

Review

A review of the preparation of carbon nitride films

Stephen Muhl*, Juan Manuel Méndez

Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Apartado Postal 70-360, Coyoacán, D.F. 04510 México

Received 30 November 1998; accepted 4 May 1999

Abstract

Using a semiempirical rule based on a range of existing hard materials, Liu and Cohen predicted that some of the crystalline forms of C_3N_4 might have values of bulk modulus close to, or even greater than, that of diamond. Subsequent theoretical work has supported this result, although modifying which of the crystal structures had the most extreme properties. Based on the assumption that hardness is primarily determined by the bulk modulus, a large number of groups initiated research to try to make this 'harder-than-diamond' material. Although today there are doubts as to the validity of this assumption, the ability to synthesise materials with such a large bulk modulus is of great interest because such substances can be expected to have extreme properties, such as thermal conductivity, compression strength, acoustic velocity, etc. A review is presented of the methods used, and the results obtained, by a variety of groups in their attempts to prepare carbon nitride films. The preparation techniques have been somewhat arbitrarily divided into the following sections: (1) atmospheric-pressure chemical processes, including pyrolysis and explosive shock; (2) ion-beam deposition, including cathode arc; (3) laser techniques; (4) chemical vapour deposition processes, including direct-current (DC) arc, hot-filament chemical vapour deposition (HFCVD) and plasma-enhanced chemical vapour deposition (PECVD); and (5) reactive sputtering, with and without deliberate substrate biasing. We have also included a section describing some of the problems associated with the analysis of carbon nitride films. A brief description of the techniques is provided and we discuss some of the problems associated with the characterisation methods that have been used in the analysis of the deposited material. A somewhat speculative set of conclusions is presented which we hope will be of assistance to colleagues working in this field. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Carbon nitride; Characterisation; Preparation

1. Introduction

The study of carbon nitride solids dates back to the last century, when Guy-Lussac discovered paracyanogen. The material was considered a troublesome by-product by chemists who dealt with reactions involving cyanogen (C_2N_2) [1], and found it very difficult to dissolve. The first deliberate attempt to make carbon nitride films was probably by Cuomo et al. in 1979 [2]. This group proposed a planar polymeric structure for the material, similar to that put forward by Bircumshaw et al. [3] for paracyanogen. However, no great interest in this material was evident until Liu and Cohen's theoretical work of 1989 [4] indicated that the properties of β - C_3N_4 might be similar or superior to those of

diamond. The now fairly well-known result of this theoretical work has been the stimulation of much research to find an adequate method to reproducibly synthesise crystalline C_3N_4 . Initially, the theoretical work was motivated by an empirical model developed to estimate the bulk modulus of tetrahedrally bonded materials. This model indicated that solids with high bulk modulus should be found in crystals with short, low-ionicity bonds between the constituents. The C–N bond, and tetrahedral crystals based on this bond, are obvious candidates for such high-compressibility solids.

To date, various C_3N_4 structures have been proposed and studied: a hexagonal β - C_3N_4 , α - C_3N_4 (analogous to β - Si_3N_4 and α - Si_3N_4), a C_3N_4 defective zinc-blende structure with carbon vacancies, cubic C_3N_4 and two graphite-like rhombohedral forms [5,6]. Additionally, various other carbon nitride compounds and structures can exist: monoclinic or triclinic forms of CN [7], paracyanogen-like CN [2,8], rhombohedral C_5N_4 [9],

* Corresponding author. Fax: +52-15-616-1251.

E-mail address: muhl@servidor.unam.mx (S. Muhl)

graphite-like C_5N [10], cubic and monoclinic C_4N_2 [6] and nanotubes of graphitic C_3N_4 and CN [11]. Fang has described these compounds in detail, but it is important to bear in mind that a given deposit will often consist of a combination of compounds of different composition and structure [12].

Various theoretical techniques have been applied to the study of the different carbon nitrides, including miscellaneous molecular-dynamics methods, first-principles pseudopotentials, routines based on Hartree–Fock and local-density approximations, etc. The cohesive energy calculated for all of the C_3N_4 compounds indicates that they should be, at least, metastable. Furthermore, from this work it is clear that the low-bulk-modulus graphite-like structures are the most stable, and that the other four high-density forms have similar but lower stabilities. There is considerable discussion as to which of the four is the most stable, as well as to the precise values of their bulk moduli. The most recent values are 448, 496, 425 and 437 GPa for the defect zinc-blende, cubic, α and β forms of C_3N_4 , respectively [13]. These values are similar to, or greater than, that for diamond at 443 GPa. Similarly, the velocity of sound in β - C_3N_4 has been estimated to be high, $\sim 10^6$ cm s $^{-1}$, meaning that the material should have a high thermal conductivity. The bandgaps of all of the high-density C_3N_4 materials are expected to be in the range 3–4 eV.

Many authors have implicitly, or explicitly, related the bulk modulus with the hardness of a material, with this being one of the principal motivations for experimental research into the preparation of C_3N_4 . This connection has been carefully discussed by Teter [13], and he concluded that from both theoretical and experimental viewpoints there is a clearer dependence between the hardness of a material and its shear modulus, rather than the bulk modulus. Under this scheme, the hardest of the C_3N_4 family would be the defect zinc-blende form, with shear modulus of 390 GPa (diamond has a shear modulus of 535 GPa and a Vickers hardness of 96 GPa). Moreover, the hardness of the zinc-blende form is predicted to be approximately 60 GPa Vickers, approximately 60% of the hardness of diamond.

There has been considerable discussion as to the stability of the various forms of C_3N_4 . Specifically, there are conflicting results as to whether the NC_3 units are planar or pyramidal. The importance of this last aspect is that some of the theoretical studies have been based on an initial, and constrained, planar structure. Similarly, *ab initio* calculations of gas-phase C_3N_4 molecules indicate that a linear chain containing sp^2 -hybridised nitrogen is more stable than the planar form, and that the pyramidal central nitrogen arrangement is even less stable. From an experimental point of view, it is not clear how much of an effect the pyramidal form would have on the calculated diffraction patterns

of these materials. Another problem related to high-density C_3N_4 structures is that the closeness of the neighbouring nitrogen atoms has a destabilising effect due to the N–N lone-pair interactions. This repulsion depends strongly on the structure considered, but can be up to 2.3 eV per formula unit. Based on this consideration, a C_4N_3 compound has been proposed where some of the N1 nitrogen atoms are replaced by carbon atoms, thus increasing the distance between nitrogen neighbours and decreasing their interaction [14]. Along the same lines, calculations using tight-binding molecular dynamics of amorphous carbon nitride indicate that the minimum of the cohesive energy occurs at lower and lower densities as the nitrogen content increases, and that there are associated changes in the bonding configuration with the nitrogen percentage. Both of these effects result in an increase in the separation of the neighbouring nitrogen atoms, and therefore a reduction in the lone-pair interaction. As mentioned later, various experimental results seem to indicate that these effects may be some of the active mechanisms impeding the inclusion of high concentrations of nitrogen in CN deposits. One of the principal implications of the above is that the nitrogen concentration of stable, or metastable, crystalline high-density carbon nitride may be less than the 57% considered for C_4N_3 .

For the purpose of this article, the sections have been classified as follows:

1. atmospheric-pressure chemical processes, including pyrolysis and explosive shock;
2. ion-beam deposition, including cathode arc;
3. laser techniques;
4. chemical vapour deposition processes, including direct-current (DC) arc, hot-filament chemical vapour deposition (HFCVD) and plasma-enhanced chemical vapour deposition (PECVD);
5. reactive sputtering, with and without deliberate substrate biasing; and
6. characterisation of carbon nitride.

The results obtained in each of the categories are briefly described. With regard to the nitrogen content of the deposits, some authors quote N/C ratios considering the nitrogen content and others state the total percentage of nitrogen, i.e., $N/(N+C)$. In this review, the data are presented as the ratio of the number of nitrogen to carbon atoms.

2. Preparation techniques

2.1. Atmospheric chemical processes

Synthesis of carbon nitride compounds has been attempted by a variety of chemical reactions, including explosive shock compression of an assortment of precursors. Wixom used shock-wave compression, up to

48 GPa, of sodium salts of tetrazole and mixtures of polymeric precursors [15]. The resultant materials were a mixture of amorphous carbon and well-ordered diamond crystallites containing little or no nitrogen. Other precursors have also been used; poly(aminomethineimine) gave an sp^2 -bonded C_2N compound which appeared to contain spherical onion-like nanostructures [16]. Explosive compression of a 36% nitrogen, linear-chain CN compound produced a crystalline material, but with characteristics similar to rhombohedral CN [17].

The results to date indicate that there is considerable nitrogen loss during the compression stage, probably due to preferential formation of the thermodynamically more stable diamond structure. In 1995, DeVries suggested the use of powder mixtures of an azide, for example LiN_3 , with a non-diamond form of carbon to form a carbon nitride compound, in a scheme analogous to that used to prepare cubic BN [18]. However, to date, no reports of the successful use of such ideas has appeared.

A number of papers have reported the synthesis and characterisation of different CNH compounds with the idea of providing information about the stability and structure of carbon nitrides. A graphite-like hexagonal polymer, $(C_3N_3)_2(NH)_3$, $N/C=1.5$, has been prepared and was found to be stable up to $500^\circ C$ [19]. An interesting ferromagnetic crystalline material, $C_3N_{4.5}O_{1.2}H_{4.1}$, was obtained from the reaction of $C_3N_3Cl_3$ and Li_3N in N_2 at $220^\circ C$ [20]. A theoretical and experimental study of various compounds containing C_3N_4 units indicated that β - C_3N_4 might be significantly different from β - Si_3N_4 [21]. The conclusion of the work was that whilst the angular geometry of the carbon and silicon atoms should be similar, for the nitrogen atoms a pyramidal configuration was favoured in carbon nitride. Additionally, there are a number of reports of high-temperature chemical processing that has produced a crystalline material whose diffraction analysis agrees quite well with the C_3N_4 structures. One involved the reaction of *N,N*-diethyl-1,4-phenylenediammonium sulfate (DPDS; $C_{10}H_{18}N_2O_4S$) with N_2 in the presence of SeO catalyst at $800^\circ C$ and the other, the annealing (again at $800^\circ C$) of the product of the ultraviolet (UV) photo-assisted reaction of sodium amide and alkyl chloride mixed with chloroform. The first material appeared to contain zinc-blende crystals and the second showed evidence of α - C_3N_4 , with both being embedded in an amorphous matrix [22,23]. However, in the second case the X-ray diffraction peaks were weak, only two or three times that of the noise level, and not all peaks could be identified with CN compounds. Unfortunately, little additional characterisation results were provided. Another study involved high-pressure (5 GPa), high-temperature ($1400^\circ C$) processing of tetracyanoethylene (C_6N_4) and 1,3,5-triazine ($C_3H_3N_3$) [10]. The tetracya-

noethylene produced a black, graphite-like solid with a composition close to that of C_5N . However, the triazine case resulted in a solid containing almost no nitrogen, with this indicating the effect of the presence of hydrogen for the inclusion of nitrogen in carbon nitride compounds.

2.2. Ion-beam deposition

2.2.1. Nitrogen bombardment of carbon

This work has been divided into groups according to the nitrogen bombardment energies used. In the high-energy range, >1 keV, a variety of carbon substrates have been used (glassy carbon, amorphous carbon and diamond) with substrate temperatures ranging from -196 to $800^\circ C$. For temperatures below $800^\circ C$, there is no significant effect on the total nitrogen content. However, there are problems related to the measurement of the nitrogen content. Since the nitrogen is implanted only into a certain subsurface volume of the carbon, the size of the volume considered during the calculation of the composition determines the percentage value. For example, implantation at 50 keV at room temperature resulted in a maximum nitrogen content of $N/C=0.33$ to 0.43, depending on the dose used; at $400^\circ C$, $N/C=0.22$ but the nitrogen was spread over a larger volume [24]. Notwithstanding these problems, the nitrogen concentration was apparently larger in diamond and glassy carbon ($N/C\sim 0.33$) than in amorphous carbon ($N/C\sim 0.18$), under the same experimental conditions. Similarly, the structure of the CN fraction was seen to be different [25]. Upon annealing, changes in the nitrogen content did not occur until $1000^\circ C$, when considerable out-diffusion was seen. However, X-ray photoelectron spectroscopy (XPS) analysis demonstrated that structural changes occurred even with $500^\circ C$ annealing [24]. There has been no evidence of the formation of either a crystalline material or a C_3N_4 compound with this technique. Significantly, hardness and Raman measurements of samples implanted with either nitrogen or carbon ions produced almost identical results [26].

At the lower energies, the N/C ratio has been reported to be controlled mainly by the ion dose, rather than the ion energy. Using 5 eV ions the nitrogen content rapidly increased with the ion dose, up to $N/C\sim 0.61$, and thereafter rose much more slowly to a saturation level of 0.67 [27]. Although the nitrogen content, measured by Rutherford backscattering spectroscopy (RBS), appeared to increase as a function of ion energy, this was due to the effect (referred to above) of the increased volume of graphite receiving nitrogen. Auger electron spectroscopy (AES) showed that the surface concentration of nitrogen did not vary significantly with the ion energy. Measurements were also made of the relative amounts of sp^3 -bonded carbon as a function of the ion

energy. A maximum was seen for an incident nitrogen energy of ~ 15 eV, with a strong decrease at higher values. This result implies that there is an energy barrier for the formation of the sp^3 phase but that energies in excess of this level cause damage to the nascent tetrahedral structures. However, no crystalline structures were observed at any ion energy.

2.2.2. Carbon beams and carbon evaporation

Freeman sources have been used to generate alternating carbon and nitrogen beams to directly deposit CN compounds. Here, both the ion energies (from 5 to 100 eV) and the relative arrival rates can be controlled [27]. The only crystalline phase that has been observed was graphite, but various important pieces of information were obtained. The sp^3C content was measured as a function of the incident ion energy, and two maxima at ~ 30 eV and < 1 eV were seen. Chemical sputtering of the carbon and CN by nitrogen was found to be of great importance, with the erosion rate depending on the incident ion energy and the binding energy of the carbon group to the substrate; no net deposit was obtained on gold substrates. Significantly, bombardment by nitrogen ions with energies greater than ~ 30 eV was seen to restrain the amount of this element in the deposit. Specifically, nitrogen bombardment was seen to remove deposited material through the formation of CN, with an etch rate of ~ 0.5 carbon atoms per incident N_2^+ ion. This process was estimated to limit the maximum nitrogen content to $N/C \sim 1.86$; however, experimental evidence indicates that the maximum may be closer to 0.67 [28]. Todorov et al. suggested that an additional mechanism involving the promotion of the formation of either molecular nitrogen or the low-boiling-point compound C_2N_2 ($-26^\circ C$) may also take place at high nitrogen contents [29]. It was also perceived that the carbon-atom arrival rate must be sufficiently low that closed carbon-ring structures do not form. This is important because the low-energy incident nitrogen atoms, required to not cause damage and other defects, cannot reorganise such rings into the desired tetrahedral phase. The N/C arrival rate should be > 3 and the incident energy < 10 eV so that surface deposition, rather than subplantation, occurs.

As is often found, annealing of the prepared material resulted in loss of nitrogen and graphitisation of the deposit. Similar work by Tsubouchi et al. reported that the structure of the CN deposit was dependent on the energy, in the range 50 to 400 eV, of both the carbon and nitrogen ions [30]. In this study, for the different energies, the relative arrival rates of the two ions were adjusted to allow analysis of films with the same $N/C = 0.4$. It was shown that the $C\equiv N$ peak intensity observed via Fourier transform infrared spectroscopy (FTIR), and the refractive index, increased strongly with increas-

ing nitrogen-ion energy but there was little change with the carbon-ion energy.

Another version of this method is electron-beam evaporation of carbon with accompanying nitrogen-ion bombardment of the substrate [31]. The experiments were performed under a high-vacuum technique with the substrate at ambient temperature. The nitrogen content was seen to change almost linearly with the N/C impingement rate, and showed no dependence on the ion energy (500–5000 eV), except at the highest energy of 10 keV. These results are somewhat expected since at such high energies any chemical sputtering effects are probably at saturation, with little dependence on the actual ion energy used. Using an arrival rate of 2:1 for $N:C$, the measured N/C value of 2 was surprisingly high. However, the film hardness and optical bandgap both decreased with increasing ion energy showing that a stable material had not been formed, and that the excessive ion bombardment had caused damage to the deposit. Basically the same technique, but using lower ion energies (< 100 eV) and a substrate temperature of $500^\circ C$, was reported to form a CN film with nitrogen concentration of $N/C \sim 0.83$ [32]. Here the nitrogen ions were generated using a microwave electron cyclotron resonance (ECR) reactor, with the carbon vapour again being formed by electron-beam evaporation of graphite. Both the composition and structure of the deposit were seen to vary with the nitrogen gas flow even though the gas pressure was kept constant at 2×10^{-4} torr. Unfortunately, this result was not explained by the authors but may indicate the importance of the formation of gas-phase precursors. From both XPS and Raman analysis, the films made at the highest flow appeared to have predominantly sp^3 -bonded carbon as well as having $N/C = 0.92$. Unfortunately, no diffraction measurements were reported.

Another study by Kohzaki et al. used the same electron-beam evaporation of carbon but at a fixed low nitrogen-ion energy of 200 eV and substrate temperatures of < 100 , 300 and $500^\circ C$ [33]. Here the N/C ratio decreased towards saturation, at a value of ~ 0.6 , as the relative nitrogen arrival rate increased with little dependence on the substrate temperature, although the FTIR spectra showed that the 2200 cm^{-1} peak ($C\equiv N$) decreased in intensity, at an approximately constant N/C value, as the substrate temperature increased. However, the XPS measurements indicated almost no change in the bonding configuration. In a second paper by the same group the deposit was reported as having a columnar structure at the highest substrate temperature but this was not crystalline [34].

There are reports of two distinct techniques that involve carbon vapours and nitrogen ions. One is the reactive ionised cluster beam and the other is by Veprek's group in Germany. In the first case polyethylene was evaporated at $300^\circ C$ through a nozzle in such a way

that the accompanying adiabatic, supersonic expansion caused condensation into clusters [35]. These were then ionised by electron bombardment and accelerated towards the silicon substrate held at 300°C. Nitrogen pressures from 3×10^{-5} to 3×10^{-4} torr were used. No composition data were provided but FTIR absorption bands in the 1000–1600 cm^{-1} range were seen to change as the nitrogen pressure increased. The authors argued that, as the two peaks observed centred at 1270 and 1420 cm^{-1} became more pronounced at higher nitrogen pressures, they were therefore probably related to single CN bonds. Raman spectroscopy showed the existence of nanocrystals of diamond at the lowest nitrogen pressures and a number of other small, diffuse peaks in addition to the normally observed D and G graphite bands. At higher nitrogen concentrations, the XPS data appeared to indicate that a larger proportion of the nitrogen was bonded to sp^3C . In an earlier paper, the same group had reported that using ammonia they had achieved N/C ratios of up to ~ 0.7 . Furthermore, electron diffraction and reflection high-energy electron diffraction (RHEED) measurements indicated the presence of crystals in the deposit, with the structure of these in good agreement with that of $\beta\text{-C}_3\text{N}_4$ [36].

The earlier work by Veprek involved chemical sputtering of graphite by an intense, high-frequency nitrogen plasma to generate large amounts of CN radicals in an excess of excited nitrogen molecules and atoms [37]. The relative concentration of CN to nitrogen could be decreased by increasing the distance between the graphite source and the substrate. At small distances the FTIR spectra were essentially of paracyanogen, with a strong absorption band at $\sim 1537 \text{ cm}^{-1}$. At larger distances the nitrogen content in the films increased to that corresponding to C_3N_4 . Biasing of the substrate caused drastic changes in the FTIR spectra; a large increase in the $\text{C}\equiv\text{N}$ peak, the disappearance of the 1537 cm^{-1} band and the growth of new bands centred at 1100 and 480 cm^{-1} . The films were amorphous by X-ray diffraction but the existence of a broad feature at $2\theta = 25^\circ$, corresponding to a lattice spacing of 3.56 nm, suggested that the material might contain rhombohedral C_3N_4 .

Yet another novel method involved various combinations of explosive evaporation of carbon, surface condensation of nitrogen, and ‘mixing’ of these layers by either intense ion or electron bombardment [38]. Four regimes were used as follows: (I) nitrogen was condensed on a graphite source electrode, then both carbon and nitrogen were explosively evaporated by electron impact; (II) nitrogen was condensed on the substrate at $\sim 80 \text{ K}$, then carbon was explosively evaporated on top with the carbon-ion energy being controlled through biasing; (III) carbon was evaporated on to the substrate, nitrogen was condensed on top, and then the two were mixed by using an intense pulse of energy-controlled electrons; and (IV) (the reverse order of III) nitrogen was con-

densed, carbon evaporated on top and the two were mixed by using a pulse of electrons. The characteristics of the deposits were independent of the type of substrate (silicon, titanium, copper, nickel and graphite). The nitrogen content could be varied up to a maximum of 59%, $\text{N/C} = 1.44$, and $1 \mu\text{m}$ films could easily be formed using multiple experiments. The X-ray diffraction (XRD) data of the $\text{N/C} = 1.33$ material showed that this was crystalline with a few strong peaks whose d -spacings agreed with those for $\beta\text{-C}_3\text{N}_4$. For all of the four regimes the threshold energy density to cause the amorphous-to-crystalline transition was reported to be 10^4 J cm^{-3} for electrons and $5 \times 10^4 \text{ J cm}^{-3}$ for ions (this was expressed as an energy density because of the different penetration depth for electrons and ions). The hardness of the films depended on the processing type used and was greatest, 20–30 GPa, for regimes III and IV. Similarly, under these conditions, the friction coefficient was quite low at 0.1, and the electrical resistance of the film was seen to decrease with increasing ‘mixing’ beam energy. One of the important aspects of this study was that chemical sputtering was avoided by using thermal condensation of the carbon and nitrogen, and that this appeared to result in significantly larger nitrogen contents in the deposit.

2.2.3. Arc deposition

Deposition using a high-current electric arc has the distinction that it is the one of the few methods by which growth can be made, almost completely, through the interaction of low-energy ionised species. Both filtered and unfiltered cathode arcs have been used in the preparation of carbon nitride compounds. The disadvantage of the unfiltered version is that macroparticles of the graphite target are nearly always incorporated in the deposit. In general, the use of an ionising source for the nitrogen improves its incorporation in the films, reflecting the large (9.9 eV) dissociation energy of molecular nitrogen; if the process is carried out in a nitrogen atmosphere significantly lower N/C ratios are normally obtained [39]. The incident energy of the carbon ions is typically $\sim 20 \text{ eV}$, but this can be increased by use of substrate biasing [40]. For nitrogen-ion energies above 100 eV, the N/C ratio increases from 0.25 to 0.4 at $\sim 200 \text{ eV}$; with little change for higher energies [41]. However, N/C values of 0.6 to 1.0 have been obtained by using nitrogen energies in the range 2.0 to 10 eV, with chemical sputtering limiting the incorporation of this element for energies in excess of 10 eV [26,28,42]. These effects can be seen to be essentially the same as those described in the previous section using carbon- and nitrogen-ion beams. Chemical sputtering has also been reported for excessive carbon-ion bombardment, but with a threshold energy of approximately 50 eV. Moreover, it is evident that the composition of the deposit is strongly dependent on the relative arrival

rates of carbon and nitrogen ions. Values of N/C greater than 0.4 are only found when significantly more nitrogen ions are incident on the growing film.

There are few reports of the effect of substrate temperature, but deposition at temperatures $\geq 300^\circ\text{C}$ strongly reduces the nitrogen content and increases the amount of $\text{C}\equiv\text{N}$ bonding [39]. Annealing of an amorphous CN film, N/C (initial) of 0.45, made using a filtered cathode arc (FCA), showed that between 0 and 200°C loosely bonded nitrogen was rapidly expelled with N/C decreasing to ~ 0.35 . From 200 to 400°C little change was observed, but from 400 to 800°C the N/C ratio again decreased to ~ 0.1 ; annealing at even higher temperatures caused graphitisation of the deposit [43]. This process of degradation with annealing is frequently observed, independently of the deposition method used.

The achievement of high N/C ratios in the deposit is only one of the necessary conditions to produce the high-density forms of crystalline C_3N_4 ; if the carbon atoms are not in the sp^3 configuration then the material is unlikely to present extreme properties. Until now, none of the deposits prepared using arcs have contained crystalline CN compounds. In all cases, as the nitrogen concentration becomes greater than $\sim 10\%$, the XPS spectra show that the amount of sp^3 bonding decreases strongly, with a concurrent increase in the peaks associated with $\text{C}=\text{N}$ and $\text{C}\equiv\text{N}$ in the FTIR spectra [39,44]. In the same way, there are reductions in the values of the associated properties, such as hardness (56 to 10 GPa), density (2.8 to 2.0 g cm^{-3}), bandgap (0.75 to 0.2 eV), refractive index (2.5 to 1.6) and residual stress (4.0 to 1.7 GPa) [39,45,46].

Merchant et al. found that CN deposits of similar nitrogen concentration, N/C ~ 0.35 , made by unfiltered cathode arc or 50 keV nitrogen implantation, were almost identical. In particular, the material contained primarily sp^2 -bonded carbon with a bond length smaller than that found in amorphous carbon. It was considered that this was due to nitrogen substituting into carbon rings up to a saturation level of about one nitrogen to three carbon atoms [47].

Unfortunately, at present, because of the limited information available concerning the structural analysis of the deposits prepared using the low-ion energy process, it is not possible to definitively ascertain if the reduction in the sp^3 bonding configuration is a consequence of the increased nitrogen content or if it is a coexistent effect due to the processing used.

A variant of the unfiltered cathode arc has been reported by Yaki et al., where the substrate was placed in close proximity to the arc but shielded from it by a stainless steel plate to interrupt the emitted macroparticles [48]. The closeness of the substrate to the source allowed much high pressures of nitrogen, up to 220 mtorr, to be used. Substrate biasing was employed from 0 to -500 V and this determined the substrate

temperature increase due to ion bombardment. Films thicker than 200 nm spalled if the applied bias was in the range -50 to -500 V . Although this indicates that such films were highly stressed, it was not clear if the effect was also seen at the highest pressure, 220 mtorr, where the mean free path of the ions would be such that ion bombardment should be negligible. The nitrogen content increased slowly from an N/C value of ~ 0.12 to 0.3 as the pressure was increased from 7.5×10^{-2} to 75 mtorr, but then rapidly increased to 0.52 at a pressure of 220 mtorr. This result is in agreement with similar observations (mentioned in other sections) that, to be able to obtain high N/C values, a greater incidence of nitrogen is required relative to the flux of carbon. Both FTIR and Raman spectroscopy of the films showed the presence of $\text{C}\equiv\text{N}$, NH, and the D and G peaks of graphite. However, a clear discussion was presented indicating important differences between the data from the two analysis techniques, with supporting data from XPS measurements. The conclusion of this was that the broad $1380\text{--}1250\text{ cm}^{-1}$ band was due to aniline-like $\text{C}-\text{N}$ stretching, the band at $1090\text{--}1080\text{ cm}^{-1}$ was related to $\text{C}-\text{N}$ stretching of aliphatic amines and that the $1540\text{--}1500\text{ cm}^{-1}$ feature could be assigned to $\text{C}=\text{C}$ and $\text{C}=\text{N}$ stretching vibrations in pyridine rings.

Yen and Chou reported the use of a high-pressure DC arc jet to make CN deposits. In this system, the arc was struck between a thoriated tungsten cone-shaped cathode and the inside wall of a graphite anode [49]. The arc is made to rotate around the anode by an external magnet and this was the source of the evaporated carbon atoms. The system was operated at high power, $\sim 400\text{ W}$, and high pressure, 60 torr, thus ensuring that the ion energy was very low. The substrate temperature depended on the substrate–arc distance and typically varied from 600 to 800°C . The N/C ratio depended on the temperature used, and at the highest temperature it was ~ 0.58 . Diffraction measurements showed the existence of small crystallites, within a carbon-rich matrix, whose lattice spacings and intensities closely agreed with those of $\beta\text{-C}_3\text{N}_4$. The c/a value at 0.39 was larger than the theoretical value and some of the observed d -spacings could not be identified. However, Raman analysis gave five small peaks whose positions were in good agreement with simulated spectra generated from the spectra of $\beta\text{-Si}_3\text{N}_4$ multiplied by the scaling factor proposed by Yen and Chen [49]. This work presents some of the most convincing evidence for the formation of crystalline C_3N_4 .

2.3. Laser techniques

Lasers have been used in two ways in attempts to fabricate C_3N_4 : ablation of graphite targets in nitrogen or ammonia atmospheres, both with and without ion

bombardment of the substrate, using excimer, Nd:YAG or CO₂ lasers [50–53]; and laser-induced chemical reactions between precursor substances, both in the gas and liquid phase [31,54,60].

In the ablation case, without additional nitrogen bombardment, or a secondary discharge to generate nitrogen ions, it is difficult to get high levels of nitrogen incorporation in the deposit. The laser-plasma plume does generate large quantities of N₂⁺ but little atomic nitrogen. The nitrogen molecules absorbed on the graphite are decomposed but the principal ablated species are C_x ($x=1-4$) and CN. The relative quantities of these depend on the ambient gas pressure, which nitrogen-containing gas is used, the laser fluence and its wavelength. In nitrogen, large amounts of CN are observed but in ammonia, C₂ dominates and there is little CN production [55,56]. Therefore, the species incident on the substrate consist, principally, of ions and radicals of C_x, CN and N₂, or NH. As described in other sections of this paper, it has been seen that N₂ species are inefficient at introducing nitrogen in the deposit and molecular nitrogen ions can remove nitrogen by chemical sputtering.

Unfortunately, most of the work using additional nitrogen-ion bombardment has employed fairly high-energy ions, > 100 eV, with this leading to graphitisation of the deposit at very high energies, and an accompanying loss of nitrogen. There are two reports of the formation of crystalline material using nitrogen-ion bombardment with laser ablation of a graphite target. The first report involved the use of 100 eV ions [57], in a manner similar to other experiments that have not produced crystalline material. However, since neither the gas pressure nor details of the substrate-ion beam geometry were given, it is unclear what was the energy of ions incident on the growing film. Similarly, the authors mentioned the importance of the inclusion of a few per cent of argon or O₂ in the ion beam, but with no other particulars given. The other paper involved either 193 or 308 nm laser ablation, and, according to the authors, cone-shaped crystalline deposits were made by using concurrent ion bombardment in the range 200–600 eV [58]. The 308 nm irradiation caused ablation of the carbon clusters and higher substrate temperatures, 700°C, were required to grow the ‘crystals’. Unfortunately, no experimental evidence was provided to support the claim that the cone-shape features seen by scanning electron microscopy (SEM) were in fact crystalline. Furthermore, the paper compared the laser results with those of the preparation of carbon nitride materials by HFCVD, implying that the work was carried out at York University, Canada. However, the photograph included of a crystalline CN deposit is from work carried out a number of years earlier, at the Institute of Physics, Beijing, People’s Republic of China. This same photograph has appeared in more than five

publications. Lamentably, this type of unclear presentation of information does not assist research in what is already a difficult field.

A somewhat more formal article by Niu et al. described Nd:YAG ablation of graphite but with an intense low-energy (1 eV) atomic-nitrogen beam incident on the substrate [59]. The N/C ratio was directly proportional to the atomic-nitrogen flux, maximum value 0.82, and was independent of the substrate temperature up to 600°C. The deposit was thermally stable up to 800°C and small crystals were observed using electron diffraction, with six *d*-spacings in close agreement with those predicted for β-C₃N₄. This work is similar to that by Xu et al., who used a novel atomic-nitrogen source with the laser ablation [39]. Very few samples were prepared and no diffraction analysis was reported, but N/C values of up to 0.6 were obtained. Significantly, XPS analysis demonstrated that the nitrogen atoms had only one bonding configuration, and the carbon-atom peaks were considered to represent graphite and CN phases. Later work by the first group showed that the nitrogen content could be increased by decreasing the carbon arrival rate at the substrate. However, FTIR data showed that was a concurrent increase in the number of C≡N bonds. A plot of %N versus the logarithm of the growth rate indicated that the saturation concentration of nitrogen was ~50%, N/C~1, and not the value of 57%, N/C=1.33, based on the C₃N₄ composition [60]. It was subsequently reported that the deposited material was made up of a mixture of a –C≡N phase and a C₂N product, and therefore it is unclear if the 50% composition result is general or specific to the mixed compound studied [61]. The C₂N compound could be purified by thermal processing, since it was stable up to ~720°C; it was shown to have many properties similar to those of diamond-like carbon (DLC) except that, because the carbon bonding was 100% sp², the deposit had low residual stress.

It is noteworthy that nearly all of the highest nitrogen concentrations, N/C~1, have been obtained by using large quantities of atomic nitrogen, either by using a remote secondary plasma together with the laser ablation, or by tuning the laser wavelength to cause decomposition of the nitrogen-containing gas. Indeed, the deposit usually contains large amounts of C≡N without the remote plasma, and very little with the plasma under the same conditions [62].

Another variant of this method involved the use of a surface-wave discharge to generate a beam of atomic nitrogen directed towards the substrate, together with the ablated carbon atoms [63]. It was shown that, for N/C ratios of less than 0.2, the nitrogen content was proportional to the incident atomic-nitrogen flux. Additionally, decreasing the KrF (248 nm) laser power from 6 × 10⁸ to 5 × 10⁷ W cm⁻² caused the nitrogen concentration to more than double, but increasing the

laser power to higher values did not alter the nitrogen content. The laser power controls the flux of carbon atoms, but it also determines the energy of the atoms. It has been reported that, as the laser power increases from 5×10^7 to 7×10^9 W cm⁻², the kinetic energy of the carbon atoms varies from a few eV to more than 100 eV [64]. The authors considered that the increased energy of the carbon atoms was the cause of saturation in the nitrogen concentration with laser power, because of chemical sputtering of the film. The cited review article [64] also states that the proportion of large carbon clusters in the emitted flux similarly increases with the laser power and this phenomenon probably also contributes to the observed variation of the composition of the deposit.

Optical emission studies of the plasma plume formed during laser ablation of graphite have shown that the laser wavelength used is also very important, since it is this that mainly determines the nature of the carbon species emitted. Relatively more carbon atoms and radicals are produced by 532 nm irradiation, whilst 355 and 1064 nm wavelengths produce more C₂ species [65].

In general, without nitrogen bombardment, the nitrogen concentration increases with the nitrogen gas pressure up to ~ 75 mtorr and remains constant thereafter. As a function of the substrate temperature, the percentage of nitrogen is almost constant up to $\sim 200^\circ\text{C}$ and decreases for higher values. In an N₂ atmosphere radio-frequency (RF) biasing of the substrate has been seen to be beneficial, as the sp³ content of the deposit increases slightly with the bias. Similarly, the sp³ content is usually found to increase as the ablation rate decreases. However, it appears clear that for many experimental conditions, with and without nitrogen bombardment, as the nitrogen concentration increases to more than ~ 15 – 20% the number of sp³-bonded carbon atoms decreases strongly together with the film density. However, Hu et al. recently (1998) reported that significant amounts of C \equiv N appeared at N/C ratios greater than that where the decrease in the sp³ content was found, and therefore considered that the two occur by independent mechanisms [66].

Most deposits to date have been amorphous forms of carbon nitride with N/C < 1. As mentioned above, there have been some reports of the formation of small crystals using laser ablation, with diffraction data containing some of the peaks calculated for β -C₃N₄ [59,70]. However, it is frequently found that some peaks are absent, others cannot be indexed, and the relative intensities often do not agree with the calculated data.

KrF or CO₂ lasers have been used to promote chemical reactions between precursor gases. In one case an ethylene–ammonia mixture was employed and an N/C ratio of 0.45 was obtained for titanium-coated quartz substrates — triple the value for uncoated substrates. The deposit also had a higher proportion of

sp³-bonded carbon, indicating the catalytic effect of the substrate [67]. The same group also reported the laser pyrolysis of acetylene/nitrous oxide/ammonia mixtures to produce a carbon nitride powder which contained both crystalline and amorphous phases [54]. The composition of the deposit was C_{2.5}N, although oxygen, fluorine and sulfur contaminants at the percentage level were also found. Notably, no —H or C \equiv N bonds were observed in the FTIR spectra. X-ray diffraction studies of the crystalline part showed 18 peaks, 11 of which coincided with those calculated for α -C₃N₄, but electron-beam irradiation caused decomposition of the crystals. This decomposition probably implies that α -C₃N₄ was not formed. However, it is not clear if the high-density forms of C₃N₄ are, in fact, stable to high-energy electron bombardment. Similarly, there is little information on the theoretical thermal stability of these materials.

An ArF laser has been used to cause the photodecomposition of ammonia during the ablation of a graphite target, with the substrate placed perpendicular to the target. Absorption by the gas limited the gas pressure to less than 1 torr. The refractive index of the films, 2.6–1.7, was inversely proportional to the nitrogen content, N/C = 0–0.79, which in turn was controlled by the gas pressure, 0–1.0 torr. However, FTIR measurements showed the presence of both CH and NH groups but very little C \equiv N was observed even at the highest N/C ratio of ~ 0.8 . The main absorption band seen was at 1625 cm⁻¹ and is thought to be related to C=N.

There are only two reports of the formation of carbon nitride compounds from a liquid, one involving the use of an ArF excimer laser to promote the decomposition of hexamine (C₆H₁₂N₄) dissolved in liquid ammonia at -60°C [68]. The deposit, grown on a tungsten substrate, was crystalline and appeared to be a mixture of the α and β phases of C₃N₄. The N/C value of 0.8 indicated that excess carbon was present, probably as amorphous carbon (a-C). However, not all of the predicted *d*-spacings were observed in the electron diffraction analysis of the material. The second work entailed using a CO₂ laser to induce microimplosions at the interface between solid ethanol and liquid nitrogen. Small crystals, 10–100 nm, were reportedly formed but no data concerning their structure or composition was given [69].

2.4. Chemical vapour deposition processes

2.4.1. Hot-filament CVD

This technique is a modified version of that used for diamond growth, but here CH₄ was mixed with either N₂ or NH₃ + H₂. In both cases the CH₄ concentration was very low; for the first instance, $\sim 1\%$ [70], and for the second, a high (98%) H₂ dilution was used with an NH₃ to CH₄ ratio of 1 [71,72]. The filament and substrate temperatures were high at 2100 and 800–900°C, respectively, and the gas pressure was between 1

and 15 torr. The modification consisted of the use of an RF or DC bias between the substrate and filament, or a grid near the filament. The bias was sufficiently higher to generate a plasma around the substrate zone and only an amorphous carbon-rich deposit was formed without this discharge [73]. Both nickel (seeded with 1 μm diamond paste) and silicon substrates have been used successfully. Initially it was reported that a crystalline deposit, with no amorphous phase, could be prepared; in a more recent paper it was reported that the N/C ratio for DC- and RF-assisted films was 0.36 and 0.16 [72], respectively, values that are very different from the N/C=1.3–2.5 reported originally [6]. Diffraction measurements were interpreted as showing the existence of a deposit of a mixture of α - and β - C_3N_4 plus two new phases which are probably monoclinic and tetragonal CN_x ($x=0.5$ –1). As is commonly found, not all of the predicted diffraction phenomena were seen, some of the intensities of the peaks did not agree with the calculated data, and some unidentified peaks were observed [74]. The crystals grown on silicon and nickel substrates had lattice constants of $\sim 10\%$ and 1%, respectively, larger than the theoretical values. Raman spectroscopy showed that no graphitic phase was present, but possibly more importantly none of the expected Raman peaks from C_3N_4 were observed.

It was argued that hydrogen plays a similar role in carbon nitride formation as it does in diamond growth and that plentiful amounts of both atomic hydrogen and atomic nitrogen are required to create C_3N_4 [75]. The results mentioned above, if the deposits are of high-density carbon nitride, indicate that there may be two regimes that can be used to grow crystalline C_3N_4 : one with high hydrogen dilution and the other with high nitrogen dilution.

2.4.2. PECVD

A considerable amount of work has been carried out on the preparation of CN deposits by means of microwave or RF plasmas. The microwave work has been motivated by the success of this technique in the preparation of diamond films. It has been shown that hydrogenated amorphous carbon nitride films, a-C(N):H, deposited by RF PECVD of methane–nitrogen mixtures can be as hard as diamond line carbon films [76]. Both RF and DC work has demonstrated that the incorporation of small amounts of nitrogen causes a considerable reduction of the internal stress, with little change in the film's hardness. This result, together with the accompanying improvement in the adhesion of the films, has made a variety of applications possible: anti-reflecting coatings in IR sensors, protective coatings for computer hard discs, etc. [77].

This section has been subdivided in accordance with the plasma frequency used.

2.4.2.1. Microwave plasmas. Such plasmas have been used at pressures from 3×10^{-3} to 80 torr. The lower values have involved electron cyclotron resonance to enhance the plasma density and electron temperature. However, the substrate is normally placed in a region free of microwave radiation, where the plasma is in a quasi-DC state. Here substrate biasing can effectively control ion bombardment, if the substrate is conductive, with the energy of the ions being determined by the voltage applied. Clearly, in the case of the growth of an insulating film, the ion bombardment changes as the film thickness increases. At the high pressure, atomic collisions produce thermalisation of the ions and the only effect created by substrate biasing is local variations in the ion/neutral/radical population in the film/gas interface region.

Microwave decomposition of a $\text{CH}_4/\text{NH}_3/\text{H}_2$ mixture at high pressure (80 torr), high power (3.5 kW), high substrate temperature (1000–1200°C) and with an adequate ratio of CH_4 to NH_3 , has resulted in the formation of an exclusively crystalline deposit of carbon, nitrogen and silicon [78,79]. If the CH_4 flow was too high, then a diamond-like deposit was formed. Although crystals with as little as 5% silicon were found, the hexagonal structure observed by XRD and electron diffraction was still significantly different from any of the proposed C_3N_4 structures. XPS analysis demonstrated that no Si–C bonds were present and therefore it was considered that the silicon was substituting the carbon in the CN matrix, such that the compound might be represented as $(\text{C}_x\text{Si}_y)_3\text{N}_4$. Interestingly, if no silicon was present, then no deposit was found; conversely, if silicon was present, a deposit could be formed even on non-silicon substrates. Raman spectroscopy showed approximately 30 sharp peaks with many of these agreeing with the calculated spectra generated from the α - and β - Si_3N_4 data, using Yen and Chou's scaling factor of 1.43 [49]. As mentioned in the Characterisation section this procedure is debatable, but the observation of sharp Raman peaks is an important manifestation. A similar procedure has recently been reported but using a 3% CH_4 in N_2 gas mixture at a somewhat lower pressure (15–20 torr) and power (1.5–2 kW) [80]. Here again a crystalline deposit was obtained, but only if a -150 V bias was applied to the substrate. The deposition involved 8 h of formation of a crystalline Si_3N_4 buffer layer on the silicon substrates followed by 10 h of processing to give the carbon nitride layer. No composition information was given, but the XPS spectra can be seen to be very similar to that given in Ref. [79] for the $(\text{C}_x\text{Si}_y)_3\text{N}_4$ compound. The X-ray data were considered to indicate that the deposit was a mix of α - and β - C_3N_4 , although various diffraction peaks were absent and the relative intensities did not agree with the predicted values.

ECR chemical vapour deposition has been carried

out using plasma excitation of the nitrogen, at pressures $<10^{-3}$ torr, extraction of this plasma to the substrate zone where methane is introduced and decomposed by the molecular nitrogen radicals and atoms [81,82]. Additional post-deposition treatment using UV illumination has also been tried [83]. The N/C ratios of the deposits are mainly determined by the N_2/CH_4 ratio but are commonly <0.3 . The films are soft, amorphous and contain quite large amounts of $C\equiv N$ bonding. The UV irradiation only affected low-nitrogen-content material, increasing the FTIR $C\equiv N$ and 1600 cm^{-1} peaks and reducing the CH absorption band. However, another group in France, using conditions almost identical to those of Ref. [82], evidently obtained a deposit with a composition of $CN_x\cdot H$, where $x > 1$ [84]. Another group using very similar conditions but with a larger range of substrate temperatures, up to 700°C , produced deposits on silicon or molybdenum substrates with a previously prepared polycrystalline diamond coating [85]. The diamond layer severely complicated the assessment of the nitrogen concentration but, as a minimum, N/C was >0.16 . The films showed good thermal stability even up to the highest temperatures. No diffraction experiments were attempted but SEM images showed the film to be made up of many small carbon nitride fibres. Most interestingly, the XPS analysis indicated a single bonding configuration for the nitrogen, consistent with it being bonded to sp^3 carbon.

2.4.2.2. RF plasmas. Most of this work has been based on the use of a standard parallel-plate type of reactor, with methane, acetylene or methylamine mixed with either nitrogen or ammonia. Gas pressures have been varied from 6 mtorr to >5 torr and substrate temperatures from lower than room temperature to $\sim 550^\circ\text{C}$; no deposit is obtainable for substrate temperatures $>600^\circ\text{C}$ [86,87]. Overall, akin to the other preparation techniques, a strong decrease was observed in the fraction of sp^3 carbon as the nitrogen concentration increased to more than $\sim 10\%$. The deposition rate also decreased severely with increasing percentage of nitrogen-containing gas in the plasma, yet again indicating the importance of chemical sputtering. Similarly, there have been few reports of deposits with N/C values in excess of 0.22 and the films typically contain between 10% and 20% hydrogen ([88] and references therein). As a consequence of this, the FTIR spectra show large absorption bands related to N–H and C–H, as well as the bands from the CN triple and double bonds. Deposition has been carried out simultaneously on the cathode (connected to the RF supply) and the earthed anode. Films grown on the anode contained more nitrogen than the cathode material, in agreement with other work that has shown that the percentage of nitrogen is inversely proportional to the electrode bias. In general, the deposition rate, refractive index, stress,

resistivity and hardness decrease as the nitrogen concentration increases above $\sim 2\%$, $N/C \sim 0.02$. Additionally, the nitrogen content of the film has been found to be proportional to the nitrogen concentration in the feedstock gas mixture, and that NH_3 is more efficient than N_2 at introducing nitrogen in the deposit; although this is accompanied by the formation of –H bonds. Furthermore, some work has been reported using CN-containing precursors such as methylamine; this has resulted in somewhat higher C/N ratios but no significant improvement in the structure of the deposit [88].

There are also a number of reports concerning the use of somewhat more unconventional PECVD systems. One paper by Wu et al. demonstrated results which are exceptions to the situation described above [89,90]. In this work, a $0.5\text{ }\mu\text{m}$ Si_3N_4 layer was first grown on a silicon wafer in a cylindrical PECVD system with an external tubular electrode. Following this, a 10:1 mixture of N_2 and C_2H_4 was used at 4.5 torr to grow the CN layer at 450°C in a 900 W plasma (200 kHz). This deposit was then annealed at 800°C for 2 h. XPS analysis showed that the nitrogen content in the deposit could be varied from $N/C=0.14$ to 1.16 by changing the nitrogen partial pressure in the gas mixture. This increased ability to incorporate nitrogen may be related to the higher-density plasma obtainable in such inductively coupled plasma systems. XRD measurements seemed to indicate that the CN film had a different preferential orientation on {111} and {100} silicon substrates, although very few diffraction peaks were observed. Deposition and high-temperature annealing of films grown on high-chromium steel substrates showed 13 diffraction peaks which the authors associated with mixed phases of α - and β - C_3N_4 . However, there was little discussion of the possibility of the coincidence of these peaks with the large number of peaks that are normally observed with such steels. The films obtained were tested in terms of their thermal and chemical stability; they were found to be resistant to attack by either HF or $HF+HNO_3$, and thermogravimetric–differential thermal analysis (TG–DTA) studies showed them to be stable up to 1200°C . The film hardness was measured as being in the range 30–50 GPa.

Another high-pressure process has been described involving a thermal plasma [91]. An argon plasma, 14 kW at 4 MHz, was ignited at 1.5 torr, then nitrogen was added and the pressure increased to ~ 830 torr. This thermal plasma heats the substrate to temperatures in excess of 600°C . Carbon was introduced by feeding fine graphite powder into the gas flow. If the feed was too high graphite inclusions were found in the deposit; however, if it was too small, no deposit was formed because of chemical etching by the nitrogen radicals. Although a high nitrogen content was obtained, with a composition of $C_3N_{4.28}O_{1.06}H_{3.09}$, the FTIR spectra showed the presence of N–H, $C\equiv N$ and $C=N$, and

all of the films were amorphous, decomposing through the emission of C_2N_2 above $700^\circ C$.

RF helicon plasma sources have also been used in carbon nitride studies [92]. This type of source operates at pressures approximately two orders of magnitude lower than conventional RF systems, and generates a much denser plasma with a substantially higher concentration of atomic nitrogen. Normally the 1×10^{-3} torr operation of this source means that substrate biasing can be quite efficient; however, the insulating nature of the CN film reduces the biasing effect. As in the ECR case, the nitrogen passes through the helicon plasma and the excited radicals and atoms are mixed with methane near the substrate. The deposits were found to have characteristics typical of those obtained with PECVD: they were amorphous, XPS showed multiple carbon and nitrogen peaks, only the Raman peaks of graphite were found, changes in the bias from 0 to 30 V reduced the nitrogen content by $\sim 2\%$, and the N/C ratios were 0.14–0.22 for substrate temperatures of 70 and $250^\circ C$, respectively.

2.5. Reactive sputtering

Reactive sputtering has been found to be able fabricate CN films with some improved properties, Tong et al. showed that such films could have extremely smooth surfaces [93] and Yeh et al. reported an important reduction in the friction coefficient compared with a-C:H films [94]. However, nearly all films grown at room temperature are amorphous mixtures of carbon and carbon nitride phases.

2.5.1. DC sputtering

Reactive DC sputtering has normally been carried out in pure nitrogen or nitrogen–argon mixtures in the mtorr pressure range, although some work has been reported at 8 torr using a nitrogen–helium mixture. In this last study, it was found that the addition of 1.5% of hydrogen drastically reduced the deposition rate, demonstrating the importance of hydrogen to the chemical sputtering phenomena [95]. A similar situation has been found with argon–ammonia mixtures, in that both the deposition rate and the nitrogen content were lower than with nitrogen gas mixtures under equivalent experimental conditions [96]. The higher-pressure work in N_2/He resulted in a deposit with an open filamentary structure, $7.5 \mu m$ long \times $0.5 \mu m$ diameter [95]. Analysis by XPS and FTIR showed that this material had only $\sim 10\%$ sp^3C , and it was concluded that it was probably a mixture of amorphous carbon and paracyanogen, N/C=1 to 0.7.

Independent of the gas mixture used, the general trends of the nitrogen content with the experimental conditions are all very similar [96–99]. The N/C ratio and the deposition rate are inversely proportional to the

substrate temperature, with little or deposit above $600^\circ C$. This observation supports the contention that the chemical sputtering process is thermally activated. The N/C ratio increases as the nitrogen concentration in the gas increases, but does not vary greatly with the gas pressure in pure nitrogen. A number of studies have produced films containing small diamond crystallites at substrate temperatures below $200^\circ C$, and a fullerene-like structure with nanometre-sized areas composed of curved and crosslinked graphite planes at higher temperatures [100]. As with other deposition techniques, the FTIR spectra show that the number of $C\equiv N$ bonds increased as the nitrogen content increased. However, the work by Wan and Egerton [112] indicated that although this was generally true, the relative sp^2 fraction decreased with the substrate temperature. Additionally, the decrease in this fraction, as a function of anneal temperature, was greatest for the material with high nitrogen content. Tentatively, it might be supposed that this decrease corresponds to an increase in the sp^3 fraction but, as mentioned by the authors, additional analysis such as by electron energy-loss spectroscopy (EELS) would be required to establish the exact bonding configuration of the carbon and nitrogen in their films.

A number of other DC sputtering arrangements have been attempted, including single and double unbalanced magnetron, and sputtering by ion extraction from helicon sources. With the unbalanced cathode work, the film characteristics and their dependence on the experimental conditions were very similar to the case of conventional DC sputtering mentioned above [101–103]. It should be mentioned that quite a lot of the unbalanced studies have used pulsed DC biasing and, unlike straightforward DC biasing, this method does effectively promote ion bombardment of the deposit. However, this has not led to significant progress towards producing crystalline high-density carbon nitride.

A novel scheme has been described that uses two facing, unbalanced graphite targets with reversed magnetic fields, with the substrate mounted perpendicular to the targets and to one side [104]. In this way the ions, from the Ar/N_2 plasma, are confined by the magnetic field and do not strike the film directly. Even so, the film properties were not remarkably different to the normal case outlined above. FTIR measurements of the films showed that the various CN bonds increased with the nitrogen content up to 20% and were constant thereafter. This was understood as showing that, using this method, only a maximum of 20% of nitrogen could be included chemically in the film. High-temperature annealing studies seemed to show that the CN triple bond is less stable than the double bond. In later work the authors described that a combination of AES, XPS and Raman spectroscopy confirmed that the increasing nitrogen content of the film promotes the formation of $C-C sp^3$ bonding rather than $N-C sp^3$. However,

because of the atypical nature of the carbon p orbital, the C=N sp² state is, in fact, more stable than the C–C sp³ phase [105].

The helicon studies have resulted in deposits with considerably higher N/C ratios of ~0.95. The procedure consisted of establishing the resonant high-density RF plasma and then using between –50 and –300 V to extract ions to sputter a cylindrical graphite target, the separately biased substrate being placed at some distance downstream [106,107]. In the first study, the power required to create the resonant condition was found to depend on the nitrogen concentration in the argon, and the target current (proportional to the physical sputtering rate) decreased with increasing nitrogen concentration. However, the deposition rate and the N/C ratio increased with increasing nitrogen gas proportion, again demonstrating the importance of chemical sputtering and the relative arrival rate to the substrate of carbon and nitrogen species. Similarly, the maximum N/C value dropped from 0.9 to 0.5 as the substrate bias increased from –100 to –300 V. XPS and Vickers indentation measurements showed that the amounts of sp² and sp³ carbon, and the film hardness, all increase at the same relative rate with increasing nitrogen concentration. Other work using a helicon source has also demonstrated the strong dependence of the N/C ratio on the relative arrival rate of the carbon and nitrogen species at the substrate [107]. Similarly, studies have shown that the plasma mainly contains N₂⁺, N⁺, CN⁺, (CN)₂⁺ and C⁺ ions, and that the CN species are created on the graphite target and then sputtered off [108,109]. The relative proportions of these species is mainly determined by the gas pressure and the plasma power; high pressures favour the formation of CN groups whilst at low pressure there are more C_x species [117].

This experimental arrangement is of particular interest since physical and chemical sputtering are involved in both the emission of the carbon species from the target and in the deposition process. Primarily, it can be concluded that chemical sputtering is controlled mainly by the impingement rate of ions and not neutral species.

2.5.2. RF sputtering

RF sputtering of a graphite target has normally been carried out in pure N₂ or N₂+Ar atmospheres; NH₃ gas mixtures have been avoided because of the danger of formation of hydrogen cyanide. In terms of the experimental parameter space, studies have been performed by using substrate temperatures from ambient to ~630°C, plasma powers from 30 to 1000 W, gas pressures from 5 to 500 mtorr and with grounded, DC-biased and pulse DC-biased substrates [108–110]. The great majority of the deposits have been found to be amorphous, with little or no deposit formation at substrate temperatures greater than 700°C. However,

often only X-ray diffraction has been used to check for crystallinity and, as exemplified by the work of Yu et al. [111], this is not necessarily conclusive. In this last study XRD analysis showed only diffraction peaks related to the silicon substrate, whilst electron diffraction demonstrated the existence of small crystalline inclusions of carbon nitride in the deposit. The crystals were only found on silicon {100} substrates, and high substrate temperatures promoted crystallisation. The diffraction patterns of these crystals were found to agree quite well with the β-C₃N₄ structure; some of the *d*-spacings could not be identified and the relative intensities of those that did were not in complete agreement with the theoretical values. The overall N/C ratio of the deposit was quite low at 0.5. The question arises, would crystals have been found in the films made by other groups if they had performed electron diffraction analysis?

In general, all groups have found that, again as observed with other deposition methods, the deposition rate decreases with both increasing nitrogen content and increasing substrate temperature [99,112]. The nitrogen content has little dependence on the gas pressure used and the maximum N/C ratios reported are from 0.4 to 1.33 [113,114]. However, almost identical works by various authors have sometimes resulted in very different N/C values; some of these differences might be explainable by the use of different analysis techniques [115–117].

All of the studies have given deposits whose Raman and FTIR spectra show the existence of C≡N, the D and G peaks from graphite, and N–H and/or C–H. The hydrogen, although not included in the process gases, is thought to come from water vapour absorbed on the walls of the reaction chamber [109]. Almost invariably the deposits are unstable to annealing at temperatures above 700°C, degrading through the emission of nitrogen, CN and (CN)₂ [116]. The inclusion of argon in the sputtering gas normally leads to lower levels of nitrogen incorporation in the deposit, probably because of increased bombardment of the deposit by high-energy argon atoms that have rebounded from the target [110].

Studies with an unbalanced magnetron system have found that the nitrogen content was controlled, in part, by the energy flux density incident on the growing film [109]. Exponential relationships between the N/C ratio and the energy flux density were observed, and in a linear–log plot this relationship was seen as three parallel lines. The authors did not fully explain this result except in terms of the possible interaction of absorbed water vapour on the film, with this somehow aiding the incorporation of nitrogen. However, a plausible explanation can be made concerning the role of electron bombardment. Different degrees of electron bombardment are to be expected for the experimental conditions corresponding to the three relationships and, in other studies, intense electron bombardment has been seen to

affect the N/C ratio [38]. However, this result does demonstrate that the properties of CN films have a complicated dependence on the plasma properties; the ion and electron fluxes and energies depend on a variety of factors such as plasma power, relative size of the electrodes, the magnetic field, the system geometry, gas pressure and gas composition.

Two groups have reported the use of RF plasma jet systems employing either a graphite nozzle or a hollow cathode in the 0.1 to 0.5 torr pressure range [118,119]. Carbon emission from the source relies mainly on chemical sputtering of the graphite although, in the hollow cathode case, ~1% of methane was added to the nitrogen flow. Optical emission studies showed that there was a very high concentration of CN radicals and atomic nitrogen in the plasma plume, and that the addition of the methane enhanced the CN production. The jet process used RF powers of less than 100 W and the hollow cathode of 300–500 W, with this resulting in quite low temperatures in the first case and substrate temperatures from 300 to 500°C for the second. Analysis of the films made by either method, using FTIR, Raman and XPS, showed a large concentrations of bonded nitrogen but that the low substrate temperatures resulted in a significant NH and CH content. The plasma jet samples were amorphous and had a composition of 17% N, 71% C and 12% Si, giving N/C=0.24. However, small crystallites embedded in an amorphous matrix were seen in the hollow cathode samples, with electron diffraction ring and dot patterns corresponding to *d*-spacings similar to that of β -C₃N₄. Composition analysis by means of energy-dispersive X-ray (EDX) analysis and secondary-ion mass spectrometry (SIMS) on optimised films gave N/C ratios of between 1 to 1.3, but because silicon substrates were used it was not established if this element was incorporated in the film.

2.5.3. Ion-beam sputtering

Two versions of ion-beam sputtering have been used to study CN films. The first involves the use of dual ion beams where one, usually of argon, in the keV range sputters carbon from a graphite target, and a second, lower-energy beam of nitrogen ions is directly incident on the substrate to nitride the film during growth. The other version used only one ion beam of high-energy nitrogen. Here the substrate is positioned so that the edge of the beam nitrifies the film while the main part of the beam sputters the target. This process is similar to that of electron-beam evaporation of carbon with ion nitriding; however, the ion-beam systems usually provide higher-energy carbon atoms and larger proportions of carbon clusters in the emitted flux [112].

Dual-beam ion sputtering has demonstrated some significant results. If only nitrogen is present then chemical sputtering predominates with the emission of CN, whilst with argon physical sputtering becomes important

with increased emission of carbon [28]. Experiments using a focused secondary nitrogen beam and a broad distribution of the arriving carbon atoms have shown that there is critical relative arrival rate for the nitrogen ions and carbon atoms [28]. At arrival rates above the critical value, no deposit was formed because chemical etching was faster than film formation. The chemical sputtering rate was seen to be ~0.5 carbon atoms per incident N₂⁺ ion, and at high energy levels nitrogen loss was accelerated by N₂ formation within the subsurface of the deposit. Chemical sputtering was also enhanced by the presence of water vapour, since this permits the formation of volatile HCN. It should be noted that the critical arrival ratio also depends on a variety of other experimental factors: substrate temperature, ion energy and probably substrate type. For values below the critical level, a variation of the ion/atom arrival rate from 0.3 to 1.0 proportionally changed the nitrogen content by approximately 50%. In general, it has been found that the N/C ratio also increased with decreasing substrate temperature or energy of the nitriding ion beam [120]. The maximum N/C values are normally from 0.35 to 0.40, but a value as high as 0.60 has been reported for experiments under almost identical conditions as for those of the typical range [121]. In this untypical study, the deposit was an amorphous CN compound with an oriented crystalline phase whose electron diffraction pattern agreed reasonably well with that of β -C₃N₄. Furthermore, X-ray reflectometry indicated that the film density was very similar to that predicted for the beta phase. Unfortunately, insufficient details were provided to explain how this unusual result was obtained. Indications of a crystalline phase were also reported by Fernandez et al. [122]. Here, four faint diffraction rings at 3.55, 2.50, 2.05 and 1.61 Å were observed which the authors claim are in good agreement with β -C₃N₄; however, no such correlation can be seen with the values shown in Table 1 below. Furthermore, it was reported that the crystallinity was improved by applying a –150 V substrate bias.

The single ion-beam work resulted in nitrogen concentrations of ~10%, N/C~0.11, with and without substrate bombardment and little evidence of any advantage of this an arrangement [123]. Furthermore, the films, in common with most of the dual-beam work, had FTIR and Raman spectra that were mainly composed of the peak of C≡N, together with broad bands due to the D and G features of graphite. Analysis by XPS showed the existence of the normally observed multi-phase carbon and nitrogen peaks.

3. Characterisation of carbon nitride

Many problems have been encountered in the precise characterisation of carbon nitride films and deposits. In this section we discuss some of the techniques used in

Table 1

Reported theoretical d-spacing values, in Å, for β -C₃N₄

<i>hkl</i>	Ref. [12]	Ref. [17]	Ref. [54]	Ref. [58]	Ref. [71]	Ref. [80]	Ref. [89]	Ref. [90]	Ref. [121]
410		0.027							
212	1.046								
330		0.948			1.071				
411	1.100		1.08		1.089		1.09		1.089
500					1.106				1.113
202					1.125				
321	1.142		1.12		1.133				1.133
112					1.141				
002	1.200		1.23		1.229				1.230
320	1.240				1.277		1.28	1.277	1.277
311				1.294	1.304				1.308
221			1.33	1.331	1.345			1.345	1.345
400					1.391				
301	1.403		1.47	1.464	1.481		1.48		1.481
310		1.051	1.52	1.537	1.543				1.544
211			1.59	1.578		1.590		1.598	1.589
220		1.094		1.600					
201				1.814	1.831	1.831			
300		1.263	1.83	1.847	1.855	1.855	1.86		1.856
111			1.95	1.920	1.953	1.953		1.953	1.953
210	2.140	1.432	2.08	2.095	2.103	2.103	2.10		2.104
101	2.210		2.25	2.202	2.259	2.259	2.26	2.259	2.250
200	2.829	1.895	2.75	2.771	2.783	2.783		2.783	2.784
110		2.188	3.17	3.200	3.213	3.213	3.21	3.213	3.215
100		3.798	5.50	5.543	5.565	5.565			5.568

the characterisation of CN films. Several of the deficiencies in the analysis techniques, and in the interpretation of the results, are highlighted in order to increase awareness of the common pitfalls found in the literature. Emphasis is placed on references to substances which contain carbon and nitrogen in an effort to help researchers in the field to use information gathered before the appearance of the Liu and Cohen paper.

3.1. FTIR

This technique has been used extensively to study carbon nitride but there is considerable discussion concerning the analysis of the spectra. Absorption bands in the infrared can give a great deal of qualitative information; however, attempts to make a quantitative analysis of the abundance of different groups are likely to fail as these require a knowledge of the relative positions of the different groups in the atomic network, which is at present not available. It is not perfunctory to remember that the position, shape and intensity of the bands associated with practically any molecular group thus far found in CN or CN:H material, are dependent on the position of other groups. The CH₃ stretching vibrations, for example, which have been used in a-C:H to estimate the percentages of sp³, sp² and sp¹ bonds, are not of much use because their position red-shifts and the intensities decrease when there is bonding to nitrogen [124,125]. Additionally, the bands are also obscured by strong overlapping hydrogen-bonding bands. Since

nitrogen in imines and pyridine-like rings has an unshared electron pair, this may form medium to strong hydrogen bonds with hydrogen atoms that are incorporated during or after deposition [126,127]. It is virtually impossible to distinguish O—H···N from N—H···O or even from O—H···O bonds when two or more of them are present [126]. So if a careful comparison between the composition and the FTIR spectra cannot be performed, no definite assignments should be made concerning the hydrogen-bonding bands. However, ignoring the presence of hydrogen bonding can lead to mistakes, such as in assigning the vibrations in the 3300 cm⁻¹ region to acetylenic groups [128] when there is no band in the 2100–2240 cm⁻¹ region to back such an assumption. Hydrogen bonding is commonly seen in porous materials and it is probably a good indicator of the softness of a film. Even when hydrogen is not incorporated deliberately in the samples, it can be present even after compression at 24 GPa [129]. Hydrogen bonding may also be responsible for the typically strong bands centred at ~3300 and 1640 cm⁻¹ [130], being the stretching and bending modes of associated N—H bonds; it should be remembered that one of the main consequences of hydrogen bonding is an increase in the absorption intensity [126].

The incorrect use of group frequencies tables can be misleading when trying to establish the sp² content, such as assigning the C=N stretching mode to what is, in fact, the bending mode of aliphatic CH₂ or CH₃ groups

[131]. The C=N frequency is reduced on conjugation but is seldom found below 1500 cm^{-1} in the IR and is relatively weak [132], unless coupled with another vibration. Furthermore, when the bond is part of a heterocycle, the vibration is difficult — if not impossible — to distinguish from the C=C vibrations [124].

At high nitrogen contents a peak at $\sim 2200\text{ cm}^{-1}$ is often seen and is accepted to be related to C≡N, but even here the situation is not simple. All of the following components have absorption bands in this region: $-\text{N}=\text{C}=\text{N}-$, $-\text{C}=\text{N}=\text{N}-$, $>\text{C}=\text{C}=\text{N}-$, $\text{C}-\text{N}^+\equiv\text{C}-$, $>\text{C}-\text{C}\equiv\text{N}$ and $>\text{N}-\text{C}\equiv\text{N}$. It should be noted that, except for the nitriles, all these groups are linear, rigid and continuous (i.e., non-terminal), and therefore impose conditions on the structure of the material which may preclude the formation of high-density C_3N_4 materials. A way to differentiate between the components is to anneal the films and look at the changes in the feature; carbodiimides and isonitriles tend to convert to nitriles or imines at relatively low temperatures (ca. 300°C) [133,134] and the lower portion of the band (below 2190 cm^{-1}) should diminish in intensity, narrowing the band.

Most authors have assumed, or even claimed, that the number of sp bonds is low on the basis of infrared spectra alone. This is a rather bold assumption, especially for films with high nitrogen content, since the absorption intensity of carbonitriles is highly dependent on their chemical environment, a fact often ignored in the CN literature. Caution should be exercised when dismissing the presence of sp-bonded nitrogen in CN materials on the grounds of a weak or non-existent vibration at 2200 cm^{-1} . For example, benzonitrile amines have very intense absorption bands, cyanopyrimidines have weak peaks and, in 2,3-cyanopyrimidine, the band is not detectable. As a rule of thumb, nitriles linked to nitrogen heterocycles have weaker absorption coefficients than those linked to unsaturated chains. Similarly, the substituents in the rings have an important effect: electron-donating groups (such as amines) increase the absorption intensity and electron-withdrawing groups (such as carbonitriles themselves) tend to decrease it [135,136]. Therefore, in samples with a high nitrogen content where a larger variety of heteroaromatic rings can exist, considering that the number of sp¹-bonded atoms is low on the basis of infrared spectral data alone is not recommended. A similar assumption is often performed with other analysis techniques, in that possible contributions of sp¹-bonded atoms in the XPS, EELS or ultraviolet photoemission spectroscopy (UPS) spectra are frequently ignored. It should be noted that sp¹ bonds contribute two π electrons so that, even for a reduced number of triple bonds, their contribution to bands or peaks should be taken into consideration.

Various broad absorption bands are found in the range $1250\text{--}1600\text{ cm}^{-1}$. Those at ~ 1570 and 1370 cm^{-1} are normally considered to be related to the

G and D peaks seen in Raman, where the incorporation of nitrogen in the carbon matrix makes the bands IR-active [137]. However, a number of articles have shown that the size and position of the D and G infrared and Raman peaks can vary in different ways with the experimental conditions [138,139]. However, more work is required in this aspect before useful information can be obtained. Different CN and CC single- and double-bond absorption bands are also found in this region. Furthermore, bands due to the different C_3N_4 structures are predicted in this range [140]. Consequently, the interpretation and association of the IR spectra is not straightforward. If crystalline C_3N_4 has the same symmetry as crystalline Si_3N_4 , then the material is expected to have both infrared- and Raman-active modes. Therefore, if Raman modes in carbon nitride are observed at wavenumbers that scale by a constant factor with those of silicon nitride, then similarly the infrared modes should scale by a matching factor. Unfortunately, the reports that give good Raman data rarely mention infrared results.

The exact position of the IR peaks also depends on the residual stress, and since it is expected that high-density forms of carbon nitride should contain considerable stress, analogous to the cases of diamond-like carbon and cubic boron nitride, such stress-related effects further complicate the precise analysis by FTIR. However, it should be noted that carbonitriles, as terminating structures, do not suffer stress-related shifts; thus if the vibrations are found below 2100 cm^{-1} , these are probably due to either a cyano ion or a different group. This is especially true when analysing the spectra of films deposited on alkali halides, since KCN and NaCN have rather strong absorption coefficients.

3.2. Thermogravimetry

Thermogravimetric studies and temperature-dependent mass spectrometry have hinted that in many cases there is an important transformation, just above 600°C and below 800°C , that is characterised by a large loss of cyano radicals, hydrogen cyanide (in the case of hydrogenated material), molecular nitrogen and cyanogen [141,142]. Curiously, a very similar effect takes place in carbon carbodiimides with the C_3N_4 stoichiometry [143], which suggests that similar structures might be present in both materials. According to Riedel et al., the decomposition involves cyanamides (i.e., nitrogen carbonitriles $\text{N}-\text{C}\equiv\text{N}$) generated from isonitriles and carbodiimides at lower temperatures. If this reaction is in some way reversible, it is not far-fetched to consider that these very same species may contribute strongly to the incorporation of nitrogen into carbon nitride films.

3.3. Raman

There are very few reports of Raman spectroscopy which show anything other than the D and G peaks, or

the photoluminescence of amorphous carbon. However, vibrational spectroscopies offer the opportunity to test whether a crystalline material has the predicted structure of the modelled carbon nitrides. By using symmetry arguments it is possible to calculate the number of modes that should be observed, check if they have a centre of symmetry or not, and then deduce whether these modes will be Raman and/or infrared-active. The position of the vibration bands obviously depends on the force constants involved; however, given a spectrum with several peaks, it should be possible to use simulation of the data and obtain these constants, especially if data are available from both the infrared and Raman modes. Unfortunately, few results from studies using both methods of analysis of the vibrational properties have appeared [144].

3.4. XPS

A similar situation exists with X-ray photoelectron spectroscopy and, although the circumstances are improving, there is still not a completely accepted identification scheme for all of the carbon and nitrogen peaks observed [145–147]. Both the XPS nitrogen and carbon peaks are normally simulated by the sum of various individual peaks related to different atomic bonding configurations. In the case of the N 1s peak, most researchers use three components near 398.5, 400.5 and 402.6 eV. However, the authors of Ref. [145] claim that a fourth peak at ~ 399.4 eV considerably improves the simulated fit and interpretation of the data. Many groups have based the analysis of films on the assignment of N 1s peaks above 400 eV to nitrogen atoms bonded to sp^2 -hybridised carbon and those below 399 eV to sp^3 carbon. However, a recent and convincingly presented paper on the XPS analysis of ion-beam deposited CN_x films arrived at the following conclusions: the 400 eV peak is related to nitrogen bonded to three carbon atoms, where these have tetrahedral coordination, and the 398 eV peak is associated with nitrogen bonded to two carbon atoms [148]. The authors dismiss the effect of nitriles on the basis that the absorption at 2200 cm^{-1} is weak; however, the chemical environment that shifts the C 1s centre line towards higher energies in substituted benzenes [149] also diminishes the intensity of the carbonitrile vibration [125]. Hence, without any other evidence, such as Raman spectra where the intensity of the nitrile vibration does not vary as much [150], it is unwise to predict a low nitrile content when the IR spectra show only a small band.

The XPS data have been simulated by assuming fixed configurations; e.g., a nitrogen atom linked to two carbon atoms for low binding energy and a nitrogen linked to three atoms for higher binding energy [148], or $N-Csp^3$ for low binding energy and $N-Csp^2$ for high binding energy [145], without considering the chemical environment and inductive effects [151].

Although this is an approach that simplifies the analysis, it should be compared with experimental results and with previous data existing in the literature. Unfortunately, it is not possible to assume that nitrogen or carbon atoms are in fixed environments; that is, not all of the trigonal nitrogens are bonded to three sp^3 -bonded atoms, such as in hexamethyltetramine, nor are all of the digonal atoms bonded to two sp^2 carbons, such as in pyridine. On the one hand, there is the nitrogen configuration of pyrrole, which is trigonal but is linked to two sp^2 -bonded carbons, and then there is also the nitrogen in monoconjugated imines, where it is linked to an sp^2 carbon and an sp^3 carbon [132]. Moreover, theoretical calculations by Weich et al. [152] show that the nitrogen atoms are in mixed environments, especially for high-nitrogen-content materials.

We therefore propose a different approach that is not fixed to any given structure, which may account for the double peaks frequently observed in a-CN for the N 1s feature. It is generally accepted that the greater the charge transfer from an atom, the higher the binding energy it will show in an XPS experiment. Additionally, it is safe to assume that nitrogen will predominantly form only three covalent bonds, leaving one lone pair not participating in any sigma bonding (although quaternary nitrogen compounds are well known, there is no evidence of their presence in CN films). So we suggest that an important part of the charge transfer will be through the 'donation' of the lone-pair electrons, and the larger the electron-withdrawing power of the group attached to the nitrogen, the larger the binding energy. This idea is supported by the values found for pyrrole and polyaniline, both trigonally bonded nitrogen compounds which tend to donate their electrons to the adjacent aromatic ring — in the first case, forming part of the aromatic sextet and, in the second case, increasing the electron density of the ring. Both structures are seen to have relatively high binding energies: 401 and 399.9 eV, respectively [153]. On the other end, we can consider pyridine and n-butylamine: one with a digonal nitrogen atom linked to two carbons in an aromatic ring, the other with a trigonal atom linked to three sp^3 -bonded (saturated) carbons, where these have relatively low binding energies (399.0 and 398.1 eV) [153]. These configurations, although structurally different, are similar in that in neither is the electron pair able to become delocalised.

Some authors have considered that a low binding energy in the N 1s band is an indication of a linkage between nitrogen and sp^3 -bonded (i.e., saturated) carbon atoms, although this might be caused by more digonal nitrogen in aliphatic chains or aromatic rings. Hence the N 1s band will have several contributions from different structures: those that allow partial or total delocalisation of the electron lone pair will be on the high-energy side, those which allow little or no delocalisation will have bands on the low-energy side.

Furthermore, since in most cases the hardness of the deposit diminishes in a drastic fashion with the incorporation of nitrogen, it may be assumed that the concurrent increase on the N 1s signal at low energies is related to digonal nitrogen in six heteroaromatic rings. Somewhere in the middle of the energy range the nitrile nitrogen atom should contribute with a band around 399.4 eV, although its exact position is probably dependent on what is attached to it. As already discussed, caution should be exercised when dismissing the presence of sp-bonded nitrogen in CN materials on the grounds of a weak or non-existent vibration at 2200 cm^{-1} . So, especially in samples with a high nitrogen content, where a larger variety of heteroaromatic rings might exist, a fit of the N 1s band without considering the nitrile bond should be viewed with suspicion.

The interpretation of the C 1s XPS peak is even more controversial. The effect of the inclusion of nitrogen causes an asymmetric broadening of this peak towards higher energies. This has been simulated by using three Gaussian components at 284.6 eV (pure carbon), 285.9 eV ($\text{sp}^2\text{C}-\text{N}$) and 287.0 eV ($\text{sp}^3\text{C}-\text{N}$). Unfortunately, this scheme is not supported by information from the Beamson and Briggs polymer database and data on several carbon compounds with different hybridisations [149]. Furthermore, this database indicates that the position of the C 1s peak depends critically on the local environment of the carbon atom in an unpredictable manner. Nevertheless, it has been reported that there is a linear relationship between the FTIR absorption at $\sim 2200\text{ cm}^{-1}$ ($\text{C}\equiv\text{N}$) and the 286.3 eV XPS peak, providing a strong indication of its identity [31]. However, this assignment is somewhat different to that found in the paper mentioned above [147]. These authors postulated the following relationships: at low nitrogen concentrations, the peaks near 284.7 eV with sp^3C in a carbon matrix and, at higher nitrogen contents, with sp^2C bonded to either carbon or nitrogen; the 285.6 eV peak to sp^3C with one nitrogen neighbour; the 286.8 eV peak to sp^3C bonded to two nitrogen neighbours. Furthermore, they proposed that the sp^3C signal in the $\beta\text{-C}_3\text{N}_4$ structure should be at 288 eV, although this peak was not observed in their films. Obviously care is required when comparing the XPS analysis of carbon nitride films performed by using the different peak assignments because a good fit is not necessarily a consequence of a correct choice of parameters (i.e., peak position, width and number of peaks) [154], and few statistical tests have been used on the fitting exercises.

There is one advantage of XPS over IR: for XPS the intensity of the line is not environment-dependent, whereas for the IR bands, as discussed above, the frequencies and intensities are dependent on the chemical environment.

Curiously, in spite of the large number of XPS studies on CN films published to date, none has studied the shake-up region, which in polymers yields valuable

information about the existence of delocalised π electrons. The effects are stronger in the C 1s region but they can also be observed in the N 1s region, as studies on heterocycles [155] and polymers such as poly(4-vinylpyridine) have demonstrated [156]. Such studies would give information about the rings present and also about the substituents.

Many of the problems related to the XPS work have arisen because the uncertainty in the absolute position of the peaks depends on the correct calibration of the instrument and because of the difficulties associated with using non-conducting standards and samples. Furthermore, the existence of a contaminated or unrepresentative surface layer can sensitively affect the shape of the XPS peaks; since this layer normally contains oxygen and adventitious carbon, it is the carbon peak that is most affected. Additionally, it is now clear that if ion-beam cleaning of the sample is used, this causes chemical sputtering which can strongly reduce the measured nitrogen content, as well as affecting the shape of the XPS peaks [146,147]. This effect can lead to much lower N/C ratios and erroneous elucidation of the initial bonding configurations. Baker and Hammer [146] have outlined a procedure by which the surface layer can be removed whilst retaining the integrity of the sample. It should be remembered that this phenomenon can be expected to occur in all elemental analysis techniques that use surface cleaning by ion bombardment. Additionally, with Auger analysis, any surface contamination can lead to incorrect N/C ratios because of the difference in the kinetic energy, and hence escape depths, of the C and N KLL Auger electrons [146]. Even when interpreted correctly, the spectroscopic techniques discussed above provide information regarding only the local or short-to-medium range bonding characteristics of the films, which can otherwise be amorphous. This is similar to the characterisation of hydrogenated diamond-like carbon or tetrahedral carbon, in that the spectroscopic techniques do not provide evidence of the existence of a crystalline structure.

3.5. Diffraction techniques

X-ray diffraction is often used to characterise the crystalline nature of the deposit but, because of the low atomic mass of both carbon and nitrogen, at least $1\text{ }\mu\text{m}$ of deposit is required to produce a clear spectrum. Additionally, as pointed out by Yu et al. [111], diffraction peaks have been observed for amorphous carbon or silicon thin films on $\{100\}$ silicon substrates which coincide with those expected from the (200) reflection of $\beta\text{-C}_3\text{N}_4$. In fact, they are thought to be due to the normally forbidden (200) reflection from silicon with this becoming feasible because of the surface stress generated by the coating. Electron diffraction is also used extensively to study the crystallinity of the deposits but sample preparation by ion milling can be expected

to cause chemical sputtering with all the associated problems. Similarly, the samples are often unstable under high-energy irradiation. Whether this lack of stability can be taken as an indication of the absence of a high-density phase is, at present, not known.

Table 1 lists a selection of the reported theoretical d -spacing values, in Å, for β - C_3N_4 . Obviously some of the data are based on different values of the lattice parameters, but even so there are a considerable number of inconsistencies. As such, a judicious choice of lattice parameter and group of reflections can be of great assistance in providing proof of the existence of crystals of the 'good' material in any particular study.

4. Discussion

There are four main issues concerning the successful synthesis of high-modulus C_3N_4 materials: (1) chemical sputtering; (2) achieving the right stoichiometry with low levels of impurities such as silicon, oxygen or hydrogen; (3) establishing the correct bonding coordination sp^3 for carbon atoms and trigonal sp^2 bonding for nitrogen atoms; and (4) the ability to produce an adequate amount of crystalline material with grains sufficiently large to allow definitive tribological testing.

Chemical sputtering is difficult to distinguish from chemically enhanced sputtering or from plain chemical erosion. In true chemical sputtering, the process gas reacts with the target to yield a compound that is easily volatilised from the target owing to its low boiling or melting point. In the enhanced case the reaction yields a product which is more easily removable by physical sputtering [157]. For the last case, the reaction takes place through a reaction between atoms in the deposit and reactive gas species from the plasma, without these becoming part of the target at any time. Since both the desorption of products and the chemical reactions are thermally activated, only with careful controlled measurements is it possible to elucidate which — if any — is the dominant mechanism. There are many studies on hydrogen chemical sputtering of carbon, but very few on the interaction between nitrogen and carbon.

The different pieces of experimental evidence show that the so-called chemical sputtering is a complicated process. At low pressures, nitrogen- and carbon-ion bombardment at energies greater than ~ 15 eV and ~ 50 eV, respectively, cause erosion of deposited CN. Furthermore, such nitrogen-ion bombardment also selectively removes nitrogen from the deposit; at present, it is not clear if carbon causes a similar effect. At low nitrogen concentration, this removal occurs through the formation of CN or C_2N_2 groups; at higher concentrations, the formation of molecular nitrogen within the film also becomes important. The presence of hydrogen is known to increase the erosion rate strongly and probably the nitrogen extraction. The two process

rates — erosion and selective nitrogen removal — also increase with increasing substrate temperature, as expected for a chemical process. From the work on diamond, glassy carbon and amorphous carbon it would appear that the extraction rate depends on the nature of the deposit. Additionally, some of the work at pressures greater than 1 torr has also reported the existence of chemical sputtering. Obviously, at such pressures, the energy of the species causing the etching is less than the 10–15 eV threshold found for low-pressure work. In this case, it has been proposed that the erosion is caused by nitrogen, or hydrogen–nitrogen, radicals and that here the process is essentially chemical erosion and not sputtering. What are the relative rates of this chemical process compared with the chemical sputtering is not known and, similarly, it is not clear at what pressure or experimental conditions the erosion process changes from one to the other. Recently, work has been published modelling the deposition and erosion processes [158], but it is clear that more and systematic research is required into the details of the various chemical sputtering processes.

Overall, it is apparent that chemical sputtering does not aid the preferential growth of C_3N_4 by removing weakly bonded carbon or CN groups, as is the situation for diamond and polymer-like deposition [130,159].

Even when a deposit is obtained containing high concentrations of nitrogen there are considerable problems in clearly establishing what is the local bonding configuration. As we have mentioned, XPS data are controversial since there are still problems as to the number of bands used to fit the spectra and their assignment to particular bonding structures. On the other hand, EELS data do show the presence of π electron states but these exist in linear and trigonally bonded carbon and nitrogen atoms, so the fine structure needs to be analysed with great care to establish to which structure the electron losses correspond. The main structural technique of nuclear magnetic resonance spectroscopy (NMR), used in organic chemistry, has not been widely employed in CN films. Very few studies have been reported, although the group at Northwestern University, Illinois, USA have reported the presence of structures related to five- and six-membered heteroaromatic rings [160]. In studies of amorphous materials, IR and Raman spectroscopy have provided information on the sp and sp^2 bonding, but not the sp^3 bonding.

Another concern is related with medium-range ordering of the atomic network. The term 'graphitisation' or 'graphitised' has been used incorrectly far too often. The term graphitisation is related to the existence of coherence between graphene planes, that is, ordering along the c -axis of graphite [161], and not to the formation of structures which are rich in π electrons. Additionally, several nitrogen–carbon compounds are non-graphitisable materials including various carbodiiimides [162]; this means that, even after heating them to

3500 K, the materials do not have a graphite crystal structure and some disorder exists along the *c*-axis [162], probably due to crosslinks between planes. Moreover, the only report of successful graphite substitutional doping involves only a very small amounts of nitrogen [163], well below the percentage level that has been usually reported when observing 'graphitisation' of CN materials. Therefore it is important to distinguish between the formation of structures bonded mainly by sp^2 hybrids and the development of a graphitic crystal-line phase.

Several reports have linked the presence of CN radicals with high nitrogen content and, in some cases, this has been associated to the presence of hydrogen and/or silicon. These observations, together with the almost unanimous existence of sp^2 C bonding in all CN materials, suggest that the formation of aromatic heterocycles may be a way to produce high-nitrogen-content material. Such an idea is based on the following: (1) the presence of cyano (nitrile) radicals can involve the formation of aromatic heterocycles [164], and this is in sharp contrast with the C_2 dimer that has been shown to play a very important role in sp^3 C (diamond) growth; (2) the presence of three-atom chains in the gas phase, with at least one nitrogen [109], can lead to cycloaddition reactions yielding five-membered rings [164]; (3) unlike only-carbon aromatic rings, aromatic nitrogen heterocycles with five atoms (azole rings) are rather stable, are π -electron-excessive systems and have at least one external atom linked to a trigonally bonded nitrogen; (4) amines and other electron-releasing groups, such as hydroxyls, stabilise six-membered rings that contain several nitrogen atoms when substituted at neighbouring carbon sites; (5) the presence of cyanogen may lead to the formation of paracyanogen which has been characterised as 'graphitic in nature'; and (6) chemical sputtering extracts nitrogen-containing species whereas carbon-only groups of atoms are more difficult to volatilise.

The formation of heterocycles with five or six atoms may explain why some researchers have observed fullerene-like structures [96]. How planar the structures are, is probably dependent on the number of six-membered rings; fivefold symmetry is, of course, forbidden in two dimensions and triazine-like rings are known to form extended but not closely packed networks [165]. Such material is yellow, and not the brown or black amorphous materials that have been synthesised to date. Hence, a curled structure made up of aromatic heterocycles is quite likely to be formed. Additional information in favour of the presence of five-membered rings comes from the relative stabilities of polycyclic heteroaromatic compounds; e.g., cyclazines with five-membered rings are usually more stable than those with only six-membered rings [166].

As we have described, there are several reports on the formation of crystalline material. However, unlike the cases of diamond and cubic boron nitride, there is

a lack of reports that reproduce results from other groups, although sputtering at relatively high pressures and powers has yielded crystalline material in several cases [104,119]. To be completely convincing, the existence of a crystalline structure must be demonstrated by at least two independent methods and the results should be mutually consistent. For example, from diffraction analysis a crystalline structure should be calculated that accounts for all the reflections and, desirably, the intensities. From the symmetry group thus obtained it ought to be possible to account for the Raman and infrared modes present in the vibrational spectra. Until now this has not been carried out; at best, what has been attempted is a comparison with other authors' calculations that do not fit the diffraction data very well and include a number of discrepancies and absences [74]. It should be remembered that there are organic crystals with high N/C ratios, relatively high melting points, low solubility, which show rich diffraction patterns and produce several lines in Raman and infrared spectra, e.g., guanine.

5. Conclusions

Many compositions of carbon nitride exist and more than a few are stable to at least 800°C. The high-density forms of carbon nitride have similar stabilities and mixed-phase deposits will nearly always be obtained. It is almost certain that the existence of crystalline C_3N_4 has not been established. Furthermore, until a cross-characterisation of crystals has been performed by at least two independent research groups, the evidence for the synthesis of high-density crystalline C_3N_4 will remain in doubt. Similarly, the thermal spike/compression process that has been used successfully for the sp^2 -to- sp^3 transition in diamond-like carbon does not occur for carbon nitride. In part, this is because there are a number of additional competing structural and chemical pathways available and, in part, because of the effect of chemical sputtering. Even so, it appears that energy spikes using electron beams or high-intensity electromagnetic radiation may be able to promote an amorphous-to-crystalline transition. The selective removal of nitrogen by chemical sputtering implies that, in order to obtain high nitrogen concentrations in the deposit, considerably more of the nitrogen-containing precursor species must be incident on the substrate. However, under such circumstances, chemical erosion can be expected to be substantial and film growth will be a fine balance between the erosion and deposition processes.

The following are probably commendable factors for the synthesis of crystalline C_3N_4 .

1. Substrate temperatures in excess of 800°C, if the process uses gaseous precursors. Such temperatures should help inhibit the formation of polymeric and inorganic CN_x compounds.

2. Atomic nitrogen and CN are probably preferable as precursors rather than molecular nitrogen and hydrocarbon ions and radicals. The use of a CN precursor is likely to help prevent the formation of stable carbon-ring structures.
 3. At low pressures, ion energies below 10 eV are necessary to avoid chemical sputtering and the concurrent reduction in nitrogen content.
 4. For gas-phase processes, the use of medium to high pressures helps to ensure that the kinetic energy of the incident neutrals is kept below 10 eV. Use of high to ultrahigh pre-deposition vacuums is recommendable to minimise the residual concentration of water vapour in the reaction chamber. As mentioned earlier, the presence of hydrogen increases the chemical erosion rate considerably.
 5. Substrate effects are complex but important; reasonable adhesion between the carbon nitride and the substrate is needed but without compound formation as in the case of silicon. Additionally, some substrate materials may enhance carbon nitride formation. There are indications that there are advantages in using nickel, titanium or Si₃N₄ coated substrates.
- In relation to characterisation of the deposits, the following may be stated.

1. Various characterisation techniques should be employed in parallel. The existence of crystalline C₃N₄ cannot be established definitively by incomplete XRD or electron diffraction data. However, evidence from diffraction data together with consistent information from Raman analysis would constitute a solid indication of the presence of crystalline C₃N₄.
2. Measured non-optimum N/C ratios do not mean necessarily that crystalline C₃N₄ does not exist within the deposit.
3. Low sp¹ bonding cannot be assumed only by the presence of small peaks in the 2000 to 2200 cm⁻¹ region of FTIR spectra.
4. Effects of the chemical environment cannot be ignored in XPS or other techniques that are sensitive to the energies of valence electrons.

References

- [1] T.K. Brotherton, J.W. Lynn, *Chem. Rev.* 59 (1960) 841.
- [2] J.J. Cuomo et al., *J. Vac. Sci. Technol.* 16 (1979) 299.
- [3] L.L. Bircumshaw, F.M. Tyler, D.H. Whiffen, *J. Chem. Soc.* 4 (1954) 931.
- [4] A.Y. Liu, M.L. Cohen, *Science* 245 (1989) 841.
- [5] D.M. Teter, R.J. Hernley, *Science* 271 (1996) 53.
- [6] A.Y. Liu, *Phys. Rev. B* 50 (14) (1994) 10362.
- [7] Y. Chen, L. Guo, F. Chen, E.G. Wang, *J. Phys.: Condens. Matter* 8 (1996) L685.
- [8] S. Veprek, *Z. Phys. Chem.* 86 (1973) 95.
- [9] J.D.H. Dannay et al., *Crystal Data*, ACA Monograph vol. 5 (1963) 118.
- [10] T. Sekine et al., *J. Mater. Sci. Lett.* 9 (1990) 1376.
- [11] Y. Miyamoto, M.L. Cohen, S.G. Louie, *Solid State Commun.* 102 (1997) 605.
- [12] P.H. Fang, *J. Mater. Sci. Lett.* 14 (1995) 536.
- [13] D.M. Teter, *MRS Bull.* 23 (1) (1998) 22.
- [14] T. Hughbanks, Y. Tian, *Solid State Commun.* 96 (1995) 321.
- [15] M.R. Wixom, *J. Am. Ceram. Soc.* 73 (1990) 1973.
- [16] T. Komatsu, M. Samejima, *J. Mater. Chem.* 8 (1998) 193.
- [17] M.B. Guseva et al., *Diamond Relat. Mater.* 6 (1997) 640.
- [18] R.C. DeVries, *Diamond Relat. Mater.* 4 (1995) 1093.
- [19] M. Kawaguchi, *Chem. Mater.* 7 (1995) 257.
- [20] M. Kawaguchi et al., *Chem. Lett.* 10 (1997) 1003.
- [21] A. Jockisch, A. Schier, H. Schmidbaur, *Chem. Ber./Recueil* 130 (1997) 1739.
- [22] J. Martin et al., *J. Appl. Phys.* 81 (1997) 255.
- [23] T.-R. Lu, *Thin Solid Films* 308/309 (1997) 126.
- [24] A. Hoffman et al., *Surf. Coat. Technol.* 68/69 (1994) 616.
- [25] C. Palacio et al., *Vacuum* 48 (1997) 709.
- [26] D.H. Lee, H. Lee, B. Park, *J. Mater. Res.* 12 (1997) 2057.
- [27] K.J. Boyd et al., *J. Vac. Sci. Technol. A* 13 (1995) 2110.
- [28] P. Hammer, W. Gissler, *Diamond Relat. Mater.* 5 (1996) 1152.
- [29] S.S. Todorov et al., *J. Vac. Sci. Technol. A* 12 (1994) 3192.
- [30] N. Tsubouchi et al., *Appl. Phys. Lett.* 72 (1998) 1412.
- [31] K. Ogata, J.F. Diniz Chubaci, F. Fujimoto, *J. Appl. Phys.* 76 (1994) 3791.
- [32] A. Boussetta, M. Lu, A. Bensaoula, *J. Vac. Sci. Technol. A* 13 (1995) 1639.
- [33] M. Kohzaki et al., *Jpn. J. Appl. Phys.* 36 (1997) 2313.
- [34] M. Kohzaki et al., *Thin Solid Films* 308/309 (1997) 239.
- [35] H.W. Lu, X.R. Zou, J.Q. Xie, J.Y. Feng, *J. Phys. D: Appl. Phys.* 31 (1998) 363.
- [36] J. Feng, Y. Zheng, J. Xie, *Mater. Lett.* 27 (1996) 219.
- [37] S. Veprek, J. Weidmann, F. Glatz, *J. Vac. Sci. Technol. A* 13 (1995) 2914.
- [38] S.A. Korenev et al., *Thin Solid Films* 308/309 (1997) 233.
- [39] N. Xu et al., *J. Phys. D: Appl. Phys.* 30 (1997) 1370.
- [40] J.P. Zhao et al., *Mater. Lett.* 33 (1997) 41.
- [41] C. Spaeth, M. Kühn, U. Kreissig, F. Richter, *Diamond Relat. Mater.* 6 (1997) 626.
- [42] J. Hartman et al., *J. Vac. Sci. Technol. A* 15 (1997) 2983.
- [43] D.G. McCulloch, A.R. Merchant, *Thin Solid Films* 290 (1996) 99.
- [44] J.K. Walters et al., *J. Appl. Phys.* 83 (1998) 3529.
- [45] M. Chhowalla et al., *Thin Solid Films* 290 (1996) 103.
- [46] Y. Taki et al., *Jpn. J. Appl. Phys.* 36 (1997) 4901.
- [47] A.R. Merchant et al., *J. Appl. Phys.* 79 (1996) 6914.
- [48] Y. Taki, T. Kitagawa, O. Takai, *Thin Solid Films* 304 (1997) 183.
- [49] T.-Y. Yen, C.-P. Chou, *Appl. Phys. Lett.* 67 (1995) 2801.
- [50] J. Bulir et al., *Thin Solid Films* 292 (1997) 318.
- [51] R. Gonzalez et al., *Appl. Surf. Sci.* 109/110 (1997) 380.
- [52] X.-A. Zhao et al., *Appl. Phys. Lett.* 66 (1995) 2652.
- [53] C.W. Ong et al., *Thin Solid Films* 280 (1996) 1.
- [54] R. Alexandrescu et al., *Appl. Phys. A; Mater. Sci. Proc.* 65 (1997) 207.
- [55] E. Aldea et al., *Jpn. J. Appl. Phys.* 36 (1997) 4686.
- [56] S. Acquaviva et al., *Appl. Surf. Sci.* 109/110 (1997) 408.
- [57] Z.M. Ren et al., *Phys. Rev. B* 51 (1995) 5274.
- [58] D.J. Johnson, Y. Chen, Y. He, R.H. Prince, *Diamond Relat. Mater.* 6 (1997) 1799.
- [59] C. Niu, Y.Z. Lu, C.M. Lieber, *Science* 261 (1993) 334.
- [60] Z.J. Zhang, S. Fan, J. Huang, C.M. Lieber, *Appl. Phys. Lett.* 68 (1995) 3582.
- [61] Z.J. Zhang, S. Fan, J. Huang, C.M. Lieber, *Appl. Phys. Lett.* 68 (1996) 2639.
- [62] C. Jama et al., *Thin Solid Films* 302 (1997) 58.
- [63] P. Merel et al., *Appl. Phys. Lett.* 71 (1997) 3814.
- [64] A.A. Voevodin, M.S. Donley, *Surf. Coat. Technol.* 82 (1996) 199.

- [65] Z.M. Ren et al., *Appl. Phys. A; Mater. Sci. Proc.* 65 (1997) 407.
- [66] J. Hu, P. Yang, C.M. Lieber, *Phys. Rev. B* 57 (1998) 3185.
- [67] R. Alexandrescu et al., *Appl. Surf. Sci.* 109/110 (1997) 544.
- [68] A.K. Sharma et al., *Appl. Phys. Lett.* 69 (1996) 3489.
- [69] S.A. Uglov, V.E. Shub, A.A. Beloglazov, V.I. Konov, *Appl. Surf. Sci.* 92 (1996) 656.
- [70] Y. Chen, L. Guo, F. Chen, E.G. Wang, *J. Phys.: Condens. Matter* 8 (1996) L685.
- [71] Y. Zhang, Z. Zhou, H. Li, *Appl. Phys. Lett.* 68 (1996) 634.
- [72] H.K. Woo et al., *Diamond Relat. Mater.* 6 (1997) 635.
- [73] Y. Watanabe et al., *Proceedings of Fall MRS Meeting, Boston, MA, 1997, Materials Research Society, Pittsburgh, PA, 1997.*
- [74] Y. Chen, L. Guo, F. Chen, E.G. Wang, *Mod. Phys. Lett.* 10 (1996) 615.
- [75] P.H. Fang, *Appl. Phys. Lett.* 69 (1996) 136.
- [76] A. Grill, V. Patel, *Diamond Films Technol.* 2 (1992) 25.
- [77] F.L. Freire Jr., *Jpn. J. Appl. Phys.* 36 (1997) 4886.
- [78] D.M. Bhusari et al., *J. Mater. Res.* 12 (1997) 322.
- [79] L.C. Chen et al., *Thin Solid Films* 303 (1997) 66.
- [80] S.L. Sung et al., *Jpn. J. Appl. Phys.* 37 (1998) L148.
- [81] M. Zhang, L. Pan, T. Miyazaki, Y. Nakayama, *Jpn. J. Appl. Phys.* 36 (1997) 4897.
- [82] D. Tanaka, S. Ohshio, J. Nishino, H. Saitoh, *Jpn. J. Appl. Phys.* 35 (1996) L1452.
- [83] M. Zhang, Y. Nakayama, *J. Appl. Phys.* 82 (1997) 4912.
- [84] M. Diani et al., *Diamond Relat. Mater.* 3 (1994) 264.
- [85] K. Wu, E.G. Wang, J. Qing, G. Xu, *J. Appl. Phys.* 83 (1998) 1702.
- [86] P. Wood, T. Wydeven, O. Tsuji, *Thin Solid Films* 258 (1995) 151.
- [87] F.L. Freire Jr., D.F. Franceschini, *Thin Solid Films* 293 (1997) 236.
- [88] M.M. Lacerda et al., *Diamond Relat. Mater.* 6 (1997) 631.
- [89] D.W. Wu et al., *Solid State Commun.* 103 (1997) 193.
- [90] D. Wu et al., *Phys. Rev. B* 56 (1997) 4949.
- [91] S. Matsumoto, K.K. Chattopadhyay, M. Mieno, T. Ando, *J. Mater. Res.* 13 (1998) 180.
- [92] J.H. Kim, D.H. Ahn, Y.H. Kim, H.K. Baik, *J. Appl. Phys.* 82 (1997) 658.
- [93] C.J. Tong, J.M. Sivertsen, J.H. Judy, C. Chong, *J. Mater. Res.* 5 (1990) 2490.
- [94] Y.A. Yeh, C.L. Lin, M. Siverstsen, J.J. Judy, *J. Magn. Mater.* 120 (1993) 314.
- [95] B.C. Holloway et al., *Thin Solid Films* 290–291 (1996) 94.
- [96] H. Sjöström et al., *J. Mater. Res.* 11 (1996) 981.
- [97] W.T. Zhang et al., *J. Vac. Sci. Technol. A* 14 (1996) 2696.
- [98] M. Friedrich et al., *Diamond Relat. Mater.* 6 (1997) 33.
- [99] N. Axen et al., *Surf. Coat. Technol.* 81 (1996) 262.
- [100] N. Hellgren et al., *Phys. Rev. B* 59 (1999) 5162.
- [101] W.T. Zheng et al., *J. Electron Spectrosc. Relat. Phenom.* 87 (1997) 45.
- [102] Y. Marumo, Z. Yang, Y.P. Chung, *Surf. Coat. Technol.* 86/87 (1996) 586.
- [103] D. Li et al., *Surf. Coat. Technol.* 68/69 (1994) 611.
- [104] A.K.M.S. Chowdhury et al., *Thin Solid Films* 308/309 (1997) 130.
- [105] A.K.M.S. Chowdhury, D.C. Cameron, M.S.J. Hashmi, *Proceedings of the Borides, Carbides and Nitrides Symposium of the 1998 TMS Conference, San Antonio, TX (1998)* 61.
- [106] J.Q. Zhang, Y. Setsuhara, S. Miyake, B. Kyoh, *Jpn. J. Appl. Phys.* 36 (1997) 6894.
- [107] Y. Ohtsu et al., *Jpn. J. Appl. Phys.* 36 (1997) 4620.
- [108] T. Okada, S. Yamada, Y. Takeuchi, T. Wada, *J. Appl. Phys.* 78 (1995) 7416.
- [109] R. Kaltofen, T. Sebald, G. Weise, *Thin Solid Films* 308/309 (1997) 118.
- [110] D. Li et al., *J. Vac. Sci. Technol. A* 13 (1995) 1063.
- [111] K.M. Yu et al., *Phys. Rev. B* 49 (1994) 5034.
- [112] L. Wan, R.F. Egerton, *Thin Solid Films* 279 (1996) 34.
- [113] S. Kumar, T.L. Tansley, L.S. Wielunski, *J. Phys. D: Appl. Phys.* 28 (1995) 2335.
- [114] M.M. Lacerda et al., *J. Vac. Sci. Technol. A* 15 (1997) 1970.
- [115] Y. Li, Z. Zhang, S. Xie, G. Yang, *Chem. Phys. Lett.* 247 (1995) 253.
- [116] M.M. Lacerda, F.L. Freire, G. Mariotto, *Diamond Relat. Mater.* 7 (1998) 412.
- [117] R. Kaltofen, T. Sebald, G. Weise, *Thin Solid Films* 290 (1996) 112.
- [118] G. Dinescu et al., *Nucl. Instrum. Methods B* 120 (1996) 298.
- [119] S. Muhl et al., *Thin Solid Films* 308/309 (1998) 249.
- [120] P. Hammer, M.A. Baker, C. Lenardi, W. Gissler, *J. Vac. Sci. Technol. A* 15 (1997) 107.
- [121] J.P. Riviere et al., *Mater. Lett.* 22 (1995) 115.
- [122] A. Fernandez et al., *Appl. Phys. Lett.* 69 (1996) 784.
- [123] S. Kobayashi et al., *Thin Solid Films* 281/282 (1996) 289.
- [124] L.J. Bellamy, *The Infrared Spectra of Complex Molecules*, Chapman and Hall, London, 1975.
- [125] D. Hadzi, *Characteristic features in the spectra of organic molecules*, in: M. Davies (Ed.), *Infra-red Spectroscopy and Molecular Structure* Elsevier, Amsterdam, 1963., Chapter VII.
- [126] G.A. Jeffrey, *An Introduction to Hydrogen Bonding*, Oxford University Press, Oxford, 1997.
- [127] H. Yasuda, *Plasma Polymerization*, Academic Press, London, 1985.
- [128] S.R.P. Silva et al., *J. Appl. Phys.* 81 (1997) 2626.
- [129] J. Zhao, R.Z. Che, J.R. Xu, N. Kang, *Appl. Phys. Lett.* 70 (1997) 2781.
- [130] S.F. Durrant et al., *Thin Solid Films* 259 (1995) 139.
- [131] S.F. Lim, A.T.S. Wee, J. Lin, D.H.C. Chua, K.L. Tan, *J. Mater. Res.* 14 (1999) 1153.
- [132] C. Sandorfy, *General and theoretical aspects*, in: S. Patai (Ed.), *The Chemistry of Functional Groups, The Chemistry of the Carbon–Nitrogen Double Bonds*, Interscience Publishers, London, 1970.
- [133] R. Riedel et al., *Chem. Mater.* 10 (1998) 2964.
- [134] , in: S. Patai, Z. Rappoport (Eds.), *The Chemistry of Functional Groups, Supplement C: The Chemistry of Triple-Bonded Functional Groups*, John Wiley and Sons, Chichester, 1983.
- [135] I.N. Juchinovski, I.G. Binev, *Infrared spectra of cyano and isocyanogroups*, in: S. Patai, Z. Rappoport (Eds.), *The Chemistry of Functional Groups, Supplement C: The Chemistry of Triple-Bonded Functional Groups*, John Wiley and Sons, Chichester, 1983, pp. 107–135.
- [136] *The Aldrich Library of FT-IR Spectra*, 2nd ed., vols. 2 and 3 Sigma Aldrich Publications, USA, 1997.
- [137] J.H. Kauffman, S. Metin, D.D. Saperstein, *Phys. Rev. B* 39 (1989) 13053.
- [138] Y. Taki, T. Kitawaga, O. Takai, *Thin Solid Films* 304 (1997) 183.
- [139] J. Schwan et al., *J. Appl. Phys.* 84 (1998) 2071.
- [140] J. Widany et al., *Diamond Relat. Mater.* 5 (1996) 1031.
- [141] R. Soto et al., *Carbon* 36 (1998) 781.
- [142] F. Falk, J. Meinschien, K. Schuster, H. Stafast, *Carbon* 36 (1998) 765.
- [143] R. Riedel et al., *Chem. Mater.* 10 (1998) 2964.
- [144] J.M. Mendez, A. Gaona-Couto, S. Muhl, S. Jimenez-Sandoval, *Mater. Res. Soc. Proc.* 441 (1997) 687.
- [145] J.M. Ripalda, I. Montero, L. Galan, *Diamond Relat. Mater.* 7 (1998) 402.
- [146] M.A. Baker, P. Hammer, *Surf. Interface Anal.* 25 (1997) 301.
- [147] D. Marton et al., *Phys. Rev. Lett.* 73 (1994) 118.
- [148] C. Ronning et al., *Phys. Rev. B* 58 (1998) 2207.
- [149] P.K. Ghosh, *Introduction to Photoelectron Spectroscopy*, P.J. Elving, J.D. Winefordiner (Eds.), *Chemical Analysis* vol. 67, John Wiley and Sons, New York, 1983.

- [150] B. Schrader, *Infrared and Raman Atlas of Organic Compounds*, 2nd ed. VCH Publishers, New York, 1989.
- [151] A. Mansour, D. Ugolini, *Phys. Rev. B* 47 (1993) 10201.
- [152] F. Weich, J. Widany, Th. Frauenheim, *Phys. Rev. Lett.* 78 (1997) 3326.
- [153] K. Siegbahn, D.A. Allison, J.H. Allison, in: W. Robinson (Ed.), *Practical handbook of Spectroscopy, Section 2: ESCA Photoelectron Spectroscopy*, CRC Press, Boca Raton, FL, 1991.
- [154] G. Leclerc, J.J. Pireaux, *J. Electron Spectrosc. Relat. Phenom.* 71 (1995) 141.
- [155] A.R. Katritzky, *Handbook of Heterocyclic Chemistry* Pergamon Press, Toronto, 1985., Chapter 2.
- [156] D.T. Clark, A. Dilks, *J. Polym. Sci., Polym. Chem.* 15 (1977) 15.
- [157] J. Roth, *Chemical sputtering*, in: R. Behrish (Ed.), *Sputtering by Particle Bombardment, Topics in Applied Physics* vol. 52 Springer, Berlin, 1983., Chapter 3.
- [158] F.D.A. Aarao Reis, D.F. Franceschini, *Appl. Phys. Lett.* 74 (1999) 209.
- [159] H. Chatei et al., *Diamond Relat. Mater.* 6 (1997) 107.
- [160] D. Li et al., *J. Vac. Sci. Technol. A* 12 (1994) 1470.
- [161] A.D. McNaught, A. Williamson, *International Union of Pure and Applied Chemistry, Compendium of Chemical Terminology*, 2nd ed., Blackwell Science, Cambridge, 1997.
- [162] Y. Yamashita, M. Shioya, S. Kondo, T. Hashinet, A. Takahu, *Carbon* 37 (1999) 71.
- [163] C.A. Kuper, M.M. Labes, *Chem. Mater.* 11 (1999) 408.
- [164] T.L. Gilchrist, *Heterocyclic Chemistry*, Addison-Wesley Longman, Singapore, 1997.
- [165] J.A. Redemann, S. Lucas, *J. Am. Chem. Soc.* 61 (1939) 3420.
- [166] W. Flitsch, U. Kramer, *Cycalazines and related N-bridged annulenes*, in: A.R. Katritzky, A.J. Boulton (Eds.), *Advances in Heterocyclic Chemistry* vol. 22, Academic Press, New York, 1978, pp. 321–365.