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13. ABSTRACT (Maximum 200 words)  We have constructed and tested new higher-temperature ceramic (ZrO <sub>2</sub> and SiC) pyrolysis nozzles that can operate continuously at 1700°C for several hours. The two successful designs were used to generate intense (10 <sup>16</sup> sec <sup>-1</sup> ) beams of CH <sub>3</sub> by thermal decomposition of azomethane. We probed the pyrolysate by vacuum-UV photoionization mass spectroscopy and (mass-resolved) resonant multiphoton ionization spectroscopy and determined that the ratio of CH <sub>3</sub> /C <sub>2</sub> H <sub>2</sub> in our source is greater than 100:1. This should make it an ideal source of methyl radicals for deposition. A chamber with the pyrolysis nozzle and a separate electric discharge nozzle source of H <sup>•</sup> was constructed. The two jets were directed onto a thermostatted molybdenum foil. Micro-Raman assays (NRL with Jim Butler) of deposited material showed good-quality diamond, but we could not rule out Raman signals from diamond seed crystals with which the surface was scratched. We designed an efficient synthesis for <sup>13</sup> CH <sub>3</sub> -N=N-CH <sub>3</sub> as a source of 50% <sup>13</sup> C-enriched methyl radicals. Micro-Raman showed no evidence of <sup>13</sup> C-enriched diamond, from which we conclude that we were previously seeing only the seed crystals. We are currently working on <i>in situ</i> probes to quantify the H <sup>•</sup> concentration, and also trying different substrates.				
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Technical Report No. 2

*Supersonic Pyrolysis jets for Diamond Film Deposition*

by

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## TECHNICAL REPORT FOR GRANT #N00014-91-J-1012

### *Supersonic Pyrolysis Jets for Diamond Film Deposition*

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Harvard University

May 21, 1992

#### Introduction.

We have developed clean supersonic nozzle sources for radicals. This project aims to apply this nozzle technology to: (1) the mechanism of diamond growth from hydrocarbon gases, and (2) selective functionalization of diamond surfaces by reaction with well-characterized gas-phase reactive intermediates. A particular emphasis in this stage of the project is growth from well-characterized methyl radical,  $\text{CH}_3$ , sources, in the absence of higher hydrocarbons, e.g. acetylene,  $\text{C}_2\text{H}_2$ . We hope to use the separation of  $\text{CH}_3$  production from  $\text{H}^\bullet$  production from deposition to isolate and probe details of the mechanism for growth of diamond from the gas phase.

#### Progress for 1991-92.

The nozzle development reported in last year's report is done, giving us a reliable, reproducible source of  $\text{CH}_3$  and other radicals. We found that pyrolysis of azomethane,  $\text{CH}_3\text{-N=N-CH}_3$ , at  $1200^\circ\text{C}/10 \mu\text{sec}$  in 1 atm helium carrier gas gives quantitative conversion to methyl radicals and  $\text{N}_2$ . The 10.49 eV vacuum-UV photoionization mass spectrum showed no higher mass species. Acetylene, because of its importance as a potential growth species, was probed for with resonant multiphoton ionization spectroscopy. We established our detection limits by obtaining an unambiguous spectrum with calibrated partial pressures of  $\text{C}_2\text{H}_2$ , and then determined that, under the conditions where we could achieve  $\text{CH}_3$  fluxes of  $10^{16} \text{ sec}^{-1}$ , the ratio of  $\text{CH}_3/\text{C}_2\text{H}_2$  is

greater than 100:1. The absence of equilibration between  $\text{CH}_3$  and  $\text{C}_2\text{H}_2$  is one important way in which our thermal radical source differs from the conventional hot filament reactors.

We have constructed a deposition chamber in which there is provision for up to two separate nozzles that can be run as either pulsed or continuous flow supersonic jets. One was set up as an electric discharge nozzle for the production of  $\text{H}^\bullet$  from mixtures of  $\text{H}_2$  in helium, and the other was set up as a pyrolysis nozzle for  $\text{CH}_3$ . We could confirm production of atomic hydrogen by rapid etching of graphite placed in the gas flow. Electrically-heated molybdenum foils at temperatures ranging from room temperature to  $800^\circ\text{C}$  were used as substrates, with and without scratching of the surface with 0.1-0.5  $\mu\text{m}$  diamond powder. Micro-Raman spectra (performed at NRL by Jim Butler) of samples grown under a variety of conditions showed diamond on those samples which had been scratched with diamond powder. Either we could grow diamond only on a pre-scratched surface, or we were seeing only residual diamond powder left from the scratching. We attempted to distinguish between residual powder and new growth by examination of the crystallite size, but the results were unconvincing either way.

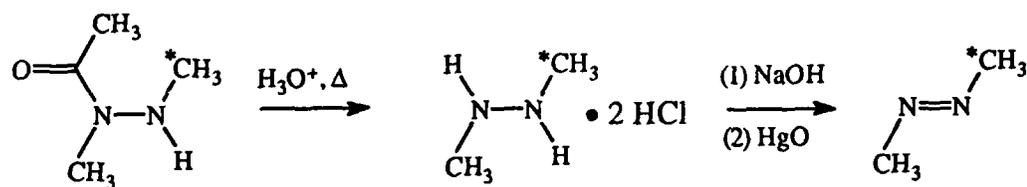
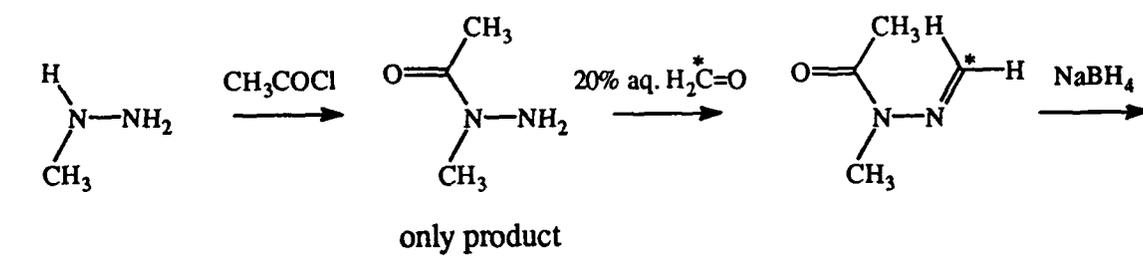
An unambiguous distinction could be made if we used  $^{13}\text{C}$ -labeled methyl radicals and  $^{12}\text{C}$  diamond powder because the isotope shift in the Raman spectrum is large. We developed an efficient synthesis for 50%  $^{13}\text{C}$ -enriched azomethane, with  $^{13}\text{C}$ -labeled formaldehyde (relatively inexpensive and available) as the source of the isotopic label. The synthesis of  $^{13}\text{CH}_3\text{-N=N-CH}_3$  can be done on the gram scale for approximately \$1000/gram. The procedure is shown in Scheme I. Micro-Raman spectra of diamond grown from the isotopically-enriched methyl source showed no evidence of  $^{13}\text{C}$  incorporation. We conclude that the previous results were due to aggregates of the diamond powder used to scratch our surfaces.

Prospects for 1992-93.

There are several possibilities for the lack of diamond growth. We had used only one substrate, molybdenum, for which it is known that the sticking coefficient of  $\text{CH}_3$  is low. We are now trying copper, silicon, and CVD diamond. For the latter, we plan to use  $^{13}\text{C}$  incorporation as the way to distinguish between the original material and any new growth. We have also completed the modifications to the chamber to allow optical access for laser-induced fluorescence probes of  $\text{H}^\bullet$  concentrations. We will now be able to optimize the atomic hydrogen production, just as we had previously optimized the  $\text{CH}_3$  production. We have not yet explored the use of heteroatom-substituted carbenes to functionalize a diamond surface. We will try to see insertion of  $:\text{CF}_2$ ,  $:\text{CCl}_2$ , and  $:\text{C}(\text{SR})_2$  into surface C-H bonds from the gas phase. Fluorination may impart oxidation resistance. The pendant  $-\text{CHCl}_2$  group from dichlorocarbene insertion is convertible to a surface vinyl group by hydrolysis and Wittig reaction. This will provide the functional handle to build postulated surface structures that may reconstruct upon thermal cycling. Surface sulfur groups may improve adhesion of metal films. These possibilities have not yet been explored.

## CAPTIONS

**Scheme I.** Synthetic scheme for the synthesis of  $^{13}\text{C}$ -labeled azomethane. All of the steps subsequent to addition to the labeled formaldehyde can be run nearly quantitatively on the gram scale.



SCHEME I

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