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Characterization of high nitrogen content carbon nitride thin films by RBS and infrared techniques [1]

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Abstract

Carbon nitride compounds have attracted much interest due to the predicted superior properties of C_3N_4. Carbon nitride thin films have been produced by reactive DC magnetron sputtering and rf PECVD. Of paramount importance to study the growth of CN films is the accurate determination of their composition in order to evaluate whether an ideal phase can be obtained. The film composition and density were obtained using 1.94 MeV $^4He^+$ RBS. The films have been also characterized by FTIR spectroscopy, profilometry and ellipsometry. © 1998 Published by Elsevier Science B.V.

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1. Introduction

Carbon nitride compounds have recently been a subject of great interest due to the hypothetical superior properties that β and cubic phases of C_3N_4 would have [1]. Methods that involve plasmas, used to produce other metastable hard materials such as diamond and cubic boron nitride, have been employed in the numerous attempts to produce thin layers of C_3N_4 [2–5]. However, most experimental efforts to synthesise these forms have lacked sufficient nitrogen incorporation or failed to produce crystalline materials; it is then very important to establish the mechanisms whereby more nitrogen can be incorporated into the material being produced, and to this end a reliable and precise technique to determine composition has to be used in its characterization. Being composed of light elements, CN does not always allow an easy determination of the exact stoichiometry, either due to the lack of sensitivity of the techniques employed or to the preferential nitrogen loss during sputtering of the films. Nuclear techniques offer an exceptional method to determine composition and to observe its evolution with growth, which can give clues to how nitrogen is incorporated into the grown films.

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In this paper we study the composition of C–N films and relate them to the preparation conditions used in two plasma methods: plasma enhanced chemical vapour deposition (PECVD) and reactive magnetron sputtering (RMS). These relationships have given some important information about the growth of such films, indicating that at low ion bombardment conditions nitrogen is incorporated mainly through the retention of nitrogen-containing species which possesses a dipole moment.

2. Experimental details

Films were prepared in two systems: a conventional parallel plate capacitively coupled rf PECVD reactor and a magnetron sputtering reactor. The samples produced in the former system were deposited onto crystalline (1 0 0) silicon substrates, placed both on the powered and grounded electrodes. Pressure was varied between 90 and 300 mTorr. The rf power was varied from 50 to 300 W. No external heating was used. The total gas flow was kept constant at 50 sccm and the ratio of N_2 to CH_4 was varied from 1 to 9. The sputtered samples were deposited onto (1 0 0) c-Si wafers placed 4 cm below the graphite (99.99% purity) target, using currents which varied from 0.1 to 1 A and sputtering voltage between 550 and 625 V. Argon and nitrogen were used as the sputtering and reactive gas, varying the argon flow fraction (Ar/Ar + N_2) from 0 to 1 in 0.25 steps; the total gas flow being between 30 to 35 sccm. Deposition pressure was varied from 10 to 40 mTorr, following a base pressure of the order of 10^{-6} Torr. These samples were heated by means of a resistive heater to temperatures between 50°C to 520°C. The substrate holder was biased externally by a DC power supply between 0 and −400 V.

Ion beam analysis (IBA) techniques were carried out with the 5.5 MV van de Graaff accelerator at the National University of Mexico. The atomic concentration was measured with the RBS technique, using 1.94 MeV α particles, that were elastically scattered from the sample and detected by a solid state surface barrier detector subtending a solid angle of 1.8 msr, set at a laboratory angle of 165°. The total energy resolution of the RBS spectrometer was 25 keV. The quantitative analysis of the samples was performed by simulating the backscattered α particle spectra obtained in the measurements with the RUMP software [6].

Other ex situ techniques were used to characterize the films. Vibrational spectra were obtained with the aid of a Nicolet 205 FTIR spectrometer. Ellipsometry measurements on a Gartner ellipsometer were also taken from some of the films to determine the index of refraction at 632 nm, as well as to estimate the thickness. A Dektak II profilometer was used to determine thicknesses which were used then to derive the films' mass densities from the atomic areal densities set in the RUMP simulations. Most films were 2000–4000 Å thick as deposition times were typically 30 min.

3. Results and discussion

Fig. 1 shows the backscattering spectrum of a CN_x film prepared by RMS using a 50–50 mixture of argon and molecular nitrogen and applying a −200 V to the substrate holder, which was kept at a temperature of 150°C. Argon incorporation

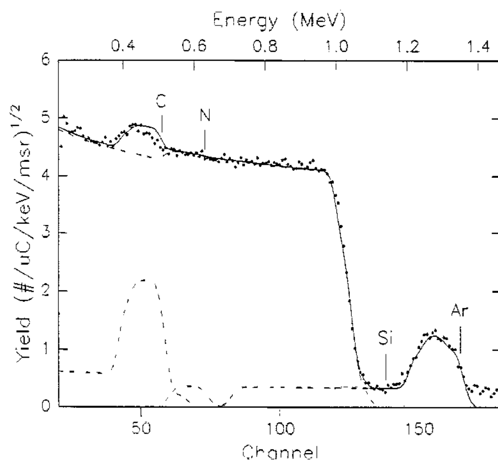

Fig. 1. A typical backscattered spectrum (dots) of 1.94 MeV $^4H^+$ ion incident on a thin CN_x film layer on a silicon substrate. Scattering geometry is set up for normal incidence and $\theta = 165°$, $\Delta\Omega = 1.8$ msr. The solid line in the spectrum simulation using the RUMP program. The dashed lines are the partial simulation of the component (C, N, Si and Ar) of the spectrum.

into the film through to the silicon–CN_x interface can be identified from the spectral information between channels 142 and 169; also present in the interface are silicon and carbon which might have formed silicon carbide and may be responsible of a high hardness values reported earlier [7]. Fig. 2 shows the composition ratio x (N/C) averaged through the whole thickness, deduced from RBS measurements, and the deposition rate (determined from dektak measurements) as a function of the fraction of argon flow (Ar/Ar + N_2). The greater the argon flow, the lower the deposition rate and apparently the nitrogen content; it can be noticed though that one of the N/C values determined for a sample prepared using only argon is different from zero, this is due to the fact that it was prepared after a deposition run that used a nitrogen and argon gas mixture without thoroughly cleaning the reactor, suggesting that one of the sources of nitrogen are the deposits on the walls. Examples of similar "contamination" or "memory effects" have been reported [8,9] in sputtering systems where carbon nitride was prepared.

Using optical emission spectroscopy we have detected the presence of CN in the plasma through the identification of some of its emission lines [7], finding that as the deposition pressure is increased the emission intensity grows as probably does the density of this radical in the gas phase. Results that confirm this have been reported by Kaltoffen et al., who used mass spectrometry in a sputtering system [10]. We have also observed that as the pressure increases from 10 to 20 mTorr the nitrogen content increases dramatically when a nitrogen-only plasma is used in RMS.

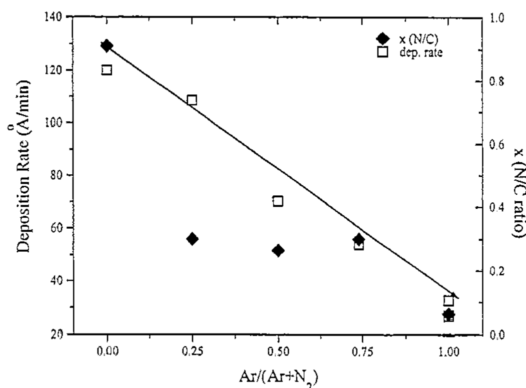

Fig. 2. Composition ratio x (N/C) averaged through the whole thickness and deposition rate as a function of the argon fraction of total gas flow, for samples prepared at 150°C applying a negative bias of 200 V to the substrate holder. The arrowed line is only a guide to the eye.

Another condition necessary for relatively high nitrogen content in RMS samples is the utilization of low sputtering powers. In our case, the range needed to obtain N/C ratios higher than 0.75 (>40% atomic nitrogen) was from 55 to 125 W; when the sputtering current was set at values equal to or greater than 0.5 A, the nitrogen content went down. There are other examples in the literature that confirm this is indeed true [3,10,11]. Kaltoffen et al. suggest that low power produces high nitrogen content because little energy, in the form of bombarding ions, is supplied from the plasma to cause the desorption of volatile species, which in the RMS case contain nitrogen (N_2^+, CN, etc.) and have a dipole moment, so Van der Waals forces can keep them bound to the surface. The data in Fig. 2 seem to support this model: less nitrogen in the plasma diminishes the formation of volatile nitrogen-containing radicals at the same time that argon impinging on the surface impedes the adsorption of nitrogen-containing radicals or even knocks off some of them from the surface. It can be argued of course, that the diminishing deposition rate is due to the reduction of the chemical sputtering rate of the carbon target [11]; although this may account for part of it, the fact that we and other researchers have observed that: (a) deposition rate and nitrogen content diminish with temperature [5,12] and (b) that both parameters also decrease at higher biases [11], suggests that volatilisation of nitrogen-containing species impedes the growth of CN_x films in RMS reactors and also reducing the value of x. We notice that low power supplied by the plasma may imply that energetic ions can bombard the surface but in small numbers, or that many ions bombard the surface but with rather reduced energies. In either case the plasma can also supply enough nitrogen-containing species to the growing surface in order to compensate for those that have been lost due to bombardment.

Densities of the films were estimated to be between 1.6 and 2.8 g/cm^3. The index of refraction tended to track the density values, i.e. the denser the film the higher the index of refraction. The index of refraction was smaller for samples prepared without nitrogen.

For the PECVD samples, the IBA techniques proved to be very useful for those deposited at the grounded electrode; they were polymer-like and electron-based techniques such as EDS that caused the loss of nitrogen and damage to the films; RBS did not visibly affect these films. Samples prepared using a N_2/CH_4 gas ratio of 9 and 1, in both cases on the grounded electrode, with rf power and pressure kept constant, were analysed using this technique. The best fit for the former sample yields a value of $x = 1$, whereas for the latter $x = 0.33$. From the IR spectra, in Fig. 3, where the absorbance due to triple and double cumulated bonds (in the 2000–2250 cm^{-1} region) is remarkably increased when the N_2/CH_4 ratio is increased, one may conclude that this increase is largely due to the incorporation of more nitrogen. Notice that as the carbon-nitrogen bond species increase in number, those attributed to C–H (2850–2950 cm^{-1} stretching modes and 1430 cm^{-1} wagging modes) and to N–H (3200–3400 cm^{-1}, 1630 cm^{-1}), tend to diminish. A similar

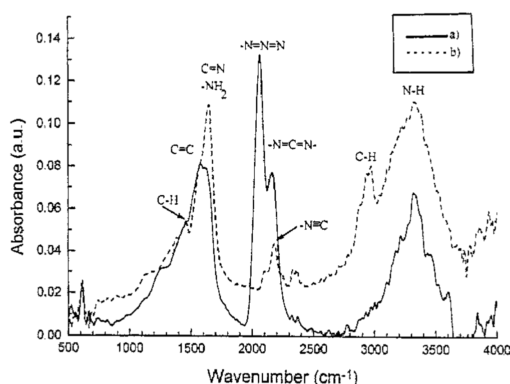

Fig. 3. Infrared absorption spectra of two samples prepared by PECVD using 200 W of rf power and a deposition pressure of 250 mTorr. Sample (a) using a N_2/CH_4 gas ratio of 9; sample (b) using a N_2/CH_4 gas ratio of 1. The double feature in the 2300–2400 is from CO_2 in the air of the spectrometer sample chamber.

trend was observed when pressure was varied: strong C≡N and/or N=C=N absorption bands developed as pressure was reduced and C–H bonds tended to disappear. This indicates that nitrogen tends to replace hydrogen in the material, that nevertheless retains a soft, polymeric character when prepared on the grounded electrode. Under the preparation conditions mentioned above, no film grew on the powered electrode, arguably due to the intense ion bombardment caused by the self-bias. At lower plasma powers, samples with low nitrogen content ($x \approx 0.1$), which also contained hydrogen, were produced, on both the grounded and powered electrodes, obtaining hard films on the latter electrode but soft ones on the former.

It is known that when the pressure is reduced in an rf PECVD reactor, or the rf power is raised, the self-induced bias on the powered electrode is increased [13]; this was confirmed experimentally in our system. As well, we observed that the self-bias was enhanced at higher N_2/CH_4 gas ratios [7]. So, there seems to be a relationship between the conditions which enhance self-bias at the powered electrode and nitrogen incorporation in the samples held at the grounded electrode. This information suggests that nitrogen incorporation into the films follows a multi-stage mechanism, further that large amounts of nitrogen in the films do not necessarily imply high-hardness. It is possible to exclude the possibility that nitrogen incorporation is due to implantation of nitrogen ions or charged radicals; implantation energies would cause the film to lose its polymeric character, since bombardment would promote crosslinking [14]. Hence, nitrogen must arrive and remain in the films in some other way. The strong signals of groups like isonitrile (–N≡C), ketene-imine (>C=C=N–), diazo (>C=N=N) and carbodiimide (–N=C=N–) [8], suggest that CN radicals as well as nitrogen-containing molecules (like HCN, C_2N_2) help in the incorporation of nitrogen to the films growing on the grounded electrode. Durrant et al. have shown that CN radicals are formed at carbon rich surfaces in the presence of a nitrogen-only rf plasma [15], indicating that radicals are not only formed in the gas phase but also at the reactor walls (including the powered electrode). This obviously does not preclude the incorporation of nitro-

gen by other means, like reaction of other nitrogen radicals with the surface.

At higher plasma powers more energy is available to produce reactive nitrogen species, but this can either go into the film or produce CN after reacting with carbonaceous material on the reactor walls. At lower pressures, electrons have a larger mean free path and hence the energy that they can acquire is larger, having the same effect: more reactive species that contain nitrogen are generated. Increasing the N_2/CH_4 ratio has obviously similar effects as more nitrogen is available for reaction. Why CN could be necessary for a higher nitrogen content in the films may be explained by the fact that the radical has already a bond formed between carbon and nitrogen, so that no extra energy is needed to break a nitrogen–nitrogen bond in order to link the nitrogen into the growing material. One has also to consider that the carbon in the CN radical has at least an unpaired electron which may help in the bonding to the surface, so even if no bond is to be broken, it is easier to incorporate nitrogen via CN radicals. Another possibility is through Van der Waals forces as discussed above.

4. Summary and conclusions

IBA techniques are useful in the study of composition of light elements materials and can help in understanding its growth and properties. We have been able to study the composition of carbon nitride films prepared under different plasma techniques and conditions. For the PECVD samples we have confirmed that the increase in the absorption intensity of triple and double cumulated bonds is due to an increase of the nitrogen content and not only to the stronger dipole moment of the groups. The existence of molecular structures with dipole moments is thus confirmed and strongly suggests that nitrogen incorporation is enhanced when these sorts of structures are impeded from leaving the growing surface of either PECVD or RMS prepared samples.

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