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(NASA-CR-165285) VAPOR PHASE DIAMOND GROWTH  
TECHNOLOGY Final Report (Case Western  
Reserve Univ.) 17 P HC A02/MF A01 CSCL 20L

N81-24965

Unclas  
G3/76 42469

**FINAL REPORT**

on

**Contract NAS 3-21965**

**"Vapor Phase Diamond Growth Technology"**

submitted by

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**January 30, 1981**



## ABSTRACT

This report summarizes the work performed under contract NAS-3-21965, "Vapor Phase Diamond Growth Technology." During the contract period primary emphasis was placed upon: 1) advising NASA LeRC personnel on appropriate techniques for growth of ion beam deposited diamond like films, 2) developing and applying analytical techniques for characterization of the ion deposited films, 3) making preliminary measurements of film quality.

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## I. INTRODUCTION

The primary purpose of Contract NAS 3-21965 was twofold: 1) to aid in the development of a capability at NASA LeRC for growing ion deposited diamond like carbon films and 2) to develop specialized capabilities for characterization and understanding of this unusual material. Both objectives have been achieved.

In the following sections of the report a brief summary of the status of the work is given.

## II. DEVELOPMENT OF EXPERIMENTAL CAPABILITY

NASA Lewis Research Center personnel, primarily Mr. Thomas J. Riley, had responsibility for design and construction of the several ion beam deposition chambers to be used for carbon film generation. Mr. Stan Domitz developed specific ion beam sources. The CWRU personnel provided consultation and advice on the crystal growth aspects of the work during this phase of the research.

The equipment has been constructed and some initial films are being grown in one of the systems. Details of these systems are not given here. We only note that the devices provide: 1) carbon ion energies down to  $\sim 50$  eV, 2) in situ surface monitoring with HEED, 3) provision for flooding the surface with ultra violet radiation, 4) infrared laser heating of substrate, 5) residual gas monitoring, 6) provision for several source gases, including diborane for doping studies, 7) growth from either hydrocarbon source gases or from carbon/argon arc sources.

### III. DEVELOPMENT OF ANALYTICAL TECHNIQUES FOR CHARACTERIZATION OF FILMS

Introduction. In this section a summary of the techniques for characterization of the ion deposited carbon films is given.

The techniques we are employing are primarily directed towards establishing the nature of the chemical bonding and crystallographic structure of the films. Ultimately, we wish to examine the electrical properties of the films, especially doped films, as well. To this end additional tests will be performed, for example, measurements of breakdown, dielectric constant and Seebeck coefficient.

The emphasis in this report is on a brief discussion of the tests themselves.

H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> Etch. A quick and dirty (more dirty than quick) method for quickly testing film quality is to subject the film to a solution of 1 part HNO<sub>3</sub> to 3 parts H<sub>2</sub>SO<sub>4</sub> (concentrated acids, by volume) at ~82°C. This treatment quickly dissolves all non-diamond carbon. For example, graphite powder and high density polyethylene are essentially dissolved within one hour. Diamond was untouched after twenty hours.

Treatment of ion deposited films obtained from Mr. Mike Mirtich of NASA Lewis showed varied results. Sample 11-21-80-1, a blue-green film on a Si substrate was untouched after 20 hours in the reagent. Sample 11-21-80-1 on a quartz substrate was also untouched except for a dark spot in the film which dissolved within 15 minutes. Sample 11-7-80-1, a golden, otherwise transparent film on quartz, came off from the substrate and broke up within 5 minutes.

We believe that this test, crude though it may be, will distinguish graphitic like carbon and will also tell which films are poorly bonded to the substrate.

One can perform these tests in small open beakers on a hot plate, but a better procedure is to use a small distilling flask and condenser.

Resistance Measurements. Measurement of the film resistance using a mercury drop electrode was first done by Mr. Tom Riley. We have repeated these measurements using samples of known thickness and find resistivities on the order of  $10^{10}$  ohm-cm for film grown on Si substrates obtained from Mike Mirtich of NASA Lewis.

This method may not be particularly good for testing film continuity because of the large surface tension of mercury. Strongly wetting liquids, i.e, water with a surfactant, could be used if an easy way of containing the liquid within a controlled area could be found.

Hardness Tests. We are attempting to measure the Vickers microhardness of the ion deposited films. The measurements themselves are extremely simple and quick to make. However, we have not yet established whether we can accurately separate out the film hardness from the substrate hardness. To do this will require several films of different thickness, but with otherwise identical properties. These films should range from one to several microns thick.

We have not yet attempted a scratch hardness test. However, if it proves impossible to get accurate Vickers hardness measurements, scratch hardness testing may be the best alternative.



Fourier Transform Infrared Spectroscopy (FTIR). Fourier Transform Infrared Spectroscopy (FTIR) has proven to be a very useful tool for determining some aspects of the film's molecular structure. In particular, the presence of hydrogen, and the form in which it is chemically combined, has been determined. The characteristic C-H stretching frequency is clearly visible in films obtained from both Gulf and Western and NASA LeRC.

Furthermore, it seems that it will be possible to get a rough estimate of the amount of hydrogen present by comparison with samples of polyethylene films of known thickness.

With a little luck we may also be able to say something about the carbon skeletal structure of the films. Comparison of the observed spectrum with natural diamond and the molecular compound adamantane will be instructive here.

The FTIR work performed to date clearly shows the need for high quality infrared transparent substrates. The alkali halide substrates are the best, but the high resistivity Motorola Si wafers are also suitable.

Scanning Auger Microscopy (SAM). Scanning Auger Spectroscopy (SAM) has proven very useful in identifying the major elements present in the films (apart from hydrogen which cannot be detected). We have confirmed that the films obtained from Gulf and Western and from NASA are essentially carbon, with minor amounts of oxygen and argon. The oxygen is removed by argon ion sputtering and hence is presumably only an adsorbed surface layer. The argon without doubt is incorporated into the lattice from the argon ions in the incident beam during growth. The amount of argon incorporated in the films has not been determined because of the lack of any known standards.

We have made some attempts to distinguish various types of carbon-carbon bonding by examining the line shape of the carbon Auger signal. Some differences have been observed. However, more careful, high resolution spectra are being taken on natural diamond, highly oriented pyrolytic graphite, and ion deposited carbon films to establish whether the differences can be used as an unambiguous means of identification.

Electron Spectroscopy for Chemical Analysis (ESCA). We have used the ESCA at the Case Western Reserve Major Analytical Instrumentation Facility for simple elemental analysis. We believe, however, that Auger analysis, when available, or EDAX analysis is better suited for our purposes because of the spatial resolution one can obtain with the primary electron beam compared to X-ray excitation.

However, the ESCA line shapes and shifts may be a good means of determining something about the nature of the carbon-carbon bonding. ESCA has, for example, been very useful in examining organic systems and polymers. The extremely high resistances of the present films, however, lends to charging and makes quantitative ESCA studies difficult. More time could profitably be devoted to this problem when good films become routinely available.

Electron Diffraction and Energy Dispersive X-Ray Analysis. Electron diffraction can provide the ultimate, convincing test of the presence of a long range crystalline order in the films. Our electron diffraction results, obtained on samples from Gulf and Western, showed only diffuse scattering, i.e., an amorphous or exceedingly finely divided polycrystalline film.

There are a number of possible outcomes from the diffraction studies. First, and highly unlikely, is the observation of a monocrystalline diamond

film giving rise to the characteristic diffraction pattern associated with a single crystal of diamond. Second, and more likely, is the observation of sharp diffraction rings characteristic of a randomly oriented, polycrystalline film. Thirdly, and perhaps even more probable, one can observe essentially diffuse scattering with no well defined spots or rings. This latter outcome can arise from a truly amorphous, random network of atoms, or from a film made up exceedingly small microcrystallites, perhaps containing as few as ten atoms each. There are means of distinguishing between these two cases, but they are definitely non-trivial (1,2).

Other possible outcomes are possible, for example, a polycrystalline film comprised of crystallites with preferred orientation. This can eliminate or suppress rings one might otherwise observe.

The availability of films on substrates other than silicon, for example Ni or, even better, alkali halide, will facilitate the electron diffraction work.

Energy dispersive X-ray analysis (EDAX) is easily performed in the electron microscope at the same time the diffraction studies are done.

Electron Energy Loss Spectroscopy (EELS). This relatively new technique will apparently be available to use on a Case Western Reserve electron microscope. It may permit us to learn something about the state of bonding of the carbon atoms, i.e., may permit the distinction between graphitic and diamondlike carbon.

Density Measurements. It may be possible to measure the density of the films directly using a microbalance technique. A film 1000 Å<sup>0</sup> thick and 1 cm<sup>2</sup> in area would weigh

$$(1000 \times 10^{-8} \text{ cm}) (1 \text{ cm}^2) (3.5 \text{ g/cm}^3) = 35 \times 10^{-6} \text{ g}$$

if it were diamond. Microbalances with sensitivities of  $10^{-6}$  g are rather routinely available. It would seem feasible, therefore, to make a direct determination of density by measuring the mass of the deposited film. This measurement would be done by difference, i.e., separately weighing the substrate and the substrate plus film.

It would be necessary to deposit a layer of known area and uniform thickness. Perhaps a circular mask of accurately known diameter could serve to delineate the deposition area. A possible source of error could be the measurement of an average thickness. A good profilometer will permit measurements of vertical displacements to within  $25\text{\AA}$ , which is well within the required range. However, the uniformity of the film thickness may cause problems.

Despite these difficulties, an attempt to measure density should probably be made after good quality films are routinely available. Density is a very useful parameter to know because it depends directly upon the molecular structure. For example, a film that is all carbon and has a density of close to  $3.5 \text{ g/cm}^3$ , can only be composed of tetrahedrally bonded carbon atoms.

Secondary Ion Mass Spectroscopy (SIMS). This technique gives a direct mass spectroscopic analysis of material sputtered from the film. It is of special utility to us because it can give a semiquantitative estimate of the amount of hydrogen present in the films.

Our work with SIMS has been somewhat frustrating. Early runs gave good SIMS spectra which were easily interpreted. Later runs on the same samples gave no results whatsoever. No sputtered ions were observed.

This may be caused by a large positive surface charge which deflects the primary ion beam. The earlier, successful experiments may have been caused by contaminants in the vacuum system which adsorbed on the sample surface lowering its electrical resistance.

There are several possible schemes for eliminating the problem which can be tried. For example, the sample could be flooded with electrons from an adjacent filament. The use of oxygen ions rather than inert gas ions is another possibility. Dr. Nicholas Baldwin of the Case Major Analytical Instrumentation Facility is looking into this problem.

High Energy Electron Diffraction. This in-situ probe will be of obvious utility in examining the surface of the films immediately after and perhaps during growth. It can be especially useful in monitoring film quality and obtaining some clues about growth mechanisms.

Electron Spin Resonance (ESR). In polycrystalline or microcrystalline diamond like carbon film there can be a number of so called "dangling bonds" at the periphery of the crystallites. These can be saturated by making crosslinks with neighboring crystals or by the addition of another atom e.g., hydrogen. However, many of these electrons may remain unpaired. The electron spin resonance spectrum will give a measure of the number of these unpaired electrons and, consequently, some indication of the structure of the films.

#### IV. STRUCTURE OF FILMS AND GROWTH MECHANISM

Structure of Films. At the present stage of the work not enough films have been examined to permit many conclusions about their structure. It has been established that they contain chemically bound hydrogen and some argon is included. It is very likely that the film may be somewhat analogous to "amorphous silicon" (1,2,3). The films, may, for example, be made up of a truly amorphous, random network of atoms or, alternately, could be a finely divided polycrystalline film.

The structure is certainly a strong function of growth conditions. Other work suggests that the films grown by a radio frequency discharge in a hydrocarbon may be more amorphous or polymeric in character (4). Films grown from carbon ions extracted from carbon/argon arc may be more crystalline (5,6,7).

Doping of the films to produce semiconducting films may be possible in both instances. Boron is known to be the P-type electrically active impurity atom in diamond. It has been successfully incorporated into diamond during low pressure epitaxial growth by chemical vapor deposition by the Principal Investigator in earlier work (8). There is still considerable controversy over the production of N-type diamond. Most recent efforts have focused on ion implantation as a means of introducing N-type doping agents (9).

Mechanism of Film Growth. Very little can be said about the mechanism for film growth. It is, in fact, extremely surprising that diamond or "diamond-like" phases arise from this process. Conventional arguments would lead one to believe that a diamond seed crystal is necessary to initiate metastable diamond growth (10).

We believe that diamond nuclei, or precursors, arise statistically on the bombarded surface. These may be stabilized by electrons from the negatively charged surface. These nuclei may be thought of as small carbanions with  $sp^3$  hybrid orbitals. The nuclei grow by direct attachment of mobile  $C^+$  ions or neutral C atoms on the surface. Nuclei and structures with non-diamond like structure ( $sp^2$  and  $sp$  configurations) are preferentially sputtered away by the impinging ion beam.

The above mechanism is extremely speculative and much more remains to be done to confirm or deny it. In particular, the structure of charged clusters of group IV atoms (C, Si and Ge) should be investigated as well as the structure of negatively charged diamond surfaces. The details of the energy and momentum transfer and the probable point of charge transfer should be considered using existing theories developed for ion implantation. This work will be part of the continuation of the present effort.

## V. PERSONNEL

Professor John C. Angus was the Principal Investigator and had primary responsibility for the research described here. Professor J. A. Mann also contributed to several aspects of the research, especially to the in-situ analytical capability (HEED).



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