Study of carbon nitride films deposited using a Hall-type ion source

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Abstract. The Hall-type ion source operated with nitrogen has been used in two ways in the synthesis of carbon nitride films: by ion beam nitridation of a graphite target and by simultaneous deposition on a collector (silicon wafer and nickel foil) of sputtered carbon atoms and nitrogen atoms from the surrounding nitrogen plasma. We present Rutherford backscattering spectroscopy, x-ray photoelectron spectroscopy and x-ray excited Auger electron spectroscopy results on the carbon and nitrogen atom fraction and chemical bonding state in carbon nitride films. The C 1s XPS peak of a sample deposited on silicon wafer was deconvoluted into three peaks at 284.7, 286.7 and 288.8 eV. The peak at 286.7 eV by analogy with polymethacrylonitrile (C≡N, 286.74 eV) can be identified as C≡N, the peaks at 284.7 and 288.8 eV as C–C and O=C–N, respectively. The N 1s peaks were also deconvoluted into three peaks at approximately 398.3, 400.5 and 402.6 eV. According to the N(E) CKVV spectra the surface samples contain an equal number of sp^2 and sp^3 bonds of carbon atoms.

1. Introduction

The large interest in producing carbon nitride material is driven by the possibility of obtaining the superhard β-C_3N_4 compound, which according to Liu and Cohen [1] might be harder than diamond. This hypothetical compound has not only attracted attention for its hardness, but also for the predicted optical properties: the films might be transparent for visible and/or UV light. In order to obtain information about the chemical state of the carbon and nitrogen atoms often x-ray photoelectron spectroscopy (XPS) is used. Numerous publications are devoted to the identification of the chemical C–N bonds by use of the C 1s and N 1s XPS spectra [2–6]. In these publications the C 1s peak has been deconvoluted into two, three or four peaks with binding energies of approximately 284.6, 285.9, 287.7 and 288.2 eV. The intensities of these peaks differ very strongly from situation to situation. In some studies the main intensity of the C 1s XPS peak is situated at 284.6 eV. For example, Boyd *et al* [4] prepared thin carbon–nitrogen films by direct impingement of 5–100 eV C^+ and N^+ or N_2^+ ions upon solid surfaces, as well as by 5–350 eV N^+ bombardment of graphite surfaces. They identified the peak at 284.6 eV as adventitious carbon. Ronning *et al* [6] also prepared the films by mass selected ion beam deposition, the intensity of the peak at 284.7 eV was equal to 31% of the total intensity, at an ion ratio of C/N = 4/6. In the work of Fujimoto *et al* [2] and

Diani *et al* [3] the main intensity of the C 1s peak was near 287 eV.

Boyd *et al* [4] used the C 1s and N 1s XPS data for standard chemical compounds such as pyridine and hexamethylene–tetramine to identify chemical interaction in their samples. This method is now accepted since until now there have been no experimental XPS data for the four C–N bonds which should be present in the β-C_3N_4 compound.

There are some discrepancies in the structure and binding energy of the N 1s XPS spectra. Boyd *et al* [4] deposited carbon nitride films by ion beam deposition and deconvoluted N 1s XPS spectra into three peaks with two main binding energies: 398.3 eV due to β-C_3N_4 bonds and 400.0 eV due to C=N bonds. Rossi *et al* [5] attributed the peaks at 398.2 and 400.2 eV to C≡N and N=C bonds, respectively.

The large variety of data shows the complexity and nonequilibrium of the physical and chemical processes encountered in the carbon nitride synthesis. The interpretation of the C 1s and N 1s data is at present ambiguous due to the absence of a reliable XPS fingerprint of a one-phase carbon nitride compound with four C–N bonds. Obviously the β-C_3N_4 phase should have C 1s and N 1s peaks with only one feature at a position defined by the electronegativity of four C–N bonds.

Most of the work described above was performed using low ion current densities (e.g., 1 μA cm^{-2} for C^+, and 2 μA cm^{-2} for N^+ [4]). For the deposition of carbon nitride

films we have used an intense source, the gridless Hall-type ion source. The purpose of this paper is to present XPS, XAES (x-ray excited Auger electron spectroscopy) and RBS (Rutherford backscattering spectroscopy) measurements of CN_X films deposited using this ion source.

2. Experimental set-up

2.1. Regimes of material deposition

The nitrogen ion beam produced by the gridless, Hall-type, ion beam source SPT-50 (denoted Stationary Plasma Thruster, SPT, because of its applications in electric space propulsion) has been used in the following two ways in the experiments for producing hard carbon nitride:

(a) ion beam nitridation of a graphite target;
(b) simultaneous deposition on a collector of sputtered carbon atoms and of nitrogen atoms from the nitrogen plasma formed by the neutralized ion beam. In this case the neutralized ion beam was used to sputter carbon from the graphite target, to heat the collector and to deposit nitrogen atoms on its surface. Two collector materials have been tested simultaneously: silicon wafer (100) and polycrystalline nickel foil.

We also attempted to enhance the graphite sputtering rate by operating the ion beam source with a nitrogen–xenon mixture flow.

2.2. The ion beam source

A Hall-type ion source, described in [7], was operated with nitrogen and has been used both for nitridation of graphite and for sputtering carbon to be deposited on a collector.

The following operation parameters of the Hall-type ion source in nitrogen were used in the present experiments: nitrogen flow 0.77 cm^3 s^{-1}, applied discharge voltage 250 V, discharge current 0.8–1 A. The experimental chamber was pumped by a cryogenic pump, backed by a turbomolecular pump and a primary pump. The pressure measured in the test chamber was 1.5×10^{-4} mbar. The above operation parameters were used both in regime A and also in regime B (see section 2.1) when only nitrogen was used.

In the case of regime B using a nitrogen–xenon mixture, the following parameters were used: nitrogen flow 0.55 cm^3 s^{-1}, xenon flow 0.083 cm^3 s^{-1}, applied discharge voltage 200 V, discharge current 1.1 A. Thus, the nitrogen flow was reduced to 71% of the value in pure nitrogen operation, while the xenon flow was 50% of that used for pure xenon operation.

In both regimes the hollow cathode was operated with a xenon flow of approximately 0.1 cm^3 s^{-1}.

2.2.1. The graphite target.
The square graphite target (12.2×12.2 mm^2), 2.5 mm thick, was exposed to the nitrogen beam. It was of 99.95% purity (reference C 000440 from Goodfellow) and was located 11 cm from the ion beam source exit.

One of the difficulties in working with ion beam material deposition and processing is trying to avoid sputtering of impurity materials (from metal holders, thermocouples, wires

for biasing the target) along with the sputtering of the wanted target material, carbon. Graphite (from which the carbon atoms are sputtered) has the lowest sputtering yield among all studied materials. The strategy used to avoid contamination consisted of the following.

- Locating the target very close to the ion beam source, where the beam density is highest.
- Locating the holders, which unavoidably cross the beam, far behind the target.
- Using an insulating material (Al_2O_3) for these holders, since this material has a lower sputtering yield than metals (although approximately three times higher than that of carbon).
- Avoiding metal wires crossing the beam.

We optimized the configuration in the following ways. Note that the axis of the ion beam was horizontal.

(a) By fixing the target on a horizontal alumina rod, 6 cm long and 5.3 mm in diameter. The rod had four tubular holes along its length, which allowed the insulation of the wire used for biasing the target and the thermocouple wires without crossing the beam. A hole with a diameter of 5.3 mm, 2 mm high, was drilled on the back side of the target, which could thus accommodate the alumina rod holder. Therefore, the target was closer to the ion source by 6 cm compared to the vertical section of the alumina rod which was connected to the horizontal section using an insulating cement 'Sauereisen' No 31 (essentially Al_2O_3 and silicate).
(b) No metal wire providing the electrical connection of the target and no thermocouple wires were exposed to the ion beam. This was achieved by inserting a disk of tantalum foil (0.1 mm thick) at the front end of the alumina holder rod, on which the Chromel–Alumel thermocouple, as well as the tantalum wire which provided the electrical connection for the graphite target, were welded. The tantalum disk was in close contact with the graphite target, inside the hole 5.3 mm in diameter on the back of the target. The above-mentioned three wires passed through three of the four tubular holes of the alumina holder rod.
(c) The alumina holder, made of two perpendicular sections, was fixed on an insulator mounted on an upper flange of the test chamber. The tantalum and thermocouple wires were connected to the leadthroughs located behind the ion source. They were insulated in Teflon tubes, which were fixed to the chamber wall.

2.2.2. The collector.
We chose to install the collector material on a graphite disk 2 cm in diameter and 4 mm thick. This disk was located 4.5 cm from the graphite target, inclined with respect to the beam axis by 45°. The silicon plate (a quadrant of a 50 mm diameter wafer) and the polycrystalline nickel foil (10×15 mm^2) were fixed on the graphite disk using a bent tantalum wire, which was inserted into two small openings drilled in the graphite disk. The collector was electrically connected to the hollow cathode of the ion beam source. This means that it could collect the primary ion beam and the ion beam scattered from the target.

The upper part of the collector was located 10 mm lower, with respect to the lowest point of the target, i.e. approximately 16 mm from the target axis. During deposition the collector was at the potential of the hollow cathode. Therefore, the Si and Ni samples located on the front side of the collector received carbon atoms sputtered from the target and were also hit by nitrogen atoms and thermal ions from the nitrogen plasma surrounding the collector. Let us recall that the Hall-type ion source produces a plasma flow with equal velocities of electrons and ions, the ion energy being much larger than that of the electrons. The collector (i.e. the graphite disk with the silicon and nickel samples) is heated by ion–electron recombination at its surface. Its temperature during the experiments was in the range of 350–400 °C.

The collector was maintained on a thin copper rod which could be inserted into a small hole made in the back side of the graphite disk. The thin copper rod was inserted into an alumina tube.

3. Experiments with ion beam nitridation of graphite (regime A)

Three experiments were performed with a simple configuration in which the graphite target was installed on the alumina holder. In these experiments the target was first cleaned by xenon ion bombardment for 10–15 min. During bombardment with xenon ions the target bias with respect to the hollow cathode was only −50 V; this low bias was applied in order to read the ion beam current, which was 10–15 mA. The xenon ion energy was thus approximately 300 eV. With a target area of 1.49 cm^2, the current density J (Xe$^+$) was estimated to be 6.7–10 mA cm^{-2}. The graphite samples produced in these experiments are designated as C(1)–C(3).

In the experiment with C(2), after the end of cleaning with xenon ions, bombardment with nitrogen ions was initiated and the bias applied to the target was gradually enhanced up to −600 V. Since the applied discharge voltage was 250 V, the nitrogen ion energy was at most 850 V. The target current at this voltage was 15 mA (i.e. 10 mA cm^{-2}). The target temperature was monitored by the Chromel–Alumel thermocouple reading and by an infrared pyrometer based on recording the intensity of four different wavelengths, which directly indicated the temperature of the target. The indications of the thermocouple and the pyrometer were in good agreement. The maximum target temperature was 520 °C and we maintained the sample at this temperature under nitrogen beam irradiation for 120 min. This duration was only 50 min in the experiment with C(1).

In the experiment with C(3), the bombardment with nitrogen ions was performed with a bias applied to the target of up to −1150 V. Since the applied discharge voltage was 250 V, the nitrogen ion energy was at most 1400 V. The target current at this voltage was 23 mA (i.e. 15.3 mA cm^{-2}) and the maximum temperature attained by the target was 660 °C. The target was maintained at a temperature in the range of 600–660 °C for 120 min.

4. Experiments with simultaneous deposition of carbon and nitrogen on the collector (regime B)

Two experiments were effected with two different collector samples, but a single target, C(4).

In the first experiment the ion beam source was operated with pure nitrogen only. A maximum bias voltage of −1.000 V was applied to the graphite target. The ion energy was in this case at most 1.250 V, since the applied discharge voltage was 250 V. The current to the target was 25 mA, i.e. the current density on the target J^+ was 16.67 mA cm^{-2}. The target temperature attained with this bias was 670 °C.

The collector was connected to the hollow cathode via a milliammeter (see section 2.2.2). The current to the collector was at most 17 mA and the collector temperature attained by the target was 360 °C. The film obtained on the silicon target was in part transparent and seemed quite thin. The silicon and nickel samples prepared in this experiment will be denoted as Si(1) and Ni(1).

In the second experiment the ion source was operated with a nitrogen–xenon mixture. A maximum bias voltage of −800 V was applied to the graphite target in this case. The ion energy was 1.000 V, since the applied discharge voltage was 200 V. The current to the target was 30 mA, i.e. the current density on the target was 20 mA cm^{-2}. The target temperature with this bias was in the range of 670–700 °C. In this case the current to the collector was 19.6 mA at most and the collector temperature attained was 400 °C.

The silicon and nickel samples prepared in this experiment will be denoted as Si(2) and Ni(2).

5. Results of surface analysis

5.1. RBS

All the samples mentioned in sections 3 and 4 were studied by RBS. Most of the results are presented in table 1. This analysis gave information about the following.

(a) The nature of the atoms present in the surface film (i.e. in the film close to the surface). RBS has shown that the surface film was essentially formed of carbon and nitrogen atoms. Some impurity atoms such as oxygen, iron and xenon were also found in some samples.

(b) The stoichiometric composition of the surface film and the ratio of nitrogen/carbon atoms present in this film. An example of the stoichiometric formula is reported for C(2): $C_1N_{0.15}Fe_{0.002}Xe_{0.002}$. From this formula we deduce the atom fraction of nitrogen with respect to carbon as 0.15.

In another example, sample Si(1), the formula is $C_{0.66}N_{0.295}Fe_{0.004}$. We deduced from this that the atom fraction of nitrogen with respect to carbon was 0.45, which is the highest such atom fraction observed.

The lowest atom fraction of nitrogen with respect to carbon, 0.05, was observed in C(4), which was bombarded with a mixture of xenon and nitrogen ions during experiment No 2.

(c) The areal density of the surface film. The areal density varied between 3×10^{17} atom cm^{-2} for C(2), and 3.6×10^{18} atom cm^{-2} for Ni(2).

Table 1. Experimental conditions for sample preparation and data obtained from RBS.

Substrate	Gas	Ion energy (eV)	Target temperature (°C)	Areal density (10^{15} atoms cm^{-2})	N/C
C (2)	N_2	850	520	300	0.15
C (3)	N_2	1400	660	450	0.12
C (4)	N_2 + Xe	1000	660	400	0.05
Si (1)	N_2		340	1600	0.45
Ni (1)	N_2		340	2300	0.20
Si (2)	N_2 + Xe		390	2600	0.25
Ni (2)	N_2 + Xe		390	3600	0.20
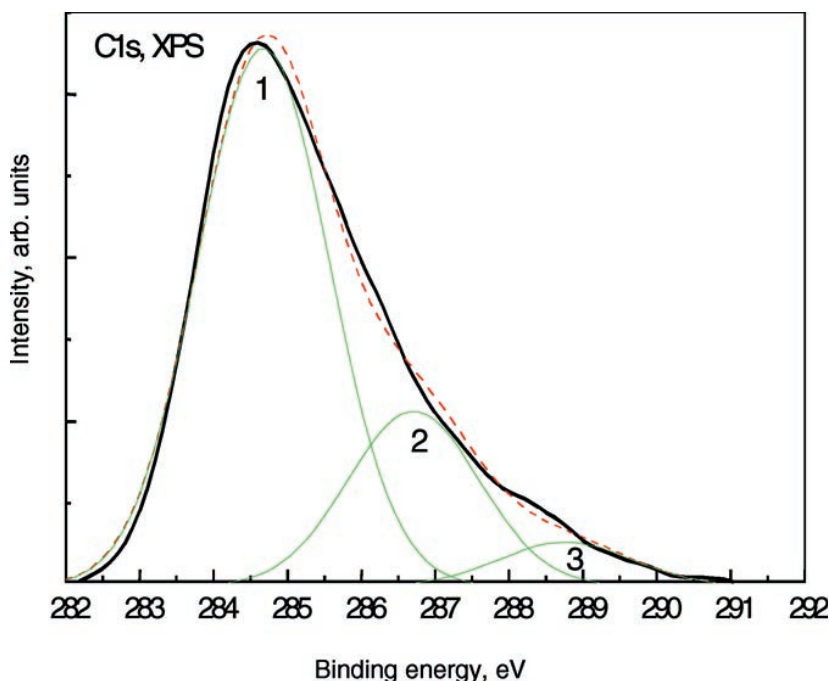
Figure 1. XPS C 1s core-level spectrum of sample Si(2).

The areal density went up by 50% when the ion energy was enhanced from 850 to 1.400 eV (compare data for the films obtained for C(2) and C(3)).

The highest areal density was observed for the collector samples exposed in experiment No 2: Ni(2) and Si(2), had areal densities of 3.6 and 2.6×10^{18} atoms cm^{-2} respectively (see table 1). Meanwhile, the areal densities observed on the collector samples exposed in the first experiment were lower: the sample Si(1) had a film of 1.6×10^{18} atoms cm^{-2}, but this film had the highest content of nitrogen (45%).

We can conclude that using nitrogen only in the neutralized ion beam source is more suitable for producing a high atom fraction of nitrogen in the film obtained by graphite sputtering than using a nitrogen–xenon mixture.

5.1.1. Other conclusions of RBS analysis. The RBS analysis of samples obtained by deposition on silicon and nickel did not show the presence of these elements in the surface film. This indicates that there is no formation of a compound by the deposited carbon and nitrogen atoms with the substrate.

Table 2. Data on carbon, nitrogen and oxygen concentration obtained from XPS analysis.

Substrate	Atom fraction			
	C	N	O	N/C
C (3)	0.75	0.17	0.08	0.23
Si (2)	0.72	0.19	0.10	0.26
Ni (2)	0.74	0.12	0.14	0.16

In the case of films deposited on silicon, it seems that the carbon density increases from the surface to the substrate, while the nitrogen density does not exhibit this feature.

The impurities (iron, xenon) are usually distributed uniformly in the film bulk, with one exception: in the sample Si(1) the xenon seems to be implanted on the film surface, but not in its bulk.

5.2. XPS

XPS and XAES were used to examine the chemical bonding state of carbon–nitride films. The XPS and XAES data were obtained using a MK II VG Scientific spectrometer.
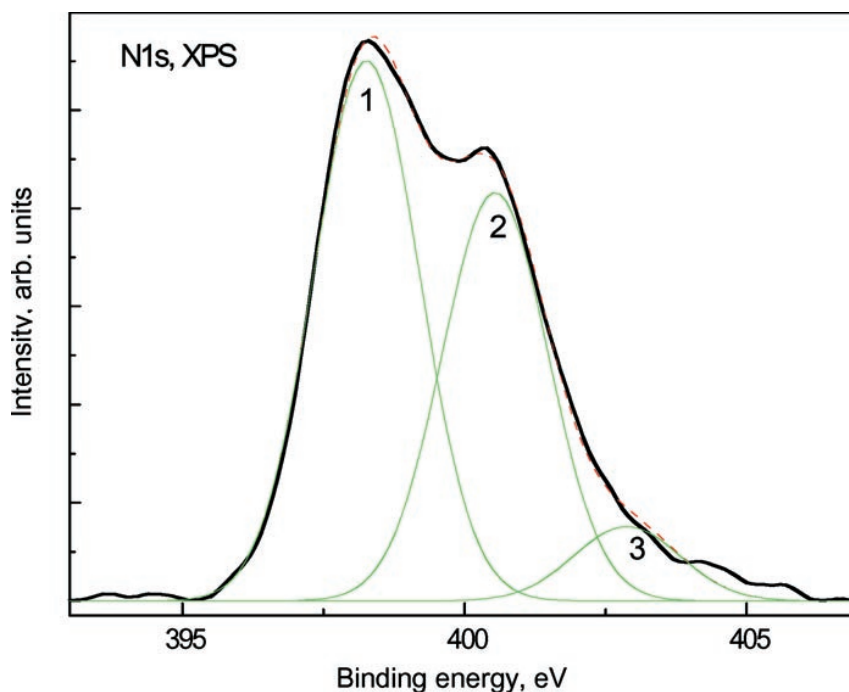
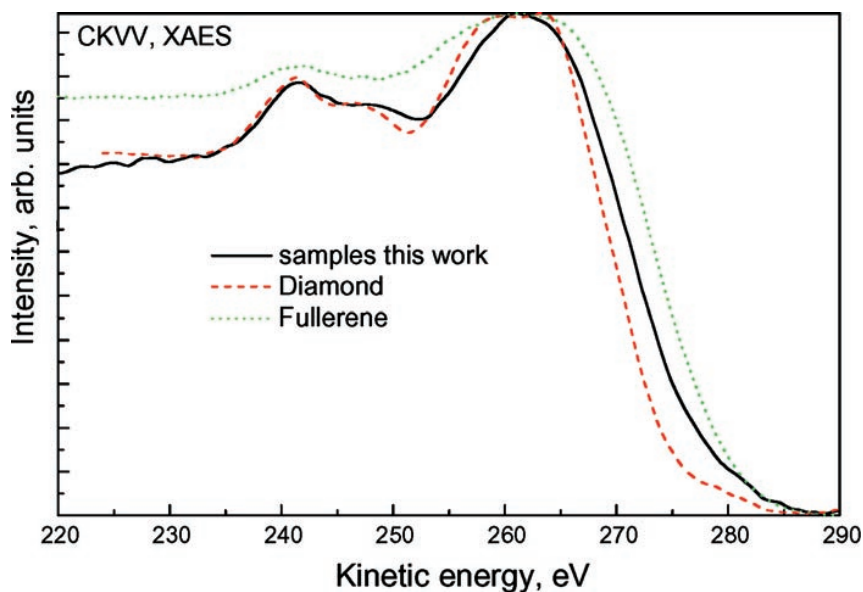**Figure 2.** XPS N 1s core-level spectrum of sample Si(2).

Figure 3. Comparison of the N(E) CKVV spectra for the sample Si(2) with those for diamond and fullerene.

Photoelectron processes were excited by an Al Kα x-ray source with photon energy of 1486.6 eV. The vacuum in the analysis chamber was 10^{-9}–5×10^{-10} Torr. The spectra were collected in the analyser constant energy mode, with pass energy of 10 or 20 eV for XPS and 50 eV for XAES. The C 1s, N 1s and O 1s XPS spectra were acquired with a 0.1 or 0.05 eV step size. Under this condition the FWHM of the Au4f peak were 1.2 and 1.1 eV, respectively. The XAES spectra were collected with a 0.25 eV step size.

Figure 1 shows the C 1s XPS peak of the sample Si(2) deconvoluted into three peaks at 284.7, 286.7 and 288.8 eV. The structure of the C 1s XPS spectrum is typical

for all our samples and is very close to spectra reported in [4, 6]. According to Boyd *et al* [4] the peak at 284.7 eV is identified as carbon that has no nitrogen neighbours. One can identify the peak at 286.5 eV by analogy with hexamethylene–tetramine (sp^3 bonding, 286.74 eV, [8]) or with polymethacrylonitrile [9] (C≡N, 286.74 eV). The peak at 288.8 eV should be assigned to O=C–N interaction on the basis of data for polyacrilamide [9].

Figure 2 shows the N 1s XPS peak of the same sample Si(2) deconvoluted into three peaks at 398.3, 400.5 and 402.6 eV (see also table 3). The structure of this N 1s XPS spectrum is typical for all our samples and coincides

Table 3. Data from the deconvolution of XPS spectra.

		Peaks						
		C 1s			N 1s			
Substrate		1st	2nd	3rd	1st	2nd	3rd	O 1s
C(3)	Position	284.7	286.7	288.8	398.9	401	403.4	532.3
	Area	9033	5759	1900	4332	2610	494	590.3
	FWHM	1.6	1.6	1.6	1.9	1.9	1.9	2.5
Si(2)	Position	284.7	286.7	288.8	398.3	400.5	402.6	532
	Area	7328	2379	593	2578	1936	330	4175
	FWHM	1.8	1.8	1.8	1.9	1.9	1.9	2.4

with the spectra given in [4]. According to Boyd *et al* [4] the peak at 402.5 eV is assigned to N–O interaction and/or N_2 formed during the deposition and trapped within the film. A similar spectrum to that shown in figure 2 was observed in [10] for *in situ* nitrogen implantation without any oxygen contamination. This information supports the second hypothesis about trapped N_2.

According to [4], the peak with the binding energy 398.3 eV is assigned to sp^3 bonding and the peak at 400.3 eV is attributed to N–C sp^2 bonding.

The XPS data for the studied samples are presented in table 2.

5.3. XAES

In order to identify the chemical states of carbon atoms on the sample surface we used Auger spectroscopy with x-ray excitation. Figure 3 shows the comparison of the N(E) CKVV spectra for the sample Si(2) with that for diamond and fullerene. The CKVV spectra for other samples had the same structure. According to the interpretation of [11] the surface contains an equal number of sp^2 and sp^3 bonds of carbon atoms.

6. Conclusion

The study by RBS of the samples prepared both by graphite nitridation (regime A) and by simultaneous deposition of nitrogen and sputtered carbon on silicon and nickel substrates (regime B) indicates that the N/C ratio is in the range from 0.12 to 0.45 for all the samples, except the graphite sample exposed to the mixture of nitrogen and xenon, C(4). This is in fair agreement with XPS results. Total nitrogen areal densities of up to 7×10^{17} atoms cm^{-2} were found in the films deposited in regime B, approximately a hundred times more than reported in [6].

C 1s and N 1s XPS peaks show some chemical states of carbon and nitrogen atoms. The nitrogen atoms have three states that show nonequilibrium distribution of atoms in the samples. One can suppose that during implantation, not only a single state C–N interaction occurs, but possibly trapped molecular nitrogen also reacts. The coincidence of

our N 1s spectra with those in [4, 10] show that as a result of ion implantation nitrogen atoms are formed in the same states and these states do not depend on the ion energy.

The C 1s and N 1s XPS peaks show strong C–N interaction with C–3N bonds. The CKVV spectra show a mixture of sp^2/sp^3 bonds in the upper layer of the samples.

Further work will be dedicated to improving the stoichiometry, in order to reach that suggested in [1]. From a physical point of view this would correspond to an optimum mixture of sp^2/sp^3 bonds, the measurement of which has been accomplished in this work. In our opinion, these successive steps will bring improvements to the desired parameters, such as microhardness and optical properties, which will also be investigated.

Acknowledgment

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