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SYNTHESIS OF CARBO-NITRIDE FILMS USING HIGH-ENERGY SHOCK PLASMA DEPOSITION

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ABSTRACT

The present work reports on the properties of nitrogen rich carbon films produced by an intense gas discharge between carbon electrodes in a nitrogen atmosphere. The energy of the discharge, initial nitrogen pressure, number of discharges and geometry are varied to establish their effect on the nitrogen content and the mechanical, structural and morphological characteristics of the deposited carbon-nitride films. The structural diagnostics include optical and scanning electron microscopy, as well as Auger and Raman Spectroscopes and Rutherford Backscattering. The C-N films formed fell into two categories, differing in morphology and mechanical properties. Type I are C-N films, containing up to 35 at. % nitrogen, and which have an amorphous structure. These films are formed at relatively low plasma shock pressure and exhibit relatively low microhardness, ~ 2 GPa. In a relatively narrow range of the plasma shock pressure and temperature the second type of C-N deposition is observed consisting of high density, closely-packed crystal-like grains growing perpendicular to the substrate surface and displaying a cauliflower-like morphology. The microhardness of these films reaches 15 GPa, as measured by the Vickers method.

INTRODUCTION

Recent theoretical work has predicted a new ultra-hard compound should be able to be synthesised with a composition C_3N_4 and a hardness to rival that of diamond [1]. These predictions sparked considerable interest in attempts to experimentally realise this compound. Attempts to date to synthesise C_3N_4 have used a variety of techniques such as: ion implantation [2], rf sputtering of carbon targets in a nitrogen gas ambient [3], plasma decomposition of various hydrocarbons [4], nitrogen ion bombardment with simultaneous carbon vapour deposition [5], dc magneuron sputtering of a graphite target in a nitrogen ambient [6], shock wave compression of carbon nitride precursors [7], plasma enhanced chemical vapour deposition [8], ion assisted dynamic mixing [9] and laser ablation of carbon target in a stream of atomic nitrogen [10]. The majority of the experimental work reports the formation of amorphous nitrogen rich carbon films. The investigations show that an enhanced nitrogen content improves wear resistance, hardness, tribological and other properties of these films. As reported in [10] a deposition with an average of 40 at. % of nitrogen is likely to contain a crystalline component related to the β-C_3N_4 phase. Exploration of new techniques for carbon-nitride synthesis is a key to further progress in this area. The aim of the present work is to test whether an intense pulsed-plasma can be used for carbon-nitride synthesis. The combination of high energy density, temperature and pressure in the carbon-nitrogen plasma produced by this method makes the synthesis conditions distinctly different from those reported earlier. The present work analyses the effect of the deposition parameters on the nitrogen content, mechanical properties and morphology of the C-N films produced by this pulsed plasma method.

EXPERIMENTAL

The experimental arrangement used for the deposition of nitrogen rich C 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 nitrogen pressure in the chamber is controlled by adjusting the rates of nitrogen supply and pumping speed. The discharge is triggered by lowering the nitrogen pressure in the chamber until the breakdown value. After the first discharge the pressure is maintained constant, so that further discharges proceed at the same breakdown voltage. Under these conditions the frequency of discharges is controlled by the charging rate of the capacitor. The time interval between

discharges was 1 - 2 seconds. The breakdown nitrogen pressure was varied by changing the inter electrode distance, while the energy released in the gap between the electrodes was varied by charging the capacitor battery to different voltages.

In this method high energy density is achieved by allowing the energy to be released in a relatively small volume between the electrodes during a short period of time. During the discharge a carbon-nitrogen plasma is formed in which the nitrogen component is provided by the nitrogen gas available in the discharge volume, whereas carbon ions are supplied by ablation from the carbon electrodes. The electrical characteristics of the discharge were measured from the e.m.f. waveform generated in a loop inductively coupled with the discharge system. A heavily damped oscillatory discharge was observed with ~95% of the energy being released during first 4 μsec. The capacitance used was 13 μF and the voltage 3 kV, giving a released power of approximately 15 MW.

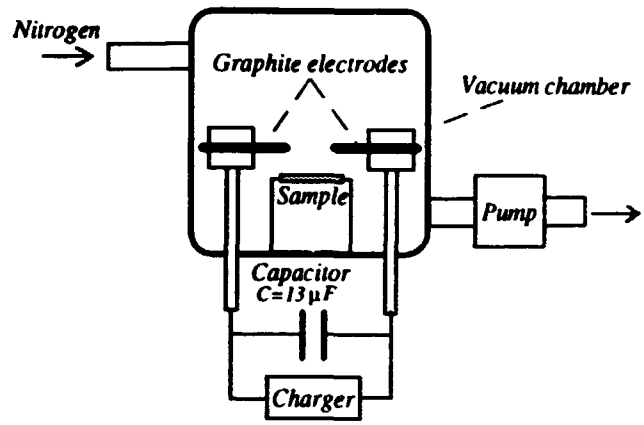

Fig. 1. Experimental arrangement.

At high temperature a major mechanism of energy loss by plasma is due to light irradiation. In this case the plasma temperature is usually estimated by assuming an equilibrium between the power supplied by the capacitor battery and the power lost by the plasma due to light irradiation [11]. Assuming the power input as $CV^2/2\tau$ (τ is the duration of the discharge) and a power loss according to Boltzman's law as $\sigma T^4 A$ (A is the area of the plasma cluster), then a rough estimate of the plasma temperature is $T = (CV^2/2\tau\sigma A)^{1/4}$. The area A is estimated as the surface area of an inter electrode space, taken as a cylinder. Then $A = 2\pi rL$, where r is the electrode radius and L is the inter electrode distance. The substitution of the parameters used in the experiment: C = 13 μF, τ = 4 μs, r = 1.5 mm and L = 2 mm, gives the plasma temperature ~ $2x10^4$ K for V = 1 kV and ~ $4x10^4$ K for V = 4 kV. At the temperature of $1.5x10^4$ K and the density of 10^{-2} g_o (g_o is density of nitrogen at STP) the nitrogen gas is completely dissociated and 92% of it is one fold ionised [12]. According to the Paschen curves [13] the breakdown voltage of 1 kV for an electrode separation of L = 2 mm corresponds to the density of ~10^{-2} g_o. Hence, in the present experiments we expect our nitrogen plasma to be almost completely dissociated and one fold ionised.

The pressure in the carbon nitrogen plasma can be roughly estimated as P = 4 Po T / To, where Po and To are the initial breakdown pressure and temperature and the factor of 4 takes into consideration the dissociation of nitrogen molecules and the release of carbon in the amount equal to that of nitrogen. Then, the plasma shock pressure is of the order of 400 Po, which gives P = ~2 MPa at V = 1 kV and L = 1 mm.

RESULTS AND DISCUSSION

Typically the nitrogen rich carbon films were deposited on Si substrates placed at a distance of 1-2 mm from the electrodes of 3 mm in diameter. The films were obtained under different deposition conditions: variable voltage at a constant electrode separation and variable electrode separation at a constant voltage. The increased voltage increases the breakdown nitrogen pressure and the energy released in the gap. The effect of increasing discharge voltage on nitrogen concentration is shown in Fig. 2, which displays a maximum of 35 at. % of nitrogen content, observed for a voltage of 2.5 kV. The increase of the electrode separation for a constant voltage decreases the breakdown nitrogen pressure and at the same time increases the inter electrode volume where energy is released. This results in a steady increase in the nitrogen content in the deposition as demonstrated in Fig. 3. Raman spectroscopy shows a clear peak at

2229 cm^{-1}, which is characteristic of carbon-nitrogen stretch and indicates that nitrogen is chemically bonded by a triple bond to carbon in the CN_x film [14].

The concentration of nitrogen in the deposition layer was measured by Auger spectroscopy and Rutherford back scattering techniques. The data in Fig. 2 and Fig. 3 are related to the nitrogen concentration on the surface of the films as measured by Auger spectroscopy. The Auger measurements from successively sputtered layers show that the nitrogen content drops to approximately half of its surface value below ~10 nm and then stabilises. However, the RBS measurements in selected samples demonstrated that the nitrogen content throughout the thickness of the films corresponds to the surface value, given by the Auger spectroscopy, or in some cases even to higher values. One possible explanation for this inconsistency is that the Ar ion bombardment used in the sputter depth profiling of the C-N films may possibly destroy C-N bonds and allow the nitrogen to escape. Hence the Auger depth profile may significantly underestimate the nitrogen content of the films.

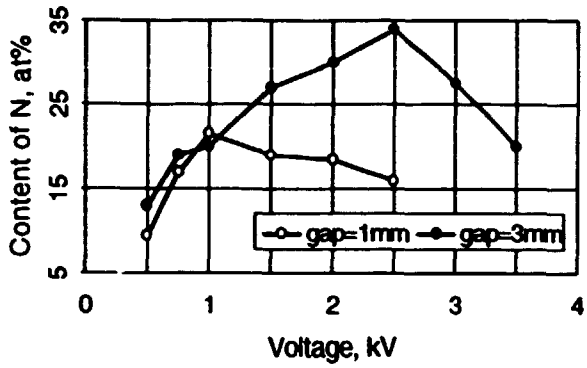

Fig. 2. Surface concentration of nitrogen in the films versus inter electrode voltage as determined by Auger spectroscopy.

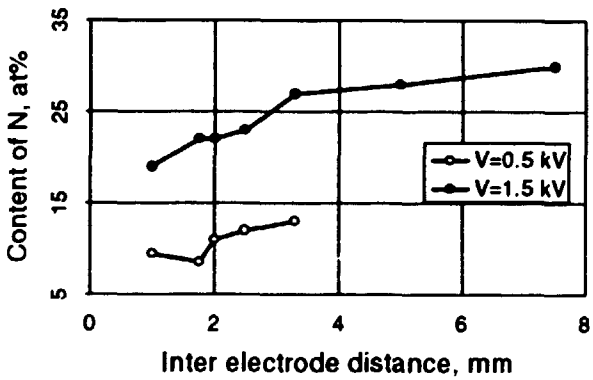

Fig. 3. Surface nitrogen content in the films versus electrode separation.

The thickness of the deposited films was measured to be ~10 μm after 10^3 discharges, which gives the thickness increment of ~10 nm per a discharge. From the thickness of the deposited film and its nitrogen concentration it is possible to estimate the amount of nitrogen incorporated in the film and to compare it with the amount of nitrogen available in the inter electrode discharge space. Assuming that plasma expands uniformly in a radial direction before being condensed on a substrate the thickness of the deposition layer can be shown to be $h = (M_n + M_c) / 4 \pi R^2 \rho$, where M_n and M_c are the masses of nitrogen and carbon available in the plasma, which are subsequently incorporated in the film, R is the distance of the substrate from the electrode axis and ρ is the density of the carbon-nitride film. If α is the mass fraction of nitrogen in the film, then the mass of nitrogen in plasma, which is incorporated in the film, is $M_n = \alpha 4 \pi R^2 \rho h$. Assuming experimental values: R = 3.5 mm, L = 2 mm, h = 10 nm and the density of C-N deposition to be 2.2×10^3 kg m^{-3} as for graphite, then for the deposition containing 30% of nitrogen, $\alpha = 0.3$, the mass of nitrogen incorporated into the film is $M_n \approx 1.5 \times 10^{-10}$ kg. On the other hand the mass of nitrogen contained in the inter electrode volume just before the breakdown is $M_n' = m_n P_0 V_0 / kT_0$, where m_n is the mass of nitrogen molecule, P_0 is the breakdown pressure, T_0 is the room temperature and V_0 is the inter electrode volume, assumed to be a cylinder so $V_0 = \pi r^2 L$. For V = 2 kV and L = 2 mm the breakdown pressure from the Paschen curve is $P_0 = 1.3 \times 10^4$ Pa. This gives $M_n' = 2 \times 10^{-9}$ kg and $M_n / M_n' \approx 0.1$. Thus about 10% of nitrogen available in the discharge space is finally incorporated in the carbon film.

The results presented in Fig. 2 and Fig. 3 suggest that the nitrogen content in the film is related to its concentration in the plasma. The increasing voltage requires the discharge to start at a higher pressure of nitrogen, thus increasing the amount of nitrogen in the inter electrode space. However, because of the increased energy of the discharge the carbon mass released from the electrodes is increased as well. Assuming the rate of ablation from carbon electrodes to be

proportional to the power released in the plasma, then the mass of carbon entering plasma is $M_c' \sim V^2 A / A_o$, where A the electrode area in contact with plasma and Ao is a total area of the inter electrode volume where the energy is released. Then, since $A/A_o = r/(r+L)$ and $M_n' \sim P_o r^2 L$, the plasma composition is $M_n'/ M_c' \sim P_o L(L+r) / V^2$. The ratio P_o/V^2 is evaluated for L = 2 mm using the Paschen curves, which relate the breakdown pressure P_o with voltage. This ratio is found to have a maximum near $V \approx 1$ kV. Thus, the maximum in the nitrogen content, observed in Fig. 2, is likely to be related to the change of plasma composition with voltage. In addition from the Paschen data at a constant V the quantity $P_o \sim 1/L$, and then $M_n'/ M_c' \sim L$. This result is consistent with the experimental data presented in Fig. 3.

The thickness of the layer and the nitrogen content is not uniform. The maximum thickness and higher concentration of carbon is commonly observed in the deposit formed closest to the electrodes. The nitrogen concentration is greatest in the section far away from the electrodes in the peripheral area of the deposition. This effect is obviously due to an intensive ablation from electrodes, which increases shock pressure and ousts nitrogen to the front of the shock wave.

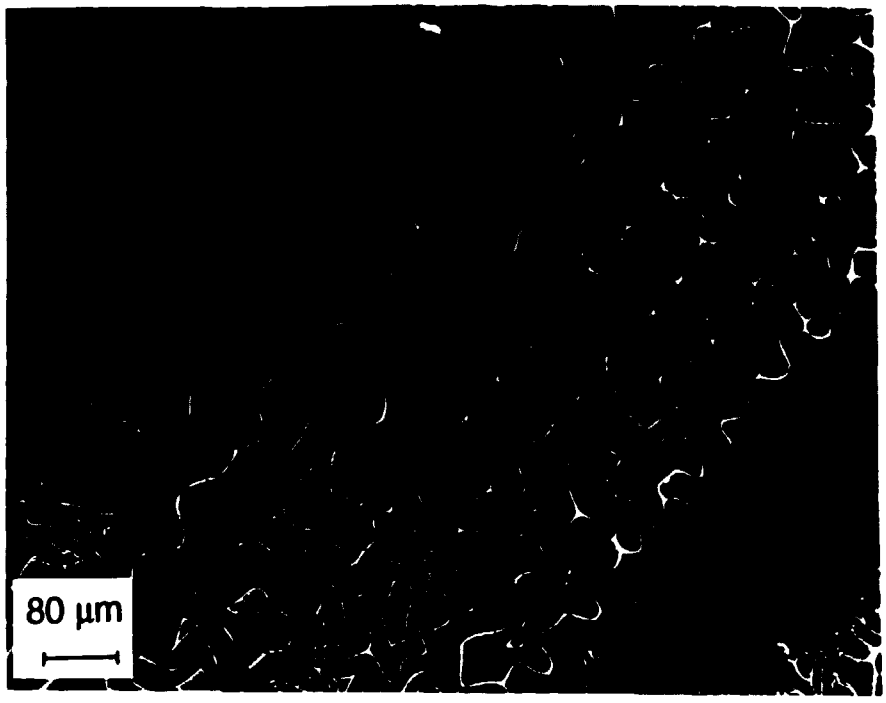

Fig. 4. Optical photograph of type I amorphous C-N film showing buckling structure. P_o = 2 Torr, discharge power 1.6 MW, 25 pulses.

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. The type I C-N films have a uniform amorphous morphology as viewed under the optical (Fig.4) 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, increasing from ~2.0 GPa to ~3.0 GPa when the nitrogen content is increased from 10 at. % to 32 at. % respectively. These films are formed in a relatively wide range of deposition parameters.

The type II "crystal-like" depositions are formed in a relatively narrow range of plasma pressure and temperature, corresponding to voltage range of 1-1.5 kV and the electrode separation of 2.0-2.5 mm. This deposition consists 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 as shown in Fig. 5. 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 [5] and by dc magnetron sputtering [6].

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 top of a type I film after 600-800 discharges, i.e. the type I film acts as a seed for type II growth. It is quite possible that multiple thermal cycling, produced by plasma discharges, contributes to the formation of the type II morphology.

The typical Auger fine structure peaks, adjacent to the main carbon peak, are shown in Fig. 6 for the type I films with different nitrogen content. There is an energy shift of ~4.5 eV between the fine structure peaks. The curves 1 and 2 indicate that at a low nitrogen concentration in the film the graphite and amorphous carbon phase with sp^2 bonding are dominant. The double peak structure shown in curve 3, (which corresponds to films with a higher nitrogen concentration) most likely indicates the presence of a number of phases, including a diamond-like carbon constituent with sp^3 bonding.

The effect of nitrogen on Raman spectra, related to ~1390 cm^{-1} (D peak) and ~1560 cm^{-1} (G peak), is illustrated in Fig. 7. The peak D is assigned to "unorganised carbon", possibly related to boundaries in small crystallites, while the G peak corresponds to carbon in the graphitic state and is the only band observed in single-crystal graphite. The spectra display broadening of the peaks and the vanishing shoulder between the peaks due to the increased nitrogen content. These results indicate that the presence of nitrogen has inhibited the formation of graphite crystallites. This fact coupled with the observation of a peak at corresponding to C ≡ N type bonds indicates that the nitrogen is most likely chemically incorporated into the film and is not just present as gas

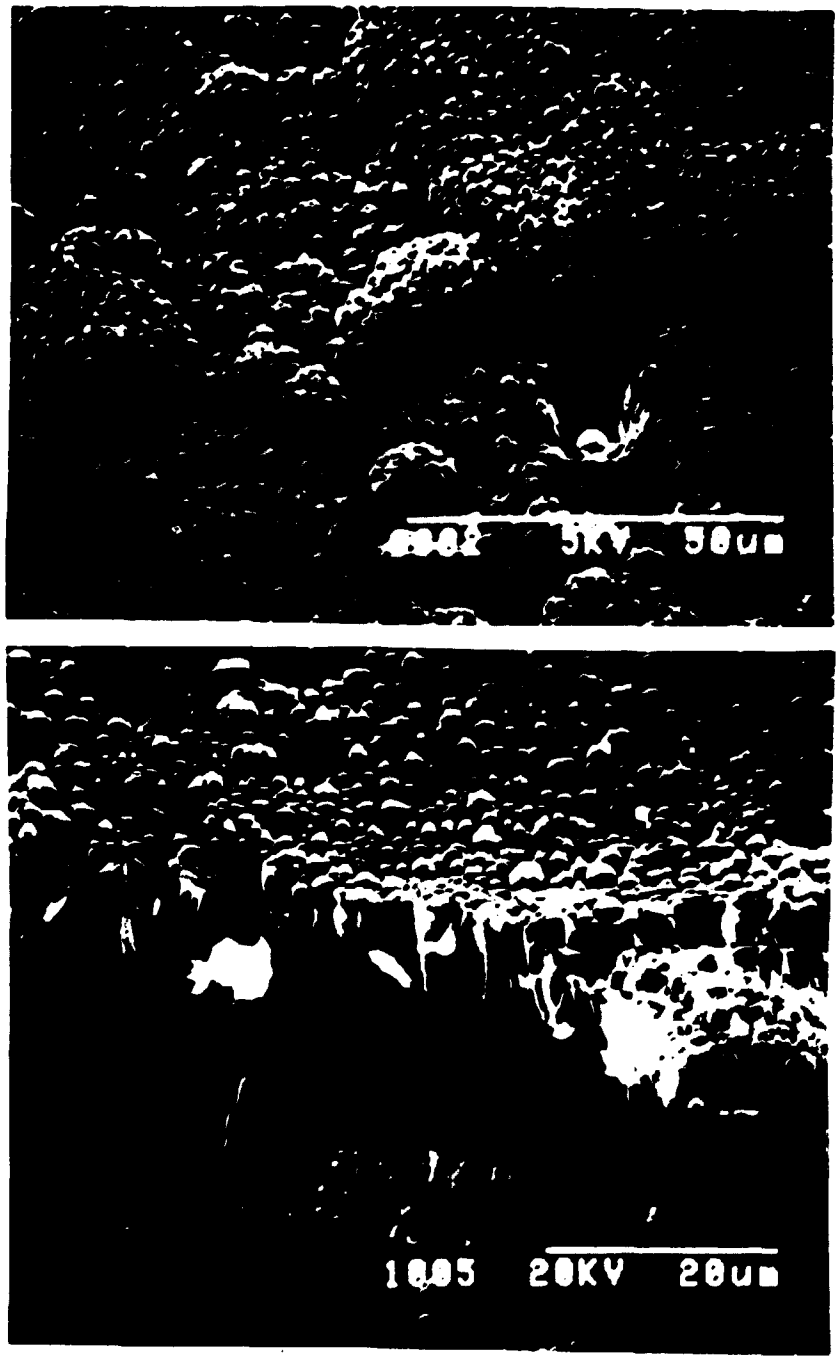

Fig. 5. SEM micrographs of type II C-N films showing cauliflower morphology (above) and columnar structure (below). P_o = 100 Torr, discharge power 6 MW, 1000 pulses.

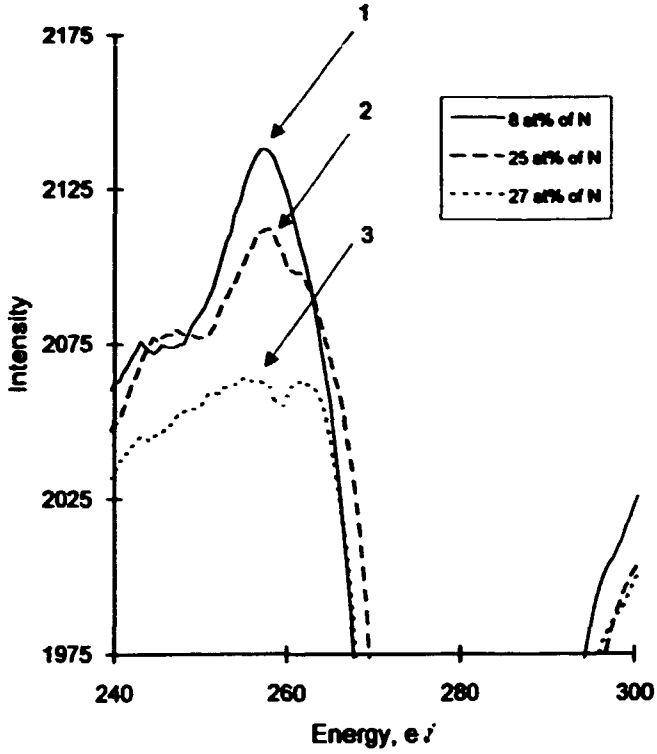

Fig. 6. Fine structure of the Auger line shape.

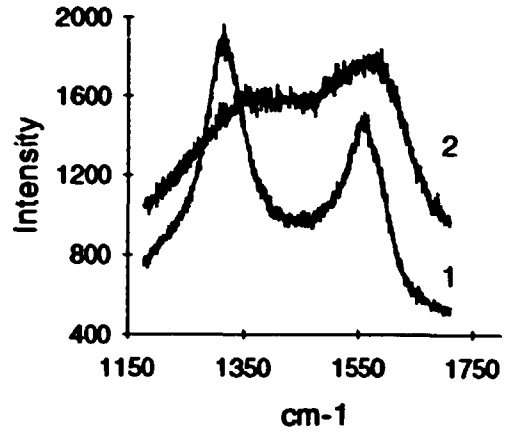

Fig. 7. Raman spectra of C-N films containing 9 at. % of nitrogen (curve 1) and 21 at. % of nitrogen (curve 2).

bubbles. The exact nature of the C-N bonding within the films will require further investigations which are currently in progress.

CONCLUSIONS

The carbon-nitride films containing up to 35 at. % of nitrogen were prepared using high intensity plasma discharge between carbon electrodes in nitrogen atmosphere. The analysis showed that two major types of C-N depositions, differing in morphology and mechanical properties, are present. Under optimum conditions carbon nitride films can be prepared with microhardness up to 15 GPa, which is higher than for most alloys and ceramics.

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