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Deposition of carbon nitride films using an electron cyclotron wave resonance plasma source

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Abstract

Hydrogenated amorphous carbon nitride (a-C:N:H) has been synthesised using a high plasma density electron cyclotron wave resonance (ECWR) technique using N_2 and C_2H_2 as source gases, at different ratios and a fixed ion energy (80 eV). The composition, structure and bonding state of the films were investigated and related to their optical and electrical properties. The nitrogen content in the film rises rapidly until the N_2/C_2H_2 gas ratio reaches 2 and then increases more gradually, while the deposition rate decreases steeply, placing an upper limit for the nitrogen incorporation at 30 at%. For nitrogen contents above 20 at%, the band gap and sp^3-bonded carbon fraction decrease from 1.7 to 1.1 eV and ∼65 to 40%, respectively. The transition is due to the formation of polymeric $>$C=N, $-$C≡N and $>$NH groups, not an increase in CH bonds. Films with higher nitrogen content are less dense than the original hydrogenated tetrahedral amorphous carbon (ta-C:H) film but, because they have a relatively high band gap (1.1 eV), high resistivity (10^9 Ω cm) and moderate sp^3-bonded carbon fraction (40%), they should be classed as polymeric in nature. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Bonding; Nitride; Optical properties; Plasma-assisted CVD

1. Introduction

The deposition of nitrogen-containing amorphous carbon has received particular attention since the theoretical predictions of a metastable silicon-nitride-like phase, i.e., β-C_3N_4 [1,2]. According to these predictions, this phase would have insulating properties, hardness and thermal conductivity comparable to those diamond. However, most attempts have yielded amorphous material with a nitrogen content lower than that expected (57 at%) and a low fraction of sp^3-bonded carbon [3–5].

C_3N_4 is typical of a number of superhard phases which include tetrahedral amorphous carbon and its hydrogenated counterpart (ta-C and ta-C:H, respectively). Each phase is metastable, sp^3-bonded and has greater density than the competing sp^2 phase. The degree of sp^3 bonding in these materials can be optimised by deposition from a highly ionised beam of medium-energy ions (around 100 eV) with a narrow energy distribution. Much of the work on carbon nitride has been carried out on systems with a low ionisation of the deposition flux, such as radio-frequency (RF) or direct-current (DC) magnetron sputtering [6–9] or plasma-enhanced chemical vapour deposition (PECVD) [10–12]. Relatively few attempts have been made using ion-beam sources [13–15], in which the deposition is driven by ions of controlled energy. In this work, we describe the deposition and characterisation of carbon nitride films deposited from a low-pressure plasma ion source [an electron cyclotron wave resonance (ECWR) source] at the same conditions under which ta-C:H films were previously deposited [16].

2. Experimental

The ECWR plasma beam source has been described elsewhere [16,17]. It is operated at low pressure (10^{-4} mbar) and uses a low-strength magnetic field (∼12 Gauss) to provide a high-density plasma with a high degree of ionisation. The ion energy and ion-current densities are controlled independently and the

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ion energy can be kept constant even with small variations in the pressure. The films were deposited over silicon ⟨100⟩ and Corning glass substrates as a function of the nitrogen-to-acetylene flow ratio, N_2/C_2H_2, while keeping the ion energy fixed at 80 eV. The ion energy and current density were monitored with a Faraday cup mounted in the substrate plane. Rutherford backscattering, channelling (RBS-c) and elastic recoil detection analysis (ERDA) were used to determine the nitrogen and hydrogen contents of the films using a self-consistent analysis based on the simulated annealing algorithm [18]. The bonding structure was determined by infrared spectroscopy (BONEM DA-3) in the range 400 to 4000 cm^{-1}. The sp^2-bonded carbon fraction was determined by electron energy-loss spectroscopy (EELS) carried out in a Vacuum Generator HB501 scanning transmission electron microscope with a dedicated parallel EELS spectrometer. Optical absorption spectra were derived from transmission and reflection measurements in an ATI-Unicam UV2-200 UV-VIS spectrometer. Resistivity measurements were carried out in the coplanar configuration using single gap cells at room temperature and as a function of the temperature.

3. Results

The deposition of CN films is limited by a decreasing deposition rate as N_2/C_2H_2 flow ratios are increased, see Fig. 1a. This is a consequence of the decrease in the concentration of CH growth species at high N_2/C_2H_2 flow ratios. In addition, bombardment of the growing films by nitrogen ions promotes the etching of the film [19]. The etch rate was measured by exposing a previously deposited a-C:H film to a nitrogen plasma at different ion energies. The results show that, for 80 eV and a current density of 0.15 mA cm^{-2}, the etching rate was 0.15 nm s^{-1}, which is comparable to the growth rates for high N_2/C_2H_2 ratios.

Fig. 1b shows the nitrogen atomic fraction as a function of the N_2/C_2H_2 flow ratio. The results indicate a rapid incorporation of nitrogen for N_2/C_2H_2 ratios below 2, while at higher N_2/C_2H_2 ratios the nitrogen atomic fraction seems to saturate at a value of 30 at%. The hydrogen content decreases slightly from 32 at% for the non-nitrogenated sample to around 26 at% for the highest nitrogen content, in agreement with results obtained by other groups [20,21].

The infrared (IR) spectra of some samples are shown in Fig. 2. In the spectrum of the nitrogen-free sample (ta-C:H) the only feature is the C—H stretching band around 2700–3000 cm^{-1}. When the nitrogen atomic fraction is increased, the following features are observed.

1. The absorption of the CH_x stretching bands at 3000 cm^{-1} decreases, while the absorption of the N—H band around 3300 cm^{-1} increases. There may be some contributions from OH bonds caused by absorbed water after exposing the film to the atmosphere [22]. However, the oxygen concentration detected was less than 2.5 at% for all the samples and no evolution of this band has been observed, suggesting mainly N—H bonds. Moreover, water is

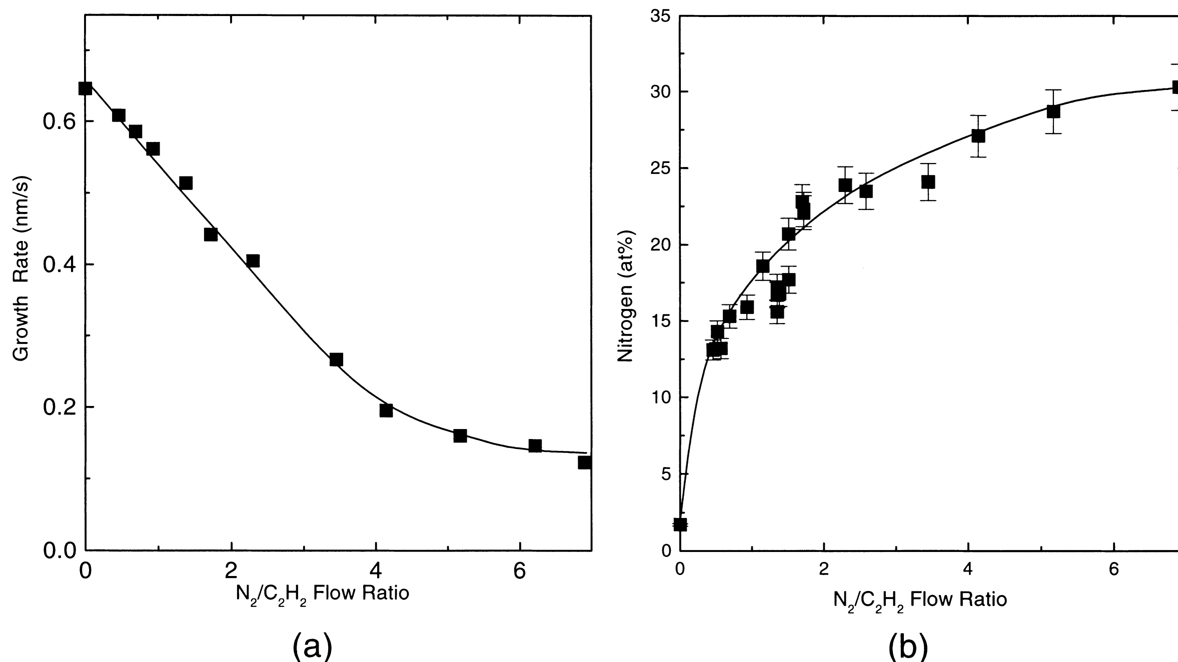

Fig. 1. (a) Deposition rate as a function of the N_2/C_2H_2 flow ratio. (b) Atomic nitrogen concentration as a function of the N_2/C_2H_2 flow ratio obtained by RBS/ERDA.

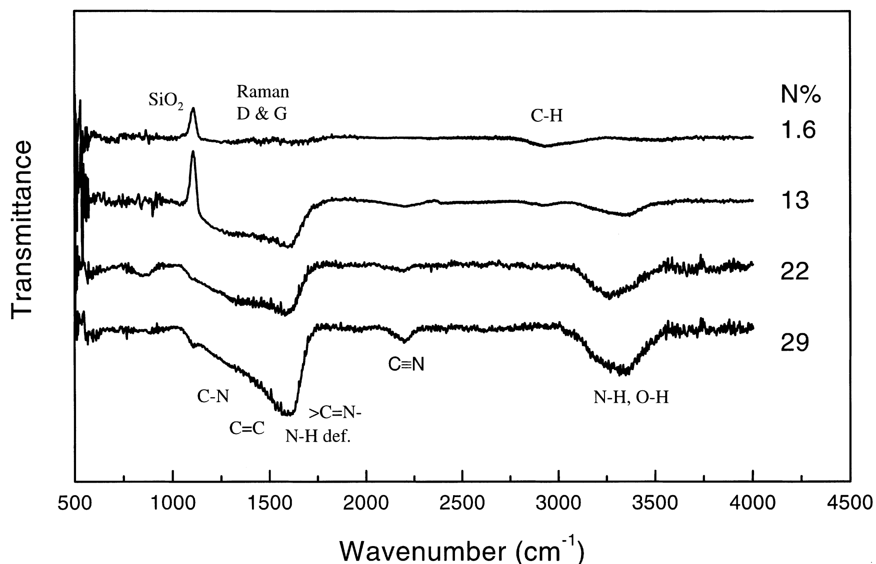

Fig. 2. Normalised Fourier transform infrared (FTIR) transmittance taken from films with increasing nitrogen content.

mainly incorporated into low-density CN films through the formation of hydrogen bonds (N—H... O, O—H...N), producing a broad IR signal that can extend from 2000 cm^{-1} to 3600 cm^{-1}.

2. The absorption in the 1500 cm^{-1} region increases and becomes asymmetric with a clear maximum around 1600 cm^{-1}, characteristic either of C=C or C=N double bonds and NH_2 bending modes. As the increase in the 1600 cm^{-1} band follows the increase in the 3300 cm^{-1} modes, we attribute the band at 1500 cm^{-1} to olefinic bonds (=N—C, =N—H and RNH_2) rather than exclusively due to the IR-active D and G bands proposed for CN films [23].
3. The C≡N absorption increases. However, the analysis of infrared bands due to C≡N in organic molecules shows strong variations in the intensity, limiting its use as diagnosis. For example, a low concentration of C≡N can give a strong IR signal when there is a nitrogen atom attached directly to the nitrile (N—C≡N), meanwhile the intensity of the C≡N signal is quenched by the presence of oxygenated groups [24,25]. In the Raman spectra, however, the band is always strong. Analyses of the films by Raman spectroscopy are in progress and will be reported elsewhere.

Fig. 3 shows the sp^2 carbon fraction of the films from EELS as a function of the nitrogen content. The carbon sp^2 fraction is calculated by modelling the π^* peak of the C-edge with a Gaussian, which is then normalised to the experimental spectra and compared with the equivalent area for a suitable standard (100% a-C). The possible source of error associated with this calculation for carbon nitride films comes from the presence of sp^1 states of C≡N groups that are unusual for carbon films, but clearly present in carbon nitride films as seen in the IR spectra. However, the main effect of the sp^1 states will be to overestimate the sp^2 carbon fraction [26], which is not the case for these films. The carbon sp^2 fraction is seen to remain within the range 30–40% up to a nitrogen content of 20 at%, where the sp^2 fraction rises sharply to about 60% and remains in that range for higher nitrogen contents. The valence plasmon energy was also measured by EELS, and used to derive the mass density. It decreases from 2.4 g cm^{-3} for ta-C:H to around 1.8 g cm^{-3}, in good agreement with the values obtained by ERDA and RBS.

The optical properties were obtained from transmission and reflection spectra measured in the ultraviolet–visible range (300–1100 nm). The complex refractive index was calculated using standard formulae for transmission and reflection of thin films deposited on transparent substrates. It is found that the refractive index decreases from 2.3 for ta-C:H down to 2.0 for a-C:N:H samples. The absorption coefficient was obtained from the imaginary part of the refractive index, and the Tauc and E_{04} gaps can both be calculated from the absorption spectra. For simplicity only the Tauc gap is shown in Fig. 4 as a function of the nitrogen content. The optical gap decreases gradually from 1.7 to 1.4 eV at 20 at% nitrogen. Thereafter, the gap falls sharply to 1.1 eV and then remains almost constant for further nitrogen incorporation. This is probably due to the increased sp^2 carbon fraction.

The room-temperature conductivity increases initially as nitrogen is incorporated from 5×10^{-9} S cm^{-1} for ta-C:H to 4×10^{-6} S cm^{-1}, but for nitrogen content >20 at% it decreases rapidly, attaining a value of 1.6×10^{-10} S cm^{-1} for 30 at% nitrogen. The activation energy was derived from an Arrhenius plot of the

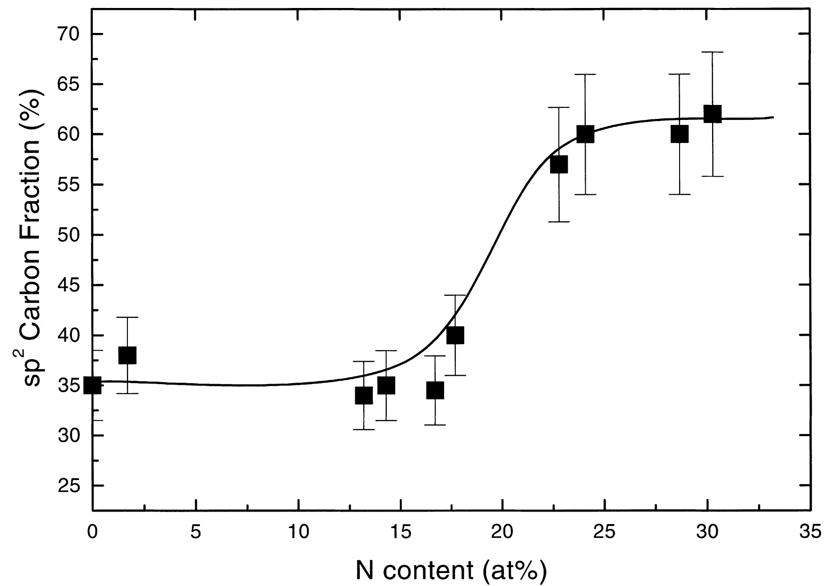

Fig. 3. The sp^2-bonded carbon fraction of the a-C:N:H films as a function of the nitrogen content, measured by EELS and calculated from the normalised area under the 1s–π^* pre-edge, which is then compared with that of a 100% sp^2-bonded amorphous carbon standard.

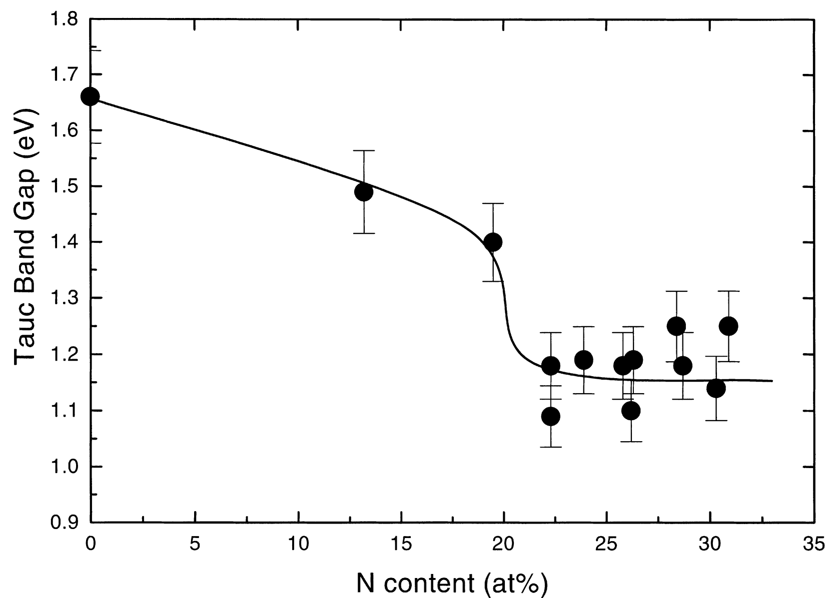

Fig. 4. Variation of the band gap as a function of the nitrogen content. For simplicity only the Tauc is shown. The E_{04} was slightly higher with a similar trend.

variation of the conductivity with $1/T$ in the temperature range 40–200°C. The results can be approximated well by a linear fit in the 40–150°C range with prefactors σ_0 in the range 10^{-2}–10^{-3} S cm^{-1}, indicating that the conduction mechanism is mainly localised state hopping in the band tails. The variation correlates with the changes in conductivity, showing a minimum for nitrogen content around 20 at% of 0.26 eV compared with 0.39 eV for ta-C:H and 0.58 eV for the 30 at% nitrogen sample. These results may suggest nitrogen doping of the ta-C:H films where no compensation is observed, as undoped ta-C:H produced from acetylene gases are n-type due to nitrogen contamination in the gas [27].

4. Discussion

We have shown that chemical etching of the carbon film by nitrogen ions imposes limits on the growth rate of carbon nitride films. The chemical sputtering process described before results in the evolution HCN and CN species, which cannot account for the low nitrogen

content since equal numbers of carbon and nitrogen atoms are removed. In addition, molecular N_2 must be formed at or below the film surface as reported elsewhere [3,28]. This N_2 can then diffuse to the surface or stay inside the film, inducing the formation of voids, which may account for the low density obtained in carbon nitride films, in combination with the formation of terminating groups such as $=N-H$ and $-C\equiv N$.

The optical, electrical, EELS and FTIR data indicate that structural modifications are induced in the deposits by increasing the nitrogen content. Below 20 at% nitrogen the sp^3-bonded carbon fraction remains constant even with the decrease in the CH bonds. Electrical measurements suggest a doping effect as the conductivity is increased by three orders of magnitude and the activation energy for conductivity decreases; however, doping itself cannot explain the decrease in the optical band gap and the nitrogen content is too high for doping. Clustering of the sp^2-bonded carbon sites induced by the incorporation of nitrogen may be responsible for the decrease in the optical gap, without affecting the sp^3 carbon fraction, so it is likely that nitrogen in ta-C:H occupies sites where doping is effective but at the same time clustering of the sp^2 carbon is promoted. For nitrogen contents higher than 20 at% the film becomes polymeric, forming olefinic, nitrogen-containing chains rather than aromatic sites, indicated by the presence of $=N-C$, $=N-H$ and RNH_2 vibrations in the IR spectra, while the conductivity decreases again.

The reason for the transition from a ta-C:H:N film to a polymeric a-C:N:H film is not clear. Other works on carbon nitride samples have shown similar transitions. Carbon nitride samples deposited by cathodic arc under different nitrogen partial pressures [29] showed a decrease in the sp^3 carbon fraction that could be attributed to the increase in the deposition pressure, as the current density and ion energy strongly depend on the mean free path. In our case the ion energy and current density were measured and kept constant for each sample, thus a different mechanism is responsible for the transition observed in these films. Hu et al. [30] noted a more drastic transition for samples deposited by plasma-assisted pulsed laser ablation at nitrogen concentrations $\sim 14\%$, which they explained as a nitrogen-driven relaxation of sp^3-bonded carbon to sp^2 bonding as a consequence of repulsion between carbon dangling bonds and nitrogen lone pairs. Alvarez et al. [31] showed a density transition for films deposited by dual ion-beam deposition around 20 at% nitrogen due to a transition from a planar structure to a more corrugated structure with the subsequent formation of voids and dangling bonds. However, this assumes an initial ordered graphitic phase instead of an amorphous phase.

So far, it is not clear what is promoting these structural changes. One possibility involves the effect of the nitrogen concentration on the relative stability of the various CN bonding configurations [20]. Alternatively, the growth process may be affected by the decrease in film density as a consequence of the lower nitrogen covalence and the formation of $N-H$ and $C\equiv N$ terminating bonds and voids. In a-C:H it is well established that the incident ions promote dehydrogenation and the formation of tetrahedral carbon bonds if they are able to densify the growing film [32,33]. Nevertheless, in a low-density or floppy film, the subsurface-implanted ions are accommodated without resistance, hence there is no possibility to further densify the film and therefore the formation of sp^3 bonds is suppressed.

5. Conclusions

a-C:N:H films containing up to 30 at% nitrogen were deposited from mixtures of N_2 and C_2H_2 using a low-energy flux of ions, generated by a low-pressure plasma source. The combination of high ionisation of the nitrogen gas and low-energy bombardment allows the nitrogen content in the films to attain higher values than those reported for conventional PECVD systems or even electron cyclotron resonance (ECR) sources. Film properties were correlated to the nitrogen content within the films. The highly tetrahedral phase of the ta-C:H sample is retained up to 20 at% nitrogen, where a transition is observed. This results in soft carbon nitride films with similar properties to polymer-like a-C:H films with the exception that, in this case, hydrogen is preferentially bonded to nitorgen and the skeletal structure is predominantly formed by $C=N$ bonds. This polymer-like structure is different from the reported paracyanogen-like carbon nitride phase in which also insulating properties are observed, since the role of hydrogen, in our films, is to saturate nitrogen bonds, inhibiting the formation of aromatic structures.

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