

CRYSTALLINE AND AMORPHOUS PHASES IN CARBON NITRIDE FILMS PRODUCED BY INTENSE HIGH-PRESSURE PLASMA

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Carbon-nitride films are prepared using a high-intensity pulsed plasma deposition technique. A wide range of nitrogen pressure and discharge intensity are used to investigate their effect on the morphology, nitrogen content, structure, bonding, phase composition and mechanical characteristics of the CN films deposited. Increasing the nitrogen pressure from 0.1 atm to 10 atm results in an increase of nitrogen incorporation into CN films to a maximum of 45 at.%. Under the high-energy density deposition conditions which involve ablation of the quartz substrate the CN films are found to incorporate in excess of 60 at.%N. Raman spectra of these films contain sharp peaks characteristic of a distinct crystalline CN phase. TEM diffraction patterns for the films deposited below 1 atm unambiguously show the presence of micron-sized crystals displaying a cubic symmetry.

INTRODUCTION

Intense theoretical and experimental interest has been focused on the possibility of synthesising new carbon-nitride materials with bulk modulus and hardness rival or exceeding that of diamond. First-principles calculations have suggested that a hypothetical material, β - C_3N_4 , may have a bulk modulus comparable to that of diamond [1]. Other forms of carbon nitrides of a composition C_3N_4 have been suggested, including α - C_3N_4 , graphitic- C_3N_4 , a cubic form of C_3N_4 [2], fullerene-like carbon nitride [3] and a crystalline carbon nitride composite [4]. The majority of the experimental work reports the formation of amorphous nitrogen rich carbon films. In [5-7] nitrogen rich carbon depositions were reported to contain small crystallites related to the β - C_3N_4 phase. Exploration of novel deposition techniques for the CN synthesis is a key to further progress in the area.

Recently we reported the production of C-N films using a shock-plasma method in a nitrogen ambient [8-10]. A number of features of the method make the synthesis conditions distinctly different from those reported earlier. These features include the high nitrogen pressure and concentration in the CN plasma, high degree of ionisation and high rate of cooling from the plasma condensation temperature, which is favourable for the formation of metastable phases. The present work analyses the nitrogen content, morphology, bonding, structure and mechanical properties of the CN films produced in a wide range of pressure and intensity of the shock plasma used. The films are characterised using optical and electron microscopy, Auger and RBS spectroscopy, XPS, TEM diffraction and microhardness measurements.

METHOD, RESULTS AND DISCUSSION

(a) Method. The experimental arrangement used for the deposition of nitrogen rich carbon films is shown in Fig. 1. Carbon electrodes of 3 mm in diameter are placed in a discharge chamber filled with nitrogen gas. A capacitor battery is discharged through a gap between the carbon electrodes. The chamber is designed to use relatively high nitrogen pressure (up to 20 atm). The discharge is controlled by introducing a third electrode near the discharge gap which is connected to a Rhumkorff coil. This third electrode produces a background ionisation near the electrode space which is necessary to trigger the discharge of the capacitor. The discharge voltage of the capacitor is controlled by the relative position of the third electrode and the power supplied by the Rhumkorff coil. A diode is inserted in the Rhumkorff coil circuit to avoid the capacitor discharge through the coil. The discharge time was $\sim 4 \mu\text{sec}$. The capacitance used was $12.5 \mu\text{F}$ and the voltage 3 kV, giving a released power of approximately 14 MW.

The CN depositions were obtained by varying nitrogen gas pressure in the chamber in the range between 0.01 atm and 8.0 atm. This allowed the amount of nitrogen in the

interelectrode space to be increased by three orders of magnitude. An estimate of peak plasma temperature gives $T \approx 3 \times 10^4$ K [10]. The plasma shock pressure is of the order of 400 MPa. The nitrogen in the plasma under those conditions is almost completely dissociated and one fold ionised.

(b) Low pressure CN deposition (below 0.1 atm).

The film composition as measured using Auger and RBS spectroscopy is found to be dependent on the nitrogen pressure. In the pressure range between 0.01 atm and 0.1 atm the maximum nitrogen content in the CN depositions reaches 35 at%. Optical and SEM examinations indicate that with the increasing number of discharges two major types of carbon-nitride depositions, differing in morphology and mechanical properties, are observed [8]. The type I CN films have a uniform amorphous morphology as viewed under the optical and scanning electron microscope but tend to develop buckling and delamination due to the build-up of compressive stresses. The microhardness of the type I morphology is relatively low, varying between ~2.0 GPa and ~3.0 GPa depending on the nitrogen content. These films are formed in a relatively wide range of deposition parameters.

The type II "crystal-like" depositions consist of high density, closely packed grains growing perpendicular to the substrate surface and producing a columnar structure. Optical observations reveal a heterogeneous microstructure and scanning electron micrographs display a cauliflower-like morphology. The grains vary in size between 5 and 10 μm and between 1 and 3 μm in diameter. The hardness of this structure is much higher than that for the type I films, reaching 15 GPa, as measured by Vickers method. Similar and even higher hardness levels were reported for carbon-nitride films prepared by ion and vapour deposition [11] and by dc magnetron sputtering [12]. The maximum microhardness for the type II morphology is observed for nitrogen concentration ~20 at%. The majority of depositions were obtained on Si substrates. However, the type II structure was also observed on glass, steel, sapphire and magnesium oxide crystals used as substrates. The type II film appears to form on the top of a type I film after 600-800 discharges, i.e. the type I film acts as a seed for the type II growth.

The columnar morphology, obtained below 0.1 atm, was found to contain a small fraction of crystalline material. The electron diffraction (ED) pattern of this material is shown in Fig. 2, which was obtained from the thin edge of a micron-sized crystal. The latter was more difficult to find and presumably constituted the minor fraction of the specimen with respect to the amorphous component and graphite. The axial ratio of $\sqrt{2}$ and the spot spacings and interplanar angles are characteristic of those expected for the [011] zone axis pattern of a face-centred cubic crystal having cell parameter approximately $a = 0.630$ nm. This structure exhibited observable reflections and overall intensity typical of the NaCl-type space group Fm3m. ED patterns showing the corresponding [001] and [111] zone axis patterns were also obtained confirming the presence of a f.c.c. structure. Quantitative parallel electron energy loss (PEELS) analyses suggest that the nitrogen content in the crystals reaches ~20 at%. The maximum microhardness, which is observed at ~20 at%N, is apparently related to the crystalline component observed by ED. PEELS analyses indicate that there is a significant degree of sp^3 character for the carbon, while for the nitrogen the sp^2 character is dominant. These results indicate that further structural complexity in the CN system may exist. In the depositions, obtained below 0.01 atm and nitrogen content less than 35 at%, we were unable to find either single crystal patterns or diffuse powder patterns consistent with the $\beta\text{-C}_3\text{N}_4$ phase predicted by Liu and Cohen [1].

(c) High pressure CN deposition (above 1.0 atm).

For the high pressure depositions above 1.0 atm the morphologies are not as pronounced. The grain size of the columnar morphology is ~0.2-0.3 μm which is significantly smaller than that for the low pressure depositions. Microhardness for these films was impossible to measure since they proved to be very brittle and cracked before any impression of the indenter appeared.

The increase of the nitrogen pressure in the deposition chamber to 8 atm increases the nitrogen concentration in the films to a maximum of 45 at%. The nitrogen distribution

changes with depth and across the surface in a radial direction. When a substrate is placed close to the center of the discharge the plasma density and temperature are high enough to produce ablation of the substrate. In this case the central section of the plasma affected area on the substrate is free from deposition since the ablation rate in this section exceeds the deposition rate. The deposition zone adjacent to the ablation area is found to contain the amount of nitrogen in excess of 60 at% which is sufficient to form the C_3N_4 stoichiometry. This zone is found to contain some amount of silicon which originates from the decomposition of the quartz substrate in the ablated area. A presence of Si obviously facilitates nitrogen incorporation into the films. Optical observations and Raman spectroscopy clearly identify small regions of pure silicon in the deposition.

The phase composition of the material in the zone is still to be investigated using high resolution TEM and electron diffraction. However, the Raman data clearly indicate the presence of a crystalline CN phase in the deposition. The spectrum in Fig. 3 was recorded using the exciting wave length of 514.5 nm in a region of the deposit adjacent to the central ablated area of the quartz substrate. This region was morphologically distinct from the rest of the deposit. It appeared lighter under the optical microscope and smoother under the SEM, compared to the rest of the film. The spectrum shows lines from the silicon along with a rising background from the luminescence of the disordered material. In this sample silicon originates from the ablation and decomposition of the quartz (SiO_2) substrate in the central most hot plasma affected area. The peaks seen on this background above 1200 cm^{-1} are probably due to the presence of amorphous carbon - nitrogen compounds. The spectrum also contains a number of sharp peaks at 1600 , 1030 , 1000 and 620 cm^{-1} with the strongest one at 1000 cm^{-1} . The sharpness of these peaks indicates that these lines arise from a well defined crystalline material. The occurrence of the peak at 1600 cm^{-1} strongly suggests that the peaks originate from the phase consisting of light elements such as CN, rather than from that which could possibly be formed by silicon with carbon, nitrogen or oxygen such as SiC, Si_3N_4 , or polycrystalline SiO_2 . The phase which gave rise to the sharp peaks was found to be unstable under the laser beam, decomposing completely after around 10 minutes exposure to this laser power. This may be due to heating from the absorption of the laser by the dark coloured material surrounding this region.

The XPS spectra are presented in Fig. 4. The energy values of the peaks c_1 and c_2 indicate that they are related to the C-C and C-N single bonds respectively. According to the area under the peaks the single bonds are predominant. The c_3 peak suggests that double and/or triple CN bonds are also present. The peaks corresponding the nitrogen also indicate the presence of a single N-N bonds in the high-pressure CN depositions.

CONCLUSION

There is a considerable difference in the morphology, composition and structure of the films produced under low and high nitrogen pressure. The films produced under pressure below 0.1 atm incorporate a maximum of 35 at%N. TEM diffraction patterns for these films unambiguously show the presence of micron-sized crystals displaying a cubic symmetry. The nitrogen content in this crystals is below the C_3N_4 stoichiometric ratio. The results suggest that a further structural complexity in the CN system exists. Increasing the nitrogen pressure up to 8 atm results in an increase of nitrogen incorporation into CN films to a maximum of 45 at.%. At the same time there are zones adjacent to the ablated area on the quartz substrate where the CN films are found to incorporate in excess of 60 at.%N. Raman spectra indicate the occurrence of a definite crystalline phase in the zones.

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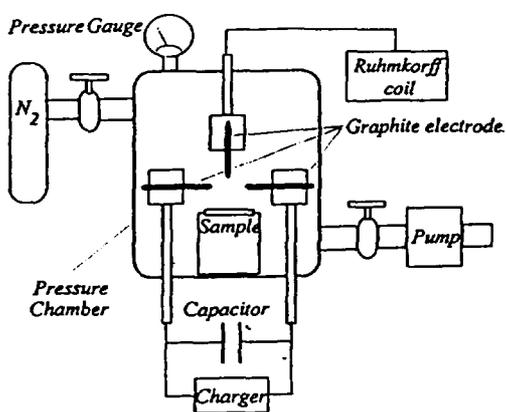


Fig. 1. Experimental arrangement.

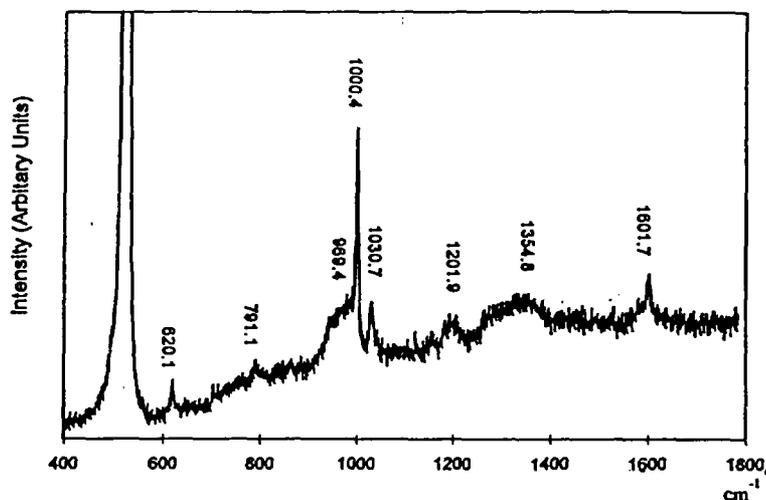


Fig. 3. Raman spectrum containing peaks from a crystalline phase; $P_0 \approx 8$ atm, 2000 pulses.

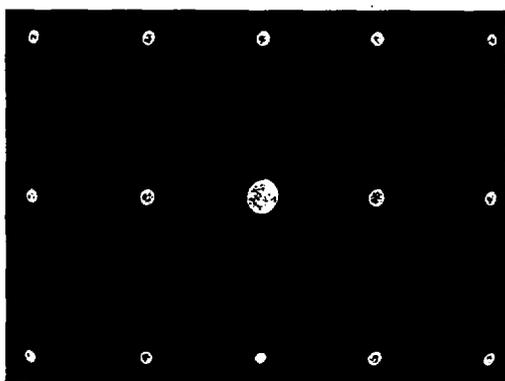


Fig. 2. Electron diffraction pattern from a 1 micron crystallite; note ratio $\sqrt{2}$ for a fcc crystal viewed along [110]. $P_0 \approx 0.05$ atm, 3000 pulses.

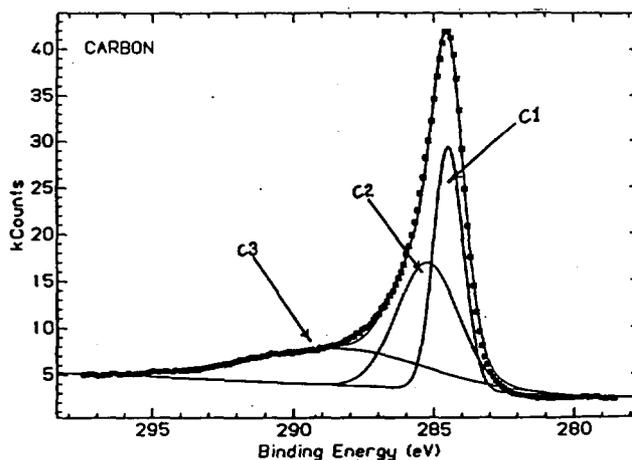


Fig. 4. XPS spectra taken from high-pressure pulsed plasma CN deposition; $P_0 \approx 5$ atm, 2000 pulses