Fundamental studies of chemical vapor deposition
diamond growth processes

CONF-9107115 --10

DE91 015324

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ABSTRACT

We are developing laser spectroscopic techniques to foster a fundamental understanding of diamond film growth by hot filament chemical vapor deposition (CVD). Several spectroscopic techniques are under investigation to identify intermediate species present in the bulk reactor volume, the thin active volume immediately above the growing film, and the actual growing surface. Such a comprehensive examination of the overall deposition process is necessary because a combination of gas phase and surface chemistry is probably operating. Resonantly enhanced multiphoton ionization (REMPI) techniques have been emphasized. A growth reactor that permits through-the-substrate gas sampling for REMPI/time-of-flight mass spectroscopy has been developed.

2. BACKGROUND

Little is known at the molecular level about the details of the chemical and physical mechanisms involved in CVD film growth processes. Most of the investigations of film growth processes to date have involved Edisonian studies; that is, operating parameters were varied and the quality of the material grown under these various conditions determined. The problem with this approach is that a real understanding of the material growth process is not achieved. This optimization approach may not examine the most important parameter required for the growth of a quality material. The real goal is to learn how to control the growth process for desirable film properties, not to optimize a given experiment.

Clearly small molecules (i.e., hydrocarbon fragments -neutrals and ions) play a role in diamond CVD, as does atomic hydrogen. The latter selectively etches and removes graphitic carbon that forms during the deposition. Ion or electron bombardment of the surface resulting in further molecular decomposition and lattice cross-linking may also be important.

The spectroscopic techniques described herein promote a chemical understanding of diamond growth by providing methods capable of measuring important growth species and determining their concentration gradients. Intermediate species present in the bulk reactor volume, the thin active volume immediately above the growing film, and the actual growing surface must be measured. Such a comprehensive examination of the overall deposition process is necessary because a combination of gas phase and surface chemistry is probably operating.

3. RESULTS AND DISCUSSION

A diamond film growth reactor was assembled, employing an O-ring sealed quartz cylinder (76 mm diameter) as a replaceable reactor vessel. Access to the interior of the reactor is via a high vacuum flange that also provides a gas inlet port and electrical and thermocouple feedthroughs. The quartz envelope serves as optical access to the substrate and was designed for convenient replacement or cleaning when dark wall coatings develop over time. The filament

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under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

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is a linear coil of 0.5 mm diameter tungsten wire that is carburized in CH_4/H_2 before a substrate is introduced. It is placed approximately 5 mm from the substrate, which lies on the flat bottom of the quartz cylinder; the filament temperature is measured using an optical pyrometer. A platinum-wired alumina substrate heater provides Joule heat independent of the filament to adjust the substrate temperature. Reactant gas flow rate and reactor pressure are under active control using mass flow controllers and a pump throttle valve.

Films on single crystal silicon were successfully grown by decomposing 1% methane in hydrogen on a tungsten carbide filament heated to about 1950 °C. SEM images of the resulting films show a 10 micron typical grain size with {111} and {100} exposed facets.

3.1 Bulk gases

The bulk reactor gas is probably the easiest (although not necessarily trivial) region to investigate. Techniques that allow three dimensional species and temperature mapping of the volume are desirable. Many different reactant gases have served as the carbon source for reported diamond film growth processes; the distribution of molecular fragments can be expected to be dependent on the particular carbon source and on the activation process employed (hot filament, RF discharge, etc.).

Detection of atomic hydrogen was demonstrated in the reactor under diamond growth conditions (40 torr, 1% methane in hydrogen, 50 SCCM flowrate) using 3 + 1 resonance enhanced multiphoton ionization (REMPI) spectroscopy at 365 nm. A spectral scan is shown in Figure 1. The output from a 10 pps Nd:YAG-pumped R6G dye laser was mixed with the pump laser fundamental wavelength to create the excitation light; pulse energies of 2 mJ were thus obtained. A travelling wave geometry^{1,2} was employed, and a platinum wire, situated between the reactor filament and a molybdenum substrate, was used to collect the photo-charge. The substrate was negatively biased by 150 volts to suppress collection of electrons from the filament.

Figure 1. Spectral scan of hydrogen atom 3 + 1 REMPI.

Three 364.7 nm photons reach the hydrogen 2P level from the 1S ground state. The line in Figure 1 represents ionization driven by absorption of third harmonic vacuum ultraviolet light generated in the medium² and is at slightly higher energy than the true 1S-2P resonance due to phase matching considerations. Addition of a retroreflecting mirror to create standing wave excitation should permit ionization via the resonant process which is known to be more

efficient. The ionization signal strength due to atomic hydrogen was recorded as a function of filament temperature and found to approximately double between 1860 and 1990 °C, as expected.¹

3.2 Boundary layer gases

All chemical vapor deposition processes for diamond film growth use a mixture of gases activated by some means, such as a hot filament, rf or microwave plasmas, or a flame. The activated species are transported to the surface of the film, with reactions occurring in all regions, activation, transport, and film boundary layer where important surface reactions take place.

For the investigation of the boundary layer, we have used a technique that we have developed in our laboratory for combustion diagnostics. This technique makes use of a small orifice in the substrate that connects the reactor to a high vacuum chamber. The method has been demonstrated for an air-acetylene flame³ and also for a gasoline-burning internal combustion engine.⁴ While the sharp reduction in collisional broadening of the spectral lines removes most of the background interference, further improvement in sensitivity and specificity can be achieved with the addition of mass-selective detection.

Whenever surface or surface-enhanced reactions are occurring and transport to the surface of reactant species is diffusion limited, there will be concentration gradients near the surface in a boundary layer. Knuth⁵ has used hydrodynamic focusing arguments to show that either the boundary layer or the bulk gas above it can be sampled by an orifice, with the sampled region depending on the ratio of orifice throat diameter, d , to boundary layer thickness, δ . For $d < \delta$, the sampled gases are principally from the boundary layer. For $d > \delta$, bulk gas will be concentrated in the center of the flow and can be isolated with a skimmer. Pumping constraints favor smaller orifices so the method is ideally suited for boundary layer measurements.

For orifice sampling experiments, the growth reactor described above is inserted into a stainless steel high vacuum chamber, and a quartz reactor with an orifice in its flat bottom is employed. Both quartz capillary (0.5 mm i.d.) and removable ceramic nozzles have been investigated. The former was found to be too fragile for practical use. A matching orifice was chemically etched in a silicon substrate to accept the nozzle outside diameter; the nozzle length is such that it extends through the substrate and terminates exactly at the surface. There are chamber windows for optical studies of the reactants in the filament and transport regions as well as for observing the substrate surface.

The region downstream of the reactor nozzle is pumped by a 450 L/s turbomolecular pump to a pressure of about 1 micron. Thus the expanding reactor gases reach a collisionless environment rapidly in order to suspend any further reaction. A conical molecular beam skimmer forms an aperture into the high vacuum region (5×10^{-7} torr) of the chamber where TOF mass spectroscopy (1 meter path) is performed. Optical access exists before and after the skimmer. An electron gun permits acquisition of survey TOF mass spectra by electron impact (EI) ionization. Suprasil entrance and exit windows exposing the ion extraction region allow for mass resolved, UV REMPI spectroscopy. Data acquisition is accomplished with a 300 MHz digital oscilloscope and a personal computer.

The 1% methane in hydrogen mixture was decomposed in the hot filament reactor and the resulting gas mixture composition followed by TOF mass spectrometry. The results are summarized in Figure 2. The boundary layer gases were extracted through a 0.34 mm diameter ceramic nozzle through the substrate. Electron impact ionization was utilized, with 70 volt electrons. Figure 2A is a TOF mass spectrum with the spectrometer evacuated (i.e., no feed gas); water and its OH fragment are evident at m/z 18 and 17, respectively. A reactor pressure of 20 torr was established for Figure 2B by supplying a 100 SCCM flow of the methane/hydrogen mixture; the reactor filament is still off. Methane and its EI fragments appear along with some unidentified heavier impurities. Finally, for Figure 2C the reactor filament was heated to 1970 °C; the methane mass peaks diminish greatly, and acetylene is seen to arise at m/z 26. Atomic hydrogen was also observed, and its relative abundance noted as a function of filament temperature.

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Figure 2. TOF mass spectra by through-the-substrate sampling: A) no reactant gas; B) methane/hydrogen mixture; and C) methane/hydrogen mixture decomposed at 1970 °C.

With EI ionization, extensive fragmentation of methane is observed; thus electron ionization could potentially lead to confusing results, indicating the presence of fragment species in the reacting gas mixture. For REMPI this is not a problem, as the optical spectral signature of an intermediate must be observed when the laser is scanned to qualify it as a component of the reactor gas. For REMPI testing at room temperature, a surrogate mixture of nitric oxide in argon was employed; detection of NO was accomplished via 2+2 REMPI near 430 nm.

3.3 Film surface species

The final region to be probed is the material at the surface of the growing film itself. For an understanding of growth processes, we feel that only the monolayer of material on the surface should be examined. Two interesting new approaches to probing the surface layer of materials are second-harmonic generation⁶ and sum-frequency generation.⁷ These are optical probes of the surface that are quite sensitive to interfacial phenomena while not requiring an ultra-high vacuum environment. Sum-frequency generation is more interesting than second-harmonic generation in that *in situ* vibrational spectroscopy of molecules on the surface can be performed. A tunable infrared photon is mixed with a visible photon at the growing film/gas interface to create a higher frequency visible signal beam. Enhancement of the signal beam generation occurs near resonances of species present and vibrational spectra of molecules on the surface result as the infrared laser is scanned through molecular resonances. The second order

nonlinear susceptibility ($\chi^{(2)}$) that permits sum-frequency generation vanishes except in geometries that lack inversion symmetry, in this case the growing film/gas interface provides this asymmetry, explaining the surface selectivity of the method. Background signal from bulk material should be minimal.

We are beginning to develop a high-peak-power, picosecond-duration, tunable infrared laser source for investigation of diamond film growth. A picosecond pulsed laser is desired because low average power is necessary to prevent altering the surface chemistry with the laser itself. The most valuable spectral regions for investigation are the C-H and C-C stretching vibration regions at 2900 and 1330 cm^{-1} , respectively. An optical parametric oscillator with proustite as the nonlinear medium and a regeneratively-amplified Nd:YAG laser pump is in the early design stage.

4. CONCLUSIONS

Several tunable laser-based diagnostics are under development to probe CVD diamond film growth. The three important reactor regions -- bulk gases, film boundary layer, and growing surface -- are individually under investigation. Orifice sampling as implemented for the hot filament reactor is also directly applicable to the oxy-acetylene flame growth method.

The combined information from diagnostics and materials characterization will eventually contribute to a better understanding of CVD processes and could very well lead to modification of diamond deposition procedures. Modifications might be made to change the dominance of different molecular species present in the vapor phase to optimize material growth; alternately, it might be advantageous to introduce a new chemical species. We feel that this global approach to investigating materials synthesis from the vapor phase is a rational strategy no matter what material is being grown.

5. ACKNOWLEDGEMENTS

Research sponsored by U.S. Department of Energy, Office of Energy Research, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

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