

Maximized sp^3 bonding in carbon nitride phases

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Carbon nitride films were deposited using a low pressure, dual ion beam system consisting of a filtered cathodic vacuum arc and a plasma beam source for carbon and nitrogen ions, respectively. This system maintains highly ionized beams even at high nitrogen fluxes, unlike in single beam systems. Film composition and bonding were measured by electron energy loss spectroscopy. Films with nitrogen to carbon atom ratios (N/C) up to 0.5 are produced. The carbon bonding is found to change gradually from sp^3 to sp^2 , rather than sharply above a critical N content, as found previously. This indicates that N atoms form individual C=N bonds rather than causing a reversion of the entire C network to sp^2 . This allows us to maintain C sp^3 bonding to the highest N contents so far achieved. © 2000 American Institute of Physics. [S0003-6951(00)05336-5]

The synthesis of carbon nitride has been the focus of intense experimental and theoretical effort since the prediction that β - C_3N_4 will have hardness comparable to diamond.¹ β - and α - C_3N_4 are dense, metastable phases in which the bonding is sp^3 at the carbon site and sp^2 plus p^2 at the nitrogen site.¹⁻⁴ There have been a number of reports of crystalline phases, but most synthesis methods create amorphous (a -) $C_{1-x}N_x$ films with a nitrogen content under the desired 57% and with little sp^3 carbon bonding at high N contents.⁵

Subplantation is a general means to grow dense metastable phases using medium energy ions in which the ions penetrate the surface layer leading to the subsurface growth of a densified, quenched-in phase.^{6,7} This has been used to grow the highly sp^3 bonded tetrahedral amorphous carbon (ta -C)⁸ and cubic boron nitride.⁹ This same process can be applied to a - CN_x . The closest approach to this process is the use of alternating mass selected ion beams (MSIB) of C^+ and N^+ ions.^{10,11} However, the MSIB method is less suited to a wide-ranging study of growth conditions because of its slow growth rates.

Subplantation requires growth from a fully ionized ion or plasma beam with an ion energy of order 100 eV, so that all the growth occurs subsurface. The filtered cathodic vacuum arc (FCVA) is the simplest, laboratory scale source of a highly ionized beam of carbon atoms. Pulsed laser deposition (PLD) can also achieve this if sufficiently energetic lasers are used.^{12,13} CN_x requires the coincident deposition from both C and N ion beams. However, if a carbon ion beam from FCVA or PLD is used to ionize a background gas of nitrogen, then the N_2 pressure must be so high, over 10^{-3} mbar, to obtain sufficiently high N incorporation that this leads to a lower ionization and a loss of subplantation efficiency.¹⁴⁻¹⁶ Overall, this causes a reversion to C sp^2 bonding and lower N incorporation. This acts as a plasma limit on the growth process. Consequently, it is necessary to

use an independent source of N ions. However, most nitrogen sources such as a Kaufman source tend to have quite low ionization.¹⁷ A highly efficient, low pressure source of N ions with a low background of molecular nitrogen is needed, such as a high plasma density reactor.

In this letter, we use the FCVA as a source of C^+ ions and an electron cyclotron wave resonance (ECWR) reactor as a source of N^+ ions. A single bend, wide duct filter FCVA is used. The incident C^+ ion energy can be varied by biasing the substrate. In our system we can produce ta -C with 85% sp^3 bonding even in the absence of substrate bias because the average ion self-energy of 25–30 eV is sufficiently high to give efficient subplantation. The ECWR is an inductively coupled radio frequency source with magnetic confinement of the plasma which operates at low pressures.¹⁸ The ECWR provides a neutral plasma beam in which the ion energy can be varied independently of the ion current by a capacitively coupled bias voltage. The ECWR produces a highly ionized nitrogen plasma with the fraction of N^+ and N_2^+ ions depending on the gas residence time,¹⁸ leading to current densities similar to the FCVA.

The two sources are aimed at substrate holder. The deposition are carried out at room temperature onto Si wafers. The nitrogen pressure is maintained below 5×10^{-4} mbar during deposition. The N ion energy is 60–100 eV. This is sufficiently high to cause subplantation, but not too high to give chemical sputtering, which is another cause of reduced N incorporation.¹⁹

We first measured the effect of nitrogen pressure on the C ion flux. Figure 1 shows that a one order of magnitude increase in nitrogen pressure leads to an even larger decrease in ion current, from 0.4 to 0.01 mA/cm². Therefore, the main experiments maintained the nitrogen pressure below 5×10^{-4} mbar.

We now consider the effect of nitrogen content on C and N bonding, by varying the relative C and N ion fluxes. The composition and bonding were measured by electron energy loss spectroscopy (EELS). For this, the films were floated off

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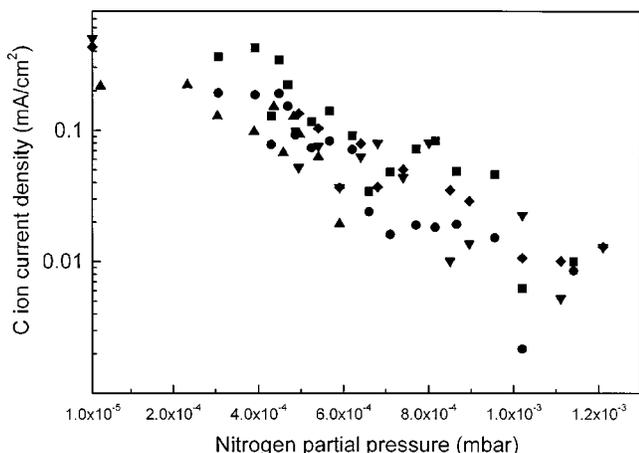


FIG. 1. Ion current density vs nitrogen pressure. Five series of runs are compared and each data point is the average of ten values to allow for fluctuations in the current density.

the substrates by dissolving the substrate in HF:HNO₃:H₂O mixture. The EELS were carried out on a Vacuum Generators HB501 scanning transmission electron microscope with a dedicated parallel EELS spectrometer of the McMullan de-

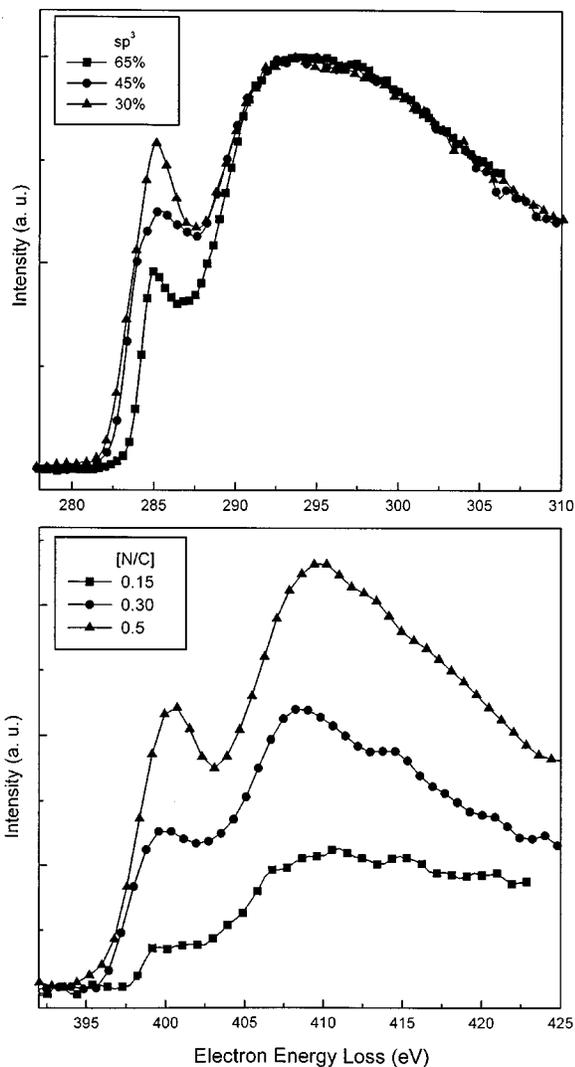


FIG. 2. C and N K edge from EELS spectra for *a*-CN_x films of three different compositions. The spectra are normalized in a window away from the edge, so the intensity reflects the change in π bonds and nitrogen content, respectively.

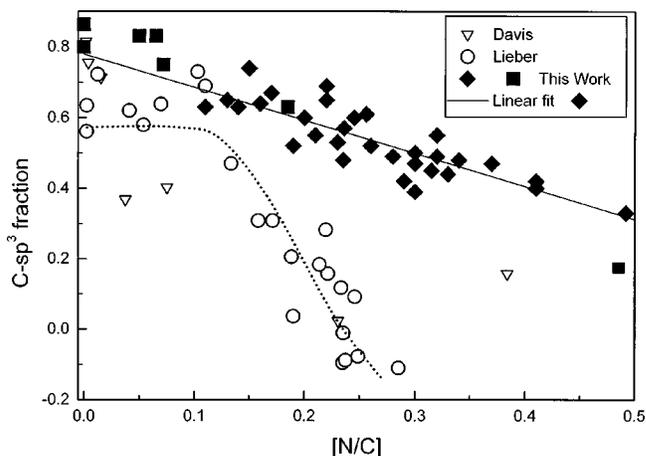


FIG. 3. Carbon *sp*³ fraction vs N/C composition ratio. Data from Davis *et al.* (see Ref. 14) and Lieber *et al.* (see Ref. 13) are included for comparison. The linear fit is obtained for samples with N/C > 0.15. Negative values in the C-*sp*³ fraction indicate C *sp*¹ bonding, probably as C≡N.

sign. The incidence and collection angles were those for the “magic angle.”²⁰

EELS spectra of films of different nitrogen content are shown in Fig. 2. The N/C ratio was derived from the relative areas of the N and C K edges, using the partial cross sections calculated by the Egerton²¹ hydrogenic model. The values were crosschecked for a batch of samples by nuclear reaction analysis.²² The C *sp*² fraction was derived from the C K edge spectra from ratio of the area of the 285 eV π^* peak to the area of a window (283.4–294 eV), to correct for differences in spectrum intensity.⁸ The ratio is normalized to the ratio for a 100% *sp*² bonded graphite standard, also measure at the magic angle. Note that *sp*¹ bonding as in $-C\equiv N$ groups can be significant in *a*-CN_x, so the π^* fraction corresponds to the sum of *sp*² sites plus twice the *sp*¹ sites (which have two π states). We cannot distinguish *sp*² from *sp*¹ by EELS, so *sp*¹ sites correspond to <0% *sp*³ bonding in the plots.

The nitrogen bonding is derived similarly from the N K edge at 400 eV and it deserves special attention. The N site in β - or α -C₃N₄ is *sp*² in the bonding plane with a filled *p*² π lone pair orbital normal to the bonding plane.⁴ Thus, there are no empty N π^* states in β -C₃N₄. The signature of C₃N₄ is an absence of both the C π^* peak at 285 eV and the N π^* peak at 400 eV. Generally, though, there are many unsaturated N configurations in *a*-CN_x, ranging from aromatic (pyridine or pyrrole) to C=N groups and nitrile ($-C\equiv N$) groups which can contribute to the 400 eV peak.

Figure 3 shows the C *sp*³ fraction as a function of N/C ratio. We see that the C *sp*³ fraction, *x*, decreases approximately linearly with N content, *n*, as

$$x = 0.78 - 0.94n.$$

The first term represents the C-*sp*³ value for N-free samples, consistent with the values measured for *ta*-C films. On the other hand, the slope, 0.94, represents the rate of decrease of the *sp*³ fraction. The fact that this value is very close to 1 suggests that the variation in C-*sp*³ fraction is mainly due to a preferential formation of C=N double bonds. This behavior contrasts with data of previous workers,^{13,14,23} also shown in Fig. 3. They found a critical N content above which the

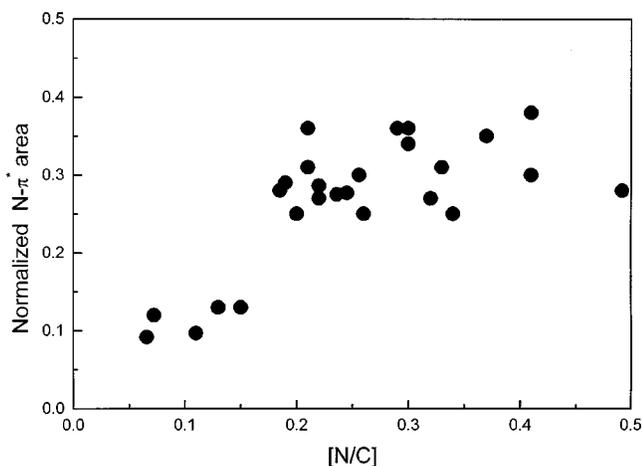


FIG. 4. Normalized π^* area of N K edge EELS spectra vs N/C composition.

sp^3 fraction falls sharply towards zero, indicating that the whole sp^3 network has reverted to sp^2 bonding.

Figure 4 shows that the N π^* fraction behaves differently. Note that these values are only qualitative as we will need a standard to get quantitative values. The N π^* fraction increases sharply from about 0.1 to ~ 0.3 at a N/C ratio of 0.2. This means that at low N content, the nitrogen is largely in $sp^2 + p^2$ bonding as in β - C_3N_4 , or N_4^+ sites with no empty π^* states, while more unsaturated π^* bonding appears above N/C=0.2.

The data of Davis *et al.*¹⁴ and Lieber *et al.*¹³ indicate a nitrogen-induced instability of C sp^3 bonding. There, N contents above a critical value cause all C atoms to revert to sp^2 bonding, not just those bonded directly to N. In our case, only those C atoms directly bonded to N revert to sp^2 bonding, which gives a gradual transition which is linear in N content. A similar effect is found in C–N molecules²⁴ and in simulations.³ Our work extends the range of high sp^3 fraction to higher N contents than in any previous work. However, so far we still get 100% sp^2 bonding at N/C=1.3. Nevertheless, our results indicate that the present direction allows progress to be made.

Concluding, the use of separate ion sources for C and N species at low operating pressures allows us to produce

hydrogen-free carbon nitride films with ~ 45 at. % N. It also shows that ion subplantation is still effective on promoting the C–C sp^3 bonding, but it is so far unable to overcome the chemical barrier to the formation of C–N single bonds. Our results confirm that plasma ionization limitations can be overcome to maximize the N incorporation and C sp^3 bonding in a - CN_x films, but that the goal of C_3N_4 remains limited by a bonding instability in the solid.

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