

Diagnostic techniques for plasma reactor temperature and species determination in advanced materials processing

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Abstract: Although plasma techniques continue to emerge as one of the more efficient means for processing advanced materials, the technology transfer, including optimization and scale-up, of plasma systems (both thermal and non-equilibrium) is hindered by a lack of understanding of the basic mechanisms which govern the plasma process. Understanding the plasma chemical reactions that occur in these reactors depends on the ability to accurately determine the plasma gas temperature and species concentration distributions. Concentration gradient measurements in turn yield information on the homogeneous/heterogeneous nature of the reactions, chemical kinetic constants, and mass transport coefficients. Detailed knowledge of the temperature and reaction rates is also essential to the success of any detailed modeling effort. Laser/optical diagnostic techniques have the capability to provide much of this crucial information. Many of these optical techniques are non-intrusive, species specific and yield excellent spatial and temporal resolution. Optical in-situ measurements, in contrast to measurements using conventional sampling probe techniques, provide valuable information on the presence of excited species (e.g., hydrogen atom concentration in the diamond deposition process) as well as the deviation from local thermodynamic equilibrium in the case of high temperature gas flows generated by plasma sources. This paper includes discussion of both optical/laser techniques and representative conventional probe techniques. Approximate temperature limitations, advantages, and disadvantages of representative temperature and species measurement techniques are summarized. A recent example of the complementary use of laser diagnostic techniques in plasma reactors for advanced material processing is presented.

INTRODUCTION

The use of both thermal and non-equilibrium reacting plasmas is attracting increasing attention as a novel approach for processing materials, especially for depositing a wide variety of coatings(1). The basic steps in the non-equilibrium coating process and the range of electron temperatures and density characteristic of the process are illustrated in Figs. 1 and 2, respectively. Principal stages of the process involve the generation of the coating material, the formation of reactant species, the transport of the reactant species to the substrate, and the final coating growth. Table I shows some examples of non-equilibrium and thermal coating and surface modification techniques in use, grouped according to the characteristic deposition process, i.e. molecular, particulate, or bulk. Listed on the far right of the table are surface modification techniques that may be applied in either a pre- or post-deposition process. Emerging applications are occurring in the fields of wear/tribology and erosion/corrosion resistance that include hard face materials, composite and nanostructural materials, metastable phase synthesis, graded composition microstructures, and stress or thermal management coatings via hybrid plasma deposition/ion implantation. Erosion and wear resistant coatings are especially important because if improvements can be made in durable protective coatings, increased utilization of current and light-weight materials under advanced development will rapidly result. Erosion and associated tribological wear aspects are responsible for an enormous expenditure of energy and fiscal resources in many applications.

Of special interest is the case of non-equilibrium plasma techniques which possess unique features not available via other commercial techniques. These include deposition with controllable environment and low bulk gas temperatures (resulting in reduced stresses in the coating). These techniques are also amenable to fully computerized process control (via in-situ diagnostics/sensors) and scale-up to production operation.

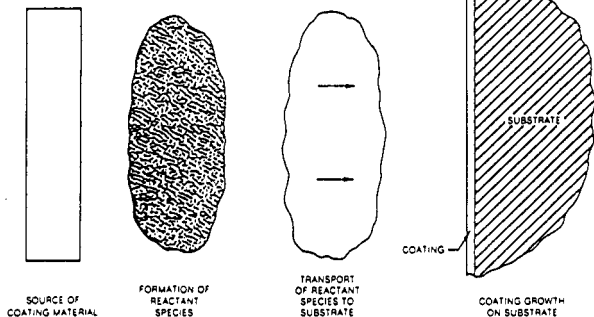


Fig. 1 Basic steps in plasma coating processes

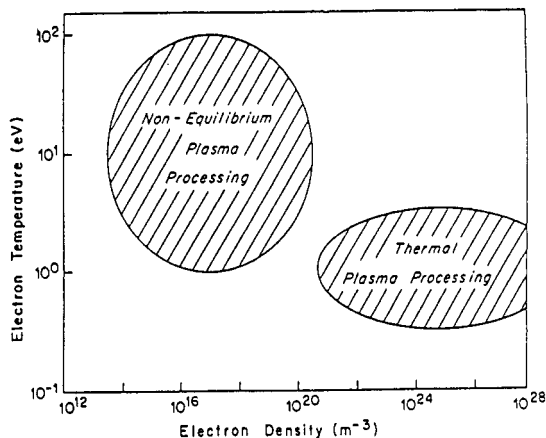


Fig. 2 Ranges of thermal and non-equilibrium plasma systems

SCIENCE BASE/NEEDS

These new applications of plasma processing are unfortunately severely limited by a lack of understanding of the mechanisms which govern the plasma molecular or atomic depositions of coatings. The properties, homogeneity and quality of these coatings are sensitive to a large number of process variables, such as gas composition and flow rate, pressure, power input, gas and substrate temperature, purity, and exposure time. As these parameters are coupled in a complicated manner, the current science base lacks an understanding of how the physical and chemical properties of coatings correlate with plasma conditions present during their formation. Critical issues are enumerated in Table II. Another problem in characterizing the chemistry in a non-equilibrium plasma is the lack of a single "temperature" as a characteristic parameter. Thus the system must be described in terms of electron, ion, excitation, vibrational, rotational, and gas temperatures.

The application of non-intrusive, non-perturbing optical/laser diagnostic techniques is a required first step for determining the chemical composition, reactive species (radicals) and corresponding concentration and temperature gradient within the plasma reaction zone(2,3). From this basic knowledge, plasma chemistry induced mechanisms can be formulated.

TABLE 1. Examples of coating techniques

ATOMISTIC DEPOSITION	PARTICULATE DEPOSITION	BULK COATINGS	SURFACE MODIFICATION
CHEMICAL VAPOR DEPOSITION <u>PLASMA ASSISTED</u>	THERMAL SPRAYING PLASMA SPRAYING D-GUN FLAME SPRAYING	WETTING PROCESSES PAINTING DIP COATING	CHEMICAL CONVERSION ELECTROLYTIC ANODIZATION (OXIDE) FUSED SALTS
ELECTROLYTIC ELECTROPLATING ELECTROLESS PLATING FUSED SALT CHEMICAL DISPLACEMENT	FUSION COATINGS THICK FILM INK ENAMELING ELECTROPHORETIC	ELECTROSTATIC SPRAYING PRINTING SPIN COATING	CHEMICAL-LIQUID CHEMICAL-VAPOR THERMAL PLASMA
VACUUM VACUUM EVAPORATION ION BEAM DEPOSITION MOLECULAR BEAM EPITAXY SPUTTER DEPOSITION ACTIVATED REACTIVE EVAPORATION PLASMA POLYMERIZATION ION PLATING		CLADDING EXPLOSIVE ROLL BONDING	LEACHING/SPUTTERING
LIQUID PHASE EPITAXY		OVERLAYING WELD COATING LASER	MECHANICAL SHOT PEENING
			SURFACE ENRICHMENT DIFFUSION FROM BULK
			ION IMPLANTATION ION MIXING
			THERMAL LASER PLASMA E-B

TABLE 2. Science Base

- Both thermal and non-equilibrium plasma reactor optimization and scale-up hindered by lack of understanding of basic mechanisms involved in deposition process
- Accurate temperature and gas composition/concentration measurements required
 - Detailed thermal profiles required for complete description of chemical environment
 - Chemical reactions depend strongly on temperature
 - Concentration gradients provide information on nature of reaction, reaction kinetic constants, and mass transport coefficients.

EXAMPLE APPLICATION

The selection of a particular deposition process depends on many factors, as illustrated in Table III. Once the selection criteria are determined, the particular process is chosen based on the individual unique features, characteristics and constraints within the given operating regime. At this point the appropriate diagnostic technique can be selected are required to optimize the process and provide the information for scale-up to a production type system.

An example of a non-equilibrium Plasma-Assisted Chemical Vapor Deposition (PACVD) type reactor used for the deposition of hard face protective coatings such as TiB₂ and diamond(4,5) is shown in Fig. 3. This longitudinal tube-type radio frequency configuration is a design that is viable for scale up to high reactant gas flows and plasma power levels. These type of reactors are typically constructed from high purity fused silica with test section diameters in the order of 5 cm. A rf power supply, operating at 13.56 MHz, with up to about 5 kW power is used to couple the rf power into the plasma in the 1-50 torr range through a work coil, as shown in the figure. The cleanliness of the substrate prior to coating deposition is a key requirement for achieving good adherence of the coating to the substrate; therefore a substrate holder and isolated load-lock and transport system are interfaced with the PACVD test section. Operational flexibility is enhanced by the simultaneous injection of different source gases at the inlet region as shown; a vacuum system is connected to the exhaust end of the reactor.

TABLE III. Basic selection criteria for deposition processes

BASIC SELECTION CRITERIA FOR DEPOSITION PROCESSES
• Deposited Material Composition
• Adhesion of Coating to Substrate
• Shape and Size of Substrate
• Purity of Source Material
• Substrate Preparation and Purity Level
• Required Deposition Rate
• Temperature Restrictions on Substrate
• Coating Thickness

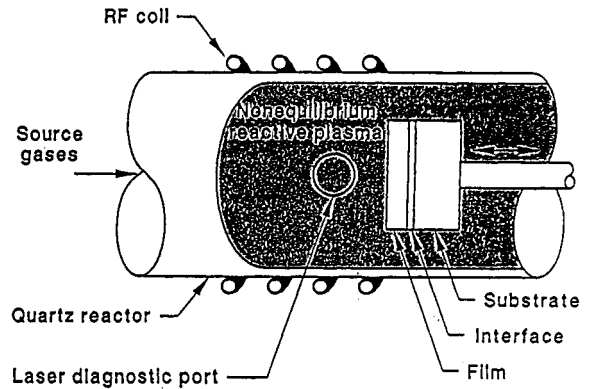


Fig. 3 Example of PACVD reactor used in deposition of hard face coatings

CONVENTIONAL TECHNIQUES FOR TEMPERATURE MEASUREMENT IN HIGH TEMPERATURE GASES

This discussion is restricted to the principal techniques applicable to plasma systems at elevated temperatures (approx. 3000° K). Other well-established conventional techniques for temperature measurement are discussed in detail in Refs. 6 and 7. Approximate temperature limitations, advantages, and disadvantages of representative temperature measurement techniques are summarized in Table IV.

Thermocouples are widely employed for sensor probe temperature measurements. Although the temperature range of 'standardized' thermocouples extends to only about 2100 K, higher temperatures are possible with the use of refractory metals, such as tungsten/rhenium, iridium/rhodium, and platinum/rhodium(6). For non-oxidizing testing applications, thermocouples based on tungsten-rhenium alloys can perform acceptably to 3030 K, or, for short periods, up to approximately 3300 K(7). Common sources of measurement error associated with thermocouples include radiation losses, conduction error, and catalytic reactions between reacting gases and the metal surface of a probe. Many of the drawbacks associated with thermocouple probes can be circumvented by the use of aspirating temperature probes, such as enthalpy probes(8) or sonic orifice probes(9). Water-cooled calorimetric or enthalpy probes have been used successfully for steady state operation at temperatures of up to 15,000 K(8). This type of probe is used to infer temperature by determining the amount of heat absorbed by the coolant. Another type of aspirating probe is the double sonic orifice probe,(9) which consists of a pair of in-line choked orifices, separated by a section of cooled duct. Aspirating probes can offer high accuracy, relative ease of calibration and measurement, and the capability to simultaneously measure several flow properties, such as temperature, pressure, gas velocity, and

chemical composition (for two-component mixtures). Use of these probes requires the gas to be in chemical equilibrium, and the probes are not capable of rapid time response.

Conventional optical techniques for temperature measurement include various types of radiation thermometers. Such thermometers include "passive" devices which analyze the radiation emitted by a substance carried by the hot gas, and "active" devices in which a probe beam is used to determine the relative populations of the energy levels of gaseous test substances(6). A major difficulty with radiant methods lies with determining the actual point of measurement within the gas medium. Optical measurements can also be affected by absorption either within the hot gas or by a surrounding cooler gas(9). These optical temperature measurement systems tend to be more complicated, and hence more expensive, than probe systems, as the optical systems require visual access, optics, reference source(s) such as cavity radiators or lamps and detectors. Transmission-type techniques for temperature measurement have utilized the temperature dependence of certain gas properties, such as electrical conductivity and sound velocity, to determine the gas temperature. While in theory well suited for high-temperature applications, these techniques can be subject to serious errors in the presence of any non-uniformities in gas properties, including boundary layers(7), and are infrequently used in practice.

TABLE IV. Conventional temperature measurement techniques at high gas temperatures

technique	temperatures	advantages	disadvantages
Thermocouples	to 3030 K	W/Re compatible with H ₂ simple inexpensive	radiation errors conduction errors probe bending intrusive catalytic effects
Aspirating Probes (e.g. enthalpy, sonic orifice)	to 15000 K	robust easily used high accuracy inexpensive Info on velocity and concentration	can require calibration require equilibrium steady-state only intrusive
Radiation/spectral thermometry	> 4000 K	rapid response non-intrusive	poor spatial resolution require optical ports may require seeding of gas must know emissivity/spectral properties
Transmission measurements (e.g. sound speed, elect. conductivity, absorption)	> 6000 K	non-intrusive rapid response	must know gas composition relies on gas uniformity

TABLE V. Conventional composition measurement techniques at high gas temperatures

technique	advantages	disadvantages
Gas sampling plus gas analyzer(s) (e.g. mass spectrometer, gas chromatograph)	high accuracy can detect ppm levels	long sampling time probe quenching effects analyzers expensive
Aspirating concentration probes (e.g. enthalpy, concentration probes)	simple do not require gas analyzer rapid time response inexpensive	must know temperature probe quenching effects cannot detect ppm levels binary mixtures only
Optical spectrometry	non-intrusive highly accurate	limited species must know temperature along optical path requires calibration requires optical access

CONVENTIONAL TECHNIQUES FOR CONCENTRATION MEASUREMENT IN GASES

Commonly employed experimental techniques for determining species concentrations in high-temperature type environments involve sample extraction by a probe for subsequent chemical analysis and optical spectrometry(10). A tabulation of the advantages and disadvantages of several composition measurement techniques is presented in Table V. The required chemical analyzers are standard, commercially available instruments and as such are not discussed in this paper. A major complication associated with gas sampling techniques is the potential for chemical reactions within the probe or transfer line, which may significantly alter species concentrations, leading to erroneous results(10,12). In addition, as with any physical probe, there is the potential perturbation of the gas flow, especially in the presence of steep temperature and concentration gradients.

A simpler and less costly alternative involves the use of aspirating probes designed to directly determine species concentrations from the bulk properties of the gas. One such probe contains a constant-temperature hot wire imbedded in the gas flow downstream of a sonic orifice(11), which allows the measurement of power losses due to convection. These types of probes require extensive calibration and create an uncertain degree of flow disturbance. Some aspirating-type probes are capable of very fast time response ($\approx 200 \mu\text{s}$)(12). Use of these types of probes also require independent knowledge of the local gas temperature and probe quenching effects are also of concern.

LASER/OPTICAL DIAGNOSTIC TECHNIQUES

Conventional diagnostics are generally not well suited to plasma materials processing experiments due to the limitations discussed above and illustrated in Tables IV and V. Many of these limitations can be circumvented by the use of laser-based optical diagnostic techniques. Table VI shows the hierarchy of optical diagnostic techniques that are currently available (in different stages of advanced development) for use in reactors for plasma processing

of materials. Since these techniques are photon-driven they provide negligible disturbance to the plasma. The main attributes of laser based systems are summarized in Table VII; a more detailed discussion is given in Ref. 13. Many of these techniques are currently applicable to a variety of hostile plasma environments. The inherent advantages/disadvantages of these optical/laser diagnostics are summarized in Table VIII. It is important to recognize that no single diagnostic technique may suffice for any given process; it will only be through the complementary use of these techniques that a fundamental understanding of the relationship between plasma process variables (temperature and species concentration) and properties of the processed material will evolve.

One example of a powerful laser technique, Coherent Anti-Stokes Raman Spectroscopy (CARS), developed at UTRC is shown in Fig. 4(14). This is a laser wave-mixing technique wherein two incident laser beams at frequencies ω_1 and ω_2 are mixed while illuminating the molecule key to the process. The frequency difference between the two wave-mixing beams is set to coincide with the Raman active vibrational resonance of the selected molecule. This excitation leads to the scattering of photons by the molecule, which results in a CARS coherent laser-like signal beam. For plasma systems, a colinear, scanned narrow band approach is normally used. In this case the laser pump energy excites a single transition of the resonant molecule at a given time and increases the sensitivity by several orders of magnitude. As the dye laser is scanned, successive transitions of the molecular resonances are excited, modulating the intensity of the CARS signal. The result is a spectrum of the rovibrational manifold of the medium from which identification of species, their concentration and temperature (vibrational and rotational) can be obtained (see Figs. 6 & 7).

TABLE VI. Hierarchy of optical diagnostics

- Emission spectroscopy
 - Black Body
 - IR
 - Visible/UV
- Absorption spectroscopy
 - FM
 - Intracavity
 - FTIR
 - Diode laser absorption spectroscopy
- Laser Induced fluorescence (LIF)
 - Multi-photon LIF
- Spontaneous Raman scattering
- Nonlinear scattering
 - Coherent anti-Stokes Raman spectroscopy (CARS)
 - Degenerate four wave mixing (DFWM)

TABLE VII. Attributes of laser-based diagnostics

- Non-perturbing and mobile
 - CARS, LIF, MPLIF, DFWM
- High accuracy
 - Temperature $\leq \pm 5\%$, concentration $\leq \pm 5\%$
- Excellent spatial and temporal resolution
 - Spatial $\leq \text{mm}^3$
 - Temporal $\leq 1 \mu\text{s}$
- Many now applicable to hostile environments
 - CARS in gas turbine exhaust, internal combustion engines, scramjets, hybrid rockets
 - Raman spectroscopy in space shuttle preburner and exhaust, gas turbine combustor exit
 - LIF in gas dynamic facilities, scramjets

TABLE VIII. Optical temperature measurement techniques

technique	advantages	disadvantages	technique	advantages	disadvantages
Emission:			Absorption:		
• Black body	experimentally/theoretically easy	solids only poor spatial accuracy emissivities not generally available	• FTIR	experimentally easy ground state v/r temp. of molecules and molecular ions	difficult to interpret poor spatial accuracy
• IR	experimentally easy	molecular(m) gases only vibrational/rotational (v/r) temperature only poor spatial accuracy difficult to interpret	• Diode laser absorption spectroscopy	ground state v/r temp. of m,l	experimentally complex requires tunable diode laser poor spatial accuracy
• Visible/UV	experimentally easy applies to ions(l), atoms(a), and molecules(m)	electronic and excited excited state v/r temperatures only poor spatial accuracy difficult to interpret	Scattering:		
• LIF	species and state selective experimentally easy ground state v/r temperature used in flame studies very high species selectivity	difficult to interpret poor spatial accuracy mostly applicable to small molecules requires laser	• linear - Raman	ground state v/r temp. of m,l experimentally easy	low sensitivity poor spatial accuracy
			• non-linear - CARS	ground state v/r temp. of m,l high spatial accuracy good species sensitivity	experimentally complex
			- DFWM	ground state v/r temp. of m,l high spatial accuracy good species sensitivity	experimentally very complex difficult to interpret

Figure 5 is a simplified schematic of the type of CARS system implemented at UTRC for diagnosing the chemistry and temperatures in plasma processes used for depositing hard face coatings such as TiB₂ or diamond(14). 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 focussing 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.

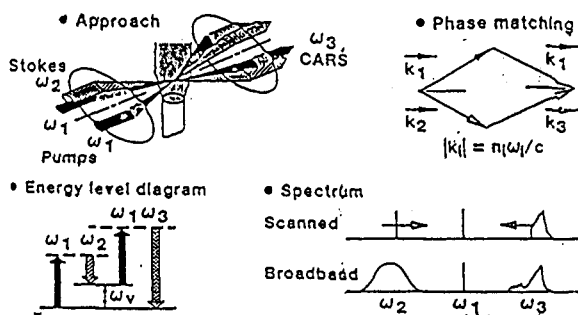


Fig. 4 Coherent anti-Stokes Raman spectroscopy (CARS)

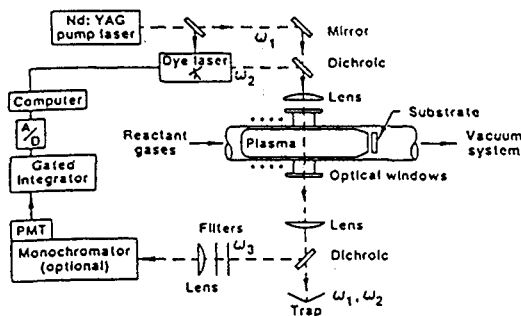


Fig. 5 Narrowband, colinear scanned CARS system for diagnostics of plasma materials processing

As molecular hydrogen is a major constituent of typical diamond-producing gases, a rotationally resolved CARS spectrum of the $v=0$ vibrational level of H₂ can be deconvoluted to yield rotational temperature, as illustrated in Fig. 7. The areas under each peak are calculated, ratioed, and compared with theoretical calculated peak ratios to assign rotational temperature.

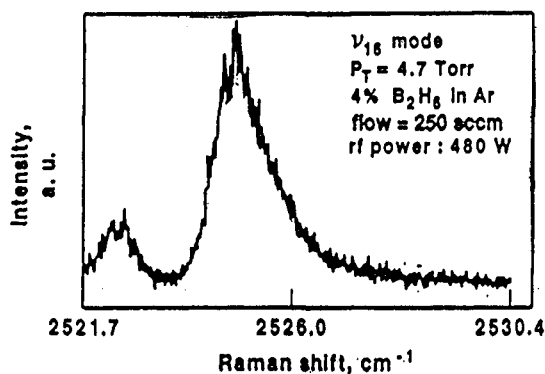


Fig. 6 Example of CARS spectrum of B₂H₆ measured in PACVD of TiB₂ process

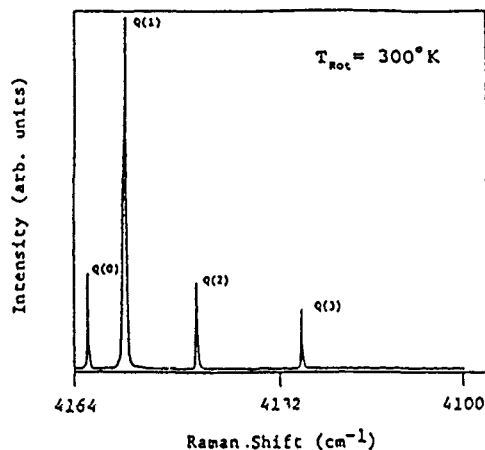


Fig. 7 Hydrogen CARS spectrum in plasma at 300 K

Laser induced fluorescence (LIF) applied to plasma diagnostics is well documented in the literature (15,16). Basically, the absorbing species is promoted to an excited state by the resonant absorption of laser radiation. Normally, the fluorescence radiation occurs at a longer wavelength than that of the absorption. The excitation

temperature is determined from the distribution of radiation from various states connected to the absorbing state. A molecule in an excited state may lose energy through a number of paths, such as dissociating internal energy transfer, energy transfer to another molecule or atom, or chemical reaction. An important advantage of this technique is that the fluorescence signal intensity is a maximum, consequently, saturation yields the highest species selection sensitivity. LIF spectroscopy has the advantage of excellent spatial resolution and high scattering cross-section. Pulsed operation can provide high temporal resolution. LIF is an incoherent technique that is applicable to minor species, as shown in the right of Fig. 8. Research involving 2-photon LIF has also been successfully used to study light reactive atoms such as O, Cl, N and H(17).

Degenerate Four-Wave Mixing (DFWM) is a variation of nonlinear scattering that has been reported in recent literature(19). This is another complementary diagnostic tool with potential application in high temperature gas (plasma) systems. Figure 8 shows how DFWM combines features of both CARS and LIF; the resultant technique provides a coherent signal with minor species detectivity well below the CARS sensitivity limits. Rakestraw et al.(20) demonstrated the use of DFWM for the quantitative measurements of OH and NH rotational distributions from which temperatures were derived. These results are in good agreement with CARS measurements and the technique offers the potential advantage of a simpler configuration because only one frequency is required for the process.

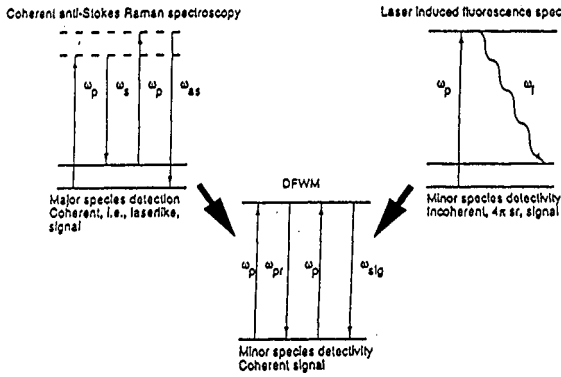


Fig. 8 Complementary aspects of laser diagnostic techniques

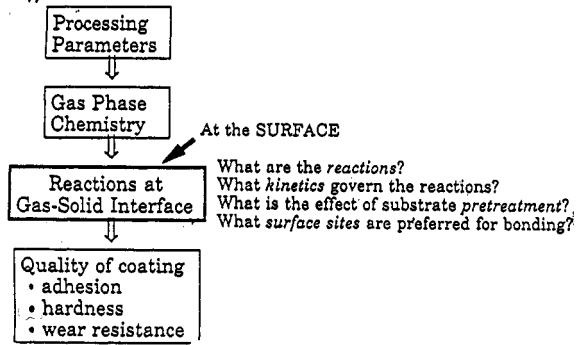


Fig. 9 Surface chemistry research issues

FUTURE DIRECTIONS

With more recent information on the gas phase becoming available, future efforts will most likely be directed at the substrate surface and the boundary layer close to the surface. The crucial importance of reactions in that region can be appreciate from the diagram depicted in Fig. 9. The coating formation process involves both homogeneous (gas) phase chemical phenomena and heterogeneous chemical reactions. The homogeneous reaction processes determine the type of reactive species necessary to initiate the surface coating phenomena and sustain the film growth. The interaction of a particular surface with the reactant species delivered through the boundary can channel the deposition process either to the desired coating composition or to an undesirable stoichiometry. Small variations in initial surface composition, surface temperature during the coating process or impurities introduced in the reaction system can conceivably have large effects on the coating chemistry path followed at the heterogeneous initiator and propagation sites. In short, given a constant phase precursor reaction network, slight changes in the surface conditions can lead to coatings having undesirable properties. Conversely, for a given surface reaction system, slight changes in the homogeneous reactant system could lead to an undesirable heterogeneous process. A more complete understanding of these processes will require laser/optical diagnostic techniques such as those described in this paper.

SUMMARY

Novel complementary laser/optical diagnostic techniques described above are candidates for application as plasma materials processing diagnostic tools, each with its own inherent advantages and associated limitations. This capability should ultimately lead to simple process control strategies to ensure high quality, economical, reproducible plasma processing of advanced materials in a production-scale environment.

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