

Conversion Efficiency of Alkoxide Precursor to Oxide Films Grown by an Ultrasonic-Assisted, Pulsed Liquid Injection, Metalorganic Chemical Vapor Deposition (Pulsed-CVD) Process

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Polycrystalline coatings of an oxide, with a columnar grain morphology, were grown on metal substrates from metalorganic precursors using the pulsed-CVD process. In a model study, films of the rutile phase of titanium dioxide were grown on nickel by thermal decomposition of titanium isopropoxide. Growth rates of up to 0.3 $\mu\text{m}/\text{min}$ were obtained with conversion efficiencies (mole oxide per mole precursor) approaching 100%. The high growth rates and conversion efficiencies portend the application of this method for the manufacture of films and coatings on large surface areas, as, for example, required in the deposition of zirconium dioxide on nickel-based superalloys to serve as thermal barrier coatings on turbine blades.

I. Introduction

EARLIER work from this laboratory has demonstrated that a simple pulsed-CVD method, illustrated schematically in Fig. 1, can be used to grow high-quality heteroepitaxial films of LiTaO_3 ¹ and TiO_2 ^{2,3} on sapphire from a single source of metalorganic precursors. The use of pulsed liquid injection with an ultrasonic nozzle is a unique feature of this method. It allows excellent control of the injection rate of the precursor while maintaining a differential between the ambient pressure of the liquid and a low pressure in the reactor. The ultrasonic nozzle nebulizes the injected liquid, which then vaporizes completely before arriving at the hot substrate, where it is decomposed to the oxide. In this way, molecular deposition is achieved. The parameters of the pulsed injection, particularly the waiting period between pulses, permits a marriage between the injection rate and the reaction kinetics for decomposition and crystallographic growth to achieve high-quality single-crystal thin films of oxides at relatively low temperatures. The thin films of LiTaO_3 grown by this method¹ have low optical absorption and nonlinear optical properties that approach the handbook values for single-crystal LiTaO_3 . Pulsed-CVD may have further advantages to the spray pyrolysis approach to CVD,⁴⁻⁶ because the former is designed for molecular impingement of the liquid precursor on the substrate. The molecule-by-molecule growth of the oxide film may offer greater control over the microstructure than if small droplets of the precursor are deposited on the substrate and then decomposed.

In this communication, we report the application of the pulsed-CVD method to grow films that are polycrystalline, albeit textured. Although these polycrystalline films can have applications in electronics, for example, as dielectric layers, our attention is focused on structural applications, such as ther-

mal barrier coatings for superalloys in the shape of turbine blades. In these large-scale applications, the conversion efficiency of the precursor to the oxide is of concern because of cost. Also, because such coatings are often 10–100 μm thick, the rate of growth must be of the order of 1 $\mu\text{m}/\text{min}$. The objective of this communication is to show that the pulsed-CVD method can provide conversion efficiency that approaches 100% and growth rates that are quite amenable for the manufacture of thick films. These results are demonstrated with a model material, TiO_2 , grown from the precursor titanium isopropoxide. Equivalent precursors for growing film of ZrO_2 , which is the major constituent of thermal barrier coatings, are readily available.

II. Experimental Procedure

A schematic of the apparatus used in this study is shown in Fig. 1. A precise volume of liquid precursor solution is injected directly into the cold-wall reaction chamber through an ultrasonic nozzle. The precursor consists of a dilute solution of the metalorganic in a low-vapor-pressure solvent. In this study, we use 1.8 mol% $((\text{CH}_3)_2\text{CHO})_4\text{Ti}$ in toluene. The pulse timing is controlled by a personal computer, and the pulse volume is simply the internal volume of the valve (C) plus the volume in the supply line (L). The fine droplets (15 μm) produced at the tip of the ultrasonic nozzle rapidly evaporate in the low pressure (0.1–10 torr (13–1300 Pa)) inside the chamber. The precursor molecules arrive at the hot substrate, where they are thermally decomposed. The substrate is heated by mounting it on to a susceptor heated by a halogen lamp encased within heat shields. The deposition temperature is controlled by a propor-

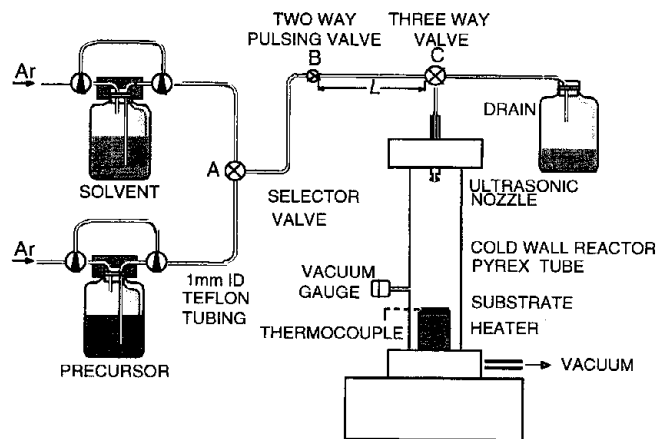


Fig. 1. Schematic diagram of the pulsed-CVD experimental reactor. Valve B is open to fill supply tubing, L, with overflow to the drain, while valve C is closed to the nozzle. Liquid precursor pulse is delivered to the chamber when valve B closes and valve C opens to the nozzle. Reaction chamber is evacuated by a rotary vacuum pump through the base of the chamber.

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tional controller with input from a thermocouple embedded in the susceptor. The low pressure in the reactor is maintained by a rotary vane pump with a liquid-nitrogen trap placed between the reactor and the pump.

All the experiments reported below were conducted at a pulse rate of 12 pulses/min and an integrated flow rate of 250 $\mu\text{L}/\text{min}$. The typical surface area of the substrates was 1 cm^2 . The principal variable in the experiments was the substrate temperature, which ranged from 400° to 700°C .

The growth rate of the films was measured by two methods. When the films were less than a few micrometers thick, the growth rate was determined by the color-chart method⁷ after calibrating the film thickness for green and red colors using ellipsometry. The thickness of the films also was measured at the end of the experiment and then divided by the duration of the experiment to obtain an average value of the growth rate. The final film thickness was determined by edge mounting a sample, grinding and polishing, and measuring with a stage micrometer on an optical microscope. The morphology of the resulting films was studied by optical and scanning electron microscopy, and their structure and texture by X-ray diffraction (XRD).

III. Analysis and Results

The conversion efficiency of the precursor to the oxide deposited on the substrate was estimated by comparing the measured growth rate to the maximum possible (the upper bound) growth rate calculated by the method given below.

Because the walls of the cold-wall reactor remain clear, we assume that the injected precursor is either deposited on to the substrate or removed at the base of the reactor (see Fig. 1) through the pump. It remains now to assume the form of the concentration profile of the precursor in the vapor phase, just above the substrate, across the cross section of the vertical glass tube in the reactor. An *upper bound* for the concentration can be obtained by assuming that the concentration is uniform across the entire cross section of the reactor tube, because any nonuniformity is always such as to lower the precursor concentration in the center region, where the substrate is placed relative to the circumferential region through which the vapor flows past the heater to the pump. Later we show that the growth rates are very similar to the value estimated from this upper-bound calculation, suggesting that, under the current operating conditions (low pressure), the uniform concentration assumption is valid. The assumption of uniform concentration is further supported by the uniform thickness of the films: the thickness varies by $<2.5\%$ over a surface area of $\sim 1\text{ cm}^2$.

The maximum growth rate can be calculated as follows. Let us say that the injection rate of the precursor solution is f_{inj} in units of $\mu\text{L}/\text{min}$ and that v_{mo} is the volumetric concentration of the precursor in the solution. The reactor cross section is A_{r} . If ρ_{mo} is the density of the precursor, ρ_{ox} the density of the oxide produced from the decomposition of the precursor, M_{mo} the molecular weight of the metalorganic precursor, and M_{ox} the molecular weight of the solid oxide, then the (maximum) growth rate (in units of film thickness per unit time), GR_{max} , is given by

$$\text{GR}_{\text{max}} = \frac{v_{\text{mo}} f_{\text{inj}}}{A_{\text{r}}} \frac{M_{\text{ox}} \rho_{\text{mo}}}{M_{\text{mo}} \rho_{\text{ox}}} \quad (1)$$

The result in Eq. (1) is independent of the net surface area of the substrate, because we have assumed that the concentration profile in the vapor phase is uniform across the cross section of the reactor. The experiments appear to be consistent with this statement; that is, films grown on substrates of different surface areas have the same growth rates.

In the current set of experiments, the parameters on the right-hand side of Eq. (1) are held constant, and have the following values $f_{\text{inj}} = 250\ \mu\text{L}/\text{min}$, $v_{\text{mo}} = 0.0476$, and $A_{\text{r}} = 0.0024\text{ m}^2$ (corresponding to a tube diameter of 55 mm). The

values for the remaining parameters are as follows: $\rho_{\text{mo}} = 0.955\text{ g}/\text{cm}^3$, $\rho_{\text{ox}} = 4.26\text{ g}/\text{cm}^3$, $M_{\text{mo}} = 284.26\text{ g}/\text{mol}$, and $M_{\text{ox}} = 79.9\text{ g}/\text{mol}$. Substituting these values into Eq. (1) gives $\text{GR}_{\text{max}} = 0.32\ \mu\text{m}/\text{min}$.

The experimental growth rates, which are reported below, are compared to this value to obtain an estimate of the conversion efficiency, which is defined as the measured growth rate divided by the upper bound for the growth rate as calculated by Eq. (1).

Measurements of GR as a function of temperature are shown on the Arrhenius plot in Fig. 2. The temperature dependence of the conversion efficiency is also shown in Fig. 2 by the axis on the right-hand side. The latter shows that the conversion efficiency exceeded 80% in the temperature range of 550° – 650°C . This region is characterized by the temperature-independent growth rate we call stage II. At temperatures $<550^\circ\text{C}$, the growth rate follows an Arrhenius relationship, as shown by Fig. 2, which is named stage I behavior. At temperatures $>650^\circ\text{C}$, the rate of change of growth rate with temperature reverses (suggesting a negative activation energy), which is called stage III behavior. The delineation of these three stages is interesting because of the engineering applications (especially because the conversion efficiency is almost 100% in stage II) and exposition of the underlying mechanisms of film growth from metal-organic precursors by thermal decomposition. These aspects are discussed below.

Stage II behavior is the regime of engineering interest. For the pulsed-CVD to have manufacturing potential, it needs to have high growth rates and conversion efficiency, which have been achieved. However, the process also must be able to produce desirable microstructures in the coatings. Although the coatings were always dense, the morphology of the grain structure varied with temperature. The microstructure was predominantly columnar in the higher temperature regime of stage I and lower to the mid range of stage II. The microstructure became equiaxed at $\geq 650^\circ\text{C}$. An optical micrograph of the columnar microstructure obtained at 575°C , with the diffraction pattern, are shown in Fig. 3. Some degree of texture is evident upon comparing the XRD pattern obtained from the coating with the powder diffraction pattern for the rutile phase.⁸ We invariably

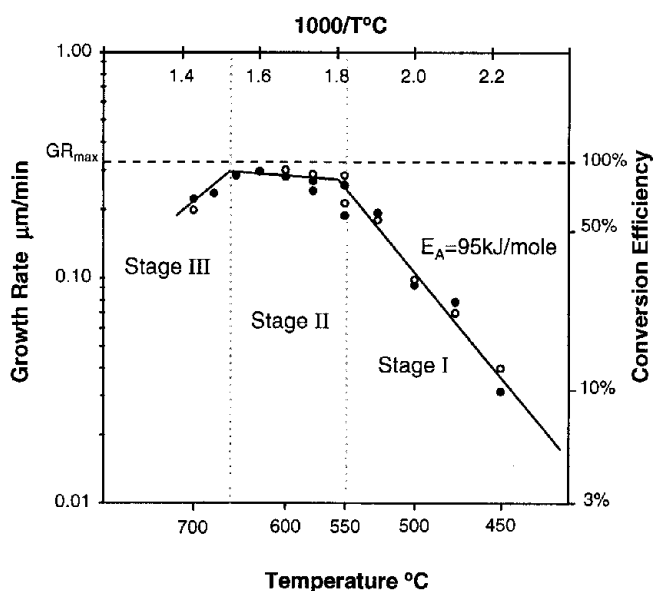


Fig. 2. Arrhenius plot of the growth rate of the film at constant flow rate of the precursor into the reactor. Upper-bound growth rate is estimated from Eq. (1). Axis on the right shows the conversion efficiency, that is, the ratio of the measured versus the upper-bound growth rate. Open circles refer to data obtained from color-change measurements, and the solid circles the data obtained from microscopic measurement of the film thickness at the end of deposition.

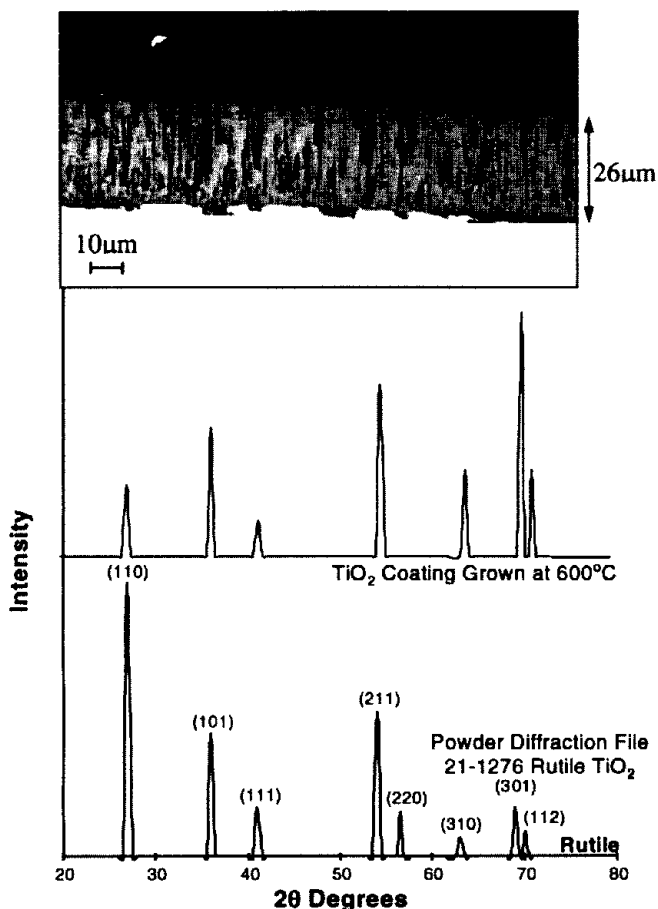


Fig. 3. Columnar microstructure of the rutile overgrowth. Total film thickness is 27 μm . Film was grown at 550°C. XRD pattern from the film shows some degree of texture when compared to the diffraction pattern expected from a powder sample of rutile.

found, as expected, that the columnar structure grew out of a thin layer of fine-grained equiaxed structure that nucleated just next to the substrate in the early stages of film growth. The columnar microstructure is desirable in thermal-barrier-coating applications.⁹ If similar results can be obtained for films of ZrO_2 , then the properties of the pulsed-CVD process portend well for application to thermal barrier coating and, possibly, to other structural coatings.

In stage I, the growth behavior is Arrhenius¹⁰ with an activation energy of 95 ± 5 kJ/mol. From the stage II data, we conclude that, $>550^\circ\text{C}$, almost all the precursor molecules arriving at the substrate decompose to the oxide. At lower temperatures, the rate of decomposition decreases, suggesting that, in stage I, the conversion rate becomes limited by the surface reaction kinetics.

The activation energy of 95 kJ/mol in the temperature range 400°–575°C is in reasonable agreement with published work. Fictorie *et al.*¹¹ have calculated an activation energy of 134 ± 2 kJ/mol using a first-order kinetic model. (Fictorie *et al.* quote

work from early studies of the heterogeneous thermal decomposition of $\text{Ti}(\text{OPr})_4$ with an activation energy of 92 ± 2 kJ/mol using the production of isopropyl alcohol as a measure of the rate of the decomposition reaction.) Wu *et al.*¹² report a value of 130–135 kJ/mol using a similar approach. However, both studies also report lower activation energies (57 kJ/mol and 85 kJ/mol, respectively) if they analyze the rate of consumption of the precursor, rather than the rate of production of the ceramic, for calculating the activation energy. Chen and Durking¹³ report a value of 87–115 kJ/mol for deposition of polycrystalline TiO_2 films. All of these experiments were conducted at conditions similar to our experiments in stage I.

The data for stage III is limited at this point, but we are certain that the growth rate begins to decrease at temperatures above $\sim 650^\circ\text{C}$. The interpretation offered for stages I and II suggest that the growth rate in stage III is *not* limited by the rate of decomposition reaction of the precursor on the substrate. Two possible explanations for the transition from stage II to stage III are that, at higher temperatures, the ceramic is deposited on the reactor tube wall because of its proximity to the susceptor, and that some fraction of the precursor molecules arriving at the surface are reevaporated before they are able to decompose on the surface.

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References

- H. Xie and R. Raj, "Epitaxial LiTaO_3 Thin Film by Pulsed Metalorganic Chemical Vapor Decomposition from a Single Precursor," *Appl. Phys. Lett.*, **63**, 3146–48 (1993).
- V. A. Versteeg, C. T. Avedisian, and R. Raj, "Metalorganic Chemical Vapor Deposition by Pulsed Liquid Injection Using an Ultrasonic Nozzle: Titanium Dioxide on Sapphire from Titanium(IV) Isopropoxide," *J. Am. Ceram. Soc.*, **78** [10] 2763–68 (1995).
- H. L. M. Chang, H. You, Y. Guo, C. M. Foster, R. P. Chiarello, T. J. Zhang, and D. J. Lam, "Structural Properties of Epitaxial TiO_2 Films Grown on Sapphire (1120) by MOCVD," *J. Mater. Res.*, **7**, 2495–506 (1992).
- W. J. DeStiso and R. L. Henry, "Preparation and Characterization of MgO Thin Films Deposited by Spray Pyrolysis of $\text{Mg}(2,4\text{-pentanedionate})_2$," *J. Crystal Growth*, **109**, 314–17 (1991).
- G. Blandinet, M. Court, and Y. Lagarde, "Thin Layers Deposited by the Pyrosol Process," *Thin Solid Films*, **77**, 81–90 (1981).
- P. Wu, Y.-M. Gao, J. Baglio, R. Kershaw, K. Dwight, and A. Wold, "Growth of Zinc Oxide Films by a Novel Ultrasonic Nebulization and Pyrolysis Method," *Mater. Res. Bull.*, **24**, 905–11 (1989).
- C. E. Morosanu, *Thin Films by Chemical Vapour Deposition*, Ch. 5. Elsevier, Amsterdam, The Netherlands, 1990.
- K. Sugiyama and Y. Takeuchi, "The Crystal Structure of Rutile as a Function of Temperature up to 1600°C," *Z. Kristallogr.*, **194**, 305–13 (1991).
- H. W. Grunling, H. Rechtenbacher, and I. Singheiser, "Some Practical Aspects of Corrosion and Coatings in Utility Gas Turbines," *Mater. Sci. Forum.*, **251–254**, 438–502 (1997).
- R. L. Moon and Y. M. Hough, *Chemical Vapor Deposition*, Ch. 6. Edited by M. L. Hitchman and K. F. Jensen. Academic Press-Harcourt Brace Jovanovich, London, U.K., 1993.
- C. P. Fictorie, J. F. Evans, and W. L. Gladfelter, "Kinetic and Mechanistic Study of the Chemical Vapor Deposition of Titanium Dioxide Thin Films Using tetrakis-(isopropoxy)-titanium(IV)," *J. Vac. Sci. Technol.*, **12**, 1108–13 (1994).
- Y. M. Wu, D. C. Bradley, and R. M. Nix, "Studies of Titanium Dioxide Film Growth from Titanium Tetraisopropoxide," *Appl. Surf. Sci.*, **64**, 21–28 (1993).
- Z.-X. Chen and A. Derking, " TiO_2 Thin Films by Chemical Vapor Deposition: Control of the Deposition Process and Film Characterization," *J. Mater. Chem.*, **3** [11] 1137–40 (1993). □