
Gas-to-Particle Conversion in the Particle Precipitation–Aided Chemical Vapor Deposition Process I. Synthesis of the Binary Compound Titanium Nitride

J. P. Dekker,^{1,2,*} P. J. van der Put,¹ H. J. Veringa,² and J. Schoonman¹
¹Laboratory for Applied Inorganic Chemistry, Delft University of Technology, Julianalaan 136, 2628-BL Delft, The Netherlands; and ²ECN, Energy Research Foundation, Westerduinweg 3, 1755 ZG Petten, The Netherlands

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 at an elevated temperature, and particles are deposited on a cooled substrate. The synthesis of titanium nitride (TiN), using titanium tetrachloride vapor (TiCl_4), nitrogen (N_2), ammonia (NH_3), and hydrogen (H_2), by the PP-CVD process is studied. TiN is formed by a heterogeneous reaction, using TiCl_4 , N_2 , H_2 , whereas simultaneously TiCl_4 and NH_3 react to form an aerosol. The activation energy of this homogeneous reaction is on the order of 100 kJ/mol. The powder formation process is determined by the dissociation of a titanium containing intermediate species. At low temperature differences between substrate and gas phase (i.e., < 2 K), only dense columnar microstructures, with growth rates of around 20 $\mu\text{m}/\text{h}$, are observed. At these temperature differences no particle deposition is observed. The layers are formed by a molecular diffusion controlled CVD growth mechanism. Porous coherent layers are found in experiments, where inter-

mediate temperature differences are applied (i.e., approximately 2–10 K). The observed interconnection of the particles has to originate from a heterogeneous reaction. Apparently, under these conditions the heterogeneous reaction is fast enough, with respect to the particle precipitation rate, to interconnect the precipitated particles. A further increase in temperature difference between the susceptor and the gas phase 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. To obtain uniform coherent porous layers two separate reaction mechanisms are required under the same experimental conditions. There should be a homogeneous reaction in the gas phase as well as a heterogeneous reaction, which is controlled by surface kinetics, in order to interconnect precipitated particles to obtain a coherent porous layer. Porous ceramic layers can be formed as long as the particle precipitation rate is slow enough with respect to the heterogeneous reaction rate.

INTRODUCTION

Chemical vapor deposition (CVD) is a well-known technique to deposit thin films of solid materials (Spear and Cullen, 1990). Gas phase reactants, diluted in a carrier gas, are introduced in a hot-wall reactor, where the reactants absorb on a substrate. These absorbed reactants will

react to form a solid film on the substrate. Typically materials formed are refractory metals, semiconductors, and inorganic materials (Pierson, 1992).

In general, powder formation in the gas phase in a CVD process should be avoided, because this will deplete the reactants necessary for the heterogeneous (CVD) reaction considerably, leading to a nonuniform film thickness. In addition, powder in the gas phase can diffuse to-

*To whom correspondence should be addressed.

wards the substrate, and deposit on the substrate. Often, this will lead to an undesirable microstructure of the film.

However, under certain experimental conditions powder formation can be used to our advantage, in that the hot-wall CVD process can be modified to control the microstructure of the layer by 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 deposited on a cooled substrate by thermophoresis, i.e., diffusion in a thermal gradient due to the difference in kinetic energy of the gas molecules which causes the particles to move from the warmer to the colder side in the reactor (Fuchs, 1964).

Particle precipitation on the substrate will result in a loose powder deposit, which has a poor mechanical stability. In order to obtain a coherent layer the powder deposit should be sintered, or a heterogeneous reaction (i.e., CVD) 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 Figure 1.

Particle deposition in a CVD process has been proven to be successful in the modified CVD (M-CVD) process (MacChesney and Digiovanni, 1990), which originally has been developed to deposit doped silica in a quartz preform for the optical fibre production. The PP-CVD process is very similar to the M-CVD process. In M-CVD the relative cold reactor wall is used as a substrate, whereas in PP-CVD a separate (cooled) substrate is introduced into the reactor. The PP-CVD process has been introduced by the group of Komiyama. They have deposited several oxides and aluminium nitride by PP-CVD (Osawa and Komiyama, 1986; Shimogaki and Komiyama, 1986). Dense to

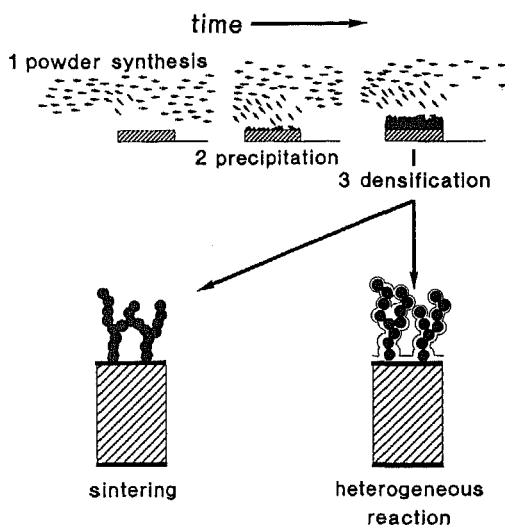
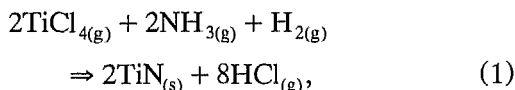


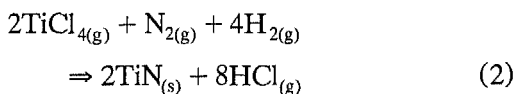
FIGURE 1. The principle of the three stages of the PP-CVD process.

highly porous layers were obtained depending upon experimental conditions.

This report will discuss the synthesis of titanium nitride (TiN) by the PP-CVD process. TiN has been chosen to investigate the possibilities of the PP-CVD process, because it is possible to synthesize TiN aerosols as well as TiN layers at the same reaction temperature and reactor pressure 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), ammonia (NH_3), and hydrogen (H_2) (Dekker et al., 1991),

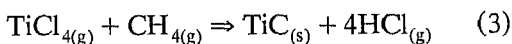


whereas TiCl_4 , H_2 and nitrogen (N_2) can only react on a surface to form TiN (Nakanishi et al., 1990).



The pores between the precipitated particles, which originate from the first reaction, should be entirely or partly filled by the solid deposit of the second reaction. It is expected that the layers formed have different porosities, depending on the ratio of particle precipitation rate over heterogeneous reaction rate. The amount of particles deposited is determined by particle concentration in the gas phase, and driving force for particle deposition (i.e., thermophoresis), whereas the heterogeneous reaction is governed by reactant concentration, and reaction rate constant. The particle concentration in the gas phase as well as the heterogeneous reaction rate constant are temperature dependent.

In principle, a variety of compounds, such as nitrides, carbides, oxides, and metals, can be deposited using this technique, provided that the gas phase reactants can serve as a source for a homogeneous reaction as well as for a heterogeneous reaction. Moreover, a variety of composites can be made by this technique as long as the formation of one solid will not be inhibited by the reactants or volatile products of the formation of the other solid. In this case, one has to separate the heterogeneous reaction and the homogeneous reaction to make two different solid phases. For example, it should be possible to make a composite layer of TiN, and titanium carbide (TiC). The synthesis of a TiN aerosol, concordant to reaction (1), can be combined with a heterogeneous reaction to form TiC using TiCl_4 , and methane (CH_4) [Aggour et al., 1975]



resulting in a composite layer of TiN particles in a TiC matrix. However, experiments are necessary to verify whether it is indeed possible to make such a composite, because it is well known that a combination of two reaction mechanisms can be

have differently than the sum of the two individual reaction mechanisms.

Formation of layers of different materials by a heterogeneous (CVD) reaction is well documented by Pierson (1992). The criteria for the synthesis of a solid in the gas phase for a given chemical mixture are not well understood. However, as a first approximation, the formation of a solid seems to be determined by the thermodynamic equilibrium constant. Kato et al. (1981) observed a tendency between powder formation (of nitrides and carbides) and the equilibrium constant. In general, a homogeneous reaction will only occur if the equilibrium constant of the reaction is high enough. This technique of making dense to porous layers offers a variety of applications, e.g., thin porous layers can be used for catalysis, membranes, or SOFC components as discussed by Van Dieten et al. (1993).

We have deposited TiN on porous alumina tubes in a cylindrical laminar flow reactor. Tubular porous alumina substrates are used in order to be able to measure the degree of porosity of the deposited layer by gas permeability measurements (Dekker et al., 1992). The influence of the reaction temperature on particle size, particle concentration in the gas phase as well as the influence of the reaction temperature, temperature gradient on microstructure, and porosity of the deposit have been investigated. Furthermore, the influence of the individual reactants on the process will be discussed.

EXPERIMENTAL ASPECTS

Synthesis of TiN

A schematic drawing of the gas distribution system of the CVD apparatus is given in Figure 2. Hydrogen is bubbled through heated liquid TiCl_4 to saturate the hydrogen stream with reactant vapor. The TiCl_4 concentration in the H_2 stream is calculated assuming the TiCl_4 vapor pressure

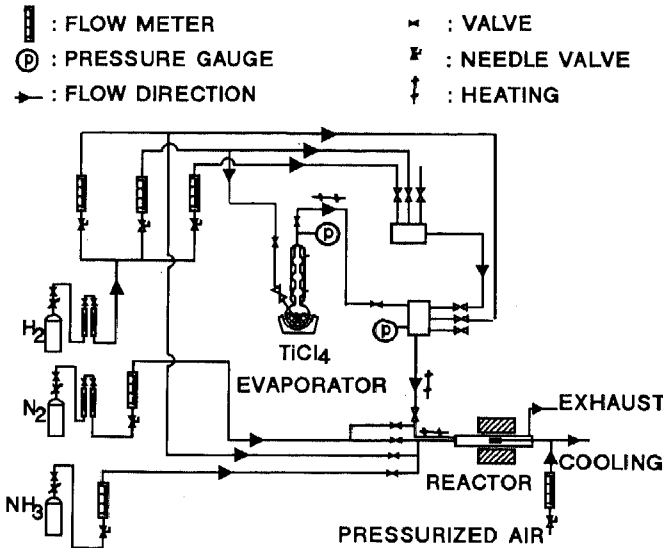


FIGURE 2. A schematic drawing of the gas distribution system of the CVD apparatus.

to be in equilibrium with the TiCl_4 liquid. The deviation in TiCl_4 gas concentration is $<10\%$ of the calculated value, as checked by monitoring the volume decrease in time of the TiCl_4 liquid. A schematic drawing of the cylindrical reactor (inner diameter 50 mm and length 700 mm) in a three-zone resistance furnace is presented in Figure 3. A nozzle is used for a separated introduction of the reactants. H_2 and NH_3 flow through the inner side of this nozzle, whereas, TiCl_4 , H_2 , and N_2 are introduced at the entrance of the reactor outside the nozzle. Thus, the reactants for homogeneous reaction (i.e., NH_3 , H_2 , and TiCl_4) are mixed in the high

temperature zone, and the reactants for heterogeneous reaction (i.e., N_2 , H_2 , and TiCl_4) are introduced at the entrance of the reactor. The susceptor for positioning the substrate consists of a dead-end hollow quartz tube. The cooling of the susceptor is regulated by an externally controlled flow of pressurized air. The axial position of the susceptor can be varied. It is positioned at the outlet of the nozzle in the middle of the reactor during the PP-CVD experiments.

Four sets of experiments have been carried out. Experimental sets 1A and 1B comprise experiments as a function of reaction temperature and temperature gra-

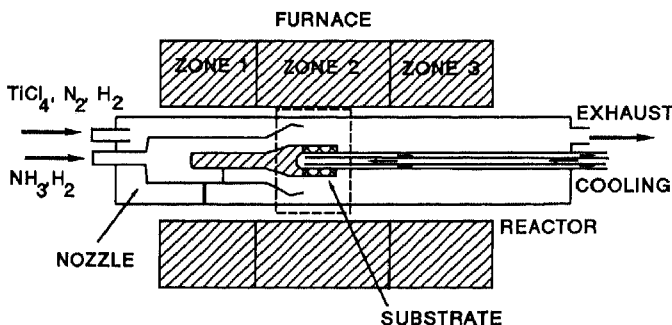


FIGURE 3. A schematic drawing of the cylindrical reactor in a three-zone resistance furnace.

dient for the synthesis of TiN layers by the PP-CVD process. Experimental sets 2A and 2B comprise experiments for the characterization of the powder formation in the gas phase. The experimental conditions are summarized in Tables 1 and 2.

A comparison between the experiments in set 1A and 1B can give information about the influence of a heterogeneous reaction, involving N_2 , on the precipitated particles. Because in set 1A a possible heterogeneous reaction can originate from the $TiCl_4$, N_2 , NH_3 , and H_2 reactants, whereas in set 1B a possible heterogeneous reaction can only originate from the $TiCl_4$, NH_3 , and H_2 reactants. The reaction temperature is varied from 923 to 1173 K, and the temperature difference between gas phase and substrate is varied from 0 to 36 K. Temperatures are measured with chromel-alumel thermocouples as illustrated in a blown up part of the center of the reactor in Figure 4. The reaction temperature is measured at the end of the gas distribution nozzle (A1 in Figure 4). The temperature of the gas phase is measured 15 mm above the substrate (A2 in Figure 4), and the temperature of the substrate is measured with a thermocouple mounted on the surface of the substrate (A3 in Figure 4). The elec-

tromotive force of the thermocouples is recorded with an accuracy of 0.01 mV, i.e., equal to an uncertainty of 0.5 K in the calculated temperature. The linear gas velocity in the inside of the nozzle, and the linear gas velocity on the outside of the nozzle are kept equal in order to avoid disturbances in the laminar flow. The layers are deposited on tubular porous alumina substrates. These substrates are slid over the cooled susceptor. The substrates have an inner diameter of 9 mm, an outer diameter of 15 mm, a length of 15 mm, an average pore size of 4.5 μm , and a porosity of 40%.

As mentioned above, the particle concentration in the gas phase is of prime importance to the PP-CVD process. It is very difficult to obtain in situ information concerning the particle formation process. Therefore, two sets of model experiments (2A and 2B) have been carried out in the CVD reactor to obtain information concerning the kinetics of the homogeneous reaction. In this case the susceptor is slid towards the third zone of the furnace (Figure 3) to rule out heterogeneous reactions. The third heating zone is kept at a relative low temperature, so the heterogeneous reaction rate is negligible. Thus, the deposited mass on the substrate can

TABLE 1. Process Parameters for the Synthesis of TiN by PP-CVD

		Set 1A	Set 1B	
Inside	NH_3 flow	17	140	$\mu mol/s$
	H_2 flow	0.7783	0.64	mmol/s
	total flow	0.78	0.78	mmol/s
Outside	$TiCl_4$ flow	35	35	$\mu mol/s$
	N_2 flow	0.49	0	mmol/s
	H_2 flow	0.49	0.98	mmol/s
	total flow	1.015	1.015	mmol/s
Reaction time		3600	3600	s
Reaction temperature		923-1173	900-1300	K
Temperature difference		0-36	0-36	K
between substrate and gas				
phase				
Reactor pressure		1×10^5	1×10^5	Pa

TABLE 2. Process Parameters for the Synthesis of TiN Powder

		Set 2A	Set 2B	
Inside	NH ₃ flow	0,17	0-140	μmol/s
	H ₂ flow	0,78, 0,7783	0,39-0,20	mmol/s
	total flow	0,78	0,39	mmol/s
Outside	TiCl ₄ flow	35	7-14	μmol/s
	N ₂ flow	0,49	0	mmol/s
	H ₂ flow	0,49	0,47-0,38	mmol/s
	total flow	1,015	0,54	mmol/s
Reaction time		3600	1800	s
Reaction temperature		923-1173	900-1300	K
Temperature difference between substrate and gas phase		65	0-65, 65	K
Reactor pressure		1 × 10 ⁵	1 × 10 ⁵	Pa

only originate from the powder present in the gas phase. In order to harvest enough powder for further analysis a larger susceptor is used than in the PP-CVD process. The temperature of the susceptor was kept constant at 800 K. This temperature was 65 K lower than the gas phase. The reaction temperature at the outlet of the nozzle was varied from 900 to 1300 K. A comparison between the experiments in set 2A, and set 2b provides information about a possible heterogeneous reaction, involving N₂, on the powder in the gas phase.

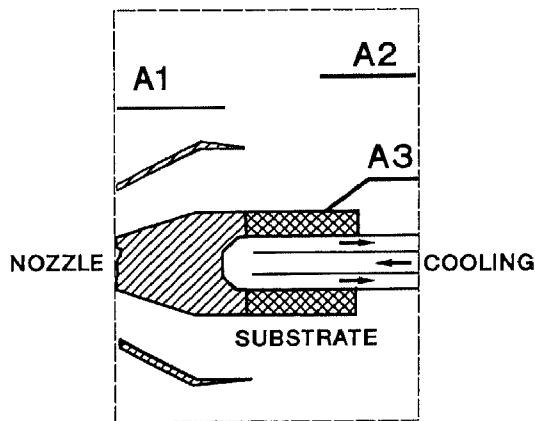


FIGURE 4. A schematic drawing of a blown up part of the center of the reactor.

Particle Analysis

Particle sizes are obtained by quasi-elastic light-scattering analysis (QELS) (Dahneke, 1983), scanning electron microscopy (SEM) analysis, (TEM) transmission electron microscopy analysis, and sedimentation field flow fractionation analysis (SF³) (Scarlett et al., 1988). In QELS or photon correlation spectroscopy, the autocorrelation function of the intensity of laser light, scattered by particles in a liquid suspension is calculated. This power spectrum of scattered light allows determination of the particle diffusion coefficient, which can easily be correlated to a particle diameter. In SF³ a suspension flows through a force field in a centrifuge. The mass distribution of the dispersed powder is exponentially distributed in the field as a result of the counteracting combination of Brownian diffusion, and centrifugal force. Owing to this induced mass distribution within the laminar flow, the retention time of particles in the apparatus is a function of their weight.

The TiN powder collected on the susceptor in the experimental sets 2A and 2B, where the susceptor is positioned at the end of the reactor in the third zone of the furnace, is suspended in an aqueous ammonia solution (0.002 M) with a powder concentration of typically 1-2 weight

percent. This suspension is fractionated by SF_3 . The fractionated suspensions are collected in optical cuvetts, and these suspensions were analyzed by QELS. TEM grids are dipped in these suspensions for SEM, and TEM analysis.

RESULTS AND DISCUSSION

The reaction of $TiCl_4$, N_2 , and H_2 did not result in any TiN powder formation within the reaction temperature region from 923 to 1173 K. Usually, these conditions are used in conventional CVD to deposit thin layers on substrates (Nakanishi et al., 1990). Therefore, it is not surprising that TiN is only observed on the reactor wall on the outside of the nozzle, and on the susceptor. Growth rates of maximal a few micrometers per hour are found. Thus, a relatively small reaction rate constant determines the growth rate. The high apparent activation energy of approximately 100 kJ/mol of this process indicates that the CVD reaction of TiN is controlled by surface kinetics (Nakanishi et al., 1990), and not by diffusional mass transport in the gas phase, because a growth rate limited by diffusional mass transport has only a small temperature dependence of typically 10–20 kJ/mol (Spear and Dirckx, 1990).

Hence, addition of NH_3 is necessary for powder formation. Powder formation, and heterogeneous deposits near the nozzle outlet are observed for all model experiments. In all cases the collected powder consists of crystalline TiN, as identified by XRD analysis. The particle sizes are obtained from TEM, SEM, QELS, and SF_3 analyses. In the temperature region from 900 to 1173 K the primary particle size varies between 100 and 200 nm, as identified by TEM analysis. The particle size appears to be unaffected by the reactant concentrations. Only at low concentrations of $TiCl_4$ and NH_3 the particle size tends to be smaller. A particle

size distribution, typical for these experiments, is shown on the TEM micrograph in Figure 5. The mean mass diameters from SF_3 analysis of the suspended powders are typically between 200 and 300 nm. The particle diameters from QELS analysis of the fractionated suspensions by SF_3 are comparable to the diameters obtained from SF_3 analysis. From these results, it can be concluded that the primary particle size is only a weak function of the reaction temperature, and that it is not likely that agglomerates in the gas phase are formed within the reaction temperature region from 923 to 1173 K. Thence, the agglomerates found on the TEM micrographs have to be a result of the preparation method for TEM samples. Agglomeration in the suspension droplet on the TEM grid occurs during evaporation of the medium. A significantly smaller particle size is found at higher reaction temperatures. The primary particle size is typically 10 nm at reaction temperatures higher than 1200 K. A possible mecha-

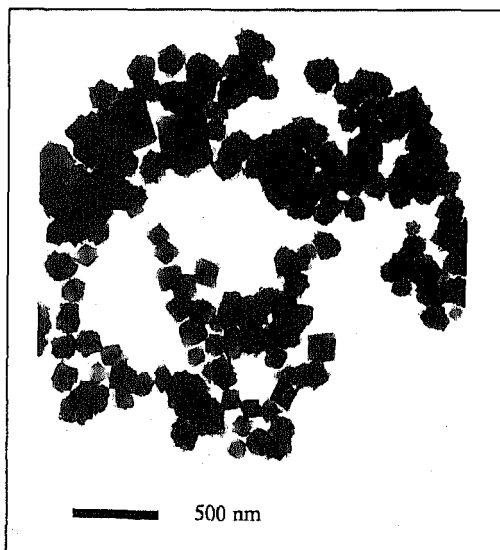


FIGURE 5. TEM micrograph of TiN powder, typical for synthesis experiments within the temperature region from 923 to 1173 K.

nism for this sudden decrease in particle size, with increasing reaction temperature, will be discussed in a forthcoming paper by Dekker et al. (1993). These high reaction temperatures are not desirable for the synthesis of coherent layers by the PP-CVD process, as will be shown.

The driving force for powder collection on the susceptor in the reactor is thermophoresis. The thermophoretic velocity (v_t) is proportional to the temperature gradient (Simpkins et al., 1979)

$$v_t = -K \left(\frac{\nu}{T} \right) \nabla(T) \quad (4)$$

where K is a constant for a given particle size, ν the viscosity of the gas, and T the temperature. In this case, where particles have a Knudsen number on the order of one, K is only a weak function of the particle diameter (Talbot et al., 1980).

For the model experiments of set 2B an increase in precipitation rate is observed, with increasing temperature difference between susceptor and gas phase, for temperature differences of > 5 K. This indicates that thermophoresis is indeed the driving force for particle deposition. The observed nonlinear increase in precipitation rate, with increasing temperature difference, is a consequence of the nonlinear temperature gradient present in the gas phase. In principle, the temperature gradient can be expressed as a function of the Reynolds number, Prandtl number, and reactor geometry (Incropera and DeWitt, 1981).

For the other model experiments, at a given concentration of TiCl_4 , NH_3 , and H_2 , the temperature of the susceptor, and the temperature of the gas phase above the susceptor are kept constant. Hence, the amount of powder harvested has to be proportional to the particle concentration in the gas phase. The weight change as a function of the temperature is presented in an Arrhenius plot in Figure 6, where a NH_3 excess of 10 with respect to the

TiCl_4 reactant is used. The gas-to-particle conversion shows an Arrhenius-like behavior within the temperature region from 923 to 1173 K. The apparent activation energy of the powder formation process is 94 kJ/mol. These experiments have been performed, at different ratios of NH_3 over TiCl_4 , in the temperature region from 923 to 1023 K. In this case the apparent activation energy varies between 89 and 96 kJ/mol, provided that there is at least a fivefold excess of NH_3 with respect to TiCl_4 . The uncertainty in the obtained activation energies are typically between 5 and 10 kJ/mol. Therefore, it is concluded that the activation energy is independent of the ratio NH_3 over TiCl_4 . No clear temperature dependence is observed for the experiments, where an excess of TiCl_4 with respect to NH_3 is used (i.e., a ratio of NH_3 over TiCl_4 of < 0.5). In this case the conversion to TiN appears only to be determined by the absolute NH_3 flux, and not by a chemical reaction mechanism. However, the conversion to TiN seems to be determined by a chemical reaction mechanism, if NH_3 is in excess with respect to the TiCl_4 concentration. Hence, the homogeneous reaction might be determined by the dissociation of a titanium containing intermediate species. It should be noted that the total conversion of TiCl_4 is unknown, because the diffusional loss of TiCl_4 in the reactor, to form TiN by a heterogeneous reaction, is unknown. Because of this uncertainty the actual activation energy of the homogeneous reaction can not be determined. However, diffusional mass transport processes have a relative small temperature dependency, thus it is expected that the actual activation energy of the homogeneous reaction is on the order of 100 kJ/mol.

From these observations one would expect it to be possible to form coherent layers by the PP-CVD process at low reaction temperatures using only TiCl_4 , NH_3 , and H_2 as reactants (experimental

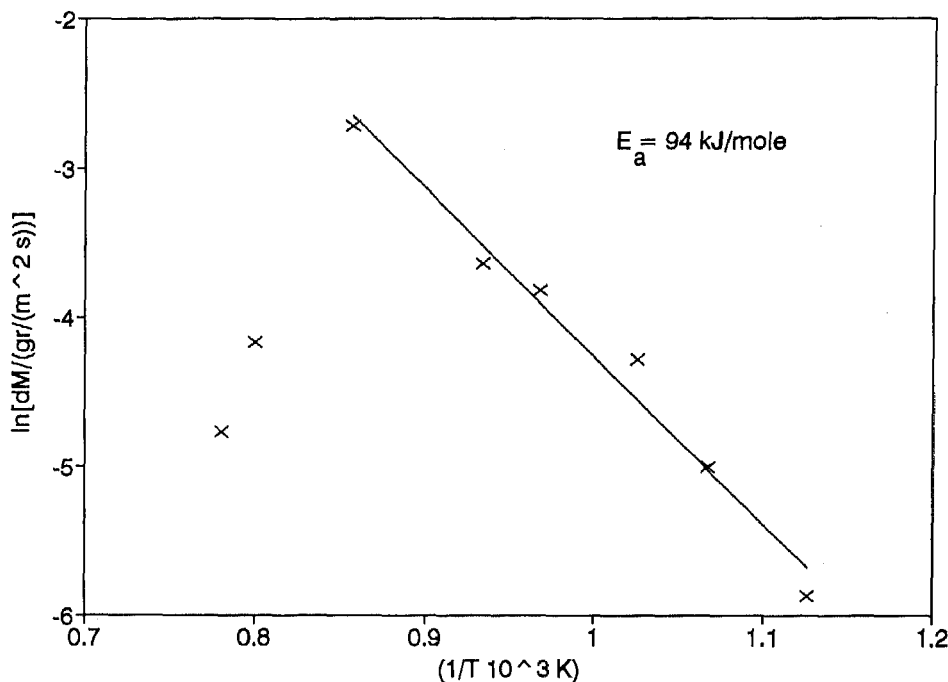


FIGURE 6. Arrhenius plot of collected TiN powder on cooled susceptor of model experimental set 2B, where a ratio of NH_3 over $TiCl_4$ of 10 is used.

set 1B), because the conversion of $TiCl_4$ to TiN powder is low at these reaction temperatures. Hence, enough reactant should be present to form TiN by a heterogeneous reaction. However, under these conditions only coherent layers are observed at the tip of the susceptor near the nozzle outlet. This is a consequence of the high reactivity of NH_3 with $TiCl_4$, which will result in a depletion of the $TiCl_4$ reactant. Similar results have been reported by the group of Komiyama. Due to the high reactivity of their reactants they could not prevent a strong depletion of the reactant, which resulted in a non-homogeneous deposit. To avoid a diffusional loss, the heterogeneous reaction should be limited by (relatively slow) surface kinetics instead of by (relatively fast) diffusional mass transport.

An excess of $TiCl_4$ with respect to NH_3 is used to prevent depletion of $TiCl_4$ in the gas phase for the experiments in set 1A. At low temperature differences between substrate and gas phase (i.e., < 2 K) only dense columnar microstructures, with a growth rate of typically $20 \mu\text{m/h}$, are observed, as can be seen in Figure 7. No individual particles in the layers have been observed. Hence, the driving force for particle movement is not high enough to induce particle precipitation on the substrate under these conditions. The grains of the layer have a tendency to become larger at higher reaction temperatures. We believe that these types of microstructures originate from a typically molecular diffusion controlled CVD growth mechanism. Similar columnar microstructures have been found for diffu-

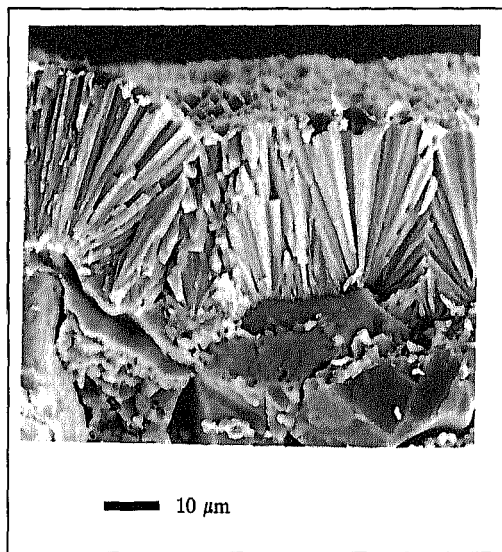


FIGURE 7. SEM micrograph of a cross section of a diffusion controlled TiN layer, which is typical for layers grown at low temperature gradients in the gas phase. This layer is grown at a reaction temperature of 973 K and a temperature difference of 2 K (the temperature of the gas phase was measured 10 mm above the substrate), using the experimental conditions in set 1B.

sion limited growth of other binary compounds, such as the growth of β -SiC using TMS (Cheng et al., 1987). A twin plane re-entrant edge (TPRE) mechanism was proposed to account for this growth of CVD β -SiC. In this mechanism step growth is facilitated by the presence of corners at the intersection of twin planes.

We suggest that the TPRE mechanism accounts for the growth of TiN, and that the mixture of N_2 , and NH_3 has to be responsible for this growth mechanism, because the microstructure observed in combination with the high growth rate is not found for the individual reactions, i.e., those involving NH_3 for a heterogeneous reaction concordant to reaction (1), or N_2 in reaction (2). Apparently, the growth rate limitation present in the formation of TiN, using $TiCl_4$, N_2 , and H_2 , which re-

sults in a growth rate of a few $\mu m/h$, disappears after an addition of NH_3 , which results in a growth rate of typically 20 $\mu m/h$. Before a rationale for this change in growth mechanism can be given some of the crystal growth characteristics during CVD have to be discussed.

CVD crystal growth by this TPRE mechanism can be limited by initiation of a new step on the crystal planes, plane growth, or diffusion in the gas phase. Plane growth occurs perpendicular to the crystal growth direction. Film growth, which is determined by surface kinetics, is limited by a slow nucleation rate on a favorable site on the crystal plane (i.e., in a groove at the intersection of two twin planes in the case of TPRE mechanism), or a low plane growth rate. The film growth rate is determined by the nucleation rate on the planes if it is assumed that the nucleation rate is slow with respect to the plane growth rate for a given chemical system. After an addition of a small amount of a species which is more *reactive* than the species already present, the nucleation rate on the planes might increase, and plane growth or diffusion in the gas phase will become rate limiting. Thus, addition of only a small amount of an extra species can enhance the film growth rate considerably, because the rate-determining step of the layer growth mechanism has been changed.

A possible rationale for the observed change in the characteristics of the TiN layers can be given similar to the discussion given above. The heterogeneous growth of TiN, using $TiCl_4$, N_2 , and H_2 , is limited by surface kinetics. This surface limitation is a consequence of a slow nucleation rate on the crystal plane, or a slow plane growth rate. For example, if it is assumed that the nucleation rate is slow with respect to the plane growth rate for the chemical system without NH_3 , then, after an addition of NH_3 , the nucleation rate on the planes will increase, and plane

growth or diffusion in the gas phase will become rate limiting. From the observed type of microstructure, as discussed above, it has to be concluded that the growth is limited by diffusional mass transport, and not by plane growth.

A further increase in temperature difference between susceptor and gas phase will result in particle deposition, which will give in a different microstructure. This is found for experiments, where intermediate temperature differences are applied (i.e., $\sim 2\text{--}10$ K). Mechanically stable porous layers are formed for the experiments in set 1A, where the reaction temperature was kept between 923 K and 1023 K. At higher reaction temperatures only loose powder deposits have been observed. The microstructure of a porous layer, typical for these experiments, can be seen in Figure 8. The primary particle sizes in these kind of layers are similar to the particle sizes, obtained from TEM analysis, formed in the model experiments, where the same reactant concentrations and reaction temperatures are used. The observed interconnection of the particles has to 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. To our knowledge no other type of CVD process is capable of making this type of porous layers.

A further increase in temperature difference between the susceptor and the gas phase only leads to loose powder deposits, as can be seen in Figure 9. These results are similar to the experiments of set 1B, where no N_2 was used. This implies that the interconnection of the precipitated particles by the heterogeneous

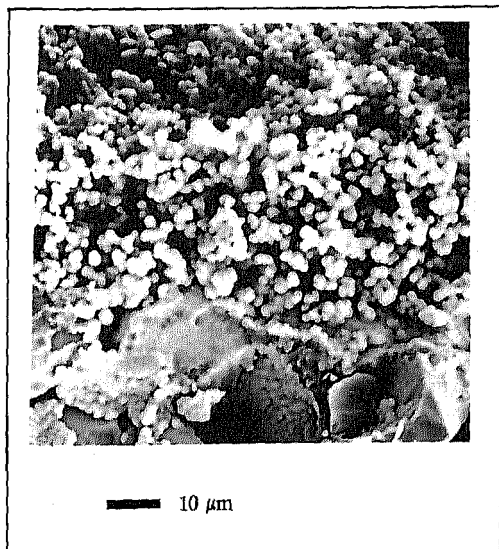


FIGURE 8. SEM micrograph of a cross section of a porous TiN layer, which is typical for layers grown at intermediate temperature gradients in the gas phase. This layer is grown at a reaction temperature of 1023 K and at a temperature difference of 3 K, using the experimental conditions in set 1B.

reaction can only take place as long as the particles are near the surface of the growing layer. No further heterogeneous reaction will occur on the particles inside the growing porous layer due to depletion of the reactants. This depletion is inevitable as the molecules diffuse within the growing porous layer, and absorb on the internal surface of the layer. Thus, the interconnection of the precipitated particles by the heterogeneous reaction can not keep up with the particle precipitation rate, which results in a loose powder deposit. It should be noted that 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

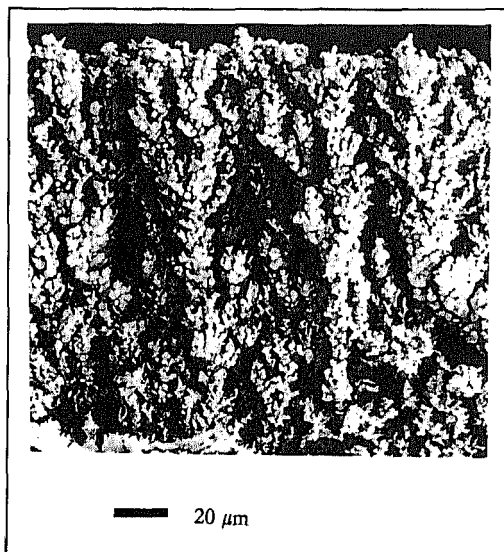


FIGURE 9. SEM micrograph of a cross section of a loose powder deposit, which is typical for layers grown at high temperature gradients in the gas phase. This layer is grown at a reaction temperature of 1023 K using the experimental conditions in set 1B.

control the temperatures within the reactor. In principle, another driving force for particle deposition such as electrophoresis can be considered. Electrophoretic velocity of the particles is probably better to control under the conditions which are typical for such a PP-CVD process. However, a disadvantage is a possible change in electric field during deposition, due to the deposition of a material with a different electrical conductivity than the substrate.

CONCLUSIONS

The reaction between TiCl_4 , N_2 , and H_2 results in a layer, formed by a heterogeneous reaction. The apparent activation energy of this process is ~ 100 kJ/mol. Thus, the film growth rate is determined by surface kinetics. An addition of NH_3

will enhance the growth rate considerably. The growth rate of these kind of layers is determined by diffusion of some gaseous species, as long as the precipitation of particles on the substrate can be neglected. This particle precipitation can be induced by applying a temperature gradient in the gas phase. This results in the formation of porous coherent layers, as long as the temperature difference between substrate and gas phase is < 10 K. The powder formation in the gas phase is a result of the reaction between TiCl_4 , NH_3 , and H_2 . The activation energy of this homogeneous reaction is on the order of 100 kJ/mol. From the experiments as a function of the reactant concentrations it is concluded that the powder formation process is determined by the dissociation of a titanium containing intermediate species.

In principle, the PP-CVD process is a suitable method for the synthesis of thin porous layers of ceramics. To obtain uniform coherent porous layers two separate reaction mechanisms are required under the same experimental conditions. There should be a homogeneous reaction in the gas phase as well as a heterogeneous reaction, which is controlled by surface kinetics. It is expected that a porous ceramic layer can be formed as long as the particle precipitation rate, controlled by thermophoresis or electrophoresis, is slow enough with respect to the heterogeneous reaction rate, because the interconnection of the precipitated particles by the heterogeneous reaction can only take place as long as the particles are near the surface of the growing layer. No further heterogeneous reaction will occur on the particles inside the growing porous layer due to depletion of the reactants. This depletion is inevitable as the molecules diffuse within the growing porous layer, and absorb on the internal surface of the deposited layer. Thus, the interconnection of the precipitated particles by the hetero-

geneous reaction can not keep up with the particle precipitation rate.

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