Particle-Precipitation-Aided Chemical Vapor Deposition of Titanium Nitride

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Particle-precipitation-aided chemical vapor deposition (PP-CVD) is a modification of the conventional CVD process, where an aerosol is formed in the gas phase and particles are deposited on a substrate. The driving force for particle deposition is thermophoresis. The synthesis of titanium nitride (TiN) has been studied. TiN is formed on the substrate, as well as in the gas phase. At low temperature differences, only dense microstructures with equiaxed grains are observed; porous coherent layers are found in experiments where larger temperature differences are applied. Additional increase in the temperature difference only leads to loose powder deposits. In principle, the PP-CVD process is a suitable method for the synthesis of thin porous layers of ceramics.

I. Introduction

IN CHEMICAL vapor deposition (CVD), gas-phase reactants, diluted in a carrier gas, are introduced into a hot-wall reactor, where the reactants adsorb onto a substrate. These adsorbed reactants will react to form a solid film on the substrate.¹ In general, powder formation in the gas phase in a CVD process should be avoided, because this will considerably deplete the reactants that are necessary for heterogeneous CVD reaction, leading to a nonuniform film thickness. Under certain experimental conditions, powder formation can be used to an advantage, in that the hot-wall CVD process can be modified to control the microstructure of the layer by using a controlled deposition of the particles on the substrate. In particle-precipitation-aided CVD (PP-CVD), an aerosol is formed at an elevated temperature, and the particles are precipitated on the substrate by introducing an external force for particle deposition, such as thermophoresis, electrophoresis, or forced flow. Particle precipitation on the substrate will result in a loose powder deposit that has a poor mechanical stability. To obtain a coherent layer, the powder deposit should be sintered or a heterogeneous reaction should occur simultaneously to interconnect the individual particles. Thus, the PP-CVD process consists of three steps, i.e., particle formation, particle deposition, and interconnection or sintering of the particles, as illustrated in Fig. 1. This technique of making dense to porous layers offers a variety of applications; e.g., thin porous layers can be used as a catalyst carrier, membrane, or porous electrode.

II. Particle-Precipitation-Aided Chemical Vapor Deposition

Particle deposition in a CVD process has been proven to be successful in the modified CVD (M-CVD) process,² which

originally has been developed to deposit doped silica (SiO₂) in a quartz preform for optical fiber production. The PP-CVD process is very similar to this M-CVD process. In M-CVD, the relatively cold reactor wall is used as a substrate, whereas, in PP-CVD, a separate substrate is introduced into the reactor. The PP-CVD process has been introduced by Komiyama and coworkers.³⁻⁸ They used titanium tetraisopropoxide (TTIP) and zirconium tetraisopropoxide (ZrTIP) for the synthesis of titania (TiO₂)³⁻⁶ and zirconia (ZrO₂),⁶ respectively, and aluminum trichloride (AlCl₃) and ammonia (NH₃) for the synthesis of aluminum nitride (AlN).⁶⁻⁸ The driving force for particle deposition was thermophoresis. Layers ranging from dense to highly porous, depending on experimental conditions, were obtained. The microstructure of the layers seemed to be determined by a combination of particle deposition, sintering, and heterogeneous reaction. In all cases, the uniformity in film thickness in the axial direction of the tubular reactor was very poor, because of the strong depletion of reactant in the gas phase. Silicon nitride (Si₃N₄) particles have been deposited on a porous substrate by electrophoresis^{9,10} or by a forced flow.¹¹ The precipitated powders were sintered afterward to form a porous layer, which resulted in a microstructure similar to a Menger sponge. The reactant mixture used in the PP-CVD process must serve as a source for the powder formation as well as for the heterogeneous reaction. In principle, two separate reaction routes, i.e., one for the powder formation and one for the heterogeneous reaction, should be used.

We have investigated the synthesis of titanium nitride (TiN) by the PP-CVD process. TiN has been deposited on porous alumina (Al₂O₃) tubes in a cylindrical laminar-flow reactor. TiN

Fig. 1. Principle of the three stages of the PP-CVD process.

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has been chosen to investigate the possibilities of the PP-CVD process because synthesizing TiN aerosols, as well as TiN layers, at the same reaction temperature and reactor pressure is possible using different nitrogen-containing reactants. A heterogeneous reaction is necessary to interconnect the precipitated particles because TiN has a poor sinterability. A TiN aerosol can be formed using titanium tetrachloride (TiCl_4), NH_3 , and hydrogen (H_2),^{12–16} whereas TiCl_4 , H_2 , and nitrogen (N_2) can react only on a surface to form TiN.^{17–19} The pores between the precipitated particles, which originate from the first reaction, should be filled entirely or partly by the solid deposit of the second reaction. The layers that are formed are expected to have different porosities, depending on the ratio of the particle precipitation rate to the heterogeneous reaction rate. The particle deposition rate is determined by the particle concentration in the gas phase and by the driving force for particle deposition, whereas the heterogeneous reaction is governed by the reactant concentration and the reaction-rate constant. The particle concentration in the gas phase, as well as the heterogeneous-reaction-rate constant, are temperature dependent. For proper process control, one must separate the heterogeneous reaction and the homogeneous reaction in PP-CVD.

III. Particle Deposition

The driving force for powder deposition on the substrate can be thermophoresis, diffusion, or gravitation. The thermophoretic velocity (v_t) is proportional to the temperature gradient:²⁰

$$v_t = \kappa \left(\frac{\nu}{T} \right) \nabla T \quad (1)$$

where ν is the kinematic viscosity of the gas, T the temperature, and κ a constant for a given particle size and gas-phase concentration. Talbot *et al.*²¹ have proposed a semiempirical formula for κ based on the formula for the thermophoretic velocity by Brock:²²

$$\kappa = \frac{2C_m C_s \left(\frac{k_g}{k_p} + C_i \text{Kn} \right)}{(1 + 3C_m \text{Kn}) \left(1 + 2 \frac{k_g}{k_p} + 2C_i \text{Kn} \right)} \quad (2)$$

where C_m , C_s , C_m , and C_i are constants, k_g is the thermal conductivity of the gas, k_p is the thermal conductivity of the

particle, and Kn is the Knudsen number ($2\lambda/d_p$; λ is the mean free path length and d_p is the particle diameter). The slip coefficient (C_s) is a function of the Knudsen number:

$$C_s = 1 + \text{Kn}[A + B \exp(-C/\text{Kn})] \quad (3)$$

where A , B , and C are constants. In gas-to-particle conversions, the particle sizes are typically $<1 \mu\text{m}$. For particle sizes of $<1 \mu\text{m}$, κ becomes equal to 0.5.²³ The influence of the thermophoretic velocity on the particle deposition in the M-CVD process has been investigated extensively.^{24–30} Comparison between the modeling results and the experimental data suggests that the thermophoretic velocity predicted by Eq. (1) is too low.³⁰ However, this equation for the thermophoretic velocity can be used for a qualitative analysis. For very small particle sizes, transport is determined by diffusion. A particle diffusion coefficient, D_p , can be described by the Einstein formula:²⁰

$$D_p = \frac{kTC_s}{3\pi\mu d_p} \quad (4)$$

where k is the Boltzmann constant and μ is the gas viscosity. A diffusional velocity can be defined using a stagnant film approximation:³¹

$$v_D = \frac{D_p}{x} \quad (5)$$

where x is a characteristic length (equal to the reactor radius). For large particles, the terminal settling velocity due to a gravitational force (v_s) cannot be neglected anymore:²⁰

$$v_s = \frac{\rho_p g d_p}{18\mu} \quad (6)$$

where g is the acceleration due to gravity and ρ_p is the particle density. The sum of these three velocities is used to evaluate the importance of thermophoresis on the mass transfer. The velocity for TiN particles, as a function of particle size, in a H_2/N_2 mixture at 1000 K is presented in Fig. 2; the constants necessary for the calculations are summarized in Table I. This figure shows qualitatively that, for particle sizes of 10^{-3} – $1 \mu\text{m}$ (1–1000 nm), the particle mass transfer is dominated by thermophoresis. This behavior is most pronounced at high temperature gradients.

From Fig. 2, however, the fact that the particle deposition might already be affected strongly by a small temperature difference can be concluded. For a more quantitative evaluation,

Fig. 2. Particle velocity, as a function of TiN particle diameter, for different temperature differences at 1000 K.

Table I. Constants for Calculation of TiN Particle Velocity in a 50/50 H₂/N₂ Gas Mixture at 1000 K

Symbol	Value
C_{th}	1.147 [†]
C_m	1.146 [†]
C_r	2.18 [†]
A	1.20 [†]
B	0.41 [†]
C	0.88 [†]
k_{TiN}	30 J·(m·s·K) ⁻¹
k_{H_2/N_2}	0.43 J·(m·s·K) ⁻¹
μ_{H_2/N_2}	3.81×10^{-5} kg·(m·s) ⁻¹
ν_{H_2/N_2}	1.9×10^{-4} m ² /s
ρ_{TiN}	5220 kg/m ³

[†]From Refs. 20–22.

the influence of a temperature gradient on the particle flux should be evaluated. However, such an analysis is difficult, because the particle concentration and the particle concentration gradient are unknown.

IV. Experimental Procedure

The synthesis experiments were performed in a stainless-steel reactor with a stainless-steel nozzle or in a quartz reactor with a quartz nozzle. Both reactors were coated with TiN before the synthesis experiments. A detailed description of the quartz reactor can be found elsewhere.^{12,13} The stainless-steel reactor differed slightly from the quartz reactor. The stainless-steel cylindrical reactor (inner diameter of 50 mm and length of 700 mm) was positioned in a three-zone resistance furnace. A nozzle was used for separate introduction of the reactants. The

NH₃-containing flow was introduced through the inside of the nozzle, whereas the TiCl₄-containing flow was introduced at the entrance of the reactor outside the nozzle. The susceptor for positioning and cooling the substrate consisted of a hollow quartz tube closed at one end that was positioned at the outlet of the nozzle in the middle of the reactor. The layers were deposited on tubular porous Al₂O₃ substrates (inner diameter of 9 mm, outer diameter of 15 mm, length of 15 mm, average pore size of 4.5 μm, and porosity of 40%). Porous Al₂O₃ substrates allowed us to measure the degree of porosity of the deposited layer by gas-permeability measurements. These substrates were slid over the cooled susceptor.

The cooling of the susceptor is regulated by an externally controlled flow of pressurized air. Temperatures are measured with chromel–alumel thermocouples, as illustrated in a cross section of the center of the reactor in Fig. 3. The reaction temperature is measured at the end of the gas-distribution nozzle (A1 in Fig. 3). The temperature of the gas phase is measured 15 mm above the substrate (A2 in Fig. 3), and the temperature of the substrate is measured with a thermocouple mounted on the surface of the substrate (A3 in Fig. 3). The relation between the temperature difference (between the substrate and the gas phase) and the pressurized air flow has been calibrated in separate experiments. Only a H₂/N₂ mixture flow equal to the gas flow used for the synthesis experiments was applied during the calibration. The electromotive force of the thermocouples was recorded, with an accuracy of 0.01 mV, i.e., equal to an uncertainty of 0.5 K in the calculated temperature. The temperature difference during the synthesis experiments was assumed to be the same as for the calibration experiments at a given pressurized flow. The experimental conditions are summarized in Table II.

Fig. 3. Schematic drawing of the cylindrical reactor in a three-zone resistance furnace.

Table II. Process Parameters for Synthesis of TiN by PP-CVD

Reaction material	Inside flow [†]				Outside flow [‡]				Reaction time (s)	Reaction temperature (K)	Temperature difference (K)	Reactor pressure (Pa)
	NH ₃	N ₂	H ₂	Total	TiCl ₄	N ₂	H ₂	Total				
Stainless steel	13.5	0.448	0.162	0.624	35.9		0.93	0.97	3600	923–1023	0–38	1 × 10 ⁵
Quartz	17		0.7783	0.78	35	0.49	0.49	1.015	3600	923–1173	0–36	1 × 10 ⁵

[†]Values for NH₃ are given in $\mu\text{mol/s}$; all others are in mmol/s . [‡]Values for TiCl₄ are given in $\mu\text{mol/s}$; all others are in mmol/s .

Argon-gas-permeability measurements are used for the characterization of the porosity of the layers. Details on the experimental aspects for the permeability measurements are given elsewhere.³² The layers are studied using scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis.

V. Results and Discussion

In all cases, the deposits consisted of crystalline TiN, as identified by XRD analysis. An excess of TiCl₄, with respect to NH₃, was used to prevent full conversion of TiCl₄ to TiN in the gas phase. The maximum conversion of TiCl₄ to TiN was always <70% over the first 15 mm in the reaction zone if NH₃ is assumed to be fully converted to TiN. Thus, a sufficient amount of TiCl₄ for a heterogeneous reaction was always present. The growth rate, as a function of the temperature difference at different reaction temperatures, is presented in Fig. 4. This plot combines experiments performed in a stainless-steel reactor and a quartz reactor. The experiments performed in the quartz reactor have been published earlier.¹² No difference in the experimental results using the quartz reactor or the steel reactor seemed to exist, despite the differences in gas composition inside and outside of the nozzle (see Table II). The reported temperature gradients^{12,13} for the experiments in the quartz reactor were derived from measurements with thermocouples in the reactor during the synthesis experiments. However, the accuracy of these *in-situ* temperature measurements was not optimal, because of the deposition of TiN onto the thermocouples. In addition, the actual temperature gradient near the substrate was unknown, because of the presence of a thermal boundary layer. Therefore, using the temperature difference as a parameter was more appropriate. The temperature differences presented in Fig. 4 were obtained by measuring the flow rate of the pressurized air during the synthesis experiments. This flow rate

was linked to a temperature difference by a calibration table, as described in the previous section. The microstructure of the films can be divided into three regions, as shown in Fig. 4: in region I, all layers have a dense structure; in region II, the layers have a mechanically stable porous microstructure; and in region III, the deposits consist of loose powder.

If no cooling is present, the experimental configuration is identical to a conventional CVD reactor and the contribution of the particles to the growth rate is expected to be low, because the diffusion rate of the particles in the gas phase is very small. To our knowledge, only Sjöstrand³³ has reported some results on the synthesis of TiN using TiCl₄, NH₃, N₂, and H₂ at atmospheric pressure and reaction temperatures of >900 K. However, Sjöstrand³³ used a cold-wall reactor instead of a hot-wall reactor. We have observed dense layers with faceted columnar grains, and no individual particles in the layers have been observed. Similar microstructures have been observed by Sjöstrand.³³ A cross section of a layer typical for the synthesis experiments where no temperature gradient was applied is presented in Fig. 5. The observed growth rates of the layers were a factor of >10 higher than the expected growth rate of TiN layers using TiCl₄, N₂, and H₂. Thus, the growth rate must be determined by the combination of TiCl₄, NH₃, N₂, and H₂. The grains of the layers have a tendency to become larger at higher reaction temperatures.

For the reaction temperature dependence, with respect to the growth rate, no Arrhenius-type behavior could be observed. The growth rate on the substrate is determined by a combination of mass transfer to the substrate, surface reactions, and conversion of reactants in the gas phase for the formation of TiN particles, which decreases the growth rate at the surface. The primary particle size in the gas phase is 100–200 nm.^{13–16} The particle concentration in the gas phase, as a function of reaction temperature, shows an Arrhenius-type behavior with an apparent activation energy of ~142 kJ/mol.¹⁶ Thus, the consumption

Fig. 4. Thickness of the TiN layer versus temperature difference at different reaction temperatures (($\blacktriangle$) 923, ($\times$) 973, ($\square$) 1023, ($*$) 1073, ($+$) 1123, and ($\blacksquare$) 1173 K). Three types of deposits are observed: region I, dense layers; region II, coherent porous layers; and region III, loose powder deposits.

Fig. 5. SEM micrograph of a cross section of a TiN layer, which is typical for layers grown without a cooling of the substrate. In this case, the reaction temperature was 1023 K.

of TiCl_4 and NH_3 for the formation of nuclei in the gas phase has a strong temperature dependence. The film growth rate using TiCl_4 , N_2 , and H_2 is controlled by surface kinetics, and the growth rate reveals an Arrhenius-type behavior.¹⁷⁻¹⁹ Whether the observed growth rate using N_2 and NH_3 is determined by surface kinetics or a diffusional mass transfer cannot be concluded, because of the complex relation between several reaction mechanisms that are interdependent. However, the observed microstructure, in combination with the high growth rate using N_2 and NH_3 , is typical for a molecular-diffusion-controlled CVD growth mechanism. Similar columnar microstructures have been found for diffusion-limited growth of other binary compounds, such as the growth of β -silicon carbide using tetramethylsilane, as has been discussed earlier.¹³

A small temperature difference of only a few degrees Kelvin has a considerable effect on the microstructure of the layers. The columnar structure disappears, and the average grain size is considerably smaller. A cross section and a surface of a layer typical for the synthesis experiments where a small temperature gradient was applied are presented in Figs. 6 and 7, respectively. Apparently, the introduction of a small temperature difference favors renucleation at the surface; as a result, virtually equiaxed

grains are formed. The temperature gradient has an influence on the particle deposition and on the thermal diffusion of relatively heavy molecules. Conceivably, the deposition of small particles, which serve as nuclei, is responsible for the change in the microstructure. The temperature difference appears to have no influence on the growth rate. Thus, thermal diffusion of molecules is not likely to be responsible for the change in microstructure.

An additional increase in the temperature gradient will result in an increase in the particle deposition rate. A cross section and a surface of a layer typical for the synthesis experiments where a temperature gradient of >5 K and a reaction temperature of 923 or 1023 K were applied are presented in Figs. 8 and 9, respectively. The observed interconnection of the particles must originate from a heterogeneous reaction. Apparently, under these conditions, the heterogeneous reaction rate is high enough, with respect to the particle precipitation rate, to interconnect the precipitated particles, whereas the heterogeneous reaction rate is not high enough to fill the voids between them. Consequently, this results in the formation of a porous layer by the PP-CVD process. The synthesis of such a mechanically stable porous layer of material with a poor sinterability is unique. To our knowledge, no other type of synthesis process is capable of making porous TiN layers at such a low temperature. Only a small window, with respect to the temperature gradient and reaction temperature, has been found where porous layers, as presented in Figs. 8 and 9, can be formed. At lower temperatures, the layers are porous and have a nonuniform film thickness. At higher reaction temperatures, the layers have a more columnar structure, as illustrated in Fig. 10.

Temperature differences of more than ~ 20 K only lead to loose powder deposits.¹³ This implies that the interconnection of the precipitated particles by a heterogeneous reaction can occur only on the particles that are near the surface of the growing layer. No more heterogeneous reaction will occur on the particles inside the growing porous layer, because of depletion of the reactants. This depletion is inevitable, as the molecules diffuse within the growing porous layer and adsorb onto the internal surface of the layer. Thus, the interconnection of the precipitated particles by the heterogeneous reaction cannot keep pace with the particle precipitation rate, which results in a loose powder deposit. Moreover, the particles that are formed in the gas phase at relatively high reaction temperatures become agglomerated in the gas phase.^{13,16,34} Consequently, agglomerates instead of individual particles will be deposited. This will result in the formation of a deposit that is more fluffy than the deposits formed at relatively low reaction temperatures, and the interconnection of the particles to form a mechanically stable

Fig. 6. SEM micrograph of a cross section of a TiN layer with virtually equiaxed grains, which is typical for layers grown with a small temperature difference. In this case, the reaction temperature was 923 K and the temperature difference was 3 K.

Fig. 7. SEM micrograph of a TiN layer, as shown in Fig. 6.

layer will be much more difficult. Therefore, for a successful synthesis of porous coherent layers, one can expect that the particles should not be agglomerated in the gas phase.

A decrease in the gas permeability of the samples existed after deposition of a layer by the PP-CVD process. The decrease in permeability is affected mainly by the type of microstructure of the deposited layer. The permeability of the substrates with the loose powder deposits remained unchanged. The relative permeability of the substrates with coherent porous layers varied over a range of 0.4–0.7 at an average pressure of 70 kPa. The relative permeability of the samples with a dense layer was always <0.2 at an average pressure of 70 kPa. In some cases for dense layers, the relative permeability was even <0.001 at 70 kPa. Illustrative examples of the argon permeability of an untreated substrate, a substrate with a coherent porous layer, and a substrate with a dense layer are presented in Fig. 11.

Notably, the control of the temperature gradient in the reactor is very delicate. Besides the choice of the reactants, the temperature gradient has a very strong effect on the final microstructure. Small temperature changes can have a dramatic effect on the microstructure. Therefore, special care should be taken to control the temperatures within the reactor.

Fig. 9. SEM micrograph of a porous TiN layer, as shown in Fig. 8.

VI. Conclusions

In all cases, the deposits consist of crystalline TiN. If no cooling is present, the experimental configuration is identical to a conventional CVD reactor, and the contribution of the particles to the growth rate is minimal, because the diffusion rate of the particles in the gas phase is very small.

A complete listing of variables used in this paper is given in Table III. We have observed dense layers with faceted columnar grains, and no individual particles in the layers have been observed under these conditions. The observed growth rates of the layers are a factor of >10 higher than the expected growth rate of TiN layers using TiCl_4 , N_2 , and H_2 . Thus, the growth rate must be determined by the combination of TiCl_4 , NH_3 , N_2 , and H_2 . The grains of the layers have a tendency to become larger at higher reaction temperatures. For the reaction temperature dependence, with respect to the growth rate, no Arrhenius-type behavior has been observed. The growth rate on the substrate is determined by a combination of mass transfer to the substrate, surface reactions, and conversion of reactants in the gas phase for the formation of TiN particles, which is detrimental for the growth rate at the surface. A small temperature difference of only a few degrees Kelvin has a considerable

Fig. 8. SEM micrograph of a cross section of a porous TiN layer, which is typical for layers grown at intermediate temperature gradients in the gas phase. This layer is grown at a reaction temperature of 973 K and at a temperature difference of 16 K.

Fig. 10. SEM micrograph of a cross section of a porous TiN layer, which is typical for layers grown at intermediate temperature gradients and a relatively high reaction temperature. This layer is grown at a reaction temperature of 1173 K and at a temperature difference of 8 K.

Fig. 11. Argon permeability as a function of the average pressure over the substrate for three different substrates ((x) untreated, (+) porous layer, and (□) dense layer).

effect on the microstructure of the layers. The columnar structure disappears, and the average grain size is considerably smaller. Apparently, the introduction of a small temperature difference favors renucleation at the surface; as a result, virtually equiaxed grains are formed. Conceivably, the deposition of small particles, which serve as nuclei, is responsible for the change in microstructure. An additional increase in the temperature gradient results in an increase in the particle deposition rate. Consequently, this results in the formation of a porous layer. The synthesis of such a mechanically stable porous layer of material with a poor sinterability is unique. To our knowledge, no other type of synthesis process is capable of making porous TiN layers at such a low temperature. Temperature differences of more than ~ 20 K only lead to loose powder

deposits. This implies that the interconnection of the precipitated particles by the heterogeneous reaction cannot keep pace with the particle precipitation rate, which resulted in a loose powder deposit.

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Table III. List of Symbols

Symbol	Definition
A, B, C	Constants for slip-coefficient formula
C_m	Momentum-exchange coefficient
C_s	Slip coefficient
C_r	Loyalka's coefficient
C_{th}	Thermal-slip coefficient
d_p	Particle diameter (m)
D_p	Particle-diffusion coefficient (m ² /s)
g	Acceleration due to gravity (m/s ²)
k	Boltzmann constant (J/K)
k_g	Thermal gas conductivity (J·(m·s·K) ⁻¹)
k_p	Thermal particle conductivity (J·(m·s·K) ⁻¹)
κ	Thermophoretic constant
Kn	Knudsen number
T	Temperature (K)
v_D	Diffusional particle velocity (m/s)
v_t	Thermophoretic particle velocity (m/s)
v_s	Terminal settling velocity (m/s)
x	Characteristic diameter (m)
λ	Mean free path (m)
μ	Gas viscosity (kg·(m·s) ⁻¹)
ν	Kinematic gas viscosity (m ² /s)
ρ_p	Particle density (kg/m ³)

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