

The Growth Kinetics of Tin Oxide Films from Tetramethyltin

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Tin oxide films have been grown employing the chemical vapor deposition technique under reduced pressure conditions using tetramethyltin as the precursor and oxygen as the oxidant. An activation energy derived for the deposition reaction under representative deposition conditions has a value of 89 ± 3 kJ mol⁻¹, suggesting a typical kinetic control. Deposition rates of tin oxide films exhibit a near first order dependence on tetramethyltin partial pressure and a zeroth order dependence on oxygen partial pressure. This study provides the first quantitative information about the growth kinetics of tin oxide films from tetramethyltin by the cold-wall low-pressure chemical vapor deposition.

Introduction

Tin oxide, SnO₂, is an electrical conductor that is highly transparent to visible light and highly reflecting to infrared wavelengths. Its unique properties make it suitable for a variety of applications both in industry and in research. Applications for SnO₂ films range from use as a transparent electrode in photovoltaic cells to use as an energy conserving coating on windows and lightbulbs.

Various techniques for growing these films have been intensively investigated during the recent past.¹⁻⁸ Chemical vapor deposition (CVD) is one of the most important techniques for producing films of transparent conducting oxides. This technique involves the reaction of one or more gaseous reacting species on or near a solid surface. The vapor of a precursor is transported to a substrate surface, where it is decomposed. The nature of the decomposition process varies according to the chemical and thermal properties of volatile transporting species. The electrical and optical characteristics of films deposited on the substrate surface are strongly influenced by the detailed process of the chemical reaction and activation mechanism. Kinetic data such as partial pressure dependence and activation energy are too limited and scattered to delineate the growth kinetics of SnO₂ films from precursors. The goal of this work is to investigate the growth kinetics of SnO₂ films from tetramethyltin, (CH₃)₄Sn by employing the chemical vapor deposition technique under reduced pressure conditions.

Experimental Section

The schematic view of low-pressure chemical vapor deposition (LPCVD) apparatus used to prepare SnO₂ films is shown in Figure 1. SnO₂ films were deposited by vaporization of (CH₃)₄Sn and its *in situ* oxidation with O₂. This organometallic compound is thermally stable and volatile, producing adequate vapor pressure (~110 torr at room temperature) and dissociating at temperatures higher than ~300 °C.⁹ (CH₃)₄Sn (Yamanaka Hutech, 99%) was placed in a glass reservoir held at room temperature through a mass flow con-

troller (Sierra Instrument, 840L) connected to five-channel Flo-Box electronics (Sierra, 905C-PS). O₂ (Dongjin Gas, 99.9%) was introduced through a metering valve into a four-way cross connected to the outlet of the mass flow controller and mixed with (CH₃)₄Sn vapor. The reactant mixture was transported into the deposition chamber through a delivery line heated at ~50 °C.

The reactor consisted of a cylindrical stainless steel deposition chamber and a cylindrical substrate heater (Omega, SUB1000) with a nozzle for the introduction of the reactant mixture. The substrates for the deposition of SnO₂ films, microscope slide glasses (Corning, 0211), were resistively heated by the heater and maintained at the desired temperature, using a temperature controller (Cole-Parmer, Digi-Sense). A thermocouple junction was spot-welded on the top surface of the heater in direct contact with the substrate. The temperature difference between the top surfaces of the heater and substrate was taken into account and corrected accordingly.

The deposition chamber was pumped down to a base pressure of $\sim 5 \times 10^{-2}$ torr by a chemical-type oil-sealed rotary pump (Alcatel, 2021C). All the partial pressures of the reac-

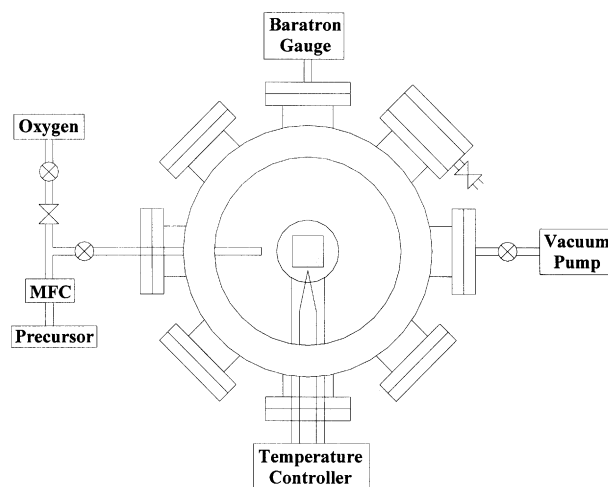


Figure 1. Schematic view of low-pressure chemical vapor deposition (LPCVD) apparatus used to prepare SnO₂ films.

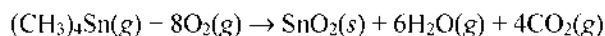
tant gases were measured by means of a minibaratron absolute pressure transducer (MKS Instruments, 750B) connected to a dual-channel digital readout (MKS Instruments, PDR-C-2C). Its anomalous behavior, due probably to the association of $(\text{CH}_3)_4\text{Sn}$ with O_2 , was observed and adequately corrected.

The deposition process sequence for a typical run was as follows. A substrate was placed on the top of the heater, the deposition chamber pumped down to the base pressure, the substrate heated to a constant temperature, and $(\text{CH}_3)_4\text{Sn}$ and O_2 admitted to commence deposition. Duration of deposition varied from 30 min to 75 min depending on desired thickness. Upon completion, flows of $(\text{CH}_3)_4\text{Sn}$ and O_2 were stopped. After the substrate was cooled in vacuum, the deposition chamber was opened for unloading.

A surface profiler (Tencor Instruments, Alpha-Step 500) was used to measure film thickness after SnO_2 films were etched with a Zn-HCl mixture to create a step for the measurement. Agreement in thickness among these measurements was within 5%. The film thickness increased linearly with deposition time. The deposition rate was calculated by dividing the film thickness by the deposition time. A four-point probe (Chang-min) was used for measuring sheet resistance of the films routinely. The Hall measurements were performed using van der Pauw geometry to determine carrier concentration and mobility. Ohmic contacts were made using silver paste. A UV-VIS-NIR spectrometer (Shimadzu, UV-3100) was used to measure transmittance for combination of the film and substrate in the wavelength ranging from 200 nm to 2000 nm. An X-ray thin film diffractometer (Siemens, D5005) employing $\text{Cu K}\alpha$ radiation was also used to identify phases present in the films. The grain size of the films was calculated using the Debye-Scherrer formula.¹⁰

Results and Discussion

The reaction leading to the formation of SnO_2 films can be written as follows.



Generally speaking, gas-phase reactions are favorable under conditions of slow gas space velocity (*i.e.*, long gas residence time) and high deposition pressure at high reaction temperature. The decomposition condition should be such that the reaction occurs only at the substrate surface and not in the gaseous phase, avoiding formation of powdery deposits, which may result in haziness in the films. The characteristics and growth rates of SnO_2 films depend on various deposition parameters, such as substrate temperature, reactant flow rates, deposition pressure, deposition time and system geometry. In order to obtain films of high quality all these parameters were optimized and controlled. A polycrystalline SnO_2 film was deposited with resistivity of $2 \times 10^{-2} \Omega \text{ cm}$ and visible transmission of $\sim 80\%$ under the optimum condition, namely, substrate temperature, 380 °C; $(\text{CH}_3)_4\text{Sn}$ partial pressure, 2.7 torr; and O_2 partial pressure, 3.0 torr. X-

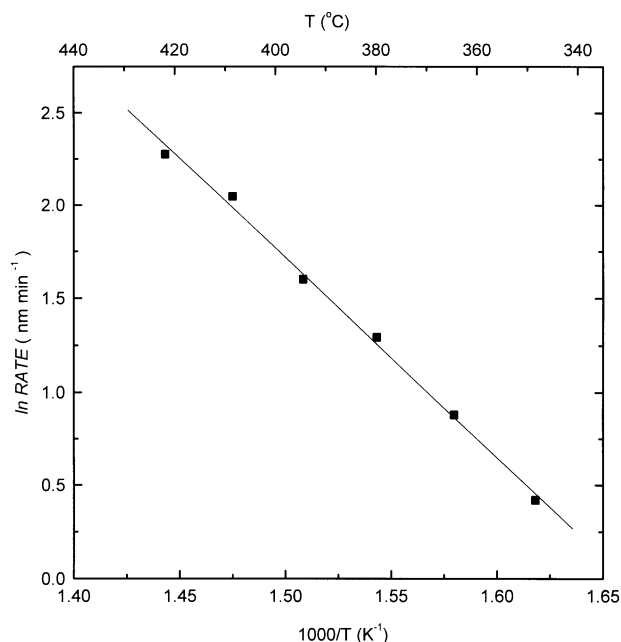


Figure 2. Plot of $\ln \text{Rate}$ versus $1/T$. $(\text{CH}_3)_4\text{Sn}$ partial pressure, 1.1 torr; O_2 partial pressure, 2.8 torr; deposition time, 60 min.

ray diffraction results showed exclusively a tetragonal rutile structure SnO_2 with a (101) preferred orientation. Next, an attempt was made to investigate the growth kinetics of SnO_2 films under the deposition conditions: substrate temperature, 345–420 °C; $(\text{CH}_3)_4\text{Sn}$ partial pressure, 1.5–3.2 torr; and O_2 partial pressure, 2.9–6.3 torr.

Figure 2 shows the plot of $\ln \text{Rate}$ versus $1/T$, where Rate is the deposition rate and T is the substrate temperature in K. From the Arrhenius plot, an apparent activation energy of $89 \pm 3 \text{ kJ mol}^{-1}$ was derived for the deposition reaction under the deposition conditions. This falls in the range of 40–210 kJ mol^{-1} for a typical kinetic process, but is lower than the reported values of 110–150 kJ mol^{-1} for SnO_2 films grown by atmospheric pressure chemical vapor deposition (APCVD).^{1–6} An activation energy as low as 55–60 kJ mol^{-1} has been reported for the hot-wall LPCVD of SnO_2 for the oxidation of $(\text{CH}_3)_4\text{Sn}$ ⁷ and SnCl_2 ⁸ with O_2 . Without a more detailed analysis it is not appropriate to speculate on the mechanistic implications of the lower activation energy.

In order to determine the dependence of deposition rate on partial pressure of $(\text{CH}_3)_4\text{Sn}$ or O_2 , SnO_2 films were grown as a function of partial pressure of either reactant. The variation of thickness, sheet resistance and resistivity as a function of $(\text{CH}_3)_4\text{Sn}$ partial pressure for SnO_2 films is shown in Figure 3. The partial pressure of $(\text{CH}_3)_4\text{Sn}$ was independently varied by adjusting the flow rate of $(\text{CH}_3)_4\text{Sn}$ at a fixed flow rate of O_2 as well as at a fixed opening of the control valve located between the deposition chamber and vacuum pump. The film thickness deposited for a constant deposition time increases linearly with $(\text{CH}_3)_4\text{Sn}$ partial pressure. By contrast, the dependence of deposition rate on O_2 partial pressure was relatively weak. Deposition rates were nearly constant under O_2 partial pressures of 2.8–6.3 torr. This indicates that O_2 diffusion is not rate-limiting at

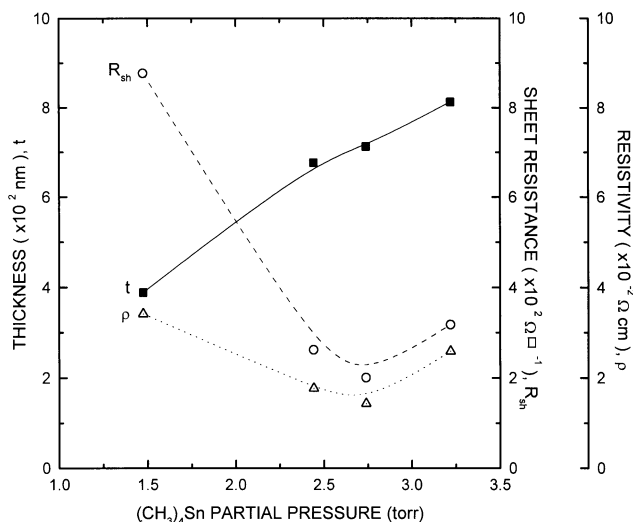


Figure 3. Variation of thickness, sheet resistance and resistivity as a function of $(\text{CH}_3)_4\text{Sn}$ partial pressure for SnO_2 films. O_2 partial pressure, 3.0 torr; substrate temperature, 380 °C; deposition time, 60 min.

low deposition rates and that O_2 adsorption is not a rate-determining step.

To examine the effect of total pressure of the deposition chamber on deposition rate, SnO_2 films were grown at different total pressures. Total pressure of the deposition chamber was varied by adjusting the conductance of the control valve located between the deposition chamber and vacuum pump at fixed flow rates of $(\text{CH}_3)_4\text{Sn}$ and O_2 . Figure 4 shows the dependence of thickness, sheet resistance and resistivity on total pressure of deposition chamber in SnO_2 films. An increase in deposition rate with an increase in the total pressure of the deposition chamber was observed. This is in good agreement with the deposition rate dependence on partial pressure of $(\text{CH}_3)_4\text{Sn}$ or O_2 since partial pressure should be

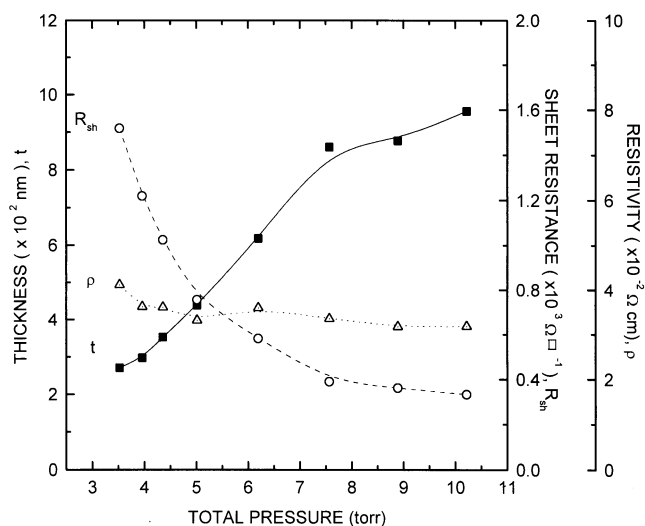


Figure 4. Dependence of thickness, sheet resistance and resistivity on total pressure of deposition chamber in SnO_2 films. Substrate temperature, 380 °C; $(\text{CH}_3)_4\text{Sn}/\text{O}_2$ partial pressure ratio, 0.4; deposition time, 60 min.

directly proportional to the total pressure thus residence time in this case.

It can be inferred that under the deposition conditions in this study the cold-wall LPCVD process was controlled by chemical kinetics based on the following reasons: the intercept of the straight line in the plot of growth rate versus substrate temperature showed a value that substantially deviates from zero, the activation energy for the reaction was close to those for a kinetic-limited processes, and the deposition rate was not independent of deposition pressure. But the mass transport effect became more pronounced at higher deposition rates, indicating a transition to mass-transfer limited regime.

Based on the observations above, deposition rates of SnO_2 films exhibit a near first order dependence on $(\text{CH}_3)_4\text{Sn}$ partial pressure and a zeroth order dependence on O_2 partial pressure. The reaction mechanism of SnO_2 film formation can be interpreted to be either homogeneous or heterogeneous. In a homogeneous reaction, $(\text{CH}_3)_4\text{Sn}$ oxidation to SnO_2 happens in the gas-phase around the substrate. The reaction product condenses onto the substrate and against the wall of the deposition chamber out of the supersaturated gas-phase to build up a continuous layer. In a heterogeneous reaction, the product SnO_2 is formed directly on the substrate surface itself. A spontaneous gas-phase reaction took place only when the total pressure of the reaction chamber was high enough, as evidenced by a leveling-off at high total pressures as well as by formation of a white powder on the inner wall of the deposition chamber. Therefore it is likely that under the representative deposition conditions, the reaction mechanism of SnO_2 film formation can be interpreted to be heterogeneous.

Considering the reaction orders, it is proposed that this heterogeneous surface reaction may follow Rideal-Eley mechanism.¹¹ This type of heterogeneous reaction would take place in different reaction steps, for instance, with the first being the adsorption of O_2 molecule on active centers of the heated glass substrate, followed by a reaction of incoming $(\text{CH}_3)_4\text{Sn}$ molecule with surface oxygen atom to form SnO_2 . After formation of a very thin continuous layer, e.g., $\text{Si-O}-(\text{SnO}_2)_n$, further film growth happens through the reaction between chemisorbed oxygen atom onto free tin coordination sites and gas-phase $(\text{CH}_3)_4\text{Sn}$ to form a continuous crystallite layer. From our experimental results and theoretical consideration the assumed mechanism seems probable though not definitely proven.

Ghoshtagore² studied the growth kinetics of SnO_2 films involving the reactions of SnCl_4 and $(\text{CH}_3)_4\text{Sn}$ by the hot-wall APCVD. It was observed that the surface reactions of both precursors took place with an adsorbed oxygen atom. Undesirable, homogeneous gas-phase volume reactions were also found for oxidation of SnCl_4 and $(\text{CH}_3)_4\text{Sn}$ above 880 °C and 490 °C, respectively. In his kinetic investigation of heterogeneous reactions, it was observed that the deposition rate is strongly dependent not only on SnCl_4 partial pressure but also on O_2 partial pressure. The deposition rate increased with increasing partial pressure of SnCl_4 or O_2 .

However, it remained constant at O_2 partial pressure higher than ~ 150 torr. These observations, at a glance, seem to contradict our growth kinetics. However, considering the substrate temperatures higher than ~ 700 °C employed for $SnCl_4$ - O_2 reaction, the different dependence of the growth kinetics on O_2 partial pressure can be understood. According to the fundamental chemisorption theory, the extent of oxygen adsorbed onto the substrate surface decreases drastically with increasing substrate temperature. Subsequently, O_2 partial pressure higher than ~ 150 torr should have been applied in order for the substrate surface to be saturated with atomic oxygen at substrate temperature higher than 700 °C; however, even a few torr of O_2 could have resulted in saturation of the substrate surface with atomic oxygen at 345–420 °C in our study. Similar growth kinetics was reported for SnO_2 films deposited using $(CH_3)_4Sn$ *via* gas-phase reaction by the hot-wall APCVD.⁵ The literature suggests that most of $(CH_3)_4Sn$ reacts in the gas-phase at least under high reactant concentration and reaction temperature conditions.^{4,6} In contrast, it was reported in the hot-wall LPCVD that the dependence of the deposition rate on $(CH_3)_4Sn$ was relatively weak, and the deposition rate was proportional to the square root of O_2 flow rate at low flow rates but constant at high flow rates.⁷ One-half order dependence of the deposition rate on O_2 partial pressure has been observed by Ghoshtagore² for the hot-wall APCVD of SnO_2 from $SnCl_4$ and $(CH_3)_4Sn$. Such marked differences imply that the growth kinetics of SnO_2 films by employing a chemical vapor deposition technique depends on substrate temperature and total pressure of the reaction chamber as well as on the chemical and thermal nature of the precursor.

Summary

We investigated the growth kinetics of SnO_2 films from $(CH_3)_4Sn$ by the cold-wall LPCVD. An activation energy derived for the deposition reaction under representative dep-

osition conditions has a value of 89 ± 3 kJ mol⁻¹, suggesting a typical kinetic control. Deposition rates of SnO_2 films exhibit a near first order dependence on $(CH_3)_4Sn$ partial pressure and a zeroth order dependence on O_2 partial pressure. It is probable that under the deposition conditions in this study, the cold-wall LPCVD process is controlled by chemical kinetics and the reaction mechanism of SnO_2 film formation can be interpreted to be heterogeneous. There is no sufficient data to make a definite conclusion, and the detailed growth mechanism of SnO_2 films is now open for further investigation.

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