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Material and Energy Efficiency Analysis of Low Pressure Chemical Vapor Deposition of TiO_2 Film

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Abstract

In this paper, Low Pressure Chemical Vapor Deposition (LPCVD) of TiO_2 thin film process is chosen as the research object to study the material and energy consumptions in this process. The material and energy utilization efficiencies have been calculated and compared under five different reaction conditions (623K, 500Pa; 673K, 500Pa; 723K, 500Pa; 673K, 400Pa; 673K, 300Pa). The material utilization efficiency result reveals that the material utilization in this process is rather low (less 1% in each condition) and increases with higher temperature and lower pressure. The energy analysis result shows that the energy efficiency is extremely low (less 0.1% in each condition) and increases with decreasing temperature and increasing pressure. The reaction condition (623K, 500Pa) is regarded as a satisfactory condition with the highest energy efficiency (0.083%) in spite of the lowest material utilization efficiency (0.5%). This research can lay a foundation for the future optimization work to improve the sustainability performance of LPCVD preparing thin films.

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Keywords: Low Pressure Chemical Vapor Deposition (LPCVD); TiO_2 thin film; material consumption; energy consumption; material utilization; energy efficiency

1. Introduction

TiO_2 thin film has been widely used in various fields such as photocatalysis, sensor, magnetic materials, environmental protection and so on nowadays and it can be prepared by different methods like, sol-gel method, Chemical Vapor Deposition (CVD), ion assisted deposition and so on. In these methods, Low Pressure Chemical Vapor Deposition (LPCVD), one of the CVD methods, is a popular method for depositing TiO_2 thin film given that it can provide high quality films. However, the problems of material and energy consumptions in LPCVD of thin films process are quite serious [1,2]. It is necessary and meaningful to analyze resources (material and energy) consumptions in LPCVD process to give insight into the causes of these problems.

To date, however, most efforts have been made to improve the thin film quality [3-5]. Little attention is paid to the problems (material and energy consumptions, low utilization efficiency, environmental effect and so on) in the film production process. Yang [6] conducted energy consumption analysis of LPCVD of TiO_2 thin film in his thesis. Some assumptions have been made and theoretical calculations are conducted under ideal conditions. What is more, the calculation results are obtained under single reaction condition. Based on Yang's work, Li [7] summarized the chemical reaction thermodynamic model of LPCVD for preparing TiO_2 thin film process.

The research described in this paper is an extension of Yang and Li's work. In this paper, Low Pressure Chemical Vapor Deposition (LPCVD) of TiO_2 thin film process is chosen as the research object. The material and energy consumptions in this process have been analyzed. The material and energy utilization efficiencies have been calculated and compared under five different reaction conditions (623K, 500Pa; 673K, 500Pa; 723K, 500Pa; 673K, 400Pa; 673K, 300Pa). One purpose of this paper is to evaluate

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the sustainability performance of LPCVD process from the aspects of material and energy consumptions and utilizations. The other one is to find a satisfactory condition under which the material and energy utilizations are better. This research can lay a foundation for the future optimization work to improve the sustainability performance of LPCVD process for preparing thin films.

Admittedly, this work is not sufficient to reflect the sustainability of the LPCVD of TiO_2 thin film process because the actual environmental impacts are not taken into account. However, the analysis of material and energy consumptions is necessary for a sustainability evaluation. A comprehensive assessment about LPCVD process should be and will be conducted in the next phase of our research.

2. Methods and Results

2.1. LPCVD of TiO_2 film process description

In LPCVD of TiO_2 film process, deposition mechanism is based on the following chemical reaction:

$$Ti(OC_3H_7)_4(g)+2H_2O(g) \rightarrow TiO_2(s)+4C_3H_7OH(g) \qquad (1)$$

The reactants ($Ti(OC_3H_7)_4$ and H_2O) are in their gas phase during the reaction. Inert gas nitrogen (N_2) is used as the carrier gas to take the reactants into the reactor and as the purging gas to clean the reactor. The reactor used to prepare TiO_2 film by LPCVD is shown in Fig.1.

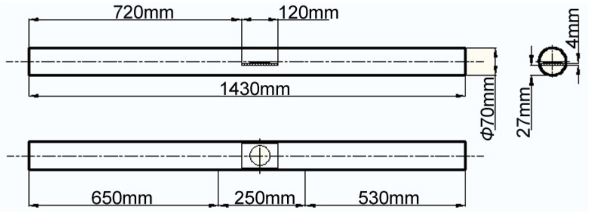

Fig. 1. The reactor used to prepare TiO_2 film by LPCVD

There are three temperature zones in the reactor: the first temperature zone (T_{01}), the second temperature zone (T_{02}), which is the reaction zone and the temperature is adjustable, and the third temperature zone (T_{03}). The pressure gradients in the three temperature zones are $\partial p_{T_{01}} / \partial x$, $\partial p_{T_{02}} / \partial x$, $\partial p_{T_{03}} / \partial x$, respectively. Here, x is the axial direction of the reactor.

There is a rectangle quartz boat in the center of the reaction zone. A silicon wafer, on which the film is deposited, is placed at the center of the quartz boat. The material of the reactor is quartz. The pressure in the reactor before reaction is p_0.

The basic and constant parameters are listed in table 1.

Table 1. Values of the constant parameters

Parameters	Values	Units
T_{01}	313	*K*
T_{03}	298	*K*
p_0	10^{-2}	*Pa*
$\partial p_{T_{01}} / \partial x$	-0.7×10^{-5}	*Pa/cm*
$\partial p_{T_{02}} / \partial x$	-3×10^{-5}	*Pa/cm*
$\partial p_{T_{03}} / \partial x$	-0.6×10^{-5}	*Pa/cm*
Reaction time	1	*hour*

Five different reaction conditions (different temperature and pressure in the reaction zone) are used to calculate and compare the material and energy consumptions in the LPCVD of TiO_2 film process. These reaction conditions are shown in table 2.

Table 2. Five different reaction conditions

Reaction conditions	Values
(T_1, p_1)	(623K, 500Pa)
(T_2, p_2)	(673K, 500Pa)
(T_3, p_3)	(723K, 500Pa)
(T_4, p_4)	(673K, 400Pa)
(T_5, p_5)	(673K, 300Pa)

2.2. Material consumption and efficiency analysis

The input materials include $Ti(OC_3H_7)_4$, H_2O and N_2. Here, only the consumption of $Ti(OC_3H_7)_4$ is taken into account considering H_2O can be reused and inert gas nitrogen is not consumed in the process. The material utilization efficiency has been calculated based on the following method:

$$\eta_{\text{material}} = \frac{M_{\text{reaction}}}{M_{\text{input}}} \qquad (2)$$

Where, η_{material} is the material utilization efficiency;

M_{reaction} is the amount of material consumed in the reaction;

M_{input} is the total amount of material supplied into the reactor.

Table 3. Material consumption and efficiency under five different reaction conditions

Reaction conditions	Input (*g*)	Consumed amount in the reaction (*g*)	Material utilization efficiency
(623K, 500Pa)	1.92	9.6×10^{-3}	0.5%
(673K, 500Pa)	1.78	10.3×10^{-3}	0.58%
(723K, 500Pa)	1.65	11×10^{-3}	0.67%
(673K, 400Pa)	1.42	8.5×10^{-3}	0.6%
(673K, 300Pa)	1.07	6.4×10^{-3}	0.6%

The total amount of $Ti(OC_3H_7)_4$ and the amount consumed in the reaction can be calculated based on the known parameters by applying the relevant knowledge of fluid mechanics and thermodynamics. The specific calculation formulae are listed in Appendix A but the specific calculation steps are omitted. The material utilization efficiency results under five different reaction conditions are listed in table 3.

The utilization efficiency results of $Ti(OC_3H_7)_4$ under five different conditions are shown in Fig.2.

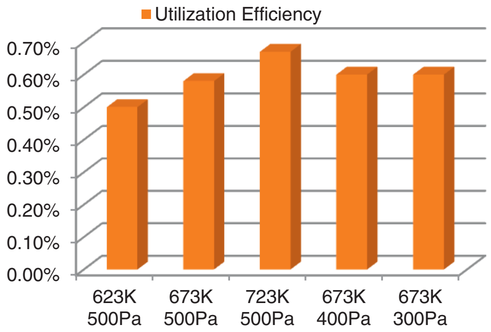

Fig. 2. The utilization efficiency results of $Ti(OC_3H_7)_4$ under five different conditions.

It can be seen from Fig.2 that the utilization efficiency of $Ti(OC_3H_7)_4$ steadily increases when the temperature changes from 623K to 723K under the condition of constant pressure (500Pa). When the temperature is constant (673K), the efficiency slightly increases with the pressure drops from 500Pa to 300Pa. The largest efficiency is obtained at the condition of (723K, 500Pa) although the value is rather small (0.67%). The result reveals that the material utilization efficiency increases with higher temperature and lower pressure. It also demonstrates that the material utilization efficiency is rather low in LPCVD process.

2.3. Energy consumption and efficiency analysis

In this paper, the energy consumption in LPCVD process is considered from the following aspects: the energy for heating the reactor, energy for pumping, energy absorbed by the input gases and the chemical reaction energy. Energy efficiency has been calculated by applying the following calculation method:

$$\eta = \frac{E_{\text{useful}}}{E_{\text{input}}} \tag{3}$$

Where, η is the energy efficiency;

E_{useful} is the useful energy;

E_{input} is the total input energy.

The total input energy, as mentioned above, contains the energy for reactor heating and for pumping. The useful energy is regarded as the energy absorbed by the input gases and the chemical reaction energy.

Heating energy

The heating energy can be calculated by applying the following method [8]:

$$Q = U + W$$

Where, U is the internal energy gain of the reactor;

W is the dissipated energy.

The internal energy gain can be calculated by:

$$U = m \times C_g \times \Delta T \tag{4}$$

Where, m is the mass of the heated component;

C_g is specific heat capacity of the material, for quartz material its value is 739 J/(kg·K);

ΔT is temperature difference.

The dissipated energy can be calculated based on the following formula [9]:

$$\begin{aligned} W &= q_{\text{convection}} \times t + q_{\text{radition}} \times t \\ &= h \times A \times \Delta T \times t + \varepsilon \times \sigma \times A \times T^4 \times t \end{aligned} \tag{5}$$

Where, $q_{\text{convection}}$ is the rate of heat dissipation on a surface by convection;

q_{radition} is the rate of heat dissipation on a surface by radition;

t is the heat dissipation time;

h is convection coefficient, here its value is 70 $W/m^2 \cdot K$;

ε is emissivity of material, ε is 0.95;

σ is Stefan-Boltzmann constant, its value is 5.67×10^{-8} $W/m^2 \cdot K^4$;

A is surface area of heat dissipation;

T is absolute temperature.

As a result, it can be obtained as follows:

$$Q = (m \times C_g + h \times A \times t) \times \Delta T + \varepsilon \times \sigma \times A \times T^4 \times t \tag{6}$$

Heating energy can be obtained by substituting the known parameters into formula (6) and the results are shown in table 4.

Table 4. Heating energy under five different reaction conditions

Reaction conditions	Heating energy (*kJ*)
(623K, 500Pa)	1.40×10^4
(673K, 500Pa)	1.66×10^4
(723K, 500Pa)	1.95×10^4
(673K, 400Pa)	1.66×10^4
(673K, 300Pa)	1.66×10^4

It can be seen from the calculation formula that the heating energy is proportional to the temperature difference and independence of pressure as a result, the value is the same when pressure is constant.

Energy for Pumping

A mechanical pump is used during the reaction process to pulse the carrier gas and reactants into the reactor and remove the residual reactants. It is operated at rated power, which is 0.55KW, during the whole process. The energy for pumping can be obtained by multiplying the power with the reaction time:

$$E_p = Pt\eta_p = 0.55 \times 1 \times 0.75 = 1485kJ$$

Where, E_p is the energy for pumping;
P is the power of the mechanical pump;
t is the operating time.
η_p is a proportional coefficient, here the value is 0.75.

Chemical reaction energy

The chemical reaction energy is determined by calculating the enthalpy change in the reaction and the calculation methods can be obtained from reference [8]. The relevant calculation formulae are listed in Appendix A. All of the gases in the reaction are regarded as ideal gas. The enthalpy change results are listed in table 5.

Table 5. Enthalpy change under five different reaction conditions

Reaction conditions	Molar enthalpy change (*kJ/mol*)	Total enthalpy change (*kJ*)
(623K, 500Pa)	69.02	2.3×10^{-3}
(673K, 500Pa)	69.56	2.5×10^{-3}
(723K, 500Pa)	70.03	2.7×10^{-3}
(673K, 400Pa)	69.56	2.1×10^{-3}
(673K, 300Pa)	69.56	1.6×10^{-3}

Energy absorbed by the input gases

The energy absorbed by the input gases ($Ti(OC_3H_7)_4$, H_2O and N_2) are analyzed by calculating the enthalpy change of each gas heated from the reference state to the reaction state. The calculation results are listed in table 6.

Table 6. Energy absorbed by the input gases under five different reaction conditions

Reaction conditions	Absorbed energy (*kJ*)			Total absorbed energy (*kJ*)
	$Ti(OC_3H_7)_4$	H_2O	N_2	
(623K, 500Pa)	-9.86	-3.11	0.18	-12.79
(673K, 500Pa)	-8.94	-2.86	0.19	-11.61
(723K, 500Pa)	-8.14	-2.64	0.20	-10.58
(673K, 400Pa)	-7.15	-2.28	0.15	-9.28
(673K, 300Pa)	-5.36	-1.71	0.12	-6.95

Energy efficiency

The energy efficiency can be obtained by substituting the known values into formula (3). The results under five different conditions are listed in table 7 and shown in Fig.3.

Table 7. Energy efficiency under five different reaction conditions

Reaction conditions	Total Input energy (*kJ*)	Useful energy (*kJ*)	Energy Efficiency
(623K, 500Pa)	15485	-12.79	0.083%
(673K, 500Pa)	18085	-11.61	0.064%
(723K, 500Pa)	20985	-10.58	0.050%
(673K, 400Pa)	18085	-9.28	0.051%
(673K, 300Pa)	18085	-6.95	0.038%

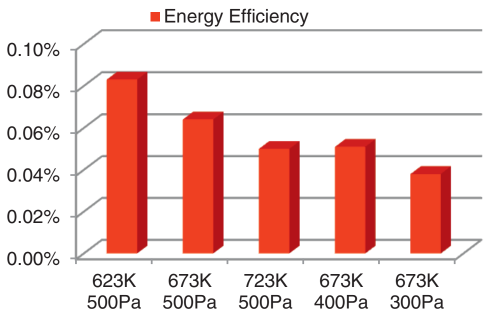

Fig.3. Energy efficiency at five different conditions

Fig.3. shows that energy efficiency decreases when temperature rises from 623K to 723K with constant pressure (500Pa). When the temperature is constant (673K) energy efficiency declines when the pressure decreases from 500Pa to 300Pa. As a result, the result shows that the energy efficiency decreases with increasing temperature and decreasing pressure. It also demonstrates that the energy efficiency is quite low in LPCVD process with the efficiency being less than 0.1% in each condition.

It can be seen from the above analyses that the material utilization efficiency is the largest (0.67%) at the condition of (723K, 500Pa) while the energy efficiency is low (not the least) at this condition. The energy efficiency reaches the highest (0.083%) at the condition of (623K, 500Pa) however, the material utilization efficiency is the lowest. As a result, it needs to weigh the parameters properly when choosing a reaction condition because it is difficult to meet the demand for both high material and energy efficiency. In this paper, the reaction condition (623K, 500Pa) is regarded as a satisfactory condition because the energy efficiency is the highest. Although the material utilization efficiency is the lowest at this condition, the values vary slightly at different conditions.

3. Conclusions

Low Pressure Chemical Vapor Deposition (LPCVD) of TiO_2 thin film process is chosen as the research object in this paper. The material and energy consumptions have been analyzed in order to give insight into the sustainability of LPCVD process. The material and energy utilization efficiencies have been calculated and compared under five different reaction conditions (623K, 500Pa; 673K, 500Pa; 723K, 500Pa; 673K, 400Pa; 673K, 300Pa). The purpose is to find a condition under which the resource utilization is better. The analysis result of material utilization efficiency shows that the material utilization in LPCVD process is rather low (less than 1% in each condition) and increases with higher temperature and lower pressure. The energy analysis result reveals that the energy efficiency is extremely low in LPCVD process (less than 0.1% in each condition) and decreases with increasing temperature and decreasing pressure. The reaction condition (623K, 500Pa) is regarded as a satisfactory condition with the highest energy efficiency in spite of the lowest material utilization efficiency considering the values of the material utilization efficiency vary slightly at different conditions.

Acknowledgements

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Appendix A.

A.1. Formulae needed to calculate the input amount of $Ti(OC_3H_7)_4$

Formulae that needed to calculate the input amount of $Ti(OC_3H_7)_4$ are listed in table 8.

Table 8. formulae that needed to calculate the input amount of $Ti(OC_3H_7)_4$

Formula name	Formulae	References
Velocity equation	$u_x = -\frac{h^2}{2\mu}\frac{\partial p}{\partial x}\left[\frac{y}{h} - \left(\frac{y}{h}\right)^2\right]$	[10]
Viscosity formula	$\mu = \frac{0.00333\left(MT_c\right)^{0.5} F}{V_c^{2/3}}$	[11]
Mixed gases Viscosity formula	$\mu_m = \sum_{i=1}^{n} \frac{\mu_i}{1 + \sum_{j=1, j\neq i}^{n} \varphi_{ij} \frac{y_j}{y_i}}$ $\varphi_{ij} = \frac{\left[1 + \left(\mu_i / \mu_j\right)^{1/2} \left(M_j / M_i\right)^{1/4}\right]^2}{2\sqrt{2}\left[1 + \left(M_i / M_j\right)\right]^{1/2}}$	[11]
Concentration function	$C(x,y) = \frac{4C_0}{\pi}\sin\left(\frac{\pi y}{2b}\right)\exp-\left(\frac{\pi^2 Dx}{4vb^2}\right)$	[12]
Diffusivity flux formula	$J(x) = D\frac{\partial C(x,y)}{\partial y}\Big\vert_{y=0}$	[12]
Initial concentration of $Ti(OC_3H_7)_4$	$C_0 = \frac{p' M}{RT}$	[8]
Diffusivity formula	$D_{im} = \left(\sum_{j=1, j\neq i}^{n} \frac{x_j}{D_{ij}}\right)^{-1}$	[13]
Film deposition rate	$\dot{G}(x) = \frac{MJ(x)}{\rho M_s} = \frac{2C_0 MD}{b\rho M_s}\exp-\left(\frac{\pi^2 Dx}{4vb^2}\right)$	[12]

A.2. calculation formulae for determining the molar enthalpy change of chemical reaction

Formulae that needed to calculate the molar enthalpy change of chemical reaction are shown in table 9.

Table 9. formulae that needed to calculate the molar enthalpy change of chemical reaction

Formula name	Formulae	References
Formula of Molar heat capacity	$C_p = a + bT + cT^2$ $c = \frac{C_{p,1}}{(T_1 - T_2)(T_1 - T_3)} + \frac{C_{p,2}}{(T_2 - T_1)(T_2 - T_3)} + \frac{C_{p,3}}{(T_3 - T_2)(T_3 - T_1)}$ $b = \frac{C_{p,1} - C_{p,2}}{T_1 - T_2} - [(T_1 + T_2)c]$ $a = (C_{p,1} - bT_1) - cT_1^2$ $c = \frac{C_{p,1}}{(T_1 - T_2)(T_1 - T_3)} + \frac{C_{p,2}}{(T_2 - T_1)(T_2 - T_3)} + \frac{C_{p,3}}{(T_3 - T_2)(T_3 - T_1)}$	[14]
Molar heat capacity of reactants and resultants	$C_p(Ti(OC_3H_7)_4) = 17.66 + 1.24T - 4.84\times10^{-4}T^2$ $C_p(H_2O) = 31.81 + 4.39\times10^{-3}T + 5.44\times10^{-6}T^2$ $C_p(TiO_2) = 25.90 + 0.12T - 7.50\times10^{-5}T^2$ $C_p(C_3H_7OH) = 5.66 + 0.32T - 1.32\times10^{-4}T^2$	[14]
Molar enthalpy change of chemical reaction	$\Delta_r H(T,p) = \sum_{\text{products}} \nu_B \Delta H - \sum_{\text{reactants}} \nu_B \Delta H = \sum \nu_B \Delta_f H_m^{\Theta} + \int_{298}^{T} \sum \nu_B C_p(B) dT$	[15]

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