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Gas evolution studies for structural characterization of hydrogenated carbon nitride samples

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Abstract

Gas evolution experiments have been performed on hydrogenated carbon nitride samples in order to study the thermal stability of such samples and to investigate the presence of molecular nitrogen within the samples. The films were deposited by a combination of nitrogen and acetylene as precursor gases using an electron cyclotron wave resonance source. The results show for the release of molecular hydrogen broad effusion transients extending from approximately 300 to 900 °C. In addition to H_2 and hydrocarbons C_xH_y, usually observed for hydrogenated carbon films, there is a significant release of HCN molecules. This effusion also sets in at temperatures near 300 °C and shows a broad maximum near 700 °C. Above approximately 500 °C, for most of the samples the evolution of nitrogen rises steadily with increasing temperature, i.e. the effusion maximum is at temperatures exceeding the temperature range (100–1050 °C) investigated. However, in the nitrogen content range from 15 at.% to approximately 25 at.%, a peak near 300 °C is also observed. It becomes less pronounced at higher nitrogen content. This peak is probably a consequence of molecular nitrogen that is included in the sample without bonding, in (isolated) voids or bubbles. The implications for film properties, composition and thermal stability are discussed.

Keywords: Carbon nitride; Thermal stability; Desorption, Tetrahedral amorphous carbon

1. Introduction

Since the theoretical prediction that if a tetrahedral-bonded carbon nitride (C_3N_4) material exists, it should be a super-hard phase [1], many works on CN compounds have been published. Most of these compounds have been prepared as thin films given that the theoretical studies indicate that the material would be metastable [2]. Now, after more than 10 years of research, three major problems in the search of the super-hard crystalline phase have been identified: (1) almost all the deposited CN films are amorphous; (2) the films are nitrogen deficient; and (3) the predominant CN bond is trigonal, not tetrahedral [3–6]. Research on CN compounds still continues in order to understand the reasons controlling the previous behavior and because CN amorphous films presented other unusual properties calling for further investigation.

One of the main routes for the production of CN thin films have been by conventional plasma-enhanced chemical vapor deposition (PECVD) systems [7,8]. In this case a combination of a hydrocarbon gas (CH_4, C_2H_2, ...) with molecular nitrogen and/or ammonia lead to the formation of hydrogenated carbon nitride films (a-CHN). Most of these films contain very low nitrogen contents, up to 15 at.%, which seem to be a consequence of the low ionization of the nitrogen gas used. In this paper we presented effusion experiments on a-CHN films prepared by a more efficient plasma source that permits N incorporation up to 30 at.% [9–11]. Nevertheless, we also observed the nitrogen content saturation reported by many other authors. It is now generally agreed that chemically enhanced preferential sputtering of N with respect to carbon is responsible for this limitation [12,13] and for hydrogenated CN films, nitrogen content is also limited by the formation of

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HCN species in the gas phase [14]. In general, effusion of volatile species, such as CN, C_2N_2, HCN and N_2 during the deposition of the films has been observed. These species remove C and N atoms leading to a lower deposition rate and to limited nitrogen content. Formation of all these molecules becomes more probable the higher the nitrogen concentration and this explains the saturation in N content [15]. If N_2 molecules are formed within the film, due to the proximity between two nitrogen atoms, and then diffused out through the voids, from the growing film, it is expected that some of these N_2 molecules stay within the film once the deposition is interrupted. However, there is very little evidence of the presence of N_2 bubbles within the film, except by Grigull and Jacob [16], where N was implanted (20 keV) in hard amorphous carbon films at both room temperature (RT) and high temperature (HT). They demonstrated that during room temperature implantation, molecular nitrogen was formed within the films.

In the search for further evidence we decided to perform effusion experiments, since any N_2 molecules may evolve (within an open network structure) at rather low temperature, as no bonds are broken. Effusion experiments are also very useful to study the thermal stability of the films, which is an important issue for any application. There are many reported works on the thermal stability of non-hydrogenated CN films. They agree in that there is nitrogen and weight loss, but the temperature at which the process starts is different from sample to sample, ranging from 300 to 600 °C [17–20]. Hydrogenated CN films have been less studied [21,22]. Franceschini et al. [21] concluded that the out-diffusion of N and H involved the formation of molecular species within the bulk followed by transport to the surface via voids in the material. N incorporation was considered to increase the interconnected network of voids and thus H effusion occurs at lower temperature than for a-CH films. There is an important difference between Franceschini's films [21] and ours. One is the higher nitrogen content in our films and the other is related to the fact that even for a-CH films the transients are different depending on the C-sp^3 bonding fraction [23,24]. Our films were produced by means of a highly energetic plasma source able to produce tetrahedral a-CH films (ta-CH), whereas Franceschini's films were produced by a conventional PECVD system and therefore the films have a very low content of C-sp^3 bonds.

In this paper, we studied the effect of nitrogen addition into ta-CH on the predominant transients observed in an experiment of thermal effusion.

2. Experimental

The ta-$C_xN_yH_z$ films were deposited onto silicon ⟨100⟩ and Corning glass substrates as a function of the nitrogen to acetylene gas flow ratio (N_2/C_2H_2), raising the nitrogen partial pressure up to 85% in the gas phase. The ion energy, pressure and power were kept fixed at 80 eV, 5×10^{-4} mbar and 300 W, respectively. The elemental composition in the deposited ta-$C_xN_yH_z$ films was determined by channeling Rutherford Backscattering (RBS) and elastic recoil detection analysis (ERDA). The bonding structure was determined by X-ray photoelectron spectroscopy (XPS). The XPS analyses were carried out with a Perkin Elmer 5500 spectrometer using the AlKα line.

For the gas evolution experiments, the as-deposited films were inserted into a quartz tube evacuated by a turbomolecular pump, and they were heated to 1100 °C at a heating rate of 20 °C/min and the effusing gases were pumped through a quadrupole mass analyzer (QMA) with which the flow of 18 different masses was recorded (almost) simultaneously. A constant and well-defined He flow through a calibrated capillary was simultaneously monitored during the effusion scans to ensure the stability of the quadrupole mass analyzer during the experiments. For a fixed pumping speed of the turbomolecular pump the partial pressure is a measure of the evolution rate dN/dt. Absolute calibration is achieved by inserting a known flow of gas through a calibrated leak.

For a correct identification of the effused species the fragmentation pattern of all the hydrocarbons caused by the ionization source of the QMA are crucial. For example, mass 26 is typical of C_2H_4, but it must appear with mass 27 of approximately the same height. However, mass 26 and mass 27 are also expected for hydrogen cyanide (HCN), but with a different ratio. In this way it is possible to assign mass 26 and 27 to HCN for the nitrogenated samples [25]. The assignment was verified by measuring more than one characteristic mass number for each gas species and by comparing the signal heights with those obtained by inserting the respective gases into the evolution apparatus.

3. Results

Fig. 1a shows the N 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 N atomic fraction seems to saturate at a value of 30 at.%. The hydrogen content (Fig. 1b) decreases slightly from 33 at.% for the non-nitrogenated sample to approximately 26 at.% for the highest nitrogen content, in agreement with results obtained by other groups [7,26]. The mass density is also plotted in Fig. 1b. Film density decreases as the nitrogen content increases and hydrogen content decreases. The decrease in film density when the hydrogen content is also decreasing is probably related to the formation of terminating bonds such as NH and CNsp^1 as evidence by infrared spectroscopy [10] and/or could

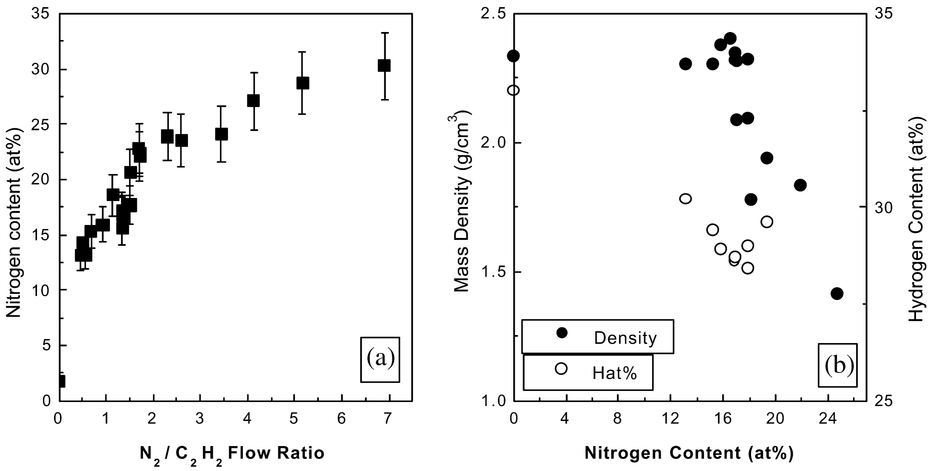

Fig. 1. (a) Nitrogen content measured with ERDA as a function of the nitrogen to acetylene flow ratio. (b) Variation of the mass density and hydrogen content with the nitrogen concentration of the films.

be related to the out-diffusion of molecules (N_2, HCN) during film growth causing a porous structure. Other film properties, such as, deposition rate, optical gap, conductivity, C-sp^3 fraction and vibrational properties have been published in previous papers [9,10].

XPS spectra for the C and N 1s peaks are shown and discussed in Rodil et al. [9]. For the purpose of this paper we are interested in studying the nitrogen peak with more detail. Fig. 2 shows the N edge before and after sputtering the film surface with 4 keV argon ions. The tail at high binding energies is usually related to NO or NN bonds. In Fig. 2 we show that after cleaning the surface, the tail has evolved into a more clear peak and its relative intensity has increased, even though oxygen has been completely removed from the surface, as was seen in a survey scan after cleaning. Thus, this peak can be undoubtedly assigned to the presence of N–N planar bonds. The high intensity also suggests that molecular N_2 is present within the films [16].

Fig. 3 shows the thermal effusion transients of three selected masses representative for the dominating species released from ta-CNH films with different nitrogen content. The transients shown are raw data not corrected for the sensitivity of the mass analyzer because, at the present stage, it was not possible to obtain the sensitivity of HCN gas due to its high toxicity. Nevertheless, we

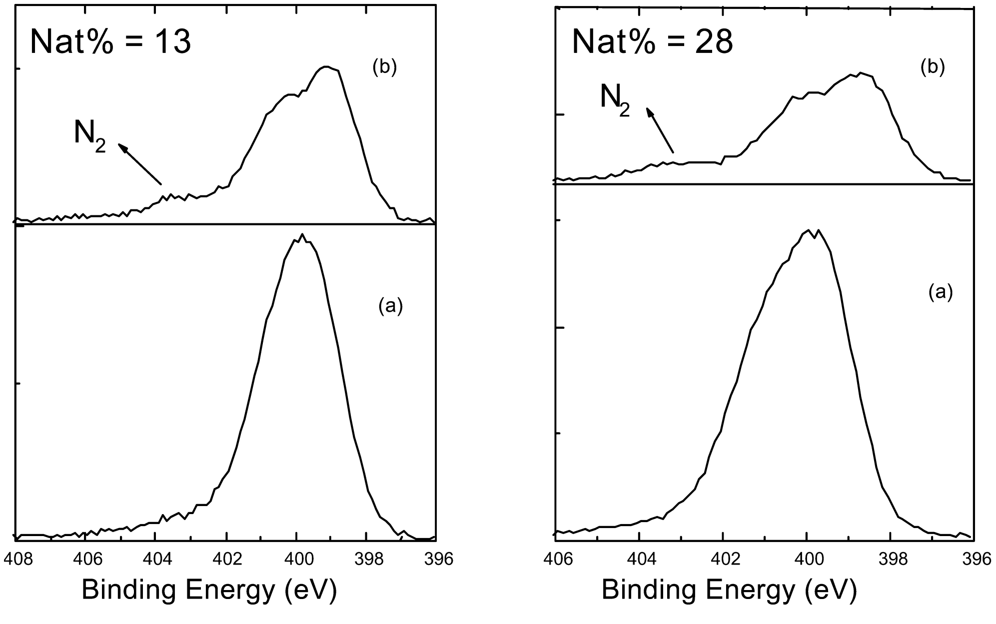

Fig. 2. XPS spectra of the N 1s level obtained (a) prior and (b) after Ar$^+$ sputtering cleaning for two representative samples with different nitrogen content.

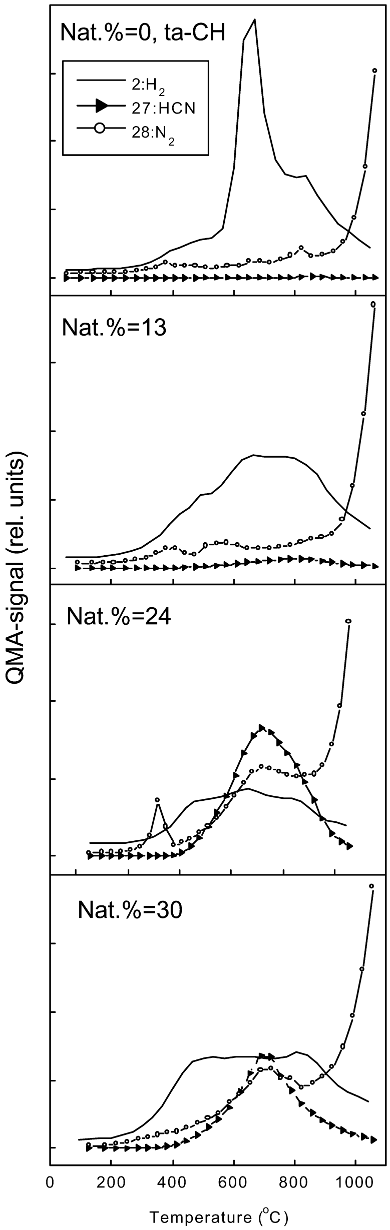

Fig. 3. Effusion spectra of H, HCN and N_2 for ta-CHN films of different nitrogen content.

compare the observed transients with the fragmentation pattern of relevant species and we can conclude that only these three species contribute notably to the effusion.

Quantitative evaluation of the atomic density for H_2 and HCN are shown in Fig. 4, using adequate sensitivity factor for H_2 but not for HCN. The atomic density of H_2 is seen to decrease in agreement with ERDA results, while the relative HCN atomic density shows an increase as the nitrogen content in the films increases.

Fig. 5 shows corrected transients of mass 28 ($=N_2$) for samples with different nitrogen content. Nitrogen is mainly released in the form of molecular nitrogen and HCN at a threshold temperature of 400 °C. Note, however, that for N% = 0 the mass 28 is clearly not N_2 but some hydrocarbon which effuses at temperatures above 1000 °C and which signal might also be present for the nitrogenated samples. It is important to note that for some samples there is a low temperature peak, approximately 300 °C, probably due to the presence of N_2 molecules.

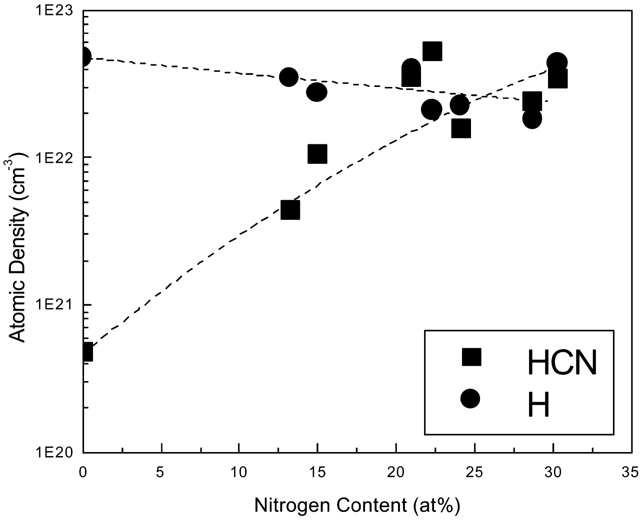

Fig. 4. Variation of the hydrogen and relative hydrogen cyanide atomic density as a function of the nitrogen content.

4. Discussion

4.1. XPS

The presence of trapped molecular nitrogen in a-CN films deposited at low energies is of importance, since

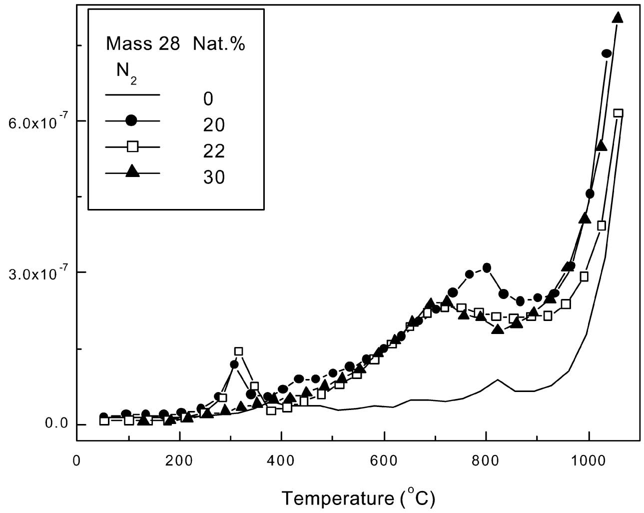

Fig. 5. Effusion transients of nitrogen (mass 28) for ta-CHN films of different nitrogen content. The vertical axis is the quadruple mass analyzer signal normalized to the studied volume and the calibration factor for N_2.

it may demonstrate that the key process responsible for the saturation of the nitrogen content within the films is the formation of molecular nitrogen either at or below the film surface. After in situ sputtering of the films, analysis of the N1s core level spectra showed a strong reduction of the nitrogen content and some structural changes induced by the bombardment as seen by other groups [27,28]. The two main components in the N1s core line were well resolved, suggesting evolution of hydrogen as a consequence of the bombardment. However, the most important result is that the peak related to molecular nitrogen (402 eV) is enhanced, suggesting the presence of N_2 bubbles embedded in the sample.

4.2. Gas evolution

For diamond-like carbon films like ta-CH shown in Fig. 3, the vast majority of hydrogen is released in the form of molecular hydrogen at a very sharp high-temperature threshold which is indicative of the sp^3-rich tetrahedral network and the predominance of a low number of isolated voids. As the nitrogen content increases the H_2 transient becomes broader and flat and threshold temperature decreases from 600 to 300 °C (see Fig. 3). This has been shown to be an indication of a replacement of the isolated voids by a network of interconnected voids for a-CH films [23,24]. However, opposite to the results from a-CH films, for the nitrogenated samples there is not significant effusion of heavy hydrocarbons, such as, methane or propane. Therefore, even if with the N incorporation film properties, such as, optical gap, sp^3/sp^2 ratio and density change in a trend indicative of a transition from DLC to polymer-like films the effusion transients of these highly N-doped films are considerably different from those of polymer-like a-CH films, suggesting that the chemical structure is different.

The other two prominent transients in the evolution experiment are HCN and N_2. Hydrogen cyanide is the second effusion mechanism for hydrogen and it increases as the nitrogen content increases. The threshold temperature for the evolution of HCN species remains unchanged for samples with different nitrogen content and lower density, suggesting that it is not related to the diffusion of HCN in the network but rather to its formation by the rupture of CH, NH, CN and/or CC bonds and the simultaneous formation of HCN molecules (and, possibly, C–C bonds) that then diffuse out the film. From the temperature of the effusion maximum ($T=700$ °C) a free energy of desorption of approximately 3 eV can be estimated [29].

For the N_2 transient shown in Fig. 5 there is a small peak at 300 °C for samples with a N content of approximately 20 at.%. For low density a-C:H [23,24] or a-Si:H [30] films a similar low temperature peak in the H_2 transient has been ascribed to the evolution of gas species bound to internal surfaces and originates from H recombination into H_2 molecules that rapidly diffuse along an open path in the material. In the case of ta-CHN, we think that this low temperature peak in the N_2 effusion transient is due to N_2 molecules trapped within the film that easily diffuse out through the interconnected network of voids as the temperature increases.

The fact that this N_2 peak is not observed for the most nitrogenated samples may be related to the probability of N_2 formation and diffusion. As the nitrogen content in the films increases the probability of formation of N_2 molecules increases, however, for the most nitrogenated films, the mass density has decreased to very low values (Fig. 1b). Therefore it is possible that the formed N_2 molecules diffuse out the films during the deposition, leaving pores in the material. As a result, the overall nitrogen content saturates and the film density decreases as shown in Fig. 1a,b.

The main effusion of nitrogen occurs at much higher temperatures than hydrogen, which is an important issue for applications. High temperature peaks in the N_2 transient occur near 700 °C and above 1000 °C. We tentatively attribute the lower temperature effusion to the formation of molecular nitrogen by the rupture of two CN bonds and the simultaneous formation of CC bonds; in the higher temperature effusion the formation of C–C may not be involved and there also might be some intensity contribution from a hydrocarbon gas, as observed for the ta-CH film.

5. Conclusions

We studied the thermal stability of highly nitrogen doped ta-CNH films showing that any possible application for such films is limited to temperatures below 300 °C. Above this temperature H and N losses would provoke severe structural changes. Effusion is dominated by H_2, N_2 and HCN species, the H atomic density decreases as the nitrogen content increases, while the HCN and N atomic density increases. The transient of the high nitrogen content films are different from those of low or no nitrogen content, indicating the different chemical environment, while other films properties are very similar. We found that the low temperature (300 °C) peak in the N_2 transient could be associated to the presence of molecular nitrogen embedded within the samples, in agreement with the XPS results and theories that associated the limited nitrogen content to the formation of volatile N_2 dimers.

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