

# From Carbon Beams to Diamond Films\*\*

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Ion Beam Deposition  
Carbon Films  
Surface Analysis

## 1. Introduction

Diamonds have attracted mankind's attention through many centuries. The quest for synthetic artificial diamonds, as well as that of artificial gold, motivated the first experiments that led to the foundation of chemistry. Bulk diamonds were successfully produced only in 1953, however, by the ASEA group in Sweden and by the General Electric team in 1955.<sup>[1,2]</sup> A specially designed reaction vessel provided the high-temperature/high-pressure conditions needed to transform graphite, the stable carbon phase under normal conditions, to cubic diamond, the precious metastable carbon phase. Artificial bulk diamonds are now commonly used in many applications. An equally challenging goal is the deposition of diamond films on various materials, which has been the subject of intense research that started about thirty years ago and has accelerated significantly during the past few years. The interest in these films stems not from their decorative value, but from the unique set of physical properties of diamond:<sup>[1,2]</sup>

- hardest known material
- excellent electrical insulator
- best thermal conductor
- high dielectric strength
- highly transparent in the UV, visible and IR regions
- chemically inert
- resistant to oxidation and corrosion
- compatible with body tissues

Attempts to fabricate true diamond films resulted in carbon films with properties varying between those of diamond and those of graphite, within a range of many orders

of magnitude.<sup>[2-7]</sup> The unique possibility of "tailoring" a combination of desired properties for a specific purpose is advantageous for a variety of applications including:<sup>[2-8]</sup>

- optical coatings suitable for hazardous environments
- protective thin films for magnetic recording materials
- heat sinks for semiconductor applications
- solid state devices
- moisture barriers
- low friction coatings for tribological applications
- hard coatings for mechanical tools
- protective coatings compatible with body tissues for medical applications

The properties of the different phases of carbon are closely related to the nature of the carbon-carbon bonds or to the electronic structure of carbon.<sup>[2,3,9]</sup> Cubic diamond has  $sp^3$  carbon atoms and a tetrahedral structure where each carbon atom is bonded to four different carbon atoms and no "dangling bonds" exist. Graphite has  $sp^2$  carbon atoms and a structure where each carbon atom is bonded only to three carbon atoms in a two-dimensional arrangement while the remaining p orbital forms a "dangling bond" (or a  $\pi$  electron band). Amorphous carbon includes a varying mixture of  $sp^1$ ,  $sp^2$ , and  $sp^3$  hybridized carbon atoms with no long range crystalline order.

Attempts to fabricate true diamond films have resulted in many deposition methods, practical processes, and films of commercial potential. Work accomplished on these topics is covered by excellent recent reviews and literature surveys.<sup>[3-5,8,10,11]</sup> Nevertheless, the understanding of the

### Abbreviations

|      |   |
|------|---|
| UHV  | Ultra High Vacuum                         |
| RF   | Radio Frequency                           |
| DC   | Direct Current                            |
| IBD  | Ion Beam Deposition                       |
| CVD  | Chemical Vapor Deposition                 |
| TEM  | Transmission Electron Microscopy          |
| XRD  | X-Ray Diffraction                         |
| SEM  | Scanning Electron Microscopy              |
| AES  | Auger Electron Spectroscopy               |
| EELS | Electron Energy Loss Spectroscopy         |
| UPS  | Ultraviolet Photoelectron Spectroscopy    |
| XPS  | X-Ray Photoelectron Spectroscopy          |
| ILS  | Ionization Loss Spectroscopy              |
| XAES | X-Ray Induced Auger Electron Spectroscopy |

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[\*\*] The authors are most grateful to T. Schaffner, W. M. Duncan, H. Y. Liu, H. L. Tsai, and M. W. Cowens of Texas Instruments, Dallas, for the TEM, XRD, Raman and FTIR analysis of the samples, to E. Rapoport, Soreq NRC, for XRD and FTIR measurements, and to S. Moss and L. Robertson, University of Houston, for XRD analysis and helpful discussions. This material is based on work supported by the National Science Foundation under Grant No. DMR-8610597.

nature of these carbon films is still very limited. This is true of almost all aspects, such as film growth processes, deposition parameter-property relationships, film characterization and nomenclature. The major reason for this situation is the complex chemical-physical nature of the deposition techniques that have been used, where the ability for separating, controlling and studying the effects of individual deposition parameters is limited.

The present work reviews recent results of the first in-situ parametric investigations of the growth of diamond films under controlled UHV conditions.<sup>[10, 12-15]</sup> These investigations were performed in the Houston facility<sup>[10, 16]</sup> that uniquely combines a controlled, mass selected (carbon) ion beam system with a UHV deposition chamber and in-situ surface analysis techniques. The work has established several surface characterization methods for studying carbon films<sup>[14]</sup> and has addressed some fundamental problems involved in diamond film deposition, such as the possibility of growing diamond films on non-diamond substrates at room temperature, the evolution of the films at different stages of growth, effects of ion parameters (e.g. ion energy), substrate parameters (e.g. material, temperature) and ambient pressure. We first briefly summarize the previous work on "diamond-like" films, including deposition methods, main processes involved in carbon film deposition, and open questions in the field. Following a short description of the system and the diagnostic techniques, the use of various surface analysis methods for the characterization of the different carbon forms related to carbon film evolution is given. Next, the first conclusive proof for diamond growth and the different stages of diamond film evolution on different substrates at room temperature are presented. The results of some parametric studies including substrate material and substrate temperature effects follow. The summary gives the most important conclusions of this work and points to future applications.

## 2. Present Status of Research on Diamond-like Films

Since graphite is the most stable phase of carbon under ambient conditions,<sup>[1, 2]</sup> simple thermal evaporation of carbon results in either graphitic or amorphous carbon films.<sup>[3-5]</sup> These films are undesirable because they have the properties of graphite, which is electrically conducting and has a high absorption coefficient in the visible and IR regions. The metastable nature of the diamond phase necessitates a combined high-pressure/high-temperature scheme for its formation.<sup>[1, 2]</sup> Such a scheme is, however, impractical for routine thin film applications. Two alternative basic approaches have thus been adopted for diamond film deposition: a) The use of energetic species (10-1000 eV) that create localized high-temperature/high-pressure regions in the growing film called "thermal spikes".<sup>[3, 6]</sup> These energetic species can be either carbon

containing or other species (e.g. Ar). In the latter case a secondary beam of carbon containing species (either energetic or thermal) impinges on the substrate simultaneously with the energetic (Ar) species. b) Chemical reactions involving hydrocarbon-hydrogen gas mixtures, usually at elevated temperatures, resulting in the formation of diamond layers on different surfaces.<sup>[11]</sup>

Three main deposition techniques have thus been developed:

- 1) Ion beam deposition techniques<sup>[3, 6]</sup> where different energetic particles (some of which contain carbon species) impinge on the substrate to be coated. IBD of carbon films was first introduced by *Aisenberg* and *Chabot*<sup>[6, 17]</sup> in 1971 and highly developed by *Weissmantel* et al.<sup>[3]</sup>. Films produced by these methods are often called i-C (ion C) or DLC films (diamond-like C). Their properties vary between those of graphite and diamond and their exact structure is still in question.<sup>[3-5]</sup> Characterization of these films revealed a dominant amorphous nature and no rigorous proof for diamond formation was given, with the exception of studies carried out with mass selected ion beams.
- 2) Plasma techniques<sup>[4]</sup> where RF, DC or pulsed plasma decomposition of various hydrocarbon gases results in the deposition of carbon films on various substrates. The first work using these techniques was published in 1955,<sup>[18]</sup> but more rigorous work was started by *Holland* and *Ojha* in 1976;<sup>[19]</sup> since then these techniques have been adopted by many others.<sup>[4]</sup> These films usually contain large amounts of hydrogen (10%-70%) and are often called a-C:H films (amorphous carbon hydrogenated).<sup>[4, 5]</sup> Though they may have properties that sometimes resemble those of diamond, they are definitely not diamond films.
- 3) CVD processes that use chemically active hydrocarbon fragments (ions and radicals) for the spontaneous growth of diamond material under rather metastable conditions.<sup>[11]</sup> These processes usually use a mixture of hydrocarbons and H<sub>2</sub> (ca. 99% H<sub>2</sub>) excited by an external source (hot filament, RF or microwave plasma) to form the carbon films on hot (800-1000°C) substrates. Work on CVD processes was started by *Eversole*<sup>[20]</sup> and *Angus* et al.<sup>[21]</sup> and was further developed by *Derjaguin* et al.<sup>[22]</sup> in Russia and the *Nirim* group<sup>[11, 23]</sup> in Japan.

Carbon films produced by the above processes have various useful properties, some close to that of diamond (e.g. hard, transparent, chemically inert, insulating films). Real cubic crystalline diamond films with crystal sizes of 1 µm and larger (identified by TEM, XRD, Raman spectroscopy and SEM) have been produced only by CVD techniques at practical (µm/h range) rates on hot (ca. 800°C) substrates.<sup>[11]</sup> Correlations between film properties and deposition parameters of specific systems have also been given.<sup>[3-5]</sup> Nevertheless, all of the systems described have a very complex nature where the different basic deposition parameters are very difficult to define and control and the

pressure is in the range  $10^{-4}$ – $10$  torr.<sup>[3–5]</sup> Many species with a complex, usually unknown, composition are involved in such deposition processes<sup>[3–5]</sup> (carbon atoms, ions and clusters, hydrocarbon ions and radicals, inert gas ions and atoms, energetic hydrogen species, impurity species due to residual gases, electrons, etc.). The energies of these species are not well defined and have wide distributions.<sup>[3–5]</sup> This results in non-reproducibility of the final product from the different deposition processes and limited understanding of the film growth mechanism. Examples of open questions, the answers for which are essential for the successful reproducible deposition of diamond films, are listed below:

- a) Mechanisms of diamond formation—"Thermal spikes" are often suggested as a possible way of obtaining the temperature and pressure needed for diamond formation,<sup>[3–6]</sup> but their role is often doubted.<sup>[4]</sup> There is no direct proof for an alternative mechanism—that of preferential etching of graphitic or amorphous constituents by energetic hydrogen or argon species.<sup>[4,6]</sup> The role of hydrogen in the stabilization of carbon  $sp^3$  bonds in the film by termination of "dangling bonds"<sup>[4,5]</sup> is only partly understood.
- b) Crystal nucleus formation and crystal growth—What are the conditions needed for the nucleation of a diamond crystal and for its further growth on an existing diamond seed?
- c) Carbon phases—What are the conditions necessary for the formation of the six known carbon phases in carbon films (graphite, cubic diamond, hexagonal diamond,<sup>[1,2]</sup> chaoite,<sup>[24]</sup> and two other carbon high pressure cubic phases<sup>[25,26]</sup>)? Very often the identification of these phases in a given film is ambiguous.<sup>[3–5]</sup>
- d) Growth mechanisms—What parameters determine amorphous-crystalline growth, crystalline size, epitaxy, adhesion to the substrate, surface morphology, etc.?
- e) Bulk properties/structure/deposition parameters relationships are not well understood.
- f) Characterization—There is no established correlation between different characterization techniques (e.g., Raman spectroscopy, TEM, XRD, and surface analysis methods). This correlation is essential for the characterization of thin ( $<1\ \mu\text{m}$ ) or microcrystalline ( $<1000\ \text{\AA}$ ) films where Raman measurements are misleading, XRD is not sensitive, and TEM is destructive and very often uncertain. Such thin films or small-crystalline material may be essential for future applications.

### 3. Mass Selected Ion Beam Deposition

Limited understanding of deposition phenomena due to the complex chemical-physical nature of many deposition systems is a general feature and not related to diamond film deposition only. Mass selected ion beam deposition has been suggested as a viable technique for fine control and separation of all the deposition parameters.<sup>[4,27]</sup> When

combined with a UHV deposition chamber and in-situ diagnostics, it offers many advantages for deposition in general and for carbon/diamond film deposition in particular:<sup>[4,10]</sup>

- Ion source parameters: Selection of only one type of carbon bearing ion from various possibilities at a specific deposition stage, control of ion energy (e.g. 10–1000 eV), ion flux, and ion beam size over a wide range.
- Dual ion beam deposition of different species (e.g., carbon ions and hydrogen/argon ions) and simultaneous doping during (carbon) deposition.
- Target parameters (temperature, in-situ pre-deposition and post-deposition treatments, nature of target) are controlled with great flexibility.
- UHV environment provides pure films on atomically clean substrates and controlled admission of gases.
- In situ parametric investigation of film growth becomes feasible using surface diagnostic tools.

Several studies on diamond deposition using mass selected carbon ion beams have been performed prior to the work conducted in Houston,<sup>[28–35]</sup> the most important of which are those of Chaikovskii et al.,<sup>[28–30]</sup> Freeman et al.<sup>[31]</sup> and Nelson et al.<sup>[32]</sup> Chaikovskii et al.<sup>[28–30]</sup> deposited diamond films in UHV using a mass selected high intensity ion beam system, obtaining small crystalline (ca. 10–100 Å) diamond films on different substrates with ion energies of 30–100 eV at temperatures of 170–293 K. The true diamond nature of these films was established by ex-situ Auger analysis and by TEM. Large diamond crystalline inclusions (up to 50  $\mu\text{m}$  size) were chaotically arranged in a finely dispersed small crystalline base. The effect of substrate temperature during deposition was also investigated and it was found that at 360 K the films were graphitic. This excellent work, which is, to the best of our knowledge, the only deposition under UHV conditions apart from the Houston work,<sup>[10,12–16]</sup> is unfortunately overlooked by later investigators.<sup>[3–5,31–35]</sup> Freeman et al.<sup>[31]</sup> found that diamond films could be deposited on existing diamond crystals at carbon ion energies of 900 eV and temperatures of ca. 700°C, using a mass selected carbon ion beam and a vacuum of ca.  $10^{-6}$  torr. The moderate vacuum conditions, however, resulted in non-reproducibility of the films. Nelson et al.<sup>[32]</sup> showed that similar temperatures (ca. 700°C) were needed for the internal growth of existing diamonds using a mass selected high energy (several kV up to 100 kV) carbon beam under high vacuum conditions.

Rabalais et al.<sup>[10,16]</sup> have developed a unique facility that combines a mass selected carbon ion beam, UHV ( $\leq 5 \times 10^{-10}$  torr) deposition environment, and several in-situ surface analysis tools. The Houston deposition system is a research facility; it has a much lower current density than the facility of Chaikovskii et al. (ca.  $0.5\ \mu\text{A cm}^{-2}$  compared to  $1\ \text{mA cm}^{-2}$ ) in the energy region of 1–300 eV.

Nevertheless, the first and only rigorous in-situ parametric investigations of diamond film growth are being conducted in this facility,<sup>[10, 12-16]</sup> some results from which are summarized in this review. Complementary investigations of thicker films, produced by a more intense facility at Soreq NRC, Israel, at similar ion energies but poorer vacuum conditions are also being performed. The purpose of the current work is to understand the basic mechanisms involved in diamond film deposition by means of energetic species.

#### 4. Surface Analysis Techniques for in-situ Investigation of Carbon Film Evolution

Differences in the electronic structure of diamond, graphite and amorphous carbon are reflected in the spectroscopic surface analysis features. Extensive work by Rabalais et al.<sup>[12-15]</sup> established the surface analysis data for diamond, graphite, and amorphous carbon as standards for further identification of the nature of deposited carbon films using Auger Electron Spectroscopy (AES), Electron Energy Loss Spectroscopy (EELS), Ultraviolet Photoelectron Spectroscopy (UPS), X-Ray Photoelectron Spectroscopy (XPS), Ionization Loss Spectroscopy (ILS), and X-Ray Induced Auger Spectroscopy (XAES). Published results were compared to those obtained in the Houston laboratory and missing data were complemented.

Figure 1 shows the surface analysis data obtained with AES, XPS, UPS and EELS for diamond, graphite, thermally evaporated amorphous carbon, and carbon films ca. 100 Å thick deposited on Ni(111) at room temperature by the Houston facility at ion energies in the range of 75–150 eV. EELS and UPS data for amorphous carbon are not presented. The features of the three different forms of carbon are different in all of these techniques, each of them being easily distinguishable. The differences lie in the line-

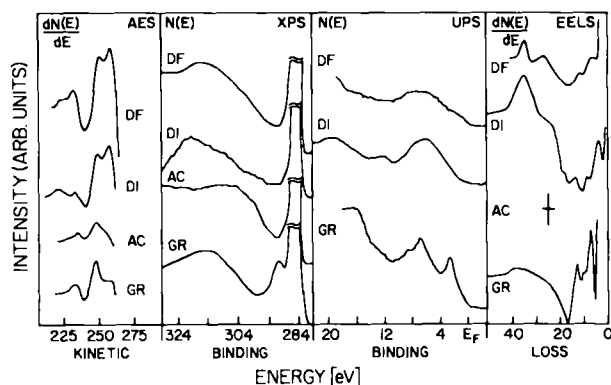


Fig. 1. Surface spectroscopic signatures of carbon in graphite (GR), amorphous carbon (AC), diamond (DI), and diamond film deposited using the Houston facility (DF), measured by AES, XPS, UPS and EELS. No information is presented for the UPS spectrum of AC. The vertical line drawn for AC in EELS indicates the energy loss position of the bulk plasmon peak. The data for GR, AC, and DI in AES, and DI in EELS are from [41] while DI in UPS is from [36].

shapes (e.g., in AES), the appearance or disappearance of peaks corresponding to  $\pi$  electrons (e.g., XPS, UPS and EELS), and the energy shift of corresponding loss peaks (e.g., XPS and EELS). It is therefore possible to identify the carbon form of the films deposited in the Houston facility.

In all four surface analysis methods, the spectra of the deposited films correspond to that of diamond and are very different from that of graphite or amorphous carbon. In the AES measurements, mild electron beam conditions are needed in order to avoid the typical electron beam damage observed for diamond surfaces.<sup>[14]</sup> Under routine experimental conditions, spectra for the electron beam damaged diamond films are measured (Fig. 2), which are

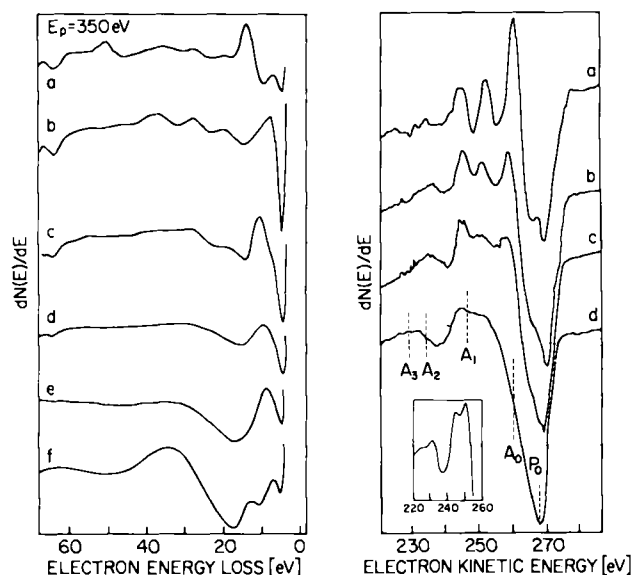


Fig. 2. Evolution of the EELS (left) and AES (right) lineshapes for 75 eV  $C^+$  deposition on Ni(111). The doses in the EELS sequence are: a) clean Ni, b)  $3 \times 10^{15}$ , c)  $5 \times 10^{15}$ , d)  $7 \times 10^{15}$ , e)  $9 \times 10^{15}$ , and f)  $> 2 \times 10^{16}$  ions  $cm^{-2}$ . The doses in the AES are: a)  $2 \times 10^{15}$ , b)  $6 \times 10^{15}$ , c)  $9 \times 10^{15}$  and d)  $> 2 \times 10^{16}$  ions  $cm^{-2}$ . The inset shows an Auger electron spectrum of a diamond film subject to minimal electron beam damage.

nevertheless more similar to that of diamond than to that of graphite or amorphous carbon. The XPS spectra of the carbon films show no  $\pi$  electron feature at 6.7 eV from the C 1s peak and the energy of the bulk plasmon loss peak is similar to that of diamond (ca. 34 eV from the C 1s peak compared to ca. 28 eV for graphite and ca. 23 eV for amorphous carbon). The UPS spectra of the films are indicative of the typical  $sp^3$  hybrid orbitals of diamond with no contribution in the  $\pi$  band region and a recession of states close to the Fermi level. The EELS spectra also exhibit the features of diamond. Additional information has also been obtained from ionization loss spectroscopy (ILS) and ellipsometry.<sup>[14]</sup>

It can thus be concluded that the short range order of the carbon films deposited at room temperature in the Houston facility is that of diamond (i.e.,  $sp^3$  hybridized

carbon atoms). This result was reproducible on every sample tested regardless of the nature of the substrate. These films are therefore different from previously reported diamond-like carbon films (DLC's) that showed surface analysis features very different from diamond, and very similar to those of amorphous carbon.<sup>[4,5,37]</sup> The only other published data where the AES features of carbon films corresponded to diamond was that from ex-situ measurements by Chaikovskii et al.,<sup>[28]</sup> where the deposition conditions were very similar to those of the Houston group. In the work of the Houston group, however, several surface analysis methods were applied to establish the same result and almost all of the measurements were done in-situ. The establishment of these surface analysis data was followed by in-situ parametric investigations of the diamond film growth that are not feasible in any other existing facility.

## 5. Parametric Investigations of Carbon Film Growth

This section reviews results from investigations of carbon film growth that are being conducted in the Houston facility.<sup>[10,12-16]</sup>

### 5.1. Stages of Diamond Film Evolution

The evolution of the diamond films on atomically clean surfaces has been investigated on different materials at room temperature using the different in-situ surface analysis techniques. The three distinct stages of a) carbidic, b) graphitic, and c) diamond were observed in the film evolution on all substrates investigated. Figure 2 shows the film evolution as monitored by AES and EELS for 75 eV C<sup>+</sup> deposition on Ni(111). At low fluxes the impinging C<sup>+</sup> ions form Ni-C bonds resulting in a typical nickel carbide signature<sup>[14,38]</sup> in both the AES and EELS spectra. At higher carbon fluxes, C-C bonds begin to form and the lineshapes change accordingly. The AES and EELS nickel peak intensities start decreasing at this stage due to formation of the carbon layer. When a complete two-dimensional carbon layer is formed, the nickel lines disappear and the carbon layer gives a graphitic lineshape. This is more obvious in the EELS data since the AES lineshape at this stage still reveals some carbidic features, probably due to a contribution from the interfacial carbidic layer. At higher carbon fluxes the thicker carbon layer forms a three-dimensional short range order for which surface analysis shows the typical diamond features as discussed in the previous section.

### 5.2. The Role of Energy

The evolution of the carbon film was investigated by AES at different energies in the range 10–300 eV. A "phase diagram" showing the C<sup>+</sup> fluxes needed for the evolution of the carbidic (A), intermediate (B), and graphitic (C)

stage on Ni(111) at room temperature was constructed (Fig. 3). The evolution of carbon layers is energy indepen-

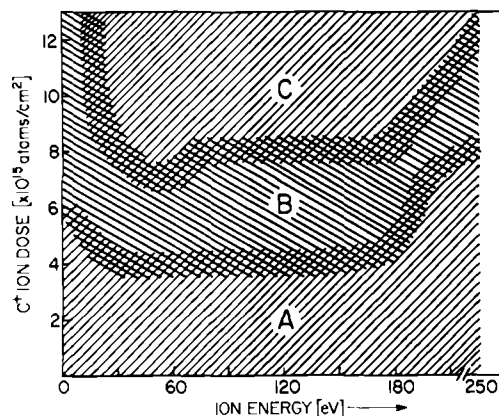


Fig. 3. Evolution of the carbon deposits monitored by AES plotted as a phase diagram of carbon ion energy and flux. Regions A, B and C correspond to deposits that have the AES lineshapes of Figure 2 (right), a, b, and c, respectively.

dent over a broad range (ca. 30–180 eV). At higher (> 180 eV) or lower (< 30 eV) energies, higher fluxes are required for the stabilization of the graphitic stage. The final diamond structure was not observed for energies below ca. 20 eV and is obtained only at a higher carbon flux for 300 eV. The energy threshold for diamond evolution can be interpreted in terms of the "thermal spike" theory.<sup>[3]</sup> At very low energies the ion induced "thermal spike" cannot provide the temperature-pressure conditions needed for stabilization of the diamond phase. At high energies the self-sputtering rate of carbon increases,<sup>[4,33]</sup> the net deposition rate at constant C<sup>+</sup> current density decreases (lower "sticking probabilities"<sup>[16]</sup>), and radiation damage may destroy the crystalline order; amorphous films are expected<sup>[33]</sup> unless the high energy deposition is performed at elevated (700–900°C) temperatures where this damage is annealed.<sup>[31-32]</sup>

### 5.3. Substrate Structure Effects

Room temperature carbon deposition on different substrates (Ni(111), Si(100), Au, T, W, Ge and Cu) exhibited similar behavior, i.e., evolution from a carbidic through a graphitic to the final diamond stage. The carbidic stage may be important for film adhesion to the substrate. Differences in the rate of film evolution on different substrates were detected (Fig. 4), indicating the possibility of different film growth mechanisms on different substrates. The rate of the initial stages of film growth was much slower on a gold substrate than on Ni and Si, possibly due to enhanced backscattering of the C from the high Z gold substrate. The substrate material was also found to influence the temperature behavior of the films as discussed in the next section.

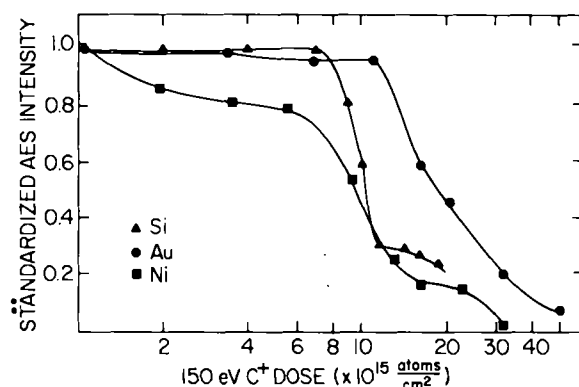


Fig. 4. Plot of the change in substrate AES peak intensity as a function of 150 eV C<sup>+</sup> flux. The substrate signals plotted are the Ni(61 eV), Si(92 eV), and Au(69 eV) transitions. The peak intensities are normalized to that for the clean surface.

## 5.4. Substrate Temperature Effects

Two kinds of temperature effects on film evolution on Ni(111) and gold were investigated, post-deposition annealing and deposition on hot substrates. The films on Ni substrates were found to be unstable under annealing. At 200°C Ni Auger lines appeared, possibly due to some Ni-C interdiffusion or film recrystallization and island formation. At temperatures exceeding 400°C carbon dissolution into the Ni associated with a graphitic transformation of the carbon was detected. This behavior is consistent with the C-Ni phase diagram.<sup>[39]</sup> Carbon ion beam deposition on the Ni substrate at 150°C resulted in graphitic films, while it was not possible to deposit carbon films on Ni at 400°C, very likely due to dissolution of C into the Ni at this temperature. Diamond films on gold were found to be much more stable under post-deposition annealing. No dissolution of the film into gold was detected, even at 875°C, although marked graphitization occurred at 650°C. Deposition of C on a gold substrate at 150°C, however, resulted in a graphitic film, similar to the results of deposition on a hot nickel substrate. This tendency to form graphitic films instead of diamond films at temperatures exceeding 100°C was also detected by Chaikovskii et al.<sup>[28-30]</sup> The explanation for this temperature behavior may relate to the graphite/diamond phase diagram<sup>[1,2,29]</sup> and is unclear at present.

## 5.5. Bulk Characterization

Bulk characterization of the diamond films is currently being performed using TEM, XRD, Raman spectroscopy, IR spectroscopy and ellipsometry. Two kinds of films are being investigated: thin (ca. 500 Å) films deposited in Houston and thick (ca. 1 μm) films deposited in Soreq NRC, Israel, under similar energy, higher current density, and poorer vacuum conditions. TEM analysis of a 500 Å diamond film deposited on Si(100) shows oriented crystals

with a diameter of ca. 1000 Å. The corresponding electron diffraction pattern confirms the existence of crystals oriented with the substrate but is very complex and has not yet been resolved. The ~1 μm samples were deposited on Si(100), Si(111), Ge and Cu. They show clear interference fringes due to non-uniformity of the film thickness indicating transparency in the visible range. Ellipsometry measurements of films on Si give refractive indices that correspond to diamond. IR spectroscopy reveals very high transparency in this region as well. XRD of the carbon film on Si(111) shows a broad peak that corresponds to diamond (111) and a crystal size of ca. 50 Å. This small size may explain the absence of a sharp 1332 cm<sup>-1</sup> diamond line in the Raman spectra, which are very similar to the Raman spectra of microcrystalline diamond films grown by CVD.<sup>[5]</sup> The bulk characterization of these films is still in progress; however, these preliminary results are consistent with the assumption that the films are made of a microcrystalline (20–50 Å) diamond matrix, with random inclusions of larger crystals. A similar interpretation has been given previously by Chaikovskii<sup>[28]</sup> and by other investigators.<sup>[3-5,40]</sup>

## 6. Summary and Conclusion

The most important general achievements of the work can be summarized as follows:

- A comprehensive surface analysis procedure has been established for carbon film characterization using the AES, EELS, UPS, XPS and ILS techniques.
- The Houston mass selected ion beam facility that combines a UHV deposition environment and in-situ surface analysis instrumentation has been established for parametric investigations of (diamond) film growth.
- Carbon films deposited by the Houston facility have been conclusively shown, by surface analysis techniques, to have the short range diamond order. This demonstrates the feasibility of reproducible diamond film deposition using pure carbon ion beams on different substrates at room temperature (in the absence of argon or hydrogen).

In-situ parametric investigations of diamond film evolution are currently being conducted, with emphasis on film evolution, effects of ion energy, substrate temperature during deposition, post-deposition annealing, substrate features and substrate material effects, ambient pressure effects, etc. Among the most important specific results obtained are:

- The film evolution has three stages; an initial carbidic stage evolves to a final diamond structure through a graphitic stage.
- The optimal carbon ion energy range for diamond film evolution at room temperature is 30–180 eV.

- Deposition on hot (ca. 100°C and above) substrates results in graphitic films.
- Substrate effects include determination of deposition rates at the initial stages and film growth modes (e.g., low deposition rates on gold) and determination of film temperature stability and the possibility of high temperature film deposition (e.g., nickel substrates are not suitable for high temperature applications unlike gold substrates).
- Bulk characterization suggests that the films have the properties of diamond and that, under proper conditions, both small and large microcrystalline diamond material can be obtained.

## 7. Future Trends

The possibility of depositing diamond films at room temperature on different substrates has been demonstrated. These films will be useful for many applications, as mentioned in the introduction. Mass selected ion beam deposition, especially under UHV conditions, has the unique possibility of controlling and separating the different deposition parameters. These possibilities do not exist in the other deposition techniques that have a complex chemical-physical nature. Mass selected IBD can thus serve several purposes:

- Parametric investigations of diamond film formation, simulating other existing deposition methods.
- Development of processes with specific deposition parameters resulting in "tailored" film properties. These processes can be attempted by other deposition methods (CVD, plasma deposition, or another ion beam deposition technique) depending on economic considerations.
- Actual fabrication of diamond films. Controlled, micro-focused beams with in-situ flexibility of changing deposition parameters, using either dual beams for doping or successive exposures of different ions for multi-layer deposition, are most advantageous for microelectronic applications.

This review has focused specifically on diamond-film fabrication. Many arguments can, however, be extended to deposition of other materials. Mass selected ion beam deposition can therefore be applied to the development of films of a variety of materials with unique and useful properties.

Received: June 13, 1988

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