

# Plasma processing of super-hard coatings

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**The outstanding properties of diamond, boron nitride and carbon nitride, including their hardness and chemical inertness have aroused tremendous interest among the scientific community during the last decade. These super-hard materials promise a variety of technological applications which could not be excelled by the use of other materials. This necessitated the development of low-cost and scalable preparation technology for the super-hard materials, and plasma processing of these materials through various chemical vapour deposition (CVD) techniques was found to be one of the most viable technology routes. In this article, we report the recent developments made by different research groups in synthesizing the super-hard materials by plasma CVD technique.**

## Diamond coating

### Introduction

Use of diamond dates back to 2000 years, when the mining and trading of diamond were mainly concentrated to the use of diamond as gems. The oldest references of the use of diamond are probably Indian in origin<sup>1</sup>. Indian diamond deposits were nearly depleted by 1725 followed by the Brazilian deposits, which were depleted after only 150 years of their discovery. The industrial use of diamond began only after the discovery of diamond deposits in South Africa. The use of diamond in the industrial domain began to increase rapidly and the demand for diamond surpassed the availability of natural diamond.

It was by then well recognized that diamond is one of the most technologically and scientifically valuable materials, which has a combination of properties unrivalled by any other known material. Due to its unusual properties (Table 1) and commercial value, synthetic production of diamond had long been a goal of numerous scientists and organizations. Scientists invented and developed the high-pressure-high-temperature (HPHT) technique<sup>2</sup> to prepare synthetic diamond. This process was also unable to cope with the increasing demand and the industrial houses wanted to produce diamond at lower temperatures and pressures than those required in the HPHT technique. Thus, the era of the metastable synthesis of diamond by the chemical vapour deposition (CVD) technique began.

The seminal work of Eversole<sup>3</sup> in the 1950s and the key contributions from Angus *et al.*<sup>4</sup>, Derjaguin and Fedoseev<sup>5</sup> and Matsumoto *et al.*<sup>6</sup> have paved the way to the current status of producing diamond films by CVD. The low capital cost, variety and versatility of the CVD processes for producing diamond have ushered renewed hope for the variety of uses of diamond by the industries.

Although still incompletely understood, the new growth process centres on the fact that carbon can bond in two forms, diamond or graphite. Diamond is comprised of inter-connected carbon tetrahedra, while graphite results from a planar, trigonal carbon bond. This results in weak inter-planar Van der Waals-type force, causing the familiar lubricating properties of graphite. The growth process consists of a competition between the formation of tetrahedral ( $sp^3$ ) or graphitic bonds ( $sp^2$ ), where the former is promoted and the latter is suppressed by appropriate means. The fabrication process generally involves dissociation of hydrocarbon (typically methane) and hydrogen gas mixtures by a variety of methods such as hot-filament CVD, dc/rf plasma CVD, acetylene torch, etc. Initially, it was believed that substrate temperature in excess of 1000 K was necessary for depositing diamond films, but at later stage it was found that diamond growth could also occur at 700 K or less. However, depending on the substrate temperature and the relative amount of hydrocarbon and hydrogen in the plasma chamber, the film morphology, especially the graphitic carbon content ( $sp^2$ -bonded carbon) in the film can vary substantially. The physical properties of the film synthesized, thus become very sensitive to the graphitic carbon content ( $sp^2$ -bonded carbon) relative to the tetrahedrally-bonded carbon ( $sp^3$ -bonded carbon) in the film.

Determination of when a carbon coating, obtained by CVD or physical vapour deposition (PVD), is diamond can be difficult. Thus, another metastable material containing amorphous carbon (a-C) with a high degree of  $sp^3$  carbon-carbon and carbon-hydrogen bonding came into being as a valuable by-product of diamond synthesis. The properties of these films are close to and sometimes advantageous to that of diamond and they are termed as 'diamond-like carbon' (DLC) films. By contrast, the DLC films are amorphous and reveal no crystallites by SEM and only broad graphitic Raman peaks ( $1300\text{--}1600\text{ cm}^{-1}$ ) are observed, with no evidence of the narrow  $1332\text{ cm}^{-1}$  diamond peak. The hydrogen content in these films profoundly affects the mechanical properties. Depending

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upon the relative amount of  $sp^2$  and  $sp^3$ -bonded carbon, as defined by a term  $R = sp^2/(sp^2 + sp^3)$ , one may have a rough guess from the  $R$  values whether the film is diamond or DLC or a-C, etc. The amorphous nature of the deposits sometimes contains the signature of Angstrom-size diamond crystallites. Generally diamond films containing diamond crystallites of the size 300 nm or less are classified as nano-diamond. In the industrial arena, nano-diamond films have their own strength in appropriate technological applications.

In the understandable excitement about diamond thin films, it is possible to overlook the potentiality of the DLC films. It is also understandable that due to the inherent amorphous character, it will have inferior properties to diamond films, which would particularly depend on the crystallinity of the film. But, for specialized applications, these films are seen to offer unusual properties. The deposition temperature of DLC films is much lower than that of diamond films, which make them suitable for deposition even on plastic-like materials. All these properties created an expectation of replacing diamond films by DLC films, and different methods of film preparation were proposed by researchers. There exists a strong potential market for diamond and DLC-based technologies.

#### Common CVD techniques used for diamond-coating

The synthesis of CVD diamond can be performed by a variety of methods using conventional laboratory equipment. Considering the great variety of applications, it is evident that quite different qualities of CVD diamond are needed. An important factor in CVD diamond production is the cost for materials and energy used. Worldwide interest in CVD diamond research has resulted in amazing innovations for the CVD process in a relatively short period. Some of these techniques are briefly described in this section.

*Hot-filament technique:* Among the multitude of low-pressure CVD processes for diamond-coating which have

been developed so far, the hot-filament CVD process (HFCVD) together with the microwave-plasma CVD method (MWPCVD) have been used most extensively by the scientists. By now, the HFCVD has become an established deposition process for diamond films. The advantage of the HFCVD over other plasma CVD methods is the adaptability to product geometries and the moderate activation temperatures. The key feature in this technique is to use a heated refractory metal wire (generally tungsten) to convert the methyl radicals in the plasma from a graphite-forming ( $sp^2$ -bonded carbon) process to a diamond ( $sp^3$ -bonded carbon) CVD method. A schematic view of the deposition chamber is shown in Figure 1.

*Microwave plasma deposition:* From the inception of the MWPCVD ( $sp^3$ ) technique in the early 1980s, it has found a lot of success because of its simplicity, flexibility and the easy commercial availability of reactors.

A typical reactor chamber is shown schematically in Figure 2. The reactor is very simple. A quartz discharge tube is inserted through the broad side of a fundamental mode rectangular wave-guide appropriate for the propagation of microwave at 2.45 GHz. Microwave power is then coupled into the chamber through a dielectric window in order to create a discharge. Hydrogen–methane plasma was formed inside the tube and was used to create the proper gas-chemistry for diamond growth. The substrate to be coated is introduced from the bottom of the discharge tube using a dielectric rod to prevent microwave leakage to the outside.

The power, size and the deposition rate that can be achieved in the microwave-plasma reactors have increased significantly over the past few years. This evolution is likely to continue as new commercial applications of diamond appear in the marketplace. The MWPCVD technique for diamond deposition is truly at the forefront of all techniques for commercial and R&D applications. The understanding of the physics of these reactors is such that the macroscopic plasma behaviour and much of the

**Table 1.** Properties of diamond

Property	Comparison with competitors	Possible application
Bandgap (eV): 5.45	1.1 for Si 1.43 for GaAs 3.0 for $\beta$ -SiC	High power electronics, high frequency semiconductor devices, hot thermistors, hot transistors, lasers, detectors.
Electron/hole mobility ( $cm^2/V.s$ ): 1900/1600	1500/600 for Si 8500/400 for GaAs	
Dielectric constant: 5.5	11 for Si 12.5 for GaAs	
Vicker's hardness ( $kg/mm^2$ ): 12000–15000	Hardest known material	Drill bits, polishing materials, cutting tools, sintered diamond compacts, wear-resistant coatings on windows and bearings.
Coefficient of friction: 0.1 in air	Very low in air (higher if kept clean in vacuum)	
Young's modulus ( $N/m^2$ ): $1.2 \times 10^{12}$	Twice the value of alumina (highest mechanical strength)	Stiff membranes for lithography masks, lightweight coatings for audio devices.
Sound propagation velocity (km/s): 18.2	$1.6 \times$ (the value for alumina)	

microscopic phenomenon are well characterized and understood. Plasma models that incorporate in a self-consistent way the electromagnetic fields inside the cavity of interest, have been developed. These models closely predict the plasma shape, position and behaviour as a function of external variables such as pressure and power.

### Results and discussion

In 1971, Aisenberg and Chabot<sup>7</sup> showed that carbon films with diamond-like properties can be prepared by using low-energy carbon ions. The most technologically important work in this area was the development of RF technique by Holland and Ojha<sup>8</sup> in 1976. Since then, a-C and an amorphous hydrogenated carbon (a-C:H) have become the focus of attention of the scientific community. Several techniques were developed for the deposition of diamond and DLC films. In general, sputtering<sup>9</sup>, DC, RF or microwave plasma CVD<sup>10,11</sup> and laser ablation<sup>12</sup> techniques are worth mentioning. It may also be worthwhile to mention the excellent work carried out by Jubber *et al.*<sup>13</sup> and John *et al.*<sup>14</sup> on the deposition of diamond films by MWPCVD. They have subsequently demonstrated commercially viable MWPCVD system for industrial application. Different characterization techniques, including mechanical and optical properties, effect of the presence of trap levels along with the density of states in the tetrahedral amorphous material have been reported<sup>15–19</sup>. Recently, a new technique<sup>20</sup> was reported for the determination of the mechanical properties of thin films from the broadening of the absorption-band tail. This non-destructive technique seems to be useful for determining the stress and strain in diamond films depo-

sited by DC plasma CVD<sup>21</sup> of  $C_2H_2 + H_2$  and that in DLC films deposited by RF plasma CVD of ethylene<sup>22</sup>. Compared to these studies, electrical conductivity and associated photo-effect have attracted lesser attention so far, although it is known that the localized trap states within the band gap of the film generally affect the carrier transport phenomenon<sup>23–25</sup>.

The use of diamond, which is generally polycrystalline in nature, is restricted due to the grain boundary effect<sup>26</sup>. Large sizes of the grains produce a very rough surface which often becomes a limiting factor in using diamond film as optical coating and low friction layer. Preparation of fine-grained diamond films was also tried by several workers<sup>27–29</sup>. The nanocrystalline diamond films are basically polycrystalline in nature with grain size in the nanometer scale. Films with grain diameter < 300 nm may be considered as nano-diamond<sup>30–34</sup>. There are various growth processes like plasma CVD<sup>30,32,33</sup>, magneto-active CVD<sup>31</sup>, detonation of trinitrotoluene (TNT) explosives<sup>34</sup>, etc. for the preparation of nano-diamond films. Highly uniform films with grain size within 100–300 nm and surface roughness ~ 14.95 nm were deposited by Gruen *et al.*<sup>31</sup> at ~ 1123 K. Zhou *et al.*<sup>29</sup> synthesized nanocrystalline diamond thin films in an argon (Ar)–methane microwave discharge without addition of molecular hydrogen. They have observed that at higher reactant gas pressure, concentration of  $C_2$  dimer increases, and concentration of  $C_2$  dimer seemed to be the key parameter for depositing nanocrystalline diamond film. Chakrabarti *et al.*<sup>26</sup> deposited nano-diamond onto fused silica and silicon substrates by CVD of camphor and hydrogen (~ 75 vol.%) mixture. They also studied the optical properties of CVD diamond synthesized from methane and hydrogen gas mixtures as precursor gases. The texture of the CVD nano-diamond from camphor and that from RF + DC plasma CVD of methane + hydrogen is shown in Figure 3 a and b respectively. Large polycrystals (with average grain size ~ 3.2  $\mu m$ ) of diamond are visible (Figure 3 b) in films deposited at 1150 K by CVD of

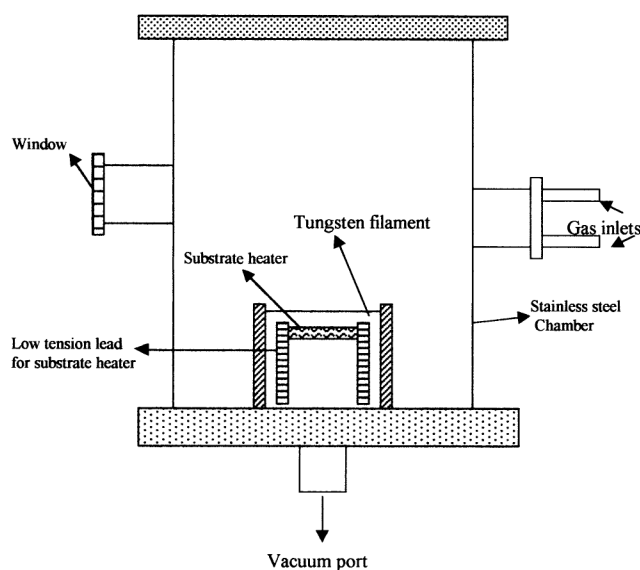


Figure 1. Schematic of a hot-filament CVD system.

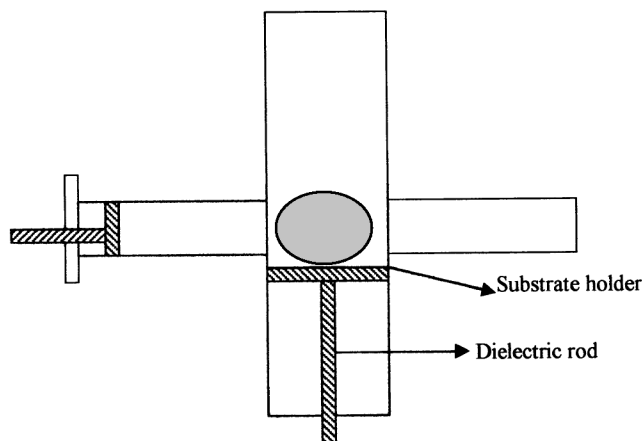
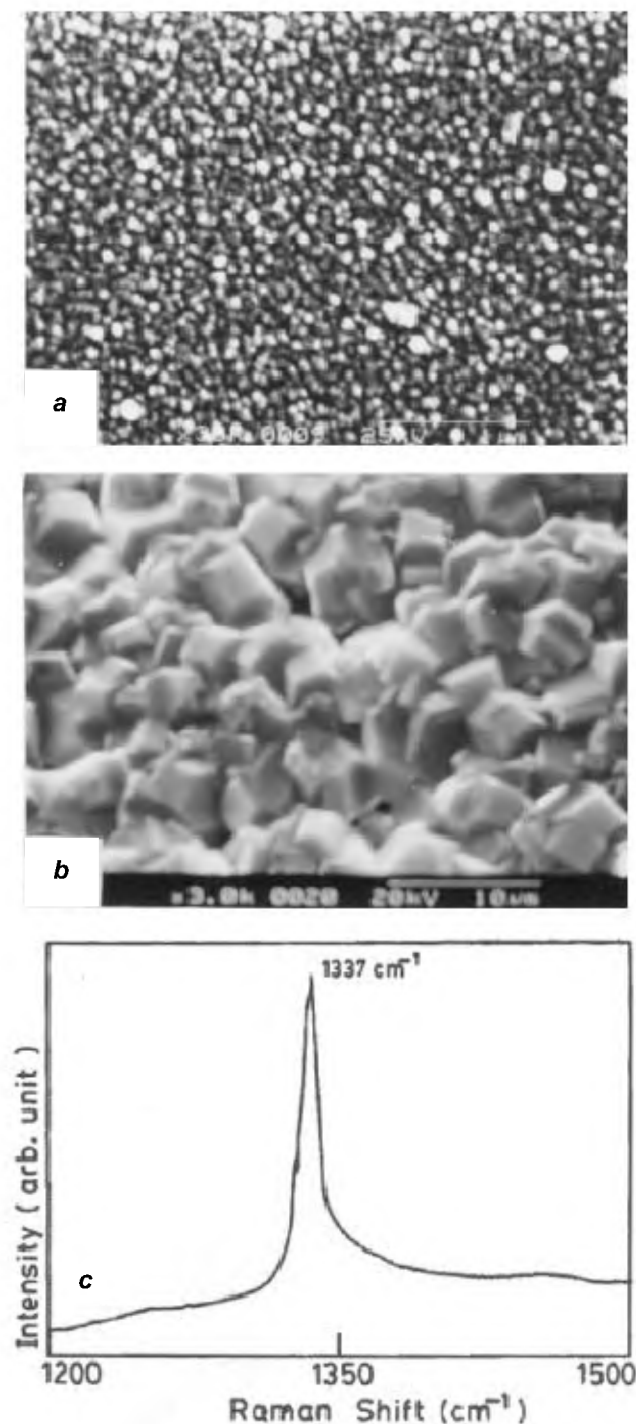


Figure 2. Schematic of a microwave plasma CVD system.

methane + hydrogen, whereas the film deposited at  $\sim 573$  K by CVD of camphor + hydrogen had much lower grain size ( $\sim 0.13 \mu\text{m}$ ). The surface of this film was quite smooth. In the FTIR spectra there was no prominent C–H absorption peak around  $2900 \text{ cm}^{-1}$ , although the presence



**Figure 3.** SEM micrograph of two representative films deposited on Si (100) substrates by: *a*, CVD of camphor + hydrogen ( $\sim 75$  vol.%) at  $T_s \sim 573$  K for nano-diamond film; *b*, CVD of  $\text{CH}_4 + \text{H}_2$  (95.2 vol.%) at  $T_s \sim 1150$  K for large-grained diamond film; *c*, Raman spectra for a nano-diamond film (*a*).

of  $\text{sp}^3$  C–C vibration  $\sim 1337 \text{ cm}^{-1}$  was indicated by Raman spectra (Figure 3 *c*). The positive shift of Raman peak from that of bulk diamond may be attributed to the compressive stress developed in the film.

Growth of high-quality homoepitaxial diamond films having large terrace width had been successful on (001) diamond substrates by Hayashi *et al.*<sup>35</sup>. They have used an end-launch type MWPCVD reactor and used methane + hydrogen gas mixture as precursor gas. They observed that macroscopic steps running parallel to (110) direction cover the film surface. The surface was found to be atomically flat with  $2 \times 1$  and  $1 \times 2$  double domain structure. Konov *et al.*<sup>32</sup> prepared nano-diamond films (grain size  $\sim 5$  nm) by plasma CVD of  $\text{CH}_4$  (10–100%) +  $\text{H}_2$  + argon mixture. They also obtained nano-diamond films without using hydrogen in the feed gas. Their films had surface roughness less than 20 nm, while the hardness varied from 70 to 85 GPa. Raman measurements of nano-diamond generally show a broad Raman peak<sup>33</sup> around  $1332 \text{ cm}^{-1}$ . This was also reported by Yoshikawa *et al.*<sup>34</sup> who studied natural diamond powder with nanometre sized grains, called cluster diamond. Jubber *et al.*<sup>36</sup> reported the atom beam treatment of the diamond films with Raman peak within  $1200$ – $1300 \text{ cm}^{-1}$ . Their nitrogen-treated samples showed a reduction in the surface roughness from 20 to 14 nm. On the other hand, Amaratunga *et al.*<sup>37,38</sup> reported mixed phase films containing diamond crystallites (10–200 nm) embedded in a non-diamond carbon matrix. Scanning tunnelling microscopy (STM) indicated their films to be smooth while the surface roughness measurements (using a profilometer) revealed features of 5–10 nm over scan lengths of several centimetres<sup>38</sup>. The existence of almost entirely  $\text{sp}^3$ -bonded a-C was proposed in 1992 by Gaskell *et al.*<sup>39</sup> on the basis of electron diffraction and neutron-scattering studies. It was suggested that DLC films might be suitable as gate dielectrics<sup>40</sup> or as passivating layers<sup>41</sup>. Films having a high chemical resistance and a good adhesion to carbide-forming materials are useful for wear protection<sup>42</sup>. Wide variation in the properties was reported by various workers depending on the deposition environment and techniques. In fact, it is not well understood till today, demanding motivated research in this important area.

Hardness and fracture toughness of CVD diamond films were measured by Novikov and Dub<sup>43</sup> using Vickers indentation method. They compared the hardness and fracture toughness of the CVD diamond with that of natural diamond. The hardness of the natural diamond varied between 64 and 67 GPa, with long radial cracks emanating from the indent corners. There was evidence of stress corrosion cracking owing to high level of residual stress around the corners. The hardness value of 75 GPa was obtained for a freestanding  $90 \mu\text{m}$  thick CVD diamond film. Friction and wear of plasma-deposited diamond films were studied by Miyoshi *et al.*<sup>44</sup>. They have used high-pressure microwave source

deposition system to deposit diamond on flat (100) silicon, polycrystalline silicon carbide and polycrystalline silicon nitride surfaces. Reciprocating sliding friction experiment in humid and in dry nitrogen and unidirectional sliding friction experiments in ultrahigh vacuum were conducted by them. The tribological characteristics of diamond films varied with environment. The equilibrium coefficients of friction for diamond films were 0.02–0.04 in humid air and dry nitrogen. In vacuum, the value increased to 1.5–1.8. Consequently, the wear factors of diamond films were considerably higher in vacuum than in humid air and in dry nitrogen. The wear factor was also found to depend on the initial surface roughness.

In general, DLC films consist of graphitic clusters linked by  $sp^2$  ( $\pi$ -bonding) or  $sp^3$ -bonding ( $\sigma$ -bonding) forming an extended carbon network, and the relative amounts of the  $sp^2$  and  $sp^3$ -bonds present in the network dictate its various properties; this permits production of tailored films for device applications. There are a large number of publications on the dependence of the properties of DLC films on the  $sp^3/sp^2$ -bonding ratio. This indicated that the electrical properties are mainly dependent on the  $sp^2$ -bonding and optical band gap depends on the lowest  $\pi$  to  $\pi^*$  transition, while the  $sp^3$ -bonding determines the mechanical properties. Recently, Mahajan *et al.*<sup>45</sup> and Mahajan<sup>46</sup> dealt with the above aspects critically.

Different methods such as plasma-enhanced chemical vapour deposition (PECVD)<sup>38</sup>, magnetron sputtering<sup>47</sup>, filtered cathode vacuum arc deposition (FCVAD)<sup>48</sup>, etc. have been used by different groups for preparing mixed a-C/diamond films with high  $sp^3$  content. However, as film properties depend on complex deposition conditions, e.g. ion energy, chamber pressure, substrate temperature, residual gaseous elements in the plasma, etc., there can be wide variations in the films produced. As the effects of the proven conditions are not yet fully understood, further research is needed.

The a-C : H films may be considered to consist of a mixed phase of tetrahedrally bonded ( $sp^3$ ) and trigonally bonded ( $sp^2$ ) carbon atoms. The optical and electrical properties of the films are dominated by  $\pi$  states of the  $sp^2$  sites which form the conduction and valence band edges and lie close to the Fermi level. These  $sp^2$  sites form clusters<sup>49,50</sup> consisting of several atoms depending on the deposition environment. Increase of  $sp^2$  cluster in the film reduces the diamond-like properties. So, films rich in  $sp^2$  carbon are not suitable for electronic or hard-coating applications. Researchers were interested to obtain  $sp^3$ -rich films in these cases. Hydrogen in the atomic state helps to stabilize the  $sp^3$  character. Many workers have used hydrogen<sup>49,50</sup> for the formation and stabilization of  $sp^3$ -bonds in the films. Although electron energy loss spectroscopy<sup>51</sup> supported the fact that hydrogen bonding to both  $sp^2$  and  $sp^3$  sites may take place with

equal probability, it was observed<sup>52</sup> that tetrahedral bonding is dominated by the presence of hydrogen and the film containing unbound hydrogen is mechanically soft. Studies of the microstructural, mechanical, electrical, optical and thermal properties of a-C : H films were reported by many workers<sup>53–55</sup>. Depending on the bias voltage, hydrogen may go to the bonded or non-bonded state. It is known that the amount of hydrogen in the bonding configuration determines the hardness, optical band gap and the electrical resistivity<sup>10,56,57</sup>, whereas the amount of non-bonded hydrogen plays a dominant role in determining the stress and adhesion of the film on the substrate. Earlier studies indicated that the partial pressure of hydrogen in the working gas mixture affects not only the bonding hydrogen concentration but also the bonding configuration ratio among CH, CH<sub>2</sub> and CH<sub>3</sub> present in the film<sup>58</sup>.

Hayashi *et al.*<sup>59</sup> investigated the effect of hydrogen on electrical and optical properties of CVD-grown homo-epitaxial diamond films. MWPCVD was used with methane and hydrogen as precursor gases for depositing undoped and boron-doped films. They have observed that both the hydrogenated and boron-doped diamond films had high concentration of holes  $\sim 10^{18} \text{ cm}^{-3}$  at 297 K. The Hall mobility of all the hydrogenated films was  $\sim 30 \text{ cm}^2/\text{V-s}$ , which was one to two orders of magnitude smaller than that of boron-doped films. Disappearance of the broad cathodoluminescent peak at  $\sim 540 \text{ nm}$  with oxidation treatment indicated the existence of hydrogen-related gap states.

Diamond and DLC films are known to contain large amount of stress. Due to the presence of high compressive stress in the films, their thicknesses are often limited to a low value. The stress depends on the lattice mismatch at the substrate surface, besides the thermal stress. In addition, the stress is determined by the dissociation energy of the ions in the precursor<sup>60</sup>. As the magnitude of the stress is also related to the amount of non-bonded hydrogen in the film, addition of nitrogen in the precursor may be useful to reduce the stress and prevent delamination of the film from the substrate due to the formation of voids in the film. The refractive index and band gap of a-C : H : N films may also be related to the stress and strain<sup>61</sup> and the  $sp^3/sp^2$  ratio. Addition of nitrogen may also influence this ratio. Franceschini *et al.*<sup>62</sup> reported the stress value of  $\sim 2.2 \text{ GPa}$  in the films deposited from rf plasma CVD of methane, which decreased by more than 35% with increasing nitrogen in the plasma.

Despite many efforts during the last two decades<sup>63–66</sup>, the exact interpretation of the close inter-relationship between the micro-hardness and residual stress is not clear. This is probably due to the latter's complicated dependence upon several growth parameters, such as the method of film deposition, the choice of the substrate material, the growth rate and the deposition temperature.

Direct measurement of micro-hardness of thin films by the indentation technique, being a destructive method, is limited by the critical thickness of the film<sup>67</sup>. Measurement of the residual strain or stress profiles from X-ray topography and optical birefringence<sup>68</sup> for determining the micro-hardness in thin films is also not that straightforward. This is basically due to the fact that the separation of two peaks (corresponding to the diffraction from the strained film and substrate) on an X-ray rocking curve is not a simple function of the difference in Bragg angles of two diffracting crystals<sup>68</sup>.

Diamond films are generally grown on Si, which without any pre-treatment of its surface, always has low nucleation density. Several methods were proposed to overcome this low nucleation density on Si substrate. Among these, scratching the substrate surface with diamond paste is very popular for polycrystalline diamond growth. Yogo *et al.*<sup>69</sup> first introduced negative bias pre-treatment of the Si substrate prior to deposition, which showed enhanced nucleation density up to  $10^8$  to  $10^{10}/\text{cm}^2$  for the growth of oriented or locally epitaxial diamond film. In recent years, Cui *et al.*<sup>70</sup> deposited diamond films by dc discharge-assisted HFCVD technique which significantly enhanced the diamond nucleation density. Textured diamond films were studied by several workers. Shang *et al.*<sup>71</sup> successfully deposited (100) textured diamond films on AlN ceramics by HFCVD. This study indicated that the growth rate of films in the  $\langle 100 \rangle$  direction is higher than that in the  $\langle 111 \rangle$  direction, and the textured degree increased with increasing deposition time. It was reported that the highest textured degree could reach as high as 94.5% for a film grown for 75 h. Application of diamond in electronic devices was anticipated from the early stages of CVD diamond research. Recently, Sakamoto *et al.*<sup>72</sup> reported fabrication of micro-patterned diamond film by site-selective plasma CVD process, since patterning of diamond film is a key technology in practical application. They showed that the nucleation density of diamond on Pt surface was much higher than that on any other surface. In particular, the difference between nucleation density on Pt and on  $\text{SiO}_2$  surfaces was of the order of  $10^6$ .

As the structure of a-C : H films strongly depends upon the ion energy impinging on the growing film surface, the effects of ion energy on the film properties have been studied by many workers. In general, it has been found that for ion energies below 800–1000 eV, the film density increases with increasing ion energy, while the hydrogen content decreases. In contrast, the effects of the variation of gaseous species in the plasma have been studied only to a limited extent. In recent years, Tei<sup>73</sup> has studied the structural changes in a-C : H films in inductively coupled  $\text{CH}_4/\text{Ar}$  plasma deposition, with a view to find the key process which plays an important role in determining the film structure. Morley *et al.*<sup>74</sup> have studied laser-induced microstructural changes of thin film a-C : H

using Raman spectroscopy, with a view to establish how sensitive PECVD a-C : H is to the typical laser intensities used for Raman excitation, and what factors affect the sensitivity. Microstructural changes in the form of the growth of graphitic crystallites, similar to that of thermally annealed samples, were observed by them. For longer laser irradiation exposure time, this graphitic component decreased, revealing an amorphous carbon structure.

## Boron nitride

### Introduction

Cubic boron nitride (c-BN) is, like diamond, a metastable material at normal pressure and temperature. This material has unique properties which include high degree of hardness, strength, chemical stability and wear resistance. In addition, in some of its material properties, such as thermal stability in oxygen atmosphere, chemical inertness with ferrous materials and possibility of *n*-type doping, c-BN is much superior to diamond. Thus c-BN is also called 'super diamond'.

The cubic phase of boron nitride has many properties similar to that of diamond. It has hardness second to diamond, a wide band gap, high thermal conductivity and good transmittance over a large spectral range. Unlike diamond, c-BN does not react with an oxide layer, it can be passivated with an oxide layer, and it can be doped both *p*- and *n*-type. At present, c-BN films are much more difficult to synthesize than diamond films. The metastable diamond phase can be synthesized using chemistry and kinetics by a variety of thermal processes (e.g. hot-filament, combustion torch, etc.). However, low-pressure synthesis of c-BN as a thin film invariably requires the use of energetic ions.

Analogous to carbon system, boron nitride forms both  $\text{sp}^2$ - and  $\text{sp}^3$ -bonded phases. Hexagonal BN (h-BN) has a layered,  $\text{sp}^2$ -bonded structure similar to that of graphite. Rhombohedral BN (r-BN) is also a layered  $\text{sp}^2$ -bonded structure, but with a different stacking arrangement of layers. The  $\text{sp}^2$ -bonded BN material can also exist in a highly disordered turbostatic (t-BN) phase consisting of random stacking of planar hexagonal networks. The cubic phase has a zinc blended crystal structure with  $\text{sp}^3$ -bonded structure.

Various near-thermodynamic-equilibrium CVD, ion-assisted PVD and non-equilibrium plasma CVD techniques have been successfully applied for the deposition of diamond and c-BN, respectively. Ion bombardment during deposition was found to be essential for the synthesis of c-BN, which evidently indicates that an ion-assisted non-equilibrium condition will be needed for the deposition of c-BN.

### Synthesis technique

The synthesis of c-BN under high pressure and temperature was first published by Wentrof<sup>75</sup> in 1957. But only from early 90s, deposition methods at lower pressures and temperatures started pouring in from different laboratories for the preparation of c-BN films. The processes adopted by these researchers include ion-beam deposition<sup>76–78</sup>, rf sputtering<sup>79–85</sup>, PECVD<sup>85,86</sup> and electron-cyclotron resonance (ECR)-PECVD<sup>87</sup>.

Several models were proposed to explain the growth process of such a metastable material. Reinke *et al.*<sup>88</sup> suggested a growth model which is based on the fact that sputter yield of c-BN was found to be lower than that of h-BN, and that c-BN deposition takes place just beneath the sputter region. However, this model cannot explain the growth of h-BN at high ion current densities reported by several workers<sup>89</sup>.

Processes for the deposition of c-BN thin films from vapour phase at lower temperatures and pressures have been investigated<sup>90,91</sup>. Recently, there has been a concerted effort by several groups to deposit c-BN at lower pressures and temperatures by PVD<sup>82,83,92–97</sup> or CVD<sup>98–100</sup> methods with ion bombardment on a growing surface. RF bias sputtering has also been tried by Mieno and Yoshida<sup>97</sup> and Bewilogua *et al.*<sup>98</sup> in which negative rf self-bias is applied to the substrate in order to enhance ion bombardment. In rf-bias sputtering, interference dephasing between the two rf power sources for target and substrate electrodes occurs. This may result in distraction of the energy distribution of charged particles and may modulate film deposition assisted by ions/or electrons<sup>101</sup>. Even though the ion-assisted methods worked well for the above groups, there are several researchers who reported the existence of a noncubic BN phase adjacent to the substrate followed by deposition of c-BN<sup>102–104</sup>. Thus a better understanding of the deposition process is necessary for improving c-BN growth. Specifically, there are still significant problems with regard to the intrinsic stress and adhesion to the substrate for c-BN films deposited by different techniques. The most advantageous technology route in this regard is yet to emerge for the fruitful exploitation of this technologically important material.

### Results and discussion

Ion bombardment during deposition by irradiation of the ion beam of substrate biasing is an essential and common feature of both CVD and PVD techniques. Interestingly, inert gases and N<sub>2</sub> are used exclusively as the ion beam and plasma gases. This suggests that H or NH<sub>x</sub> radicals dissociated from H<sub>2</sub> or NH<sub>3</sub> are detrimental to c-BN deposition, in contrast to deposition of diamond or other nitrides, and thus their concentration must be reduced as

low as possible, even though the detrimental role of H and NH<sub>x</sub> on the formation of c-BN has not yet been clarified. The ion energy used in ion-beam-assisted deposition (IABD) processes ranges from 400 to 1000 eV, depending on the ion current density and deposition rate. Note that the values of the substrate bias reported in the sputtering and CVD techniques do not refer to the bombarding ion energy, especially when the plasma is generated at a pressure higher than 10 mTorr, because of collisions in the sheath region. Even when the plasma is generated at a pressure less than 1 m Torr, the biasing value is different from the ion energy, since the potential is relatively high in high-density plasma. Therefore, the sheath potential defined by the difference between the plasma potential and the bias voltage is more meaningful, although the impinging ion energy may be scattered around the potential value due to the modulation in the sheath by the rf characteristics.

According to the threshold value of the total momentum of impinging ions per depositing boron atoms for depositing c-BN<sup>77,99</sup>,  $\sum R_j (2 m_{\text{ion},j} E_{\text{ion},j})^{0.5} > 200$  (eV × amu)<sup>0.5</sup>, (where  $R_j$  is the ratio of the  $j$ th ion flux to the atomic boron flux,  $m_{\text{ion},j}$  is the mass of the  $j$ th ion, and  $E_{\text{ion},j}$  is the energy of the  $j$ th ion), low ion energy may be compensated for by the high ion current density, namely a large  $R_j$  (ref. 76). From the physical point of view, however, there should exist a lowest ion energy threshold for c-BN deposition, which is considered to be around 50 eV based on ion–diamond interaction<sup>100</sup>. The requirement that  $R_j > 1$  means<sup>89,105</sup> that the c-BN deposition rate is limited by the ion current density. In the IABD process, a maximum deposition rate of 0.3 nm/s was reported when the ion current density used was 1.5 mA/cm<sup>2</sup> (ref. 105), which may be the highest that can be achieved by the present ion sources due to the low beam efficiency, when the ion energy is less than a few hundred eV. Accordingly, deposition rates higher than 1 nm/s require an ion current density higher than a few mA/cm<sup>2</sup> at least. This can be achieved only by using high-density plasmas ( $n_e$ ) with a high electron temperature ( $T_e$ ), namely  $n_e (T_e^{1/2}) > 5 \times 10^{11}$  cm<sup>3</sup> eV<sup>1/2</sup>. This is one of the reasons why high-density plasmas such as ECR, inductively coupled plasma (ICP) and RF with magnetic field were used exclusively for the CVD or bias sputtering techniques. Even if one can successfully apply conventional glow discharges to deposit c-BN, the deposition rate may be low as 0.001 nm/s at best, since a lower plasma density of approximately 10<sup>9</sup> cm<sup>−3</sup> and the condition  $R_j > 1$  will limit the atomic boron flux or source gas flow rate to less than 5 × 10<sup>13</sup> cm<sup>2</sup>.s or 0.01 sccm.

Ichiki and Yoshida<sup>96</sup> deposited boron nitride films by low-pressure (1 mTorr) ICP technique. They have demonstrated that ion bombardment to the substrate and high density ICP free from hydrogen were essential for the deposition of c-BN. The lowest deposition temperature reported is 423 K, although some uncertainties arise

as to the measurements performed during deposition under ion bombardment. It is a general experience that in a high-density plasma, the substrate temperature automatically reaches  $\sim 600$ – $700$  K and as such a deposition below that can only be achieved by proper substrate cooling arrangements. At this point one must remember that the surface temperature (of the film during deposition) may be entirely different from that being measured in this process. Thus it is imperative that one has to optimize the plasma density, ion energy (bias) and substrate temperature to get the best film at a reasonably lower temperature.

Influence of excited hydrogen species on the surface state of  $sp^2$  hybridized boron nitride had been studied by Konyashin *et al.*<sup>102</sup>. Termination of  $\pi$  (dangling) bonds of  $sp^2$ -hybridized boron nitride on the surface of a-BN and h-BN resulted from the surface interaction with the excited hydrogen species.

Bhattacharyya *et al.*<sup>102</sup> deposited boron nitride films onto silicon (001) and fused silica substrates by using borane-ammonia and nitrogen gas mixtures in a capacitatively-coupled plasma CVD chamber. RF power was varied within 200–250 W and the deposition was carried out under self-biased condition. AFM and SEM micrographs of a typical film deposited on Si are shown in Figure 4 *a* and *b*, respectively. The films were quite compact in nature and the surface roughness varied within 55 to 158 nm. FTIR studies indicate the presence of  $\sim 50\%$  c-BN in the films. The band gap varied within 5–6 eV depending upon the relative percentage of c-BN content in the films.

Mirkarini *et al.*<sup>103</sup> investigated how ion irradiation could selectively promote the formation of dense  $sp^3$ -bonded c-BN over the graphite-like  $sp^2$ -hybridized phase. They have deposited the c-BN films by ion-assisted pulsed laser deposition technique in an ultrahigh vacuum system. They have performed the experiment in which either the ion mass ( $m_{ion}$ ) or ion energy ( $E$ ) was varied in conjunction with the ion flux per depositing atom ( $J/a$ ). They observed that for a fixed ion energy and mass, there was a critical value of  $J/a$  above which c-BN formation was initiated. A window of  $J/a$  values could be located in which large c-BN percentages were obtained, and at a point where  $J/a$  value was so large, the films began to be completely sputtered away<sup>77,103</sup>.

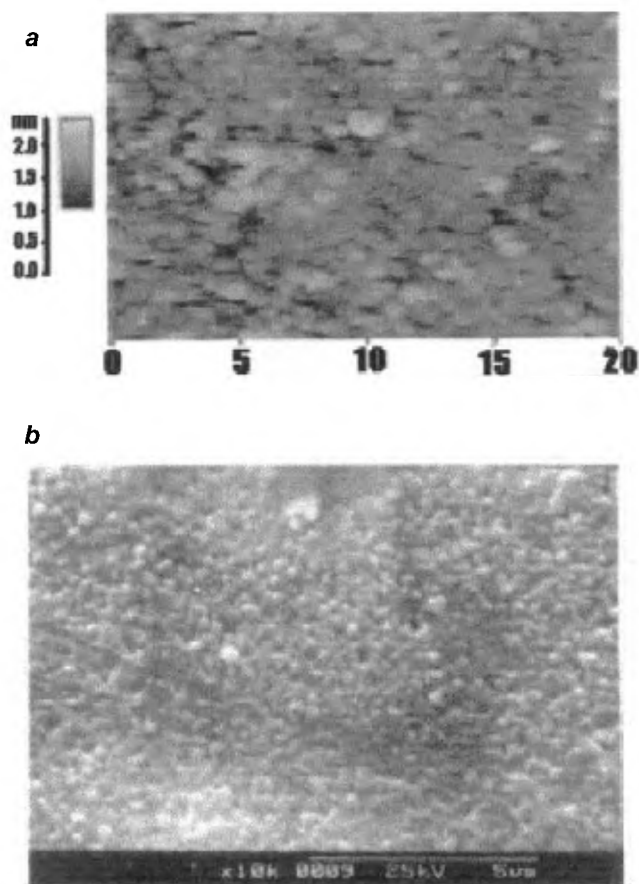
Several models were proposed to explain the mechanism of c-BN growth by use of PVD or plasma CVD:

- (i) Stress induced by the impact of high-energy ions can reach values corresponding to HPHT synthesis of c-BN (stress model)<sup>104</sup>.
- (ii) Incoming ions increase the density in the surface layer, promoting the formation of  $sp^3$ -hybridized modifications of BN (subplantation model)<sup>106</sup>.
- (iii) Ion deposition of c-BN is treated as a cylindrical, thermal spike and complete rearrangement of the spike

volume is regarded as resulting in formation of the dense modification of boron nitride (cylindrical spike model)<sup>107</sup>.  
(iv) Formation of c-BN occurs due to selective sputtering on h-BN from the growing boron nitride film compared to c-BN (sputter model)<sup>108,109</sup>.

However, the stress model explains c-BN growth as a result of internal, bi-axial compressive stress in the boron nitride film due to ion bombardment. The formation of an interlayer of  $sp^2$ -hybridized boron nitride before growth of c-BN could be easily explained by the model<sup>108,110</sup>.

The deposition techniques adopted by these groups have their own merits and demerits. It may be stated that all the deposition methods adopted by most of the groups could not increase the c-BN content by more than 80% in the film. There was seldom any regular grain shape, and peeling of the films due to poor adhesion was a very common observation by the workers. Most experiments have confirmed that the existence of interfacial mismatch and strain energies between c-BN films and the substrates are the main obstacles in the growth of high quality c-BN films. It is more or less well accepted by now that the growth mechanism of c-BN thin films are yet to be understood to dictate the terms of growing well-crystallized c-BN thin films.



**Figure 4.** *a*, AFM of a BN film deposited on Si (100) substrate at  $T_s \sim 723$  K; *b*, SEM micrograph of BN film as in (*a*).



## Carbon nitride

### Introduction

Great interest had been generated in the synthesis of carbon nitride ( $\text{CN}_x$ ) films right from the theoretical prediction<sup>111,112</sup> of the existence of a  $\beta\text{-C}_3\text{N}_4$  phase by Liu and Cohen in 1989. This complex structure was based on the  $\beta\text{-Si}_3\text{N}_4$  structure for a C–N solid in which C is substituted for Si. It was expected to have potentially useful mechanical and electrical properties. The predicted band gap of  $\beta\text{-Si}_3\text{N}_4$  is  $\sim 3.2$  eV. Corkill and Cohen<sup>113</sup> calculated the quasi-particle electronic band structure of  $\beta\text{-C}_3\text{N}_4$  using GW approximation. The indirect band gap is predicted to be 6.4 eV. The atomic coordination suggests  $\text{sp}^3$  hybridization of the carbon atoms, while nitrogen atoms are  $\text{sp}^2$ -hybridized. The predicted low bond length is  $\sim 0.147$  nm and the bond ionicity is  $\sim 7\%$ . The predicted cohesive energy is 5.8 eV and the calculated bulk modulus is 4.27 Mbar, which is close to that of diamond. This suggests that the hardness of  $\beta\text{-C}_3\text{N}_4$  would approach that of diamond. The sound velocity predicted theoretically is  $1.1 \times 10^4 \text{ m s}^{-1}$ , which suggests that this material will possess good thermal conductivity.

Several attempts were made to deposit stoichiometric carbon nitride ( $\text{C}_3\text{N}_4$ ) films consisting of carbon–nitrogen single bonds. The preparation techniques that have been tried so far include low-energy, mass-selected ion-beam deposition<sup>114,115</sup>, dual-ion-beam deposition<sup>115</sup>, particle beam-assisted laser processing<sup>117–119</sup>, reactive sputtering<sup>120–124</sup> and ECR-assisted evaporation<sup>125</sup>. But none of the above techniques were able to produce stoichiometric  $\beta\text{-C}_3\text{N}_4$  film. Films were always nitrogen-deficient, which was attributed to the energetic particle bombardments involved in the deposition process<sup>114,126</sup>. There have been a few studies to investigate the effect of substrate temperature on the phase formation and properties of  $\text{CN}_x$ <sup>126,127</sup>. All these studies resulted in the use of amorphous  $\text{CN}_x$  films for protective coatings on magnetic recording disks and have promising potential as protective coatings on space and optical devices. Recent results, however, indicate that a-C : N : H is a superior electronic material compared with a-C : N.

### Synthesis of $\beta\text{-C}_3\text{N}_4$

After the Liu and Cohen's prediction, a host of methods for synthesizing  $\beta\text{-C}_3\text{N}_4$  were tried by a number of groups. Among these methods, processes involving plasma processing may be classified into the following broad categories:

- (a) CVD<sup>128–132</sup>.
- (b) Plasma-enhanced or ion-assisted evaporation<sup>125,133,134</sup>.

A variety of hydrocarbon gases<sup>124,132,135,136</sup> were used along with nitrogen for the CVD process for synthesizing carbon nitride films. However, methane and nitrogen gas mixture was the most favoured combination used by many groups.

Most of the CVD processes used a conventional capacitively-coupled, parallel-plate electrode system placed inside a typical stainless steel vacuum chamber. RF (13.56 MHz) power was applied to produce plasma between the two electrodes. Films were deposited at various power levels and self-bias condition at chamber pressure ranging from 0.1–1 Torr.

### Results and discussion

Much work has been focused on the forming of  $\text{CN}_x$  films with high nitrogen to carbon ratios<sup>112,119,134,137</sup>. Films were always nitrogen-deficient, which was attributed to the energetic particle bombardments involved in the deposition process<sup>114,126</sup>. It is well known that the properties of films deposited using a self-negatively biased rf-PECVD system<sup>138,139</sup> depend strongly on the deposition parameters. The key parameter in determining the property of the film is the ion bombardment energy. This is a function of self-bias voltage which in turn is a function of rf power coupled to the plasma. The effect of ions on the properties (optical, electrical and structural) of carbon nitride films prepared by rf-PECVD technique was studied by Zhang *et al.*<sup>129</sup>. The apparatus used by them was a capacitively-coupled, parallel-plate electrode CVD system. The substrate was not heated. Nitrogen and methane were introduced in the chamber at a ratio of 2. The rf power was varied between 5 and 50 W, and the maximum chamber pressure was 0.8 Torr. They had observed that an increase in rf power and a decrease in gas pressure led to an increase in the self-bias voltage. This resulted in an increase in ion energy and ion bombardment. The films grown on the cathode and anode showed different properties, with or without ion bombardment, under the same deposition conditions. The films prepared with efficient ion bombardment contained lesser hydrogen, had higher electrical conductivity and greater hardness.

In another report, Zhang *et al.*<sup>140</sup> presented their work on carbon nitride prepared by ECR plasma CVD technique. The ratio of  $\text{CH}_4$  :  $\text{N}_2$  was in the range of 2 : 0.25. The microwave power and pressure were fixed at 400 W and 3 mTorr respectively. The substrate temperature was varied between 278 and 299 K. They had used optical emission spectroscopy (OES) to monitor the emissive species and studied the effect of  $\text{CH}_4$  :  $\text{N}_2$  ratio as well as substrate temperature on the N/C composition ratio and the structure of the film. It has been observed that the growth rate decreased but the nitrogen concentration increased in the film, as the gas ratio of  $\text{CH}_4$  :  $\text{N}_2$  decreased.

At lower substrate temperature, both the deposition rate and the nitrogen concentration increased. The observed reduction in the growth rate with increased nitrogen and at higher substrate temperature was ascribed to the increase in the flux of nitrogen species which caused reduction in the concentration of molecular  $C_mH_n^*$  species necessary for film formation.

Freire<sup>141</sup> deposited a-C:N:H films onto Si (100) substrates in a rf-PECVD deposition chamber. Several combinations of methane–nitrogen, methane–ammonia and acetylene–methylamine gas mixtures were used. The self-bias voltage varied between –350 and –370 V, while the total system pressure varied within 3–8 Pa. It was observed that incorporation of nitrogen into the amorphous network induced a substantial amount of  $sp^2$ -bonded carbon and the observation was found to be independent of precursor gases. Increase in the incorporation of nitrogen culminated in reduction in the internal compressive stress in these films. Effect of substrate temperature (300 to 710 K) on the structure and properties of  $CH_x$  films deposited by reactive pulsed laser deposition technique at a fixed nitrogen ambient pressure  $\sim 0.2$  Torr was presented by Ong *et al.*<sup>142</sup>. Graphite rings seen in the films. Atomic fraction of nitrogen drops from 0.27 to 0.13 as the substrate temperature increased to 710 K. Wan and Egerton<sup>143</sup> prepared  $CH_x$  films by two-arc discharge evaporation of carbon and by reactive sputtering of a graphite target in a nitrogen-containing ambient. Films were deposited with or without applied bias to the substrates (like cleaved KCl, mica and silicon) which were kept at temperatures between 173 and 873 K. The highest N/C ratio obtained by sputtering was 0.75, with deposition onto mica substrate kept at 173 K. It was observed that over 75% nitrogen was weakly bonded to carbon, and was released when the film was annealed at 1073 K. Bombardment by carbon ions during deposition was found to increase the fraction of C–N bonds.

Structural properties of a- $CH_x$  films deposited by PECVD technique onto silicon substrates were studied by Han Kim *et al.*<sup>131</sup>. The structural and compositional modifications induced by the substrate negative bias ranging from 0 to –400 V were examined. The deposition rate was found to increase with bias voltage. FTIR studies indicated a clear absorption peak at  $2190\text{ cm}^{-1}$  with stretching vibrations of a  $C\equiv N$  triple bonding (nitride). The absorption peaks centred around  $3300\text{ cm}^{-1}$  and  $2900\text{ cm}^{-1}$  were identified as due to N–H and C–H stretching modes respectively. There were broad bands in the region between  $1350$  and  $1650\text{ cm}^{-1}$ , which were assigned to the C=C stretching mode which is normally forbidden.

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## MEETINGS/SYMPOSIA/SEMINARS

### International Conference on Phonons in Condensed Materials (Phonons 2K3)

Date: 20–23 January 2003

Place: Bhopal, India

Topics include: Coherent phonons, Brillouin scattering/ultrasonic experiments, Electron–phonon interactions, Phonons at high pressure, Phonon dynamics and transport, Low dimensional systems, Neutron scattering, Defects and disorder, Nanostructures, Bose–Einstein condensate, IR/Raman spectroscopy, Phase transition and soft modes, Surfaces and interfaces, Glass and disorder systems, Nonlinear dynamics.

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### National Symposium on Mineral Phosphate Solubilization 2002 and Wet Workshop on MPS

Date: 14–16 November 2002

Place: Dharwad

Topics include: Chemistry of phosphates in soil; Biochemistry of MPS in microbes; Microbial transformation of phosphorus in soil; Agronomic response to MPS microbes; Biodiversity of MPS microbes; Interaction of MPS microbes; Molecular genetics of mineral phosphate solubilization; genetic engineering for improvement of mineral phosphate solubilization by microbes; Plant-mediated mineral phosphate solubilization; Bioprocessing of phosphate rock ores.

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