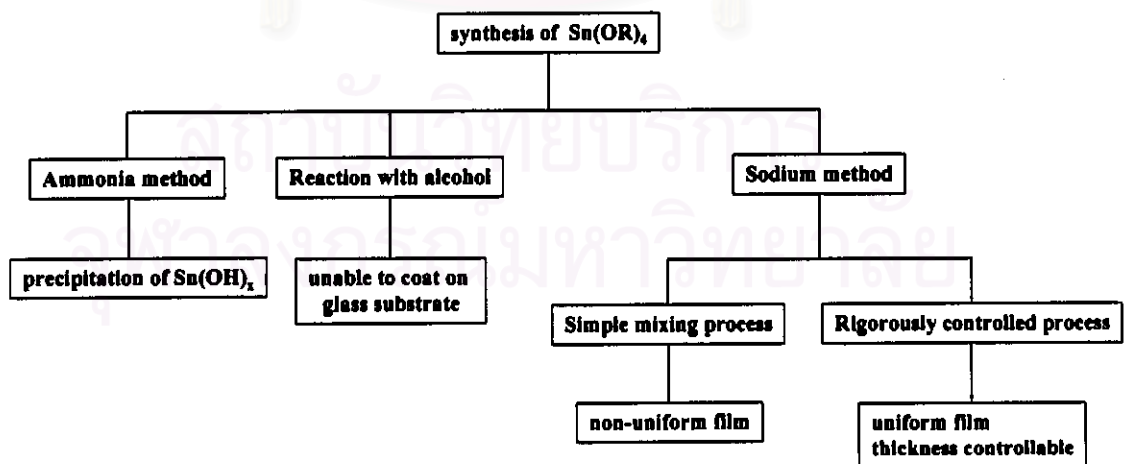


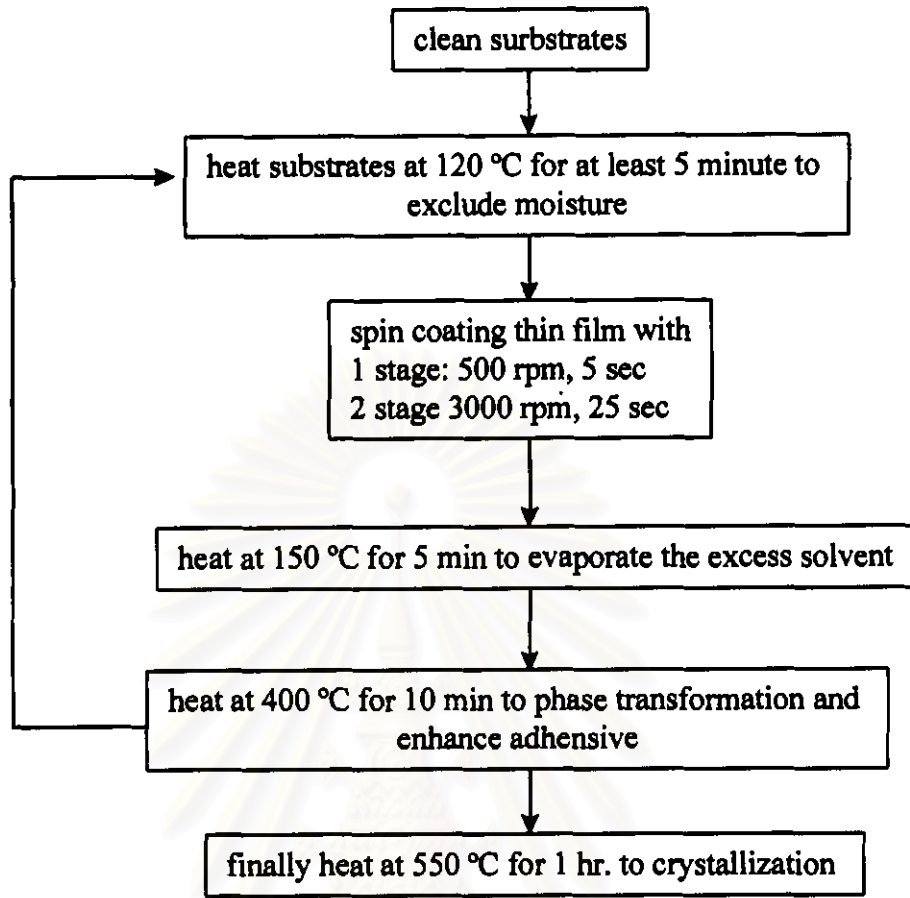
Fig. 5.10 Summary of synthesis of tin alkoxide.

### 5.3 Fabrication Processes of Gas Sensors

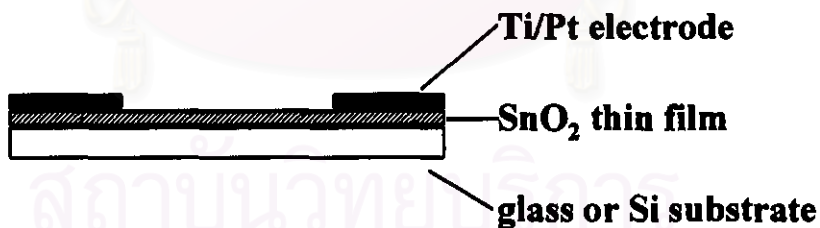
The SnO<sub>2</sub> sol solution was coated on various substrates i.e. glass and Si by spin coating technique. For the case which a modified substance was added, a solution of the modified substance was mixed directly to the SnO<sub>2</sub> solution. The added amount depended on the desire doping concentration, generally, this was calculated in percent by weight. The spin speed was set to 500 and 3000 rpm for the first stage and the second stage respectively. We could increase the thickness of SnO<sub>2</sub> thin film by increasing the number of spin as shown in Fig. 5.10(a). The thickness and refractive index of thin film on Si substrates were investigated by ellipsometry. After the film deposition process, Ti/Pt electrodes were deposited by an electron beam evaporator (EB). The thickness of Ti and Pt were 500 and 1000 Å respectively. The conditions for deposition of Ti and Pt are given in Table 5.2. Finally, SnO<sub>2</sub> thin film gas sensors were cut into pieces with the size of 5 × 10 mm. The gap between electrodes was 1 mm width. The structure of thin film gas sensor was demonstrated in Fig. 5.11(b). Fig. 5.12 shows a photograph of the fabricated sensors.

Table 5.2 Conditions for deposition of Ti and Pt by electron beam evaporator

Conditions	Ti	Pt
Thickness (Å)	500	1000
Back pressure (torr)	$2 \times 10^{-6}$	$2 \times 10^{-6}$
Substrate temperature (°C)	room temperature	room temperature
Deposition rate (Å/sec)	1	1
Rotation speed (rpm)	5	5
emission control	60	75-80
Current emission (mA)	15-20	90-110
Calibration parameter for thickness monitor:		
density (g/cm <sup>3</sup> )	4.5	21.4
Z-ratio	0.628	0.245
tooling (%)	60	60



(a)



(b)

Fig. 5.11 (a) Diagram of SnO<sub>2</sub> thin film deposition by sol-gel process and (b) Structure of thin film gas sensor.

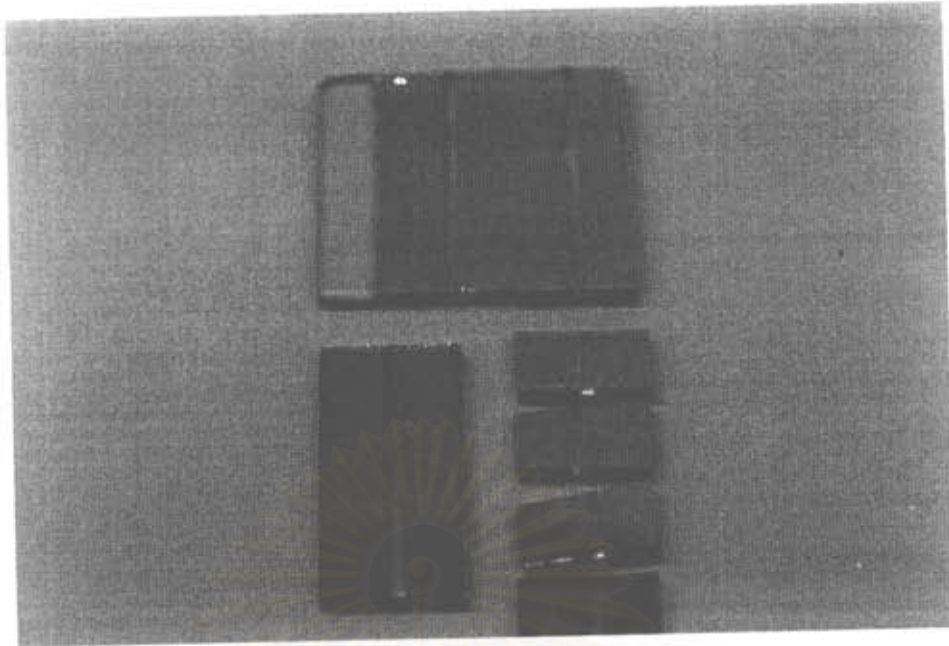


Fig.5.12 Photograph of fabricated sensors.

#### 5.4 Summary

In this chapter, Synthesis of tin (IV) alkoxide by various chemical methods have been described. It was shown that the sodium method with the rigorously controlled process gave the best results in the preparation of tin alkoxide. This tin alkoxide solution was used as a starting precursor to fabricate thin film gas sensors.  $\text{SnO}_2$  was deposited on various substrates by spin coating technique. The thickness of  $\text{SnO}_2$  thin films could be controlled by changing the number of spin. The fabrication processes of gas sensor by sol gel technique was also demonstrated.

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