Gas Phase SFF Control System for Silicon Nitride Deposition by SALD/SALDVI

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Abstract: A closed-loop laser scanning and temperature control system has been developed for SALD/SALDVI. Temperature control is especially important in SALD/SALDVI because temperature plays a defining role in both composition and deposition rate. The control system for SALD/SALDVI is presented which provides .STL file interpretation, real time temperature control, and laser response modeling, all on a PC. This control system was utilized with the SALD/SALDVI techniques for depositing silicon nitride. Characteristics of Si_3N_4 fabricated shapes are discussed, including composition, morphology, and electrical properties.

Introduction

Selective Area Laser Deposition(SALD)/SALD Vapor Infiltration(SALDVI) are gas-phase SFF approaches to forming a vast array of materials from a laser- induced, localized gas-phase reaction[1]. The deposition of ceramic shapes, such as silicon nitride, without post-processing presents one of the promising advantages of gas-phase SFF. Laser-CVD growth of silicon nitride fibers from silane(SiH_4) and ammonia(NH_3) gas mixtures has previously been shown[2]. Mixed gas environments of tetramethylsilane(TMS, $Si(CH_3)_4$) and ammonia have also experimentally produced silicon nitride deposits. A more thorough examination of the TMS and NH_3 deposition system, using thermodynamic modeling, was undertaken to understand the temperature and gas partial pressures necessary for formation of silicon nitride. With this knowledge, a gas-phase SFF computer control system, including closed-loop control of temperature, was implemented to verify the modeling predictions. These experiments were performed with a 150 watt cw Nd:YAG laser(λ=1.064 nm), an optical pryometer for temperature control, and an 8 inch diameter stainless steel vacuum chamber(the system is more thoroughly described in reference 3). In addition, the electrical and morphological nature of the formed silicon nitride shapes was examined.

Gas-phase SFF Computer Control System

Monitoring and control of both position and temperature are performed on a PC program written in-house in Visual Basic language[4]. This software is currently used on 2 gas-phase SFF systems at UCONN(references 5 to 10 detail the theory on which the control system is based).

The motion control can handle single two-dimensional layers or multiple 2D layers taken from a three-dimensional .STL or CAD models. The .STL/CAD capability requires that the 3D solid model be sectioned into 2D layers. Each layer must then be 'scanned' with the appropriate laser scan spacing to create a coordinate file for laser scan control. An in-house translation program takes the coordinate file for each layer and creates motion control code for scanning the laser. When creating a SALDVI structure, the control program also accesses a powder delivery program[11].

The original temperature control design utilized a proportional gain to vary the laser power and consequently adjust the reaction temperature to the desired target temperature, based on the following equation: $P_{laser}=P_{laser} + K * \Delta T$, where P_{laser} is the laser power, K is the gain,

and ΔT is the difference between the measured and target temperatures. This simplified control scheme was inadequate, leading to either large temperature overshoots or slow response times. As a result, a PID(Proportional Integral Derivative) filter was programmed into the control software. The PID filter functions according to the flowchart in Figure 1.

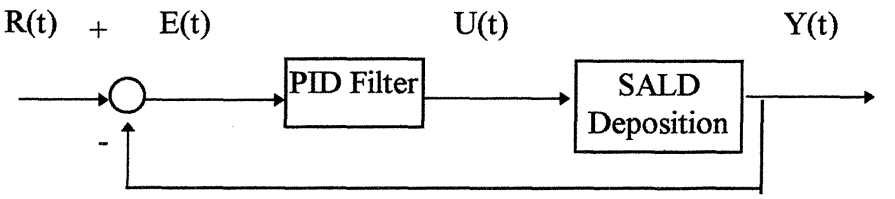

Figure 1 : PID Flowchart

R(t) is the desired target temperature, Y(t) is the measured target temperature by the optical pyrometer, E(t) is the error between measured and target temperatures, and U(t) is the PID adjustment signal to the laser controller. In a discrete time domain, where k represents a temperature measurement sampling, the PID signal is based on the equation: $U(k) = U(k-1) + K_p[E(k) - E(k-1)] + K_i E(k) + K_d[E(k) - 2E(k-1) + E(k-2)]$.

Due to the non-linearity of the laser power response to the analog control voltage from a Digital-to-Analog Card(DAC), a signal conditioner was employed to apply the PID output signal directly to the laser power. This conditioner is based on a laser calibration of the laser output power to the DAC input power, according to the equation: $V(t) = mU(t) + b$, where m is the slope and b is the y-intercept of the laser power versus DAC curve.

With the PID in place, the next step was to determine the appropriate PID parameters for small temperature overshoot and a quick response time. Experimentally, a trial and error approach could take a considerable amount of time. A first order estimation of the necessary PID values was obtained using a simple system model on a spreadsheet. The reaction zone temperature versus time response at constant laser power during deposition can be modeled using the following equation: $T(t) = P \times K(1 - e^{-\frac{t}{t_1}})$ where P is the laser power, $K = \frac{\Delta T(\infty)}{P}$, $\Delta T(\infty)$ is the difference between the steady-state temperature and the initial temperature, and $t_1 = -\frac{t_{75\%}}{\ln\left(1 - \frac{T(t_{75\%})}{P \times K}\right)}$ ($t_{75\%}$ is the time to 75% of $T(\infty)$). In order to use this modeling spreadsheet, a simple constant power, single line scan deposition experiment must be performed to obtain real values for $T(\infty)$, P, and $t_{75\%}$. After inputting these values into the worksheet, PID settings can be tested and a time-temperature response graph is generated, based on consecutive iterations of the following equation: $Y(k) + a_1 Y(k-1) = b_1 U(k-1)$, where $b_1 = K\left[1 - \exp\left(-\frac{t_0}{t_1}\right)\right]$, $a_1 = -\exp\left(-\frac{t_0}{t_1}\right)$, and t_0 is the sampling time. The graph details the expected system response of temperature overshoot and time to reach the steady-state temperature. This modeling program provided initial PID values of K_p=.01, K_i=.001, and K_d=.01

for the Nd:YAG laser. With further experimentation, the optimal temperature response and control for the YAG laser used PID parameters that are a factor of 10 less than the modeled values.

Thermodynamic Modeling of the TMS/NH3 Deposition System

A thermodynamic consideration of the tetramethylsilane and ammonia gas deposition system was performed using a modified version of software titled CET89[12]. CET89 is a Gibbs free energy minimization program for solids, liquids, and gases. The modifications made at UCONN to the routine involve the ability to calculate free energies over a specified temperature range. With this program, the deposition materials and phases of these products are projected based on what is favored by thermodynamics to be in equilibrium at selected temperatures, pressures, and molar ratios. Gas partial pressure were used as the independent variable. The effect of overall total pressure changes the temperature of transition from one region to another in the diagram below, but the net form of the map remains the same. Figure 2 shows a tetramethylsilane/ammonia gas mixture deposition map.

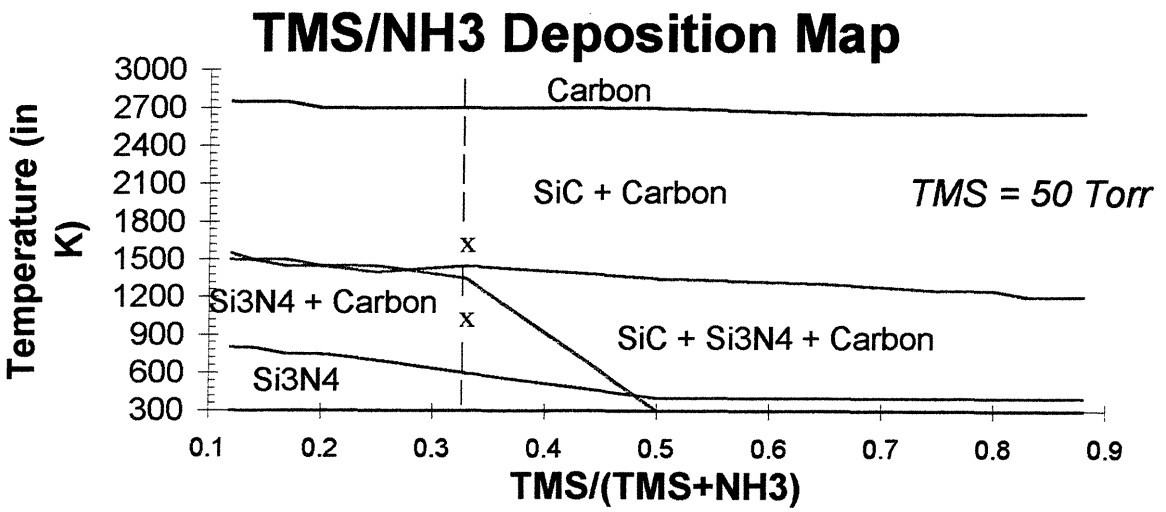

Figure 2 : TMS/NH_3 Deposition Map from CET89

Based on the deposition map, a partial pressure ratio of 1:2 for TMS:NH3 was chosen to demonstrate the ability to manipulate the product composition to form Si_3N_4.

Experimental

Selective Area Laser Deposition(SALD) of silicon nitride rods served as the initial focus of experiments to determine the composition of the formed material, utilizing x-ray diffraction spectroscopy(XRDS). Implementing the PID control computer program, deposition target temperatures from 1000^0 C to 1350^0 C were selected to achieve constant temperature growth conditions. These temperatures were based on the approximate region in the deposition map, at a 1:2 TMS/ NH_3 gas ratio, where silicon nitride would be expected to form(the experimental region can be seen on Figure 2, along the vertical line between the x's). The target temperature is actually a temperature parameter, with variations from the actual temperature due to differences in size between the heated reaction zone from the laser and the size of the sampling area of the

pyrometer. Some modeling of the relation between the actual and measured temperatures has been performed but a more complete analysis will be performed. A sample XRDS pattern in shown in Figure 3, where sample #37 was a rod grown at 1100^0 C target temperature.

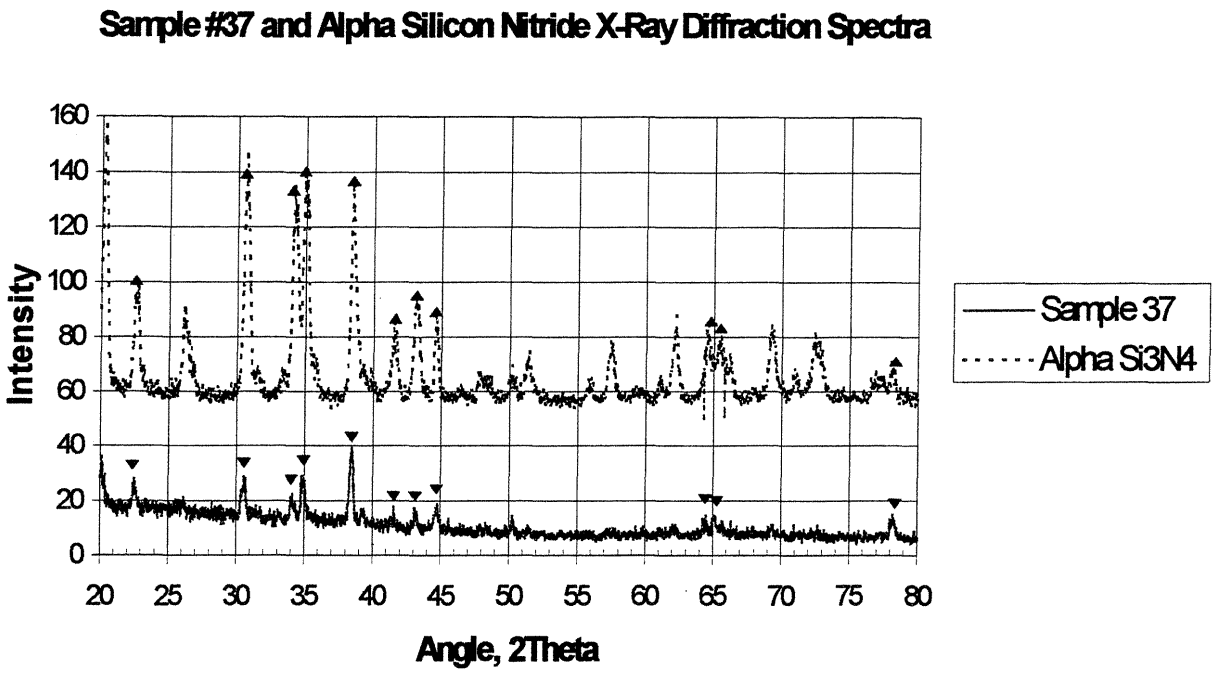

Figure 3 : X-ray Diffraction Spectra for a Si_3N_4 SALD Rod and an Alpha Si_3N_4 Standard (Note: A matched peak has an up and a down arrow associated with it)

The x-ray pattern shows a small texturing effect along the 211 plane, at $2\theta = 38.9^0$. Other rod experiments showed silicon nitride formation up to 1350^0 C deposition temperatures, which may imply a deviation from the thermodynamic modeling prediction for the transition temperature from silicon nitride to silicon carbide formation, depending on the accuracy of the temperature measurements.

The electrical resistivity of both SALD silicon nitride rods and SALDVI silicon nitride single layers was measured using a mega-ohm meter. Available literature report silicon nitride resistivity values greater than 10^{14} ohm-centimeters[12]. Resistivity(ρ) calculations are based on the following equation: $\rho = R*A/t$, where R is the resistance measured from an ohm-meter, A is the area of the sample, and t is the thickness of the sample. Both rod and layer samples exhibited resistances greater than 100 Mega-ohms, which was the maximum calibrated value of the ohm-meter used. Conservatively using this resistance, the SALD/SALDVI silicon nitride displayed resistivity of greater than 10^9 ohm-centimeters. An enhanced method for accurately determining the resistance is presently under consideration.

Infiltration of deposited silicon nitride into alpha-silicon nitride powder was performed at the 1:2 TMS/NH_3 gas ratio in a square raster scan pattern. Scan speeds ranged from 20 microns/second to 50 microns/second. A preponderance of dense SALD material, with very little

infiltration, resulted from the faster scan speed condition. At the slower, 20 microns/second scan speed, some infiltration could be seen, but there was still a great deal of SALD material growing off the powder surface. Figure 4 shows the powder/SALD growth interface of the 20 microns/second scan speed sample, with some deposited material(silver-white) infiltrated into the powder(black). A methodical assessment of the appropriate scan speed, deposition temperature parameter, and gas ratios will be undertaken to determine the best conditions for silicon nitride infiltration.

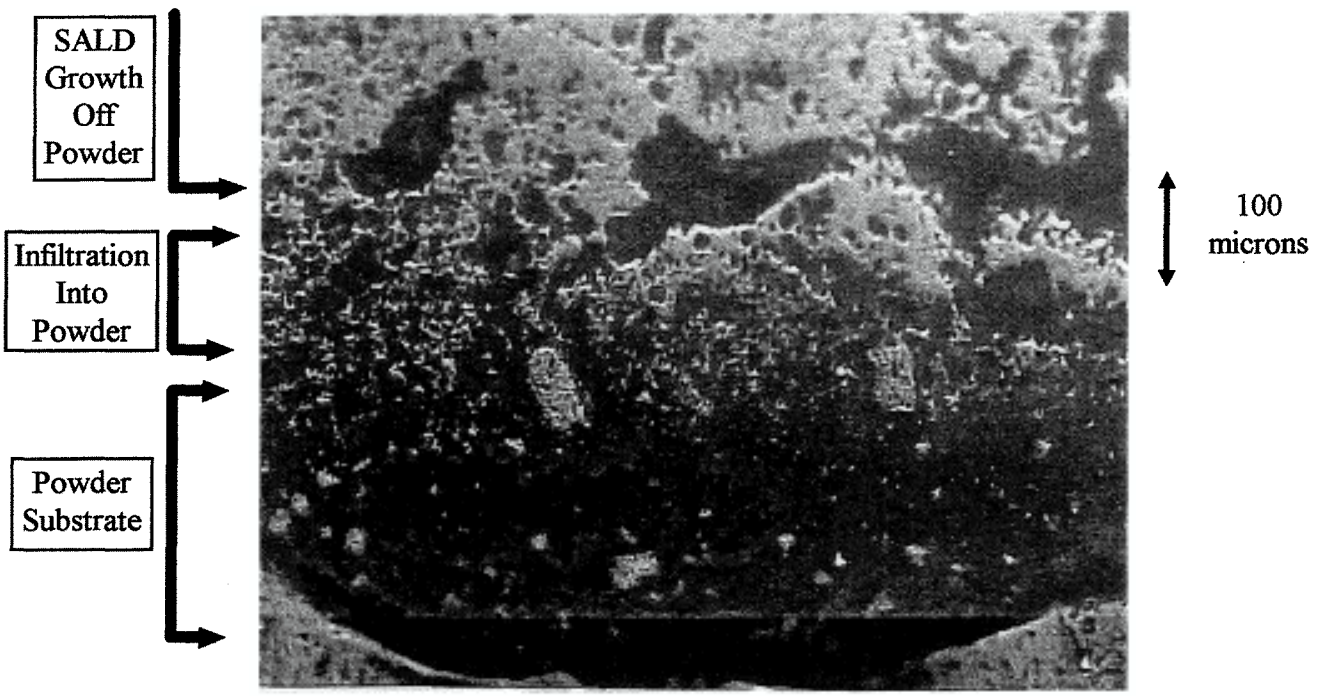

Figure 4 : SALDVI Si_3N_4 Cross-Section, Scan Speed 20 microns/second

Conclusions

A temperature and laser scanning closed-loop computer program was designed and implemented for use with the SALD/SALDVI processes.. This program utilizes a PID filter to minimize the temperature overshoot and maximize the temperature response time, in an effort to create constant temperature deposition conditions. Thermodynamic modeling, using CET89 software, predicted regions where silicon nitride would be deposited in a tetremethylsilane and ammonia gas environment. Employing the closed-loop program, the deposition of silicon nitride was demonstrated, based on gas mixture pressures and deposition temperatures from the thermodynamics. Further experimental work will focus on the deposition transition temperature from silicon nitride to silicon carbide, with comparisons to the thermodynamic model. Multi-layer SALDVI silicon nitride shapes will be attempted, and the electrical characterization of Si_3N_4 will be improved to better judge the quality of the material being deposited.

Acknowledgments

The authors wish to acknowledge the support of DARPA/ONR, contract #N00014-96-1-1299, and ONR, contract #N00014-95-1-0978.

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