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Laser Diagnostics and Modeling of Plasma Assisted CVD

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EXECUTIVE SUMMARY

Plasma assisted chemical vapor deposition (PACVD) represents a novel approach for utilizing the nonequilibrium effects of reactive plasmas for depositing a wide range of protective hardface coatings that have both wear and erosion application. The nonequilibrium plasma is the heart of this complex system and has the function of generating the reactive molecular fragments (radicals) and atomic species at concentration levels unattainable by other competing processes.

Even with the recent advances in several interfacing research areas, new applications of PACVD type reactors have still been limited by a lack of understanding of the key mechanisms (both in the gas phase and at the surface) which govern the plasma deposition of protective coatings. The properties, homogeneity and quality of PACVD coatings are sensitive to a large number of process variables that, in turn, are coupled in a complicated manner. Understanding the role of the nonequilibrium plasma gas phase, versus surface reactions is still unclear. This is particularly true of the aspects of gas "temperature", species distribution, rate determining steps, and most importantly the associated synergistic effects. To date no chemical kinetic models have been formulated. These models are critical for interpreting data but vital for the extrapolation of the gathered experimental data in the scale up to commercial reactors and production rates. In most of the PACVD systems, the multi-step mechanisms are uncertain and the rate constants unknown. This is especially true for the coating titanium diboride (TiB_2) which represents a very hard, well adherent coating with outstanding potential in erosion and wear resistance.

It is now widely accepted that such advanced protective hardface coatings materials will play a vital role in the energy technologies of the coming decades, with major applications in diverse areas ranging from aerospace and commercial propulsion systems (jet engines) to automotive components and internal combustion engines, (ceramic heat engines), cutting and machining tools, electronic packaging, thermal management, and possibly room-temperature superconductors. Wear and associated erosion aspects are responsible for an enormous expenditure of energy and fiscal resources in almost all DoE applications. Many of the results from this investigation are also applicable to other materials processing reactors such as electron beam, PVD, CVD, laser ablation, microwave, high energy cathodic arc, thermal plasma (rf or dc) and combustion spray. These also include the various hybrid systems such as the rf/dc arc as used in Japan for diamond deposition and e-beam PVD deposition of advanced titanium alloy coatings as used at the Paton Institute in Kiev, Ukraine.

IMPORTANCE TO DOE

From the standpoint of DoE relevance, it is anticipated that materials, material processing and plasma processing of materials will be key technical issues as we approach the year 2000 and beyond.

This is based on the knowledge that the present energy situation in the U. S. will require new and innovative approaches and techniques for more efficient use of energy resources over the next decade. (Ref. 1) This will not be restricted to the development of new materials but will also include the conservation of materials (e.g. via hard face protective and wear resistant coatings), the refining of materials, and the development of new processing techniques which are more energy efficient, more productive, and with minimum impact on our environment. All of these make up part of DoE's future technological charter. Electrically generated thermal plasmas and nonequilibrium plasmas with excitation temperatures far exceeding those possible with combustion processes, will play an increasingly important role in these developments. Such plasmas offer potentially unlimited possibilities for synthesis and depositing advanced protective coatings, such as diamond, diamond-like-carbon (DLC's), borides, nitrides, carbides, and oxides.

PROJECT OBJECTIVES

The proposed research effort has the objective of increasing our understanding of the principal physical and chemical processes in a critical plasma processing application. (i. e. PACVD of hard face protective coatings such as TiB_2 .) The long range objective is to establish an improved engineering science base of how hard face protective coating properties (e. g. hardness, adhesion, smoothness, and erosion and wear resistance) correlate to the plasma conditions present in the PACVD system used in their formation. The results of this research program have the potential of eliminating the traditionally used empirical/Edisonian trial and error methodology. Most important, it offers the opportunity for the U. S. to take a leadership role in the scale-up of new applications in the advanced protective coatings area. It should also be emphasized that the new and advanced diagnostic techniques developed under this program will also be directly applicable to other plasma processes. The techniques that would benefit include CVD, PVD, electron beam, microwave, ion-beam, laser-assisted, combustion driven and thermal plasma processes used in the DoE community and at the numerous government laboratories throughout the U. S.

Approach

We are studying the deposition of titanium diboride (TiB_2) from diborane (B_2H_6) and titanium tetrachloride (TiCl_4) from the basic reaction $\text{TiCl}_4 + \text{B}_2\text{H}_6 \rightarrow \text{TiB}_2(\text{s}) + \text{H}_2 + 6\text{HCl}$ in a low pressure (2–15 torr) inductively coupled rf-plasma continuous flow CVD system. TiB_2 was selected in this investigation from a variety of potential compounds for hard face coatings for several reasons. Hexagonal TiB_2 is ranked as the fourth hardest known compound with a density of 4.52 g/cc and a melting point of approximately 3200 C. It is a very stable boride at room and elevated temperatures and the only boride of titanium that is stable in the presence of carbon. This stability is related to its crystalline structure which is dominated by the 2-D network boron configuration. The thermal expansion coefficient, β , of TiB_2 ($\approx 6.5 - 8.1$ deg/C) closely matches that of Ti-6Al-4V ($\approx 7.2 - 9.6$ deg/C) which is the reference substrate material selected. Having a perfect β match is desirable, but having a substrate of slightly higher β will result in some compression during cooling which is a desirable feature. A relatively thin coating of very hard TiB_2 ($\approx 1 \mu\text{m}$) over a relatively ductile substrate of Ti-6Al-4V should provide an optimum combination. The reactor has been described previously (Ref. 2). The reactor is axially symmetric, presently consisting of a cylindrical (36 mm ID)

quartz walled test section in which quartz optical access ports have been installed. The 13.56 MHz rf field is generated using a 5 kW power supply and inductively coupled, using a multiple-turn, water cooled copper work coil, to the reactant gases. Up to five reactant or carrier gases can be simultaneously injected into the reactor through a metered flow system. The work coil and matching network are installed on a platform independent of the reactor itself and are capable of independent positioning via a motor driven worm gear. This allows spectroscopic probing at variable distances upstream or downstream from the work coil and the plasma region. The substrate holder is also independently driven by a magnetic slide mechanism, thereby allowing the substrate to be positioned at variable distances from either the laser probe beams or the plasma work coil region.

Our goal is to develop a sufficient chemical and physical data base, complemented with chemical kinetic modeling and material characterization, so as to enable a predictive capability for this type of PACVD materials process. No previous published work exists that has adequately modeled this important type of nonequilibrium plasma process. One of the main objectives of this program is the development of a detailed model describing the controlling chemical and physical processes associated with the PACVD of titanium diboride. There is very little fundamental existing knowledge on gas phase, plasma, or surface processes associated with decomposition of the proposed reactants, diborane and titanium tetrachloride, or the formation of the product, titanium diboride. Many species, including compounds/radicals may be involved in this complex process. These include B, Ti, Cl H₂, H, BH, BH⁺, BCl, TiH, BH₂, TiCl, TiB₂, BCl₃, BH₃, B₂H₅ and B₅H₁₁. Development of a useful and reliable model should entail separate development (combined with diagnostic verification) of models for decomposition of diborane, decomposition of TiCl₄, co-decomposition of the two reactants, plasma assisted decomposition of these species, deposition of boron from diborane, deposition of titanium, and co-deposition of boron and titanium.

CARS as a probe for nonequilibrium effects

Much of the laboratory effort to date has been focused on applying coherent anti-Stokes Raman spectroscopy (CARS) to gas phase precursors and major molecular by-product species. CARS is an advanced laser wave-mixing technique wherein two incident laser beams are mixed while illuminating the molecule key to the process. For plasma systems such as PACVD, a colinear, scanned narrowband approach is normally used for increased sensitivity. Figure 1 is a simplified schematic of

Fig. 1. UTRC narrowband, colinear scanned CARS system for diagnostics of plasma TiB₂ materials processing.

the CARS system implemented at UTRC for diagnosing the chemistry and temperatures in the plasma processes. The basic CARS equipment includes an injection-seeded, single-mode, Nd:YAG primary beam pump laser which is frequency doubled to produce narrow bandwidth (≈ 50 MHz), 10 nanosecond pulses at 532 nm with a 10 Hz repetition rate, and a narrow bandwidth (0.4 cm^{-1}) scanned Stokes dye laser. A major portion of the primary beam is split off to drive the dye laser. The remaining 532 nm beam serves as the pump and is combined colinearly with the Stokes beam at a dichroic prior to focusing in the test region. The frequency shifted CARS signal is formed in the laser focus and all three beams exit the reactor where a dichroic separates the CARS beam from the incident wave mixing beams. All signals from the PMT are digitized on every pulse and processed in a computer. Typically, ten CARS pulses are averaged per spectral step which corresponds to 0.1 cm^{-1} in wavenumber. In about 30 minutes spectral scans from $50\text{--}100\text{ cm}^{-1}$ can be completed.

Figure 2 is an example of the first time measured spectrum of the rovibrational manifold of B_2H_6 from which concentration and temperature (vibrational and rotational) is obtained. As molecular hydrogen is also a major constituent of typical diamond-producing gases, a rotationally resolved CARS spectrum of the $v=0$ vibrational level of H_2 can be deconvoluted to yield rotational temperature, as illustrated in Fig. 3. The areas under each peak are calculated, ratioed, and compared with theoretical calculated peak ratios to assign rotational temperature.

Fig. 2. Example of CARS spectrum of B_2H_6 measured in PACVD of TiB_2 process

Fig. 3. Hydrogen CARS spectrum in plasma at 300 K

In these experiments CARS has been successfully applied to measure concentrations and temperatures in both the $\text{B}_2\text{H}_6/\text{Ar}$ system and in the $\text{TiCl}_4/\text{B}_2\text{H}_6/\text{Ar}$ system. This resulted in the key observations (Ref. 3, 4) that:

1. Chemistry is initiated far (≈ 10 cm) upstream of the work coil, most probably due to electron impact induced fragmentation.
2. Near stoichiometric conversion of B_2H_6 to H_2 and/or H_2/HCl appears to occur upstream of the work coil/plasma glow region
3. In the absence of rf-coupling effects to the wall, all chemistry occurs near room temperature.

4. Observation of emission spectra of both systems indicate B_2H_6 and/or $B_2H_6/TiCl_4$ quenches UV emission.

Model Development

Substantial UTRC expertise has already been developed in utilizing and modifying SANDIA computer codes for treating many of the important chemical and physical processes associated with PACVD. These codes include CHEMKIN II (Ref. 5), a transport property package (Ref. 6), SURFACE CHEMKIN (Ref. 7) and many of the related codes such as SENKIN (Ref. 6), SPIN (Ref. 5) for modeling surface deposition during flow against a disc, and CRESLAF (Ref. 10) for modeling a chemically-reacting, boundary layer flow with surface deposition.

Towards the specific objectives of model development for PACVD of TiB_2 , significant advances have already been made at UTRC:

1. A detailed chemical kinetic model for the pyrolysis of diborane has been developed and compares well with literature pyrolysis data,
2. A preliminary model for the pyrolysis of titanium tetrachloride has been constructed,
3. The diborane pyrolysis model has been augmented to describe the decomposition of diborane upstream (observed with CARS diagnostics) of a plasma reactor, and
4. A preliminary model for CVD of boron in the vicinity of an argon/diborane plasma field has been developed.

but rapid recombination of BH_3 back to diborane resulted in negligible overall decomposition of diborane. With the added reactions

With these and several other reactions involving H-atom abstraction by H-atoms to form molecular hydrogen, diborane decomposition can be approximately modeled. The complete reaction sequence is reproduced in Table 1. Rate constants for decomposition via electron impact were selected to be about 20 sec^{-1} in order to model the observed decay in diborane. Assuming a rate constant of $10^{16} \text{ cc/mole/sec}$ for an electron-molecule reaction, the required rate constant suggests an average electron density of about 10^9 per cubic centimeter. This electron number density is consistent with low limit estimates for densities in plasmas which should provide a reasonable estimate for conditions

upstream of the plasma glow region. Unfortunately, the large amounts of molecular hydrogen experimentally observed could not be predicted by the model. The stoichiometric conversion of diborane to hydrogen

strongly suggests the existence of surface processes which have not yet been included.

Correlation of Material Properties to Operating Envelope

Detailed coating characterization has been accomplished (Ref. 11) on samples of rf-PACVD prepared TiB_2 using Auger, Ion Scattering and secondary ion mass spectroscopies (AES, ISS and SIMS) as well as several complementary techniques. In addition, coating characteristics such as smoothness, adhesion (UTRC custom built pin-on-disk apparatus) and hardness (state-of-the-art Nanoindenter apparatus) and erosion resistance (UTRC sand erosion test facility) have been measured. Table 2 summarizes the physical, chemical and mechanical properties that have been measured from coatings prepared in our laboratory on Ti-6Al-4V substrates. This substrate represents a critical alloy of paramount interest in many commercial and DOE applications. It's strength to weight and low temperature oxidation/corrosion resistance are excellent, but erosion and wear occurs rapidly, thus the need for applying a durable extremely hard face coating such as TiB_2 . Ion implantation has also been shown capable of improving TiB_2 tribological properties even further (Ref. 12). Near-surface hardness increases to as high as 70 GPa and the dry coefficient of friction has been shown to decrease from about 0.25 down to 0.05 (i.e. — approaching teflon).

TABLE 1
CHEMICAL KINETIC MODEL FOR DIBORANE PYROLYSIS
ENHANCED BY ELECTRON IMPACT

		(k = A T**b exp(-E/RT))		
Reactions Considered		A	b	E
1. B ₂ H ₆ →2BH ₃ (+e)		2.0E+01	0.0	0.0
2. BH ₃ +BH ₃ (+M)→B ₂ H ₆ k _∞		2.0E+13	0.0	0.0
k ₀		9.0E+18	0.0	0.0
3. BH ₃ +B ₂ H ₆ =B ₃ H ₇ +H ₂		2.5E+11	0.0	7500.0
4. B ₃ H ₇ +B ₂ H ₆ →B ₅		8.0E+11	0.0	8500.0
5. B ₅ H ₁₁ →B ₅ H ₉ +H ₂		1.0E+12	0.0	30000.0
6. B ₃ H ₇ +BH ₃ →B ₄ H ₁₀		1.0E+13	0.0	3500.0
7. BH ₃ +B ₄ H ₁₀ D→B ₅ H ₁₁ +H ₂		2.8E+11	0.0	7500.0
8. B ₂ H ₆ →B ₂ H ₅ +H (+e)		2.0E+01	0.0	0.0
9. H+B ₂ H ₅ →BH ₃ +BH ₃		5.0E+12	0.0	0.0
10.H+B ₂ H ₅ →BH ₂ +BH ₂ +H ₂		1.0E+13	0.0	0.0
11.H+B ₂ H ₅ →B ₂ H ₄ +H ₂		5.0E+12	0.0	0.0
12.B ₂ H ₅ +B ₂ H ₆ =B ₄ H ₁₀ +H		8.0E+11	0.0	8500.0
13.B ₂ H ₅ =BH ₃ +BH ₂		3.0E+15	0.0	35000.0
14.H+B ₂ H ₆ =H ₂ +B ₂ H ₅		1.0E+13	0.0	10000.0
15.BH ₂ +B ₂ H ₆ =B ₃ H ₇ +H		1.0E+13	0.0	28000.0
16.BH ₂ +BH ₂ (+M)→B ₂ H ₄ k _∞		2.0E+13	0.0	0.0
k ₀		9.0E+18	0.0	0.0
17.B ₂ H ₄ +B ₂ H ₆ →B ₄ H ₁₀		1.0E+09	0.0	0.0
18.B ₂ H ₄ →BH ₂ +BH ₂ (+e)		2.0E+01	0.0	0.0

Note: A units mole—cm—sec—K, E units cal/mole

Despite having accomplished this extensive array of characterizations, several measurements are still desirable. Since we have either established or propose to establish chemical kinetic models and laser spectroscopic measurements on the two component plasma integrated—systems involved in TiB₂ deposition, minimal characterization on both the boron deposited from the diborane/Ar plasma and on the titanium deposited from the TiCl₄/Ar plasma should be included. Trace impurities and hydrogen content can be measured by SIMS.

TABLE 2
TiB₂ COATING CHARACTERIZATION MEASUREMENTS SUMMARY

Physical: <u>Measurement</u>	<u>Technique</u>	<u>Results/Comments</u>
Structure/Orientation	X-ray	Hexagonal structure Lattice parameters correct Highly preferred orientation: (111)
Thickness	SEM, SEI	25 μm with intermixing in 0.2 μm region near interface.
Surface roughness	Sloan Dektak, STM	random roughness: 50–100 μm wavelength. peak-to-peak ampl.: 500 nm – 1 μm
Mechanical: <u>Measurement</u>	<u>Technique</u>	<u>Results/Comments</u>
Hardness	UTRC Nanoindenter	Very high hardness: 40 GPa @ 170 nm depth
Adhesion/Cohesion	UTRC Scratch Removal Technique	20 N force required to cause isolated fracture spallations @ > 20 N, transverse microcracks occur in scratch trough @ 60N separation occurs
Erosion	UTRC Sand Erosion (Sinai sand)	Survival well above other materials. No measurable erosion @ impact velocities < 200 m/s Coating fails @ 270 m/s
Chemical: <u>Measurement</u>	<u>Technique</u>	<u>Results/Comments</u>
Composition	AES	TiB _{2.17} , traces of C, O
Chemical: <u>Measurement</u>	<u>Technique</u>	<u>Results/Comments</u>
	XPS	TiB _{2.18} , trace of carbide. Broadening of B peak suggests presence of free B.
	RBS	Ti signal 20% less than expected for dense TiB ₂ . Suggests coating is TiB ₂ with 20% Ti vacancies, 10% B vacancies.

In addition, since the stoichiometry of our coatings is approximately $\text{TiB}_{2.2}$ (see Table 2), we should continue to monitor this parameter as we vary plasma parameters such as flow, pressure (both partial pressure of the reactants and total pressure), rf-power, etc. Also, as required to provide additional input on the potential species present, both time-of-flight and quadrupole mass spectroscopic systems are available at UTRC. The question we wish to answer is: 'do we always get $\text{TiB}_{2.2}$ regardless of processing test parameters?' The coatings produced during laser diagnostic experiments can be monitored for stoichiometry using AES and for impurities using SIMS. The question of stoichiometry is important to have complete information for modeling.

CONCLUSIONS

The chemical physical processes that lead to a PACVD applied TiB_2 coating are extremely complex in nature due to the extent of non-equilibrium in the low (~ 10 torr) pressure regime. It is also this effect, however, that produces desirable qualities such as low temperature deposition and species that couldn't exist thermodynamically in higher temperature regimes. It is unique to this type of process that gas phase chemistry can occur at room temperature and coexist with a highly energetic pool of electrons, ions and photons whose representative "temperature" is approximately 10,000–20,000K.

We have used laser spectroscopy, CARS, to determine that both precursors and products in this unique environment are rotationally equilibrated with the surrounding environment and the sole interaction (in our reactor) of the high temperature pool of species is to initiate the chemistry. This simplified the modeling effort. The next step is to develop pyrolytic models where the initial production of free radicals is generated thermally, compare these models with published literature for validation, and use them as a basis for modelling the low pressure plasma system. Various initiation schemes can be tested and selected based on spectroscopically observed data.

We believed that our $\text{B}_2\text{H}_6/\text{Ar}$ system could be modelled by a pyrolytical mechanism augmented by electron impact induced fragmentation of B_2H_6 . As described above, the comparison of CARS data with modelling results, led us to conclude that BH_2 production is critical to boron deposition. Even with our present model, the near stoichiometric conversion of B_2H_6 to H_2 and B observed experimentally is not adequately predicted. Our interpretation of this deficiency is that our model lacks the heterogeneous chemical reaction sequences necessary to predict total conversion of hydrides to hydrogen molecules. To understand the total PACVD of TiB_2 deposition process, continuation of the heterogeneous reaction chemistry is required.

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