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**INVESTIGATION OF PACVD PROTECTIVE COATING PROCESSES
USING ADVANCED DIAGNOSTICS TECHNIQUES**

**Performance Report for the Period
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PERFORMANCE REPORT

"Investigation of Laser Diagnostics of PACVD Processes
for Depositing Hard Face Coatings"

Principal Investigator: Ward C. Roman

Objective:

To improve the understanding of the mechanisms which govern the nonequilibrium reactive plasma atomistic or molecular deposition of hard face coatings for erosion resistant applications. The goal is to provide a predictive capability that is severely lacking in the present science base of PACVD processing for depositing hard face coatings. Advanced laser diagnostics will be used to probe the plasma for improving process control.

Problem:

Durable protective coatings and films are emerging as a critical technology for a variety of commercial applications within DOE and UTC. These range from protective coatings for propulsion systems, to films and heat sinks for semiconductors, from optical lenses and electronic devices for space environments to diamond films and free standing structures for erosion resistant windows and to tribological coatings for machining operations. The needs include developing a better understanding of processes such as Chemical Vapor Deposition (CVD) and Plasma Assisted Chemical Vapor Deposition (PACVD). Technology transfer is limited by a lack of understanding of the basic mechanisms involved in the deposition process (gas phase and surface interactions). This understanding is also vital for viable scale-up to production type DOE hardware. Numerous new and novel in-situ, nonintrusive diagnostic techniques are becoming available, but a correlation of the CVD and PACVD parameters with some of the key coating properties is required. Thus, a predictive capability that is lacking in the present science base can be established together with important phenomenological aspects needed for efficient deposition of high-quality films, coatings and free standing structures. As the mechanisms become better understood, use of remote sensors and Artificial Intelligence (AI) may then be introduced.

Approach:

Nonequilibrium reactive plasmas are recognized as a novel approach for a wide variety of material coating applications. This kind of plasma provides a unique environment wherein deposition of thin, hard face, conformal surface coatings can occur at much lower temperatures, critical

for inhibiting coating stresses, and within more complex chemical environments than are possible by conventional vapor deposition techniques. As reported in DOE ER-0241, current understanding of the mechanisms of plasma deposited thin coatings is so poor that it is impossible to alter the coating in desirable ways without extensive experimentation. To date, there is insufficient information to make definitive statements about deposition mechanisms. In order to develop a fundamental understanding of these processes, the chemical composition, reactive species, concentration/temperature gradients and synergistic effects within the plasma must be known. In this research effort, focus is on implementing complementary laser diagnostic strategies (e.g. Coherent Anti-Stokes Raman Spectroscopy, CARS, and/or Laser Induced Fluorescence, LIF) to aid in differentiating between gas phase and gas-surface chemistry in the PACVD process of depositing TiB_2 and diamond onto titanium and titanium alloy substrates. CARS is a nonlinear optical technique useful for measuring the concentration and temperature of molecules that is not normally applied to PACVD type processes because of the low pressure of the medium (10 torr). The CARS signal scales nonlinearly (approximately as the square) with the molecular number density. For the low pressures typical of the PACVD process, the normal broadband CARS technique, used at atmospheric pressure and above, would not yield a detectable signal. To increase the sensitivity of the measurement, a narrowband, scanned CARS experiment is being used for investigating these PACVD systems.

Because of its superior erosion and thermal resistance, TiB_2 was selected as the initial hard face coating material for investigation. Exploratory tests with diamond coatings have also been initiated. Another task of the program involves investigation and characterization of the substrate and coating. The principal physical characteristics being measured include microhardness (depth profiles), smoothness and adherence. The principal chemical characteristics being measured include structure, stoichiometry and impurities as a function of coating thickness. These measured physical and chemical properties of the final coatings are being used for correlation with and definition of measured critical plasma parameters.

Status to date/Progress:

The experimental arrangement is presented and discussed in detail elsewhere [3], and will be presented here only in brief. CARS is applied to the dominant species in an inductively coupled B_2H_6/Ar (5% diborane in Ar - Matheson) rf-plasma. The pump beam (ω_1) is a frequency doubled Nd:YAG laser, while the probe beam (ω_2) is provided by a tunable dye laser. The beams are collinearly combined and focused into the plasma, where they interact through the third order nonlinear susceptibility to produce a coherent signal beam ($\omega_3 = 2\omega_1 - \omega_2$) that is resonantly enhanced when $\omega_1 - \omega_2$ coincides with a Raman active molecular resonance. This technique is used to probe axial concentration profiles of both diborane and hydrogen in the rf-plasma.

A 5 kW rf power supply, operating at 13.56 MHz, is used to inductively couple the rf power into the plasma through a multiple-turn water-cooled copper work coil. Coils can be placed either upstream, downstream or about the optical access ports. If placed up or downstream, an actuated worm gear allows variation of the distance from the view port to the coils (plasma glow region). This in turn permits various species axial distributions to be determined as conditions such as flow rate or total pressure are varied.

Emission spectra are obtained with a UV sensitive Princeton Instruments CCD array. Plasma emission is collected with a fiber optic bundle and focused into a 1/4 meter monochromator which disperses the radiation onto the array.

In the initial investigation of rf-PACVD of TiB_2 , we are concentrating on a $\text{B}_2\text{H}_6/\text{Ar}$ plasma. This simplifies the overall chemistry from:

to:

and greatly reduces the complexity of the chemical kinetics. This allows our preliminary efforts at modeling to be more easily accomplished and verified.

In situ diborane CARS spectra were compared with spectra obtained in the absence of a rf field and at room temperature; no significant differences were observed. The absence of rotational broadening indicates that no significant energy transfer has occurred to rotational energy in the diborane molecule. More significant, is the hydrogen CARS spectra. A comparison of complete rotational spectra with theoretically calculated spectra and with spectra observed at room temperature indicates that the hydrogen rotational temperature is near 278 K even after flowing through the plasma glow region.

CARS spectroscopy has been applied *in situ* to obtain axial concentration profiles of both the precursor B_2H_6 and the gas phase product H_2 . Figure 1 shows the axial distribution of diborane partial pressure about the plasma glow region (work coils). Flow direction is from left (positive distance) to right. Diborane was not observed above the limit of detectability (60 mtorr) closer than 4.4 cm upstream of the plasma center, or at plasma center, or downstream. Data were obtained at 4.7 torr total pressure with a volumetric flow rate of 250 sccm of 4% B_2H_6 in Ar. The line at 188 mtorr represent the partial pressure of diborane in the absence of the rf field. The data used to compile Figure 1 are complete CARS spectra of the ν_{16} Raman active rovibrational bandhead, and were recorded both as a function of position and of rf power. These spectra are compared with spectra obtained in the absence of a rf field and at room temperature, and no significant differences are observed. This allows partial pressure determination to be made by a room temperature calibration run immediately after rf data are obtained.

Figure 2 depicts the appearance of H_2 in the rf-plasma as a function of total pressure. The conditions under which these data are obtained differ from those in which the diborane disappearance curves were obtained due to experimental difficulties encountered in establishing a stable discharge. However, the results stand alone and allow qualitative comparisons to be made. The appearance of H_2 is seen to coincide (about 10 cm upstream) with the disappearance of diborane and reaches a maximum near the point at which the diborane signal disappears (about 4.5 cm upstream). Qualitatively these observations are also in good agreement with the observation of boron wall deposition discussed previously [4]. Partial pressures are obtained from CARS spectra of the Q(1) rotational line of the hydrogen molecule. The room temperature rotational distribution allows room temperature calibration curves to be used in extracting concentrations from signal strengths.

Figure 1. The Disappearance of Diborane Upstream of the Work Coil. Flow Direction is from Left to Right

Figure 2. The Appearance of Molecular Hydrogen in the rf-plasma. Flow Direction is Left to Right

Due to our speculation over the role photochemistry plays in the reaction mechanism, we looked at emission as a function of carrier gas (Ar versus He) with and without added diborane. Figure 3 contrasts plasma emission spectra observed in pure Ar with the emission observed with 1% added diborane. The intense glow region about the work coil extends ± 2.5 cm about the zero distance point on Figures 1 and 2. In the diborane/nobel gas plasmas the emission from this region is the intense red (656.3 nm, from the singly ionized H atom) typical of a pure H_2 plasma in our system and is entirely consistent with the CARS data that indicate near total conversion of B_2H_6 to H_2 . As observed in Figures 3 and 4, the addition of diborane nearly totally quenches the emission from the nobel gas. In addition to the hydrogen emission (not shown) both spectra contain BH(A $\rightarrow$ X) rovibronic bandheads ($\nu_{00} = 23074.0 \text{ cm}^{-1}$ or 433.38 nm). This emission proves that total conversion of diborane to molecular hydrogen and boron atoms has not occurred by the time species penetrate the plasma glow region even though the CARS data suggest that near stoichiometric amounts of hydrogen have been formed. The line(s) near 496 nm have not been assigned at this point, but the absence of a rotational bandhead indicate that they probably originate from an atomic species such as boron or hydrogen atoms.

Figure 3. Emission Spectra of a) Argon Plasma and b) Argon with 1% B_2H_6 Obtained at 3 torr Total Pressure with Approximately 400 W of rf Power. Prominent Ar Peaks (a) are Quenched with Addition of Diborane and Spectra is Dominated by BH A $\rightarrow$ X Emission.

One of our long term goals is the development of a suitable model for PACVD of TiB_2 . Such a model would be useful for interpreting data as well as for extrapolation of experimental data to assist in the scale up of successful coating procedures to commercially viable conditions. The plasma decomposition of $\text{TiCl}_4/\text{B}_2\text{H}_6$ mixtures is sufficiently complex that as stated above, it is prudent to investigate a variety of simpler, but related processes in order to develop some understanding of and experience with the chemical system.

The first system selected for study is the pyrolysis of diborane. its selection was based on the expectation [4] that photochemical- or plasma-assisted pyrolysis was the cause of the observed very rapid decay of diborane and commensurate formation of hydrogen upstream of the plasma glow region. Furthermore, since the pyrolysis is based on growth processes, a study of these types of steps could help in the understanding of surface growth reactions.

A review of the literature on diborane pyrolysis indicated that there was relatively excellent agreement on measurements of overall decay rates and reaction order [5,6], yet even after 40 years since these studies there is no useful kinetic mechanism which adequately describes these phenomena. Rate constants for only two of the related reactions (i.e., for BH_3 recombination and for BH_3 addition to B_2H_6) have been measured and even the chemical sequence has not been established (despite much speculation). By using

Figure 4. Emission Spectra of a) He Plasma with 5% B_2H_6 and b) He Alone with Approximately 400 W of rf Power at Listed Pressures.

the recently calculated heats of formation from McKee [7] and the structural and thermodynamic calculations of J. Montgomery [8], we have developed the five-step mechanism and related rate constants shown in Table I. Reverse rate constants were determined from thermodynamic. Heats of formation, room temperature entropies and heat capacities for the B_xH_y species used in this study are reported in Table II. The proposed mechanism, in fact, is similar to early proposals for this process, but previously untested presumably due to lack of kinetic codes and large uncertainties in the thermodynamics of intermediate species. The two body rate constant for BH_3 recombination (k_1) is a factor of two higher than the reported value [9]. The rate constant in Table I for BH_3 addition to diborane, k_2 , is more than two orders of magnitude lower than the lower limit value as measured by Fridman and Fehlner [10]. As Fehlner recognized in [11], use of his rate constant leads to the conclusion that Reaction 2 is so fast that Reaction 1 cannot equilibrate and the reaction is controlled by the first order decomposition (Reaction 1). Since experimental data strongly supports 3/2 order (consistent with equilibration of Reaction 1 and the overall rate controlled by Reaction 2), he argued that the addition, $\text{BH}_3 + \text{B}_2\text{H}_6 = \text{B}_3\text{H}_9$ was reversible, and this reverse step was much faster than hydrogen elimination to form triborane(7). In fact, Fridman's and Fehlner's own data do not support this conclusion since the mass range of the observed reaction product (35-38) is more consistent with interpretation as triborane(7). Furthermore the peak mass occurs at mass 38 coincident with the mass of F_2 which could be formed as a trace byproduct between PF_3 and B_2H_6 . (F_3PBH_3 was used as the source of BH_3 .) Because of the extreme difficulty of this measurement, possible interferences of F_2 , and inconsistencies with overall decomposition diborane, we elect to favor a much lower value for this rate contrast. The pre-exponential and activation energy we suggest in Table I is in reasonable agreement with known values for methyl addition to hydrocarbons.

Figure 5. Thermal Decomposition of Diborane. Data Points Represent Experiments of Clarke and Pease [5]. Line Represents Calculations Based on Mechanism Proposed in Table I.

In the time scale of the present experiment and using the addition rate constant in Table I, negligible amounts of higher order boranes could be formed.

Alternatively, we also considered the photochemical decomposition to $B_2H_5 + H$. By analogy, one could argue that the B_2H_5 addition to B_2H_6 is also slow. However, in this case, recombination is sufficiently energetic that alternative reaction paths are opened. The overall reactions:

are all exothermic. The very large exothermicity of recombination to diborane (100 kcal/mole) indicates that the excited B_2H_6 product immediately decomposes into two boranes. The last process appears quite feasible. With BH_2 and B_2H_5 some additional reactions with low barriers are possible, including

Most importantly, a facile source of both BH_2 and BH_3 are available from the photochemical process. (Presumably analogous steps are possible from plasma processes). BH_2 and BH_3 , in turn, have been speculated [15] to be important growth species during deposition of polycrystalline and amorphous boron. Preliminary chemical kinetic modeling using estimated rates results in predictions of BH_2 and BH_3 concentrations as high as 1/30th of the initial diborane concentration.

To duplicate the diborane profile of Figure 1 a temperature above 600 K is required, this is not consistent with measured rotational temperatures and we consider rotational temperatures to be representative of other degrees of freedom 10 cm upstream of the plasma glow region. (This is, of course, not true in the plasma.) Therefore, the mechanism for diborane disappearance could not be pyrolytic.

We have, therefore, investigated the effect of initiating the chemistry photochemically. Kinetically, the major affect is to produce lower order boron hydrides (e.g. BH_2 and BH_3) in addition to the higher (e.g. B_5H_{11}). Since these species (BH_2 and BH_3) have been proposed as likely candidates for surface deposition of boron, and we observe significant boron deposition prior to the glow region, we conclude that chemical initiation could occur photochemically and intend to investigate this proposed mechanism as well as other aspects related to TiB_2 deposition.

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Potential Problem Areas and Solutions

None anticipated.

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