

SOME EXPERIMENTS ON THE MECHANISM OF
DIAMOND FILM GROWTH

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INTRODUCTION

Since direct crystallization of diamond from carbon atoms is thermodynamically unfavorable at low pressures, it has been suggested by Fedoseev, et al.(1) that an "organic synthesis" picture of diamond formation is more accurate. In this picture, a diamond structure is built up by chemical reaction with carbon-containing free radicals or ions, and structure formation is controlled by kinetics rather than thermodynamics. A key problem in low pressure diamond film synthesis is the lack of a generally accepted chemical mechanism for this process. (For an example of a proposed mechanism, see Tsuda, et al.(2).) Resolution of the mechanistic question will require identification of the various chemical species present in diamond synthesis systems, and correlation of the growth rate with the concentrations of the species. A complete understanding of the mechanism can provide a rational basis for the design of improved methods for diamond synthesis.

EXPERIMENT

We have constructed a simple diamond film synthesis system with the objective of gaining mechanistic information. Our laboratory is not yet able to measure the concentrations of free radicals and ions directly, so we have designed experiments to give differing initial mixtures of free radicals. The interpretation of such experiments is complicated by the fact that rapid gas-phase chemistry takes place to change the mix of radicals, but it is possible to estimate the progress of such chemistry with kinetic modeling.

The apparatus consists of a quartz bell jar on a vacuum manifold with provision for vacuum ultraviolet (VUV) irradiation of the substrate region as well as hot tungsten filament dissociation of the gas atmosphere. The VUV source is a hydrogen microwave discharge. The substrate material, usually single crystal silicon, was mounted on a silicon nitride heating element. The atmosphere was typically 1% organic vapor and 99% hydrogen gas at 10 torr, flowing at 100 sccm. The filament, when in use, was at 2000 Celsius and 5mm from the substrate, and the

substrate was at 850 Celsius. Experiments were done with methane, carbon monoxide, acetone, acetylene, and methyl bromide. Our assessment of the most probable initial species produced is based on thermochemistry for the tungsten filament (3) and known photochemistry for the VUV source (4).

Table 1 summarizes the experiments carried out. If we consider only neutral chemistry, our interpretation of these experiments is as follows: CH_3 and C_2H_2 are more likely to be reactants than are C, C_2H , or CH_2 . This conclusion must be taken with caution because of the important influence of the gas phase chemistry. For example, a crude analysis of the reaction manifold will show that methyl radicals, CH_3 , will recombine very rapidly under the conditions of the experiment, and are probably regenerated by the reaction of H-atoms with undissociated methane. This interpretation explains the apparent paradox in the table: methyl bromide is a good source of methyl radicals, yet it produces no observable diamond film. The explanation is that methyl bromide reacts rapidly with hydrogen atoms to produce a large initial concentration of methyl radicals, but these quickly recombine and leave no new source of radicals. Our experiments give no direct information about the importance of ions. In our view, ions might be generated by electron bombardment of the substrate, and therefore their possible importance cannot be ruled out in these experiments.

ACKNOWLEDGEMENT

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REFERENCES

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- 2) M. Tsuda, M. Nakajima, and S. Oikawa, J. Am. Chem. Soc. 108, 5780-5783 (1986).
- 3) J. L. Franklin, et al., Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions NSRDS-NBS 26, U. S. Dept of Commerce (1969).
- 4) J. G. Calvert and J. N. Pitté, Jr, Photochemistry, Wiley, New York, (1966).

TABLE I

SUMMARY OF EXPERIMENTS

| CARBON SOURCE | VUV | HOT WIRE | SPECIE. | RESULTS |
|------------------------------------|-----|----------|---------------------------------|-----------------------------------|
| CH ₄ | | X | CH ₃ | SMALL AMOUNT OF DIAMOND |
| | X | | CH ₂ | (no data) |
| CO | | X | CO* | DEPOSIT OF TUNGSTEN CARBIDE |
| | X | X | C | LONSDALEITE |
| (CH ₃) ₂ CO | | X | CH ₃ | ABUNDANT DIAMOND |
| | X | X | CH ₃ | ABUNDANT DIAMOND, MORE NUCLEATION |
| C ₂ H ₂ | | X | C ₂ H ₂ * | SOME DIAMOND |
| | X | | C ₂ H | SLIGHT DIAMOND, LESS THAN THERMAL |
| CH ₃ Br | | X | CH ₃ | GRAPHITE |
| | X | | CH ₃ | NO DIAMOND DEPOSIT |