

On the possibility of β -C₃N₄ carbon nitride synthesis via C and N implantation into copper

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The effects of high dose carbon and nitrogen implantations into copper on the type of chemical bonds and stoichiometry of the formed C–N phases are described. The results are compared with those obtained after nitrogen implantation into diamond like carbon (DLC) layers. The striking difference between the two experiments is the stoichiometry of covalently bonded C–N phase which corresponds to C₂N or to C₃N_{3.7} for N implantation into DLC and C and N implantation into copper, respectively. © 1999 Kluwer Academic Publishers

1. Introduction

Since the publication by Liu and Cohen in 1989 on the possible existence of β -C₃N₄ carbon nitride [1] a great interest was given to this compound. It is supposed to possess unique properties; very high hardness compared to that of diamond, high resistivity and good thermal conductivity, what make it extremely attractive for material science, especially for micromechanical applications and high power electronic devices. Numerous attempts were performed to synthesize this compound [2–6]. The methods like Physical Vapor Deposition [2], Chemical Vapor Deposition [3], Ion Implantation [4], Laser Ablation [5] or precursor thermal decomposition [6] were used. Up to now, however, there is no definitive confirmation of the continuous β -C₃N₄ layer synthesis. In most experimental data published till now and independently of the used method the final results are quite similar and far from the expected β -C₃N₄ structure. The formed layer is in general nitrogen deficient, rather soft and unstable under energetic ion irradiation. It seems that the main obstacle in C₃N₄ synthesis lies in its metastable structure [1]. The use of energetic methods, like high energy ion implantation, may lead to the decomposition of this compound and, consequently, to the formation of diverse nitrogen C–N phases, nitrogen deficient when compared with C₃N₄ stoichiometry. Another possible reason for the synthesis failure is that during the deposition process carbon is deposited mainly in the form of clusters and not as single atoms.

Consequently, the structure of the deposited layer is predetermined by the cluster structure, which is rarely covalently bonded. All these complications lead to a moderate success of β -C₃N₄ synthesis. In some experiments only the small C–N precipitates were observed having a structure close to that expected for β -C₃N₄ phase [7, 8].

The drawbacks described above point to the conclusion that nitrogen ion implantation into bulk carbon or diverse carbon layers is not a wise choice for β -C₃N₄ synthesis. Metastable structure of this compound indicates that the promising synthesis techniques should use either the low energy methods to prevent the decomposition of formed compound or synthesis conditions far from equilibrium to avoid the formation of thermodynamically stable phases. The example of the low energy synthesis methods could be carbon laser ablation in nitrogen atmosphere, the second concept could be achieved by using a high temperature or high stress process. The aim of the presented paper is to explore this latter possibility by studying the role of high compressive stress on the type of chemical bonds formed between carbon and nitrogen.

A straightforward way to introduce high compressive stress for new phase synthesis is to place a compound containing carbon and nitrogen atoms in resistant vessel and to heat it during compression. Such an experiment was already performed but did not provide the expected results. The compound formed was still a

poorly defined non-covalent, carbon rich phase [9]. It is possible that the stress level required for the formation of covalent C–N bonds was not achieved in the Sekine's experiment [9]. Another experiment based on the similar concept was performed by M.R. Wixom [10] by using shockwave compression of organic C–N–H precursors. This attempt has not led to β -C₃N₄ synthesis either, although diamond precipitates were found in the reaction products.

We decided to perform our experiment in a different way. It is known that ion implantation leads to high compressive stresses in the surface layer of metals [11]. Moreover, insoluble elements tend to form precipitates when they are implanted at sufficiently high doses. Therefore the high dose implantation of carbon and nitrogen into a metallic matrix in which both elements are insoluble should allow the formation of highly compressed C and N containing precipitates. If the stress favors the creation of covalent bonds, the β -C₃N₄ phase should be preferentially formed in C+N implanted copper sample compared to nitrogen implanted carbon. Another advantage of this kind of experiment is that the problems due to the predetermined carbon structure are avoided as carbon is introduced as isolated atoms and not as atomic clusters.

The metallic matrix chosen for the experiment is copper for numerous reasons. First of all carbon and nitrogen are insoluble in copper and do not form nitrides nor carbides [12]. Secondly copper is a good electrical conductor what facilitates the XPS and RBS measurements.

The effects of C and N implantation into copper are compared to those obtained for a DLC (diamond like carbon) layer implanted with nitrogen ions. Such a material was chosen as a reference mainly because of its covalent bonds. Moreover, the N-implanted DLC samples showed the higher retention of implanted nitrogen atoms compared to rf-sputtering deposited C layers and bulk graphite samples [13].

In this paper we will use a specific notation for the implanted samples by underlining the matrix; thus the N-implanted DLC and the C and N implanted copper samples will be labeled respectively DLCN and CuCN.

2. Experimental

In the experiment pure copper samples (>99.9% Cu) typically 1 cm² and 2 mm thick were used. DLC samples were about 200 nm thick layers deposited on the <111> Si substrates. Prior to the implantation processes the copper samples were mechanically polished and cleaned in an ultrasonic bath. The implantations were performed using a 200 kV MPB 202 RP ion implanter (IEMT Warsaw) and a 400 kV implanter (IPN Lyon). The implantation processes in Warsaw were performed at 50 keV (C⁺) and 65 keV (N⁺) whereas in Lyon they were done at 100 and 120 keV for C⁺ and N⁺ ions, respectively. All implantations were performed at room temperature. For 50 and 65 keV implantations carbon and nitrogen doses were varied from 1 × 10¹⁷ at/cm² up to 1 × 10¹⁸ at/cm². Doses of 1.25 × 10¹⁸ at/cm² of 100 keV C⁺ and 120 keV N⁺ ions were used

for the samples implanted sequentially with both elements. The implantation doses were slightly increased when compared to 50 and 65 keV implantations in order to keep the similar maximum concentration of each element. The impurity profiles as well as the retention curves were determined by means of Nuclear Backscattering Spectrometry (NBS) technique, using a backscattering resonance at 5.7 MeV (carbon) and 6 MeV (nitrogen). The type of chemical bonds were analyzed by means of X-ray Photoelectron Spectroscopy (XPS) experiments performed in the "Institut de Recherche sur la Catalyse" in Lyon. For that purpose the samples were implanted with both, carbon and nitrogen ions up to doses of 1.25 × 10¹⁸ at/cm² of each element.

The XPS study was carried out on a VG ESCALAB 200R spectrometer using the AlK_α radiation ($h\nu = 1486.6$ eV). Prior to the experiments the spectrometer was calibrated by assuming the binding energy of the Ag3d_{5/2} line to be 368.2 eV with respect to the Fermi level. In our experimental conditions the full width at half maximum, at 50 eV pass energy, was equal to 1.0 eV on the Ag3d_{5/2} peak. Data were acquired for the C1s, N1s and Cu2p_{3/2} peaks at 0.1 eV steps with a dwell time of 200 ms. In order to perform the analysis at different depths a surface etching was performed using 5 keV Ar⁺ ions. The analyzed area was equal to about 1 mm² which was much smaller than the etched zone (few cm²), the composition changes due to non-uniform etching can thus be neglected. The vacuum during analysis was typically 1 × 10⁻⁹ mbar; during the etching process it raised up to ~10⁻⁶ mbar.

After smoothing the experimental spectrum the background was subtracted using a nonlinear Shirley function [14]. In order to perform a quantitative analysis of carbon-nitrogen phases fits were carried out with a nonlinear least square curve fitting program using a gaussian-lorentzian product function. Scofield sensitivity factors [15] were used in the analysis. In our experimental conditions (constant analyzer energy (CAE) and at pass energy of 50 eV) in C and N binding energy region the product of transmission function by the mean free path is proportional to $E_c^{0.6}$. The experimental precision of XPS quantitative analysis is considered to be around 20%.

3. Experimental results

3.1. Concentration of implanted atoms

The maximum nitrogen concentration in DLCN samples was determined previously and it was found to be equal to about 25 at % [13]. The first part of the following experiments was thus devoted to the determination of carbon and nitrogen concentrations after implantation into copper. For that purpose the copper samples were implanted with increasing doses of each element. The doses used were 1 × 10¹⁷ at/cm², 2 × 10¹⁷ at/cm², 4 × 10¹⁷ at/cm², 7 × 10¹⁷ at/cm² and 1 × 10¹⁸ at/cm². The depth distributions for both, nitrogen and carbon atoms were measured by means of the NBS method. The maximum of the atomic concentrations were extracted from the NBS spectra and are shown in Fig. 1

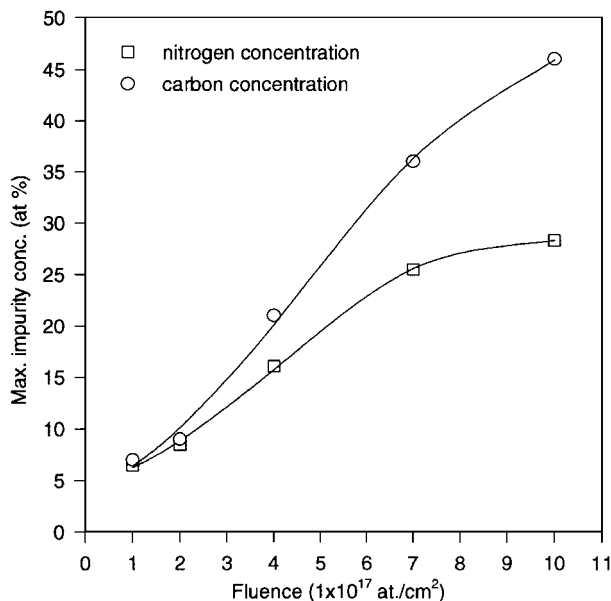


Figure 1 Maximum carbon and nitrogen atomic concentrations after implantations at various doses into copper.

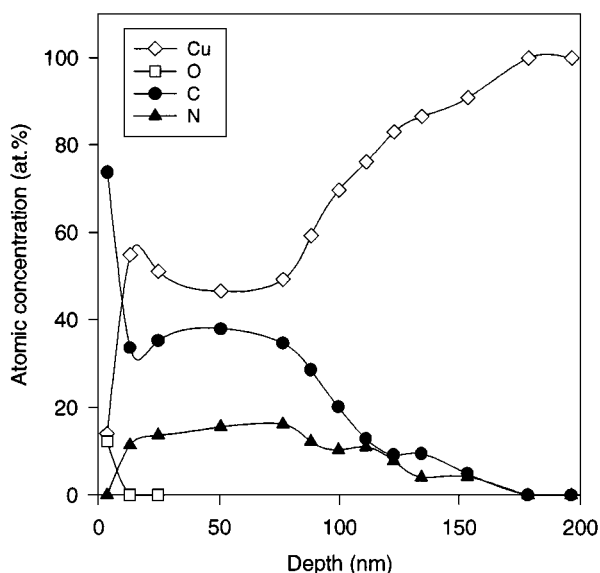


Figure 2 Depth distribution profiles of carbon and nitrogen atoms after dual C and N implantations into copper.

as a function of the implantation dose. One can note the much higher retention of carbon atoms when compared with nitrogen. These effects may be partially due to the recoil of carbon atoms originating from the pollution layer at the sample surface.

Samples used in the XPS experiments were implanted up to a dose of 1.25×10^{18} at/cm² of nitrogen followed by 1.25×10^{18} at/cm² of carbon ions. The carbon and nitrogen profiles extracted from the NBS measurements are presented in Fig. 2. One can note the high carbon concentration at the surface followed by the region in which carbon concentration is close to 40 at %. Nitrogen concentration profile is characterized by a plateau extending from the surface up to ~ 150 nm having an average concentration of about 17 at %. It is worth to point out, that after implantations with such high doses the depth concentration profiles of impurity atoms depend not only on the ion beam target sputtering but also on impurity migration and surface release processes.

3.2. XPS measurements

The XPS measurements were performed for three different sputtering times (15, 60 and 90 min for CuCN samples or 0, 10 and 20 min for DLCN samples), hereafter labeled as shallow, medium and deep. An example of a XPS photoelectron spectrum recorded in the 0–1000 eV energy range is shown in Fig. 3. One can note the presence of narrow C 1s (~ 284.5 eV), N 1s (~ 400 eV) and Cu 2p_{3/2} (~ 936.1 eV) photoelectron peaks as well as broad peaks due to Auger electrons from copper Cu LMM (~ 570 – 630 eV). XPS analysis allows one to determine the relative concentrations of each element in analyzed samples. The average atomic concentrations of carbon, nitrogen and copper extracted from XPS spectra recorded from the samples discussed in this paper are listed in Table I. The discrepancy between the NBS and XPS results (Fig. 2 and Table I, respectively) can probably be attributed to the sample roughness which is responsible for the shadowing of carbon-filled hollows at the sample surface against the etching beam. The preferential copper sputtering

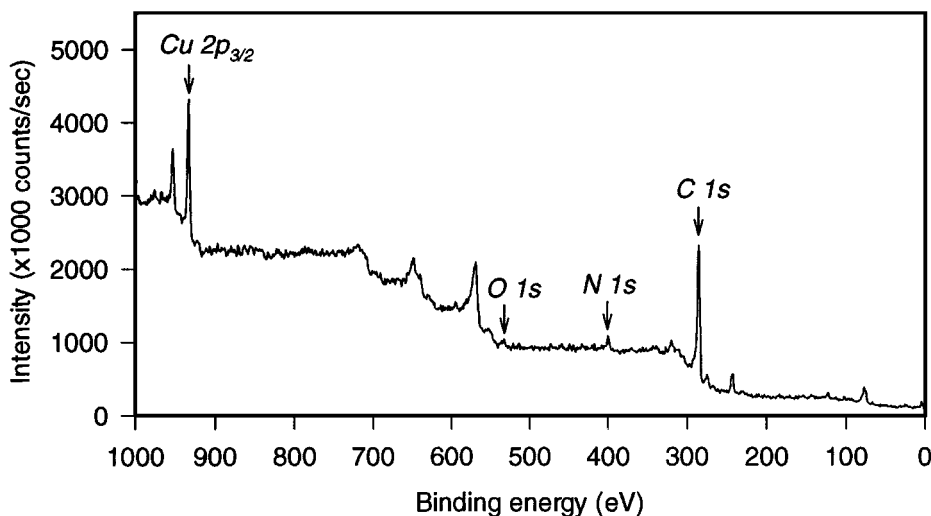


Figure 3 XPS photoelectron spectrum recorded for a CuCN sample.

TABLE I Average compositions of DLCN and CuCN samples extracted from XPS measurements

No.	Sample	Concentrations (at %)			
		C	N	Cu	O
1	DLC shallow	82	9	—	9
2	DLC medium	89	8	—	3
3	DLC deep	90	8	—	2
4	Cu shallow	59	11	30	—
5	Cu medium	59	12	29	—
6	Cu deep	69	14	17	—

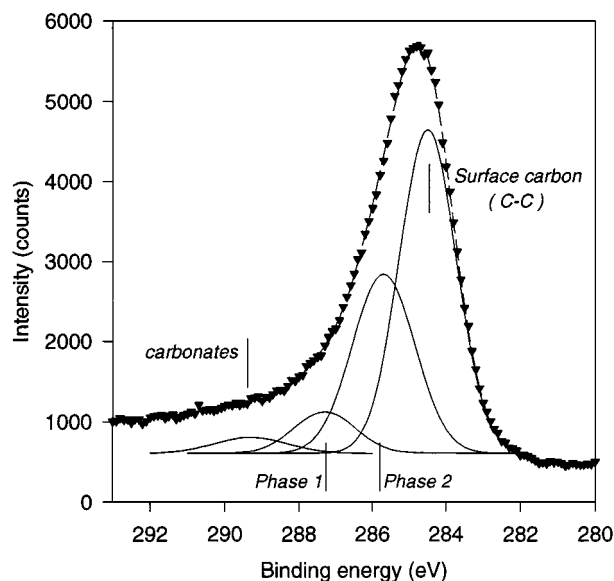


Figure 4 C1s contribution to the XPS spectrum recorded for a DLCN sample. The carbon peak is fitted with four components (see explanation in the text).

leading to the increase of carbon concentration on the sample surface or the carbon deposition on the sample surface which took place during the sputtering of the surface layer can neither be excluded.

The detailed experimental data were acquired in the vicinity of C 1s, N 1s and Cu $2P_{3/2}$ peak positions. The analysis of Cu peak did not reveal any significant changes of chemical state of copper, confirming thus that the metallic matrix did not react with the implanted elements. A typical XPS spectrum recorded for DLCN sample in carbon peak vicinity is shown in Fig. 4. The carbon part of the spectra was fitted with four components. The widths and positions of these components were kept constant for all studied samples. The peak at 284.5 eV was attributed to the carbon pollution at the sample surface (C–C bonds in so called surface carbon, [16]), the peak at 289.3 eV is characteristic to the carbon in carbonate compounds, whereas the peaks at 287.3 and 285.8 eV were attributed accordingly to the model of Marton and co-workers [17] to the carbon atoms bonded to nitrogen in so called phase 1 and phase 2 carbon nitrides. The binding energy of photoelectrons in phase 1 is supposed to be the same as in β - C_3N_4 carbon nitride [17]. One can note, that the chemical shift between phase 1, phase 2 and surface carbon is equal to 1.3–1.5 eV leading to the significant overlapping of those contributions. A better accuracy

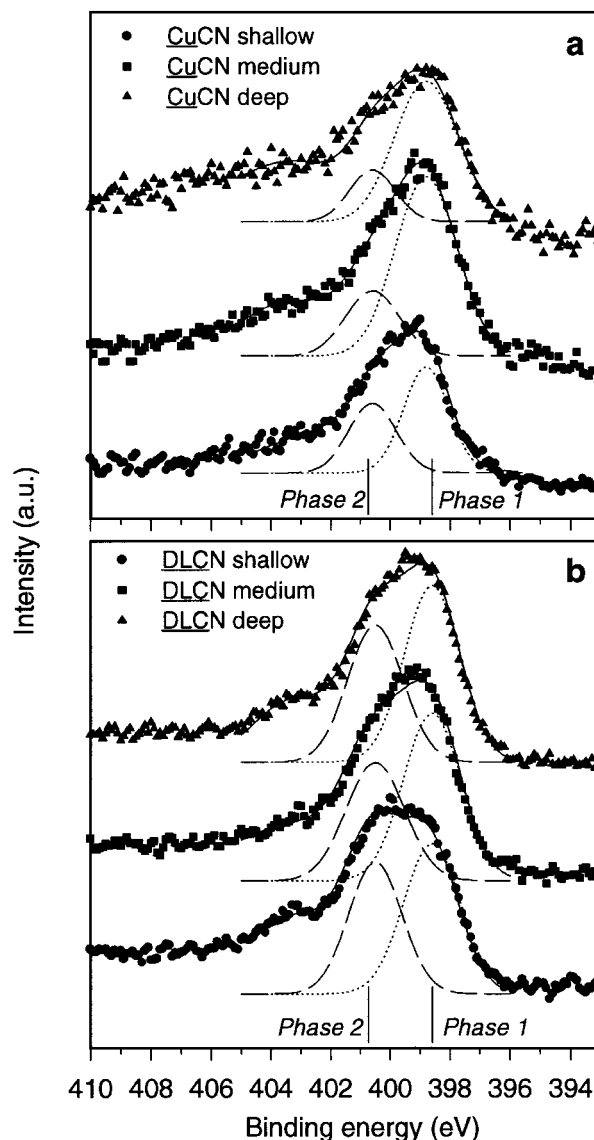


Figure 5 N1s contribution to the XPS spectra recorded at different depths for CuCN (a) and DLCN (b) samples. For the sake of clarity only the contributions of phase 1 and phase 2 are shown in this figure.

was obtained by the analysis of the nitrogen peak. First of all there is no influence of carbon contamination, secondly the chemical shifts of phase 1 and phase 2 are bigger (Fig. 5a and b). The nitrogen peak was splitted into four components; 404.9 eV, 403.2 eV (N–N or N–O bonds), 398.5 eV and 400.5 eV. The last two lines are attributed to the phase 1 and phase 2, respectively. All four nitrogen lines were used for fitting the spectra recorded on CuCN samples, whereas in DLCN samples the 404.9 eV line was not observed.

The first information that could be extracted from the XPS analysis are the fractions of atoms confined in a given phase. An example of such data is presented in Fig. 6 showing the fraction of nitrogen atoms bonded with carbon in phase 1 for DLCN and CuCN samples. One can note that the fraction of nitrogen in covalently bonded phase is higher when the synthesis was performed via C and N implantation into copper compared to nitrogen implantation into DLC layers.

The XPS technique permits also the determination of the stoichiometry of a given phase by using calculation method described in [17]. This procedure applied

TABLE II Average stoichiometry of phase 1 and phase 2 and their relative abundances extracted from XPS data

No.	Sample	Phase stoichiometry		Relative C–N phase abundance	
		Phase 1	Phase 2	Phase 1	Phase 2
1	<u>DLCN</u> shallow	C ₂ N	C ₅ N	50	50
2	<u>DLCN</u> medium	C ₂ N	C ₉ N	59	41
3	<u>DLCN</u> deep	C ₂ N	C ₉ N	56	44
4	<u>CuCN</u> shallow	C ₃ N _{3.6}	C ₅ N	26	74
5	<u>CuCN</u> medium	C ₃ N _{3.9}	C ₅ N	30	70
6	<u>CuCN</u> deep	C ₃ N _{3.75}	C ₄ N	27	73

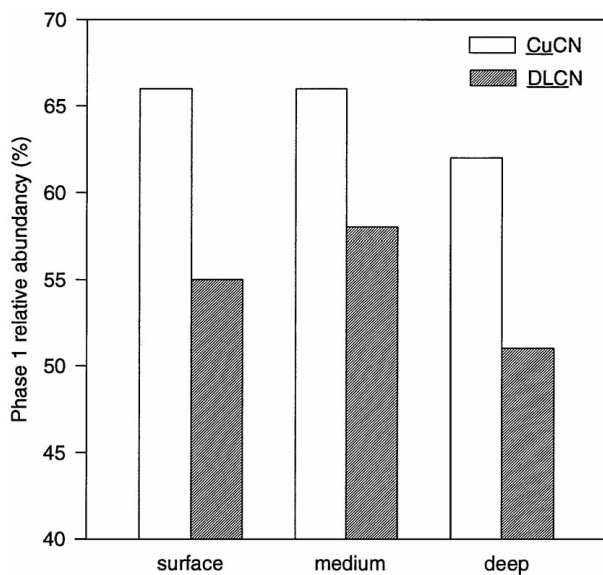


Figure 6 Fractions of nitrogen atoms in phase 1 carbon nitride in CuCN and DLCN samples.

to our experimental data allowed to detect four different C–N phases and to identify their compositions as: C₉N, C₅N, C₃N_{1.5} and C₃N_{3.7}. Detailed results of this analysis are shown in Table II. The last two columns in this table contain the relative abundances of phase 1 and 2 in the analyzed samples. The calculations were based on the fraction of atoms bonded in a given phase and on the phase stoichiometry. For example, at shallow depth in CuCN sample the XPS analysis revealed, that 19% of C and 62% of N atoms were bonded in phase 1 having the stoichiometry of C₃N_{3.6}, the rest of carbon bonded with nitrogen was confined in C₅N phase. Consequently, for each 100 C atoms 6.3 C₃N_{3.6} and 16.2 C₅N “molecules” were formed. This leads to 28% of C₃N_{3.6} and 72% of C₅N phase fractions, respectively. The same calculations performed for nitrogen atoms lead to the values of 24% of C₃N_{3.6} and 76% of C₅N phase abundances. The values listed in Table II are the average fractions obtained for both carbon and nitrogen atoms.

4. Discussion

The NBS measurements showed that by using C and N implantations into copper it is possible to form layers with high carbon and nitrogen concentrations. The

XPS analysis allowed the determination of the type of chemical bonds between carbon and nitrogen as well as the stoichiometry of the phases formed. The most important result from presented experiments is the direct observation of the covalently bonded phase having a stoichiometry very close to the value expected for β -C₃N₄. This phase was observed only in carbon and nitrogen implanted copper. After nitrogen implantation into DLC layers the stoichiometry of the covalently bonded phase (phase 1) is totally different and close to C₂N. It should be pointed out once again that the parameters used in the deconvolution procedure were exactly the same for CuCN and DLCN samples. The observed difference in covalently bonded phase composition is thus significant. The nitrogen-poor phase 2 is characterized by a stoichiometry of C₅N or C₉N. It is interesting to note, that C₅N phase was synthesized by pulse plasma method [18]. The infrared absorption analysis revealed in this case the presence of C=N and C≡N bonds. It was postulated, that C₅N phase may have a structure similar to that of chaoite (a form of carbon having -C=C- bonds).

It cannot be excluded, that the composition of the analyzed samples may be altered by the bombardment with 5 keV Ar ions. It is however unlikely that the radiation damage induced by this process will favorize the formation of metastable compound, such as C₃N₄. The bombardment with Ar ions should lead rather to the transformation of metastable phases into phases of lower values of free energy. It seems thus that this phase was formed during high energy implantation and not during the argon etching.

The obtained results give a new insight of the experimental data previously published. In most experiments the layers formed are nitrogen poor when compared with the β -C₃N₄ phase. This effect was often attributed to the formation of a mixture of C₃N₄ with various nitrogen-poor C–N phases. Our results show that ion implantation into carbon layers leads to the formation of a covalently bonded phase with a composition very different from the C₃N₄ phase. This phase could be, for example, a nitrogen doped diamond. Consequently, it seems that the observation of covalently bonded C–N phases without determination of their stoichiometry does not constitute an experimental evidence of β -C₃N₄ formation.

Detailed analysis showed that the covalently bonded phase formed in CuCN samples has a stoichiometry varying from C₃N_{3.6} to C₃N_{3.9} i.e. its nitrogen content is slightly lower than that expected by Liu and Cohen [1]. Despite of the possible experimental errors we suppose that this difference reflects a real physical fact. The calculations presented in a paper published by Hughbanks and Tian [19] indicated that in an original Liu and Cohen’s model the positions of nitrogen atoms are very close what leads to strong repulsive interactions. Consequently, the replacement of some nitrogen atoms by carbon ones was postulated to stabilize beta carbon nitride. This leads to a nitrogen-deficient phase formation (between C₃N₄ up to even C₄N₃, i.e. C₃N_{2.25}) which keeps most of structural features characteristic of C₃N₄. Our results confirm thus the calculations

performed by Hughbanks and Tian concerning the modified structure of carbon nitride.

5. Conclusions

The results presented in this paper provide a confirmation of the existence of covalently bonded C_3N_4 phase, showing that ion implantation of carbon and nitrogen atoms into an inert metallic matrix is an interesting technique allowing the synthesis of various carbon nitrides. The XPS measurements revealed that in both, DLCN and CuCN samples a mixture of two, covalently and non-covalently bonded C–N phases was detected. In copper samples implanted with high doses of carbon and nitrogen a covalently bonded C–N phase having a stoichiometry ranging from $C_3N_{3.6}$ to $C_3N_{3.9}$, i.e. very close to the value expected for β - C_3N_4 phase, was detected. The slightly lower nitrogen content confirms the hypothesis formulated by Hughbanks and Tian [19] that strong repulsive interactions between nitrogen atoms in the β - C_3N_4 structure make this structure energetically unfavorable. The preferential formation of covalently bonded phase in CuCN samples may be attributed either to a high compressive stress or to the fact that carbon was introduced into reaction with nitrogen as isolated atoms and not as clusters.

Acknowledgements

This work was partially financed by Polish State Committee for Scientific Research (SPUB research grant). The DLC films were kindly supplied by Applications Couches Minces, France. The authors are grateful to A. Plantier for C and N implantations.

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Received 22 July 1997

and accepted 22 January 1999