CHAPTER I
INTRODUCTION

1.1 Background

The synthesis of new metal alkoxides possesing unique structures and properties is important for the study of sol-gel processes and the evolution of metal alkoxide chemistry. Tin oxide (SnO_2), cassiterite structure, is a typical wide band gap n-type semiconductor and one of the most widely used semiconductor oxides due to its chemical and mechanical stabilities. It can be used as transparent electrodes for solar cells, liquid crystal displays, catalysts for methanol conversion and CO/O_2, CO/NO reactions in the control of noxious emissions, antistatic coatings and gas sensors, anodes for lithium-ion batteries, transistors, catalyst supports, nano and ultrafiltration membranes and anticorrosion coatings. Among the various applications, the most important use of SnO_2 is to be used as gas sensors. The sensing properties of SnO_2 sensors, such as sensitivity, selectivity and reproducibility depend on several factors, mainly crystallite size and specific surface area .

In this research, we are focusing on the synthesis of high surface area tin oxide using tin glycolate as a new metal alkoxide precursor via the sol-gel process. Tin oxide nanoparticles were prepared by many different wet chemical methods, such as precipitation, hydrothermal, solvothermal, gel-combusion, spray pyrolysis, electron beam evaporation, sputtering methods, polymerized complex and sol-gel method. Many methods can be used to prepare high surface area, but they require high costs and temperature. More importantly, the sol-gel technique offers many advantages over other methods, precise control of the doping level and easy to prepare three dimensional network metal oxides than other technique at low temperature .

1.2 Sol-gel Process

The sol-gel process was first started in the late 1800s. The process means the synthesis of an inorganic network by a chemical reaction in solution at low temperature. It is one of the versatile solution processes for making ceramic and glass materials having better purity and high homoginiety products. The mechanism involves the transition from a liquid (solution or colloidal solution) into a solid (di- or multiphasic gel). The goal of the sol-gel technology is to use low temperature chemical process to produce net-shape, net-surface objects, films, fibers, particulates, or composites that can be used commercially after a minimum of additional processing steps.

The sol-gel process needs metal-inorganic compound precursor, such as metal alkoxide $M(OR)_n$. The precursors are dissolved in a suitable solvent subjecting to hydrolysis and condensation reaction.

The hydrolysis of metal alkoxides occurs via the hydroxylation of alkoxy group, as shown in equation 1.

$$M(OR)n + H_2O \longrightarrow M(OR)n\text{-}1(OH) + ROH \qquad (1)$$

Where;	$M(OR)n$	metal alkoxide
	$M(OR)n\text{-}1(OH)$	partial hydrolyzed metal alkoxide
	ROH	alcohol
	H_2O	water

When a hydroxy group is generated, propagation occurs through a polycondensation process. Depending on experimental conditions, two competitive mechanisms have to be considered, olation and oxidation. Formation of hydroxo bridges and formation of oxygen bridges occur through the elimination of solvent molecules, see equation 2, and the elimination of H_2O, as shown in equation 3.

$$M(OR)_n + M(OR)_{n-1}OH \longrightarrow M_2(OR)_{2n-2} + ROH \qquad (2)$$

$$M(OR)_{n-1}OH + M(OR)_{n-1}\text{-}OH \longrightarrow M_2(OR)_{2n-2} + H_2O \qquad (3)$$

Where;	$M(OR)_n$	alkoxy group
	$M(OR)_{n-1}OH$	hydroxyl group

ROH	alcohol
H_2O	water
$M_2(OR)_{2n-2}$	metaloxane

Obviously, hydrolysis and polycondensation are invovled in the transformation of a metal alkoxide precursor into oxide network. The chemical reactivity of metal alkoxides toward hydrolysis and condensation mainly depends on the positive charge of the metal atom and its ability to increase into coordination number. The factors affecting to the sol-gel process, hydrolysis and polycondensation reaction, to form gel are :

1. The electronegativity of the metal atom to increase the coordinate number.
2. The steric hindrance of the alkoxy group.
3. The molecular structure of the metal alkoxides (monomeric or oligomeric).
4. The amount of added water in the hydrolysis and sequence of water addition.
5. pH

One property of the sol-gel process is the ability to control the process all the way, from the molecular precursor to the product. Sol-gel chemistry offers many advantages, such as a lower processing temperature that can be used for the synthesis of new materials including both organic and inorganic component, the rheological properties of sols and gels that allow fiber or films to be processed by techniques, such as spin-drawing, dip-coating or screen printing.

Generally, the sol-gel process relatively involves in 4 steps, viz, solution chemistry (gel formation), aging, drying and calcinations/sintering. The advantages of the sol-gel process are as follows :

1. The thermal degradation of any materials is minimized with higher purity and stoichiometry since the temperature required in the process is low.
2. It is easily to achieve a homogeneous control due to the fact that organometallic precursors containing different metals are frequently miscible.
3. It is likely to obtain highly porous and nanocrystalline materials.
4. There is no need for machine or melting process for casting ceramic materials or producing thin films or fibers or monoliths because of easily applicable precursors.

5. It is easier to obtain uniformity high degree in thickness, leading to applications for optical components.
6. It allows a production of amorphous materials via the low temperature, which is basically below the crystallization temperature of oxide materials.However, it should be noted that there are also some limitations from the sol-gel process. Those are:
    1. The precursors are often expensive and sensitive to moisture.
    2. The sol-gel process is time consuming, particularly where careful aging and drying are required.
    3. It is likely to occur the problem of dimensional change, such as densification, stress cracking or cracking on drying.