XPS and NRA depth profiling of nitrogen and carbon simultaneously implanted into copper to synthesize C_3N_4 like compounds

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Abstract

Carbon nitride nano-compounds have been synthesized into copper by simultaneous high fluence (10^{18} at.cm^{-2}) implantation of ^{13}C and ^{14}N ions. The implantations were performed with a 2 MV Tandem accelerator. The terminal voltage was fixed at 400 kV and the target temperature was maintained at 250 °C during the process. Depth profiling of ^{13}C and ^{14}N has been performed using (d,p) and (d,α) nuclear reactions induced by a 1.05 MeV deuteron beam. The retained dose deduced from NRA measurement is relatively close to the implanted one, which indicates that carbon and nitrogen diffusion processes were likely limited during implantation.

The chemical bonds between carbon and nitrogen were studied as a function of depth by X-ray photoelectron spectroscopy (XPS). The C 1s and N 1s core level photoelectron spectra revealed the presence of different types of C-N bonds, which correspond to specific kinds of chemical states. These results indicate that different carbon nitride compounds have been formed during the implantation.

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1. Introduction

In recent years, the synthesis of crystalline carbon nitrides has been extensively investigated as they are expected to show remarkable physical properties such as high hardness and wear resistance. A wide variety of elaboration techniques have been used such as reactive sputtering, chemical vapour deposition, pyrolysis of organic materials, laser deposition and ion implantation [1-6]. The fully crystalline phase formation remains nevertheless very difficult to achieve, whatever the technique employed. However, even amorphous carbon nitride layers may have suitable physical properties for the use in many tribological applications, for instance as protective coatings.

The aim of our study is to synthesize homogeneous, reproducible and well characterized carbon nitride compounds by means of ion implantation. For that purpose we performed simultaneous implantations of ^{13}C and ^{14}N into copper at 250 °C. Carbon and nitrogen depth distributions were determined by non resonant nuclear reactions induced by a 1.05 MeV deuteron beam. Then, the chemical bonds between carbon and nitrogen implanted atoms were studied by XPS measurements.

2. Experimental

2.1 Materials and substrate implantation

The samples are polished polycrystalline copper substrates. Simultaneous ^{13}C and ^{14}N implantations were performed using the non deflected beam line of the 2 MV ALTAÏS[1] Tandetron accelerator installed at LARN. We used a cesium sputter ion source (Snics) to perform these implantations. A copper cathode filled with a mixture of $K^{13}C^{14}N$ (30 mg) and

[1] **A**ccélérateur **L**inéaire **T**andetron pour l'**A**nalyse et l'**I**mplantation des **S**olides

Ag (60 mg) is bombarded by a Cs^+ ion beam. CN^- anions are sputtered from the cathode and accelerated in the low energy part of the Tandetron accelerator. Passing through the stripper canal, the CN^- anions hit N_2 gas molecules and a large variety of CN^+, C^{n+} and N^{q+} cations are produced and accelerated in the high energy part of Tandetron accelerator towards the copper sample. The sample was maintained at 250 °C and the vacuum pressure did not exceed 10^{-5} Pa during the implantation procedure. The terminal voltage of the accelerator was fixed at 400 kV, which gives for instance energies of respectively 608 keV and 625 keV for $^{13}C^+$ and $^{14}N^+$ (Table 1). The current density of the ion beam was measured around 80 µA.cm^{-2} and the total fluence was about 10^{18} at.cm^{-2} over an area of 3 mm in diameter.

2.2 Nuclear reactions and X-Ray photoelectron characterizations

The depth distributions of carbon and nitrogen in copper were studied using (d,p) and (d,α) non resonant nuclear reactions induced on ^{13}C and ^{14}N. The experimental set-up used to perform these measurements was presented in a previous work [7].

XPS measurements were performed to study the composition and the nature of the carbon nitride compounds formed in the implanted copper sample. XPS spectra were recorded with a SSX 100 Spectrometer system (Surface Science Instrument) equipped with a hemispherical electron analyser. All reported spectra were recorded at a 35° take-off angle relative to the substrate using monochromatized Al K_α radiation as excitation source (1486.6 eV). Nominal resolution was measured as full width at half maximum of respectively 0.92 and 1.4 eV for core-levels and survey spectra of the Au $4f_{7/2}$ peak. The argon ion gun used for sputtering was equipped with a special regulating system which enabled automated long time depth profile procedures. A depth profile procedure consists of several cycles of recording different XPS peaks followed by etching the sample. The recorded XPS peaks and the etching time have to be fixed before running the procedure and can not be changed during

its execution. All XPS procedures were performed with an ion beam raster size of about 2×2 mm^2 and an Ar^+ ion energy of 3.9 keV. The carbon and copper sputter rates obtained in these conditions were determined in order to convert the etching time in a metric scale (nm). For that purpose, a multilayer sample ($C_{50\ nm}$ / $Cu_{250\ nm}$ / Si) was prepared by physical vapour deposition. The carbon and copper layers thicknesses were measured by a stylus profilometer from Veeco Instruments (Surface Profile Measuring System Dektak). We performed 40 cycles to determine the depth profile of this sample. For each cycle, the C 1s, Cu $2p_{3/2}$ and Si 2p signals were recorded and the etching time was fixed to 60 s. The chemical composition was obtained from the areas of the detected XPS peaks, performing Shirley background subtraction and taking into account sensitivity factors for each constituent. In the same way, 28 cycles were performed to characterize the implanted samples. In this case the C 1s, N 1s, O 1s and Cu $2p_{3/2}$ peaks were studied, and the etching time was fixed to 120 s. Moreover, the spectra were referenced to the Cu 2p3/2 metallic copper line, always present in the sample, set at binding energy of 932.7 eV. The peaks were analysed using mixed Gaussian–Lorentzian curves (with a 70 % Gaussian content). Binding state information was determined from chemical shifts observed on the binding energy scale after the curve fitting of XPS peaks.

3. Results and discussion

We first present NRA results from carbon and nitrogen nuclear reactions obtained with the 1.05 MeV deuteron beam. Then, we discuss the procedure applied to convert the XPS sputtering time into the depth scale. The formation of characteristic carbon nitrogen bonds within the implanted layer is discussed on the basis of XPS measurements.

Figure 1 shows the experimental spectrum recorded at 150° (NRA detector) for the sample simultaneously implanted with ^{13}C and ^{14}N at 250 °C. The peak labelled $^{13}C_{p0}$ observed just below 6.0 MeV is due to the $^{13}C(d,p_0)^{14}C$ nuclear reaction. The very intense peak labelled $^{12}C_{p0}$ is attributed to ^{12}C surface contamination occurring during the implantation process. All other peaks are assigned to $^{14}N(d,p_i)^{15}N$ (with i = 0, 1, 2, 3, 4 or 5) and $^{14}N(d,\alpha_i)^{12}C$ (with i = 0 or 1) nuclear reactions. The simulation was performed with the SIMNRA 6.04 program [8] using the nuclear reaction cross sections measured by M. Kokkoris et al. [9], S. Pellegrino et al. [10] and J.L. Colaux et al. [11]. The copper sample used in this program was subdivided into thin layers whose composition was adapted to adjust the simulated curve to the experimental spectrum. The simulated spectrum is represented by the solid line in Figure 1. The thickness of layers provide by the SIMNRA program is given in at.cm^{-2}. The density of each layer was deduced from its composition in order to convert its thickness in a metric scale (nm). The calculated depth distributions of carbon (open circles) and nitrogen (open squares) are shown in Figure 2. A carbon surface contamination of about 20 nm is clearly observed in Figure 2.a. This may be explained by some carbon build-up phenomena during implantation as no carbon is detected on the virgin sample surface. The carbon and nitrogen depth distributions may be decomposed into a combination of Gaussian curves assigned to the different implanted ion species [12]. This decomposition is not represented in Figure 2. Nevertheless the position of each Gaussian curve maximum is reported in Table 1. We can see good agreement between the projected ranges calculated with SRIM2003 code (R_{SRIM}) [13] and the experimental results (R_{exp}). The slight difference between R_{SRIM} and R_{exp} was discussed in a previous work [14]. Finally, converting the nanometric depth scale in a 10^{15} at.cm^{-2} one, the integral of the depth profiles allows us to estimate the incorporated carbon and nitrogen atomic densities at $5.0\ 10^{17}$ at.cm^{-2} and $4.5\ 10^{17}$ at.cm^{-2} respectively. The sum of both is very close to the total implanted fluence

which was $1.0\ 10^{18}$ at.cm^{-2}. These results enable us to conclude that carbon and nitrogen diffusion is low during the implantation process.

The XPS depth profile of the C $_{50\ nm}$ / Cu $_{250\ nm}$ / Si multilayered sample is presented in Figure 3. The very sharp interface between the carbon and copper layers proves that the Ar^+ ion gun and the analysis beam are well aligned. On the other hand, the interface between copper layer and substrate (Si) is much less sharp, which suggests that the XPS depth resolution decreases with increasing depth. This may be explained by the sample roughness induced by Ar^+ ion bombardment increasing with the etching time. The carbon and copper sputter rates deduced from Figure 3 are $5.8\ nm.min^{-1}$ (S_C) and $18.2\ nm.min^{-1}$ (S_{Cu}) respectively. This large difference implicates that the total sputter rate of the implanted sample will change with depth because the carbon concentration varies strongly along the depth scale. In order to determine the equivalent width (W_{Eq}) sputtered during one etching cycle we have considered the following equation:

$$W_{Eq} = T \times \left(S_C \times A + S_{Cu} \times (1 - A)\right) \qquad \text{Equation 1}$$

where T is the etching time and A is the atomic concentration of carbon measured in the previous cycle. Note that the nitrogen concentration is not taken into account in this equation because, as will be seen later, the major fraction of nitrogen appears as gas bubbles. Moreover, as the carbon and copper sputter rates are strongly correlated to the experimental etching conditions, the sputter rates S_C and S_{Cu} has to be measured before each XPS depth profile.

The N 1s core level photoelectron spectrum, acquired at 630 nm depth, is presented in Figure 4.a. Three components (N_1, N_2 and N_3) can clearly be resolved for this spectrum. According to the literature [15-18], the N_1 and N_2 components (centered at 398.6 eV and 400.6 eV) are related to the presence of C-N bonds. The N_1 component (FWMH = 1.7 eV) is

assigned to nitriles (−C≡N) and pyridine (C−N ═C) type bonds while N_2 (FWMH = 1.8 eV) is attributed to sp^2 C−N bonds. The N_4 component (centered at 397.2 eV, FWMH = 1.7 eV) may be added in the low energy tail of N_1 peak. This can presumably be assigned to the C_3N_4 structure. The exact position and intensity of this component is nevertheless uncertain because it strongly depends on the exact background fitting. Thus the presence of C_3N_4 will be not discussed here. The much broader component N_3 (centered at 404.1 eV, FWMH = 3.6 eV) is attributed to nitrogen gas molecules [19]. The precipitation of nitrogen in large gas bubbles during the implantation was already highlighted in a previous work [12].

The C 1s core level photoelectron spectrum, acquired at the same depth, is presented in Figure 4.b. The long tail towards higher binding energies indicates the presence of low quantities of C─N and C─O bonds due to the higher electronegativity of nitrogen and oxygen. Nevertheless no clear peak components can be easily distinguished. To achieve the curve fitting, five components have been used. The major component C_0 (centered at 284.4 eV, FWMH = 1.8 eV) corresponds to carbon atoms bonded to carbon neighbours, as graphite (sp^2) or amorphous (sp^3) carbon. The C_1 (centered at 286.3 eV, FWMH = 1.6 eV) and C_2 (centered at 285.8 eV, FWMH = 1.5 eV) are related to nitrogen presence. C_1 is assigned to nitriles (−C≡N) and pyridine (C−N ═C) type bonds while C_2 is attributed to sp^2 C−N bonds [15-18]. As these positions are very close, the following constraint was imposed on the C_1 and C_2 areas to perform the curve fitting:

$$0.90 \times B(N_i) \leq A(C_i) \leq 1.10 \times B(N_i) \quad \text{for i = 1 or 2}$$

where $A(C_i)$ is the peak area of component C_i and $B(N_i)$ is the peak area of the component N_i normalized by the sensitivity factor of nitrogen. C_3 (centered at 288.0 eV) is attributed to the C−O bonds. Although no constraint is imposed on this component, the ratio between the C_3 area and the normalized area of O 1s peak (not shown here) is always observed between 0.85 and 1.15, which proves the validity of this component. Finally the much broader C_4 (centered

at 290.5 eV, FWMH = 2.8 eV), is assigned to carbon shake up. Whatever the depth analysed, this component represents about 14.0 % of the C_1 one which corresponds to the amount of shake up generally observed in literature.

These results show that several carbon nitride compounds are created during the simultaneous implantation of C and N ions into copper. Moreover, the atomic concentration of each carbon and nitrogen component can be deduced from their areas. Figure 2 shows the carbon (solid circles) and nitrogen (solid squares) depth profiles obtained by XPS. The agreement between NRA and XPS carbon depth profiles is very good, even if the XPS one is slightly broader and less intense due to the decreasing of the XPS depth resolution with etching time. The carbon retained dose deduced from the XPS results is equal to $5.4\ 10^{17}$ at.cm^{-2}, which is in very good agreement with the carbon retained dose measured by NRA. However, the nitrogen depth profile obtained by XPS is strongly different from that obtained by NRA. The nitrogen retained dose is evaluated to be $1.3\ 10^{17}$ at.cm^{-2} whereas we have found $4.5\ 10^{17}$ at.cm^{-2} by NRA. The precipitation of nitrogen into gas bubbles during the implantation can explain this strong divergence. Indeed, the gas bubbles will burst during the etching process. A large part of nitrogen will then be released in the XPS chamber and only a certain fraction is analyzed. The nitrogen retained dose without the contribution of gas bubbles was found to be $0.9\ 10^{17}$ at.cm^{-2}. We can then conclude that only 20 % of the implanted nitrogen interacts with carbon atoms to produce carbon nitride compounds.

4. Conclusion

Simultaneous implantation of carbon and nitrogen into copper was performed at 250 °C. Carbon and nitrogen depth profiles were measured using NRA and XPS. The results

obtained by NRA were compared and confirmed by SRIM2003. The very good agreement between the results obtained by NRA and XPS for carbon proves the reliance of the XPS depth profiling method. The carbon retained dose deduced from both techniques corresponded to the implanted one. That allowed us to conclude that any diffusion processes during the implantation are marginal. The long tail observed for higher binding energies in the C 1s core level spectra revealed the presence of C─N and C─O bonds, but no clear peak components can be resolved in these spectra. On the other hand the decomposition of N 1s core level spectra shown that at least two kinds of carbon nitride compounds were formed during the implantation. Unfortunately the majority of implanted nitrogen atoms precipitate in large gas bubbles and only about 20 % of them take part in the formation of carbon nitride compounds.

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Table 1: Energies and calculated (R_{SRIM}) and experimental (R_{exp}) projected ranges of CN^+, $^{13}C^{n+}$ and $^{14}N^{q+}$ ions implanted into copper with a terminal voltage of 400 kV on our Tandetron accelerator. As the CN molecule is broken hitting the surface of copper sample, the projected range of $^{13}C^{14}N^+$ corresponds to average of the ones of ^{13}C at 401 keV and ^{14}N at 432 keV.

	E (keV)	R_{SRIM} (nm)	R_{exp} (nm)
$^{13}C^{14}N^+$	833	429	440
^{13}C	208	257	280
$^{13}C^+$	608	606	650
$^{13}C^{2+}$	1008	866	910
^{14}N	225	240	260
$^{14}N^+$	625	550	600
$^{14}N^{2+}$	1025	775	820

Figure captions

Figure 1: Experimental and simulated NRA spectra recorded at 150° (NRA detector) for the copper sample simultaneously implanted with ^{13}C and ^{14}N at 250°C. Symbols represent the experimental spectrum and black line represents the simulation realized with SIMNRA code. Notations of C and N peaks are explained in the text.

Figure 2**:** Concentration depth distributions of carbon and nitrogen calculated from SIMNRA (open symbols) and CASAXPS (solid symbols) simulations for the copper sample simultaneously implanted with ^{13}C and ^{14}N at 250°C.

Figure 3**:** XPS depth profile of the multilayered sample ($C_{50\,nm}$ / $Cu_{250\,nm}$ / Si) prepared by physical vapour deposition.

Figure 4: N 1s (a) and C 1s (b) XPS spectra at a 630 nm depth for the copper sample implanted with ^{13}C and ^{14}N at 250 °C. Experimental data are represented by short dot lines. Solid lines are the results of the curve fitting Gaussian-Lorentzian components and the sum of them. Meaning of N_i and C_i notations is discussed in the text.

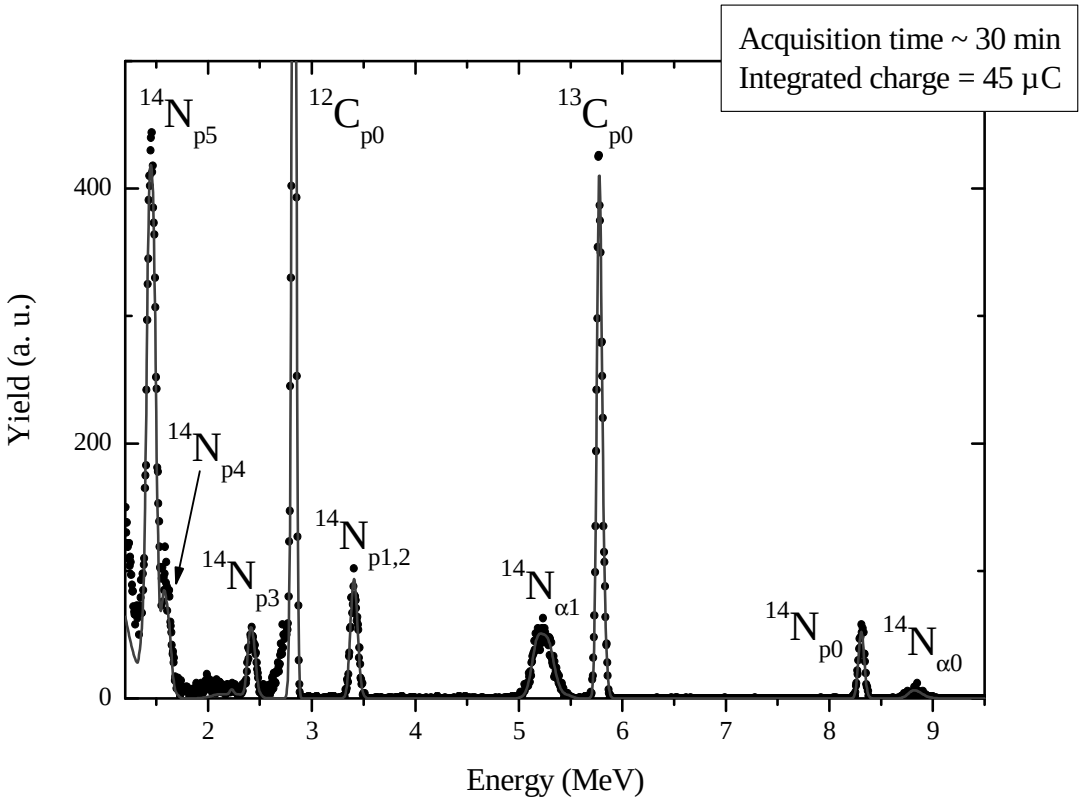

Figure 1

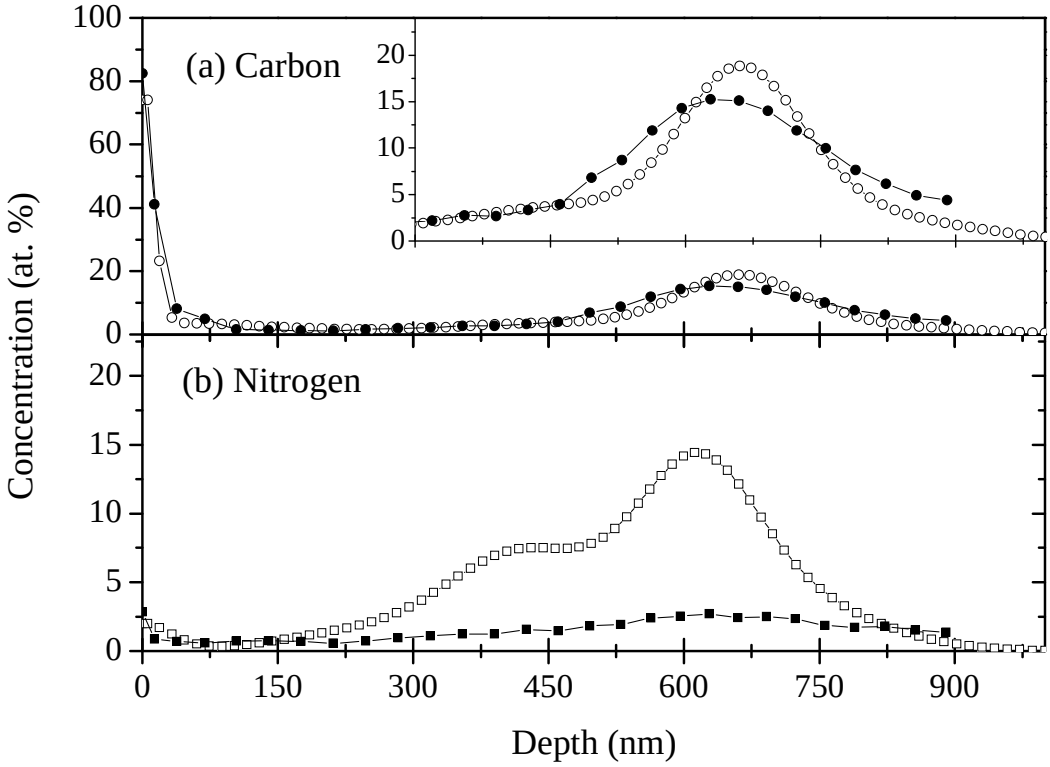

Figure 2

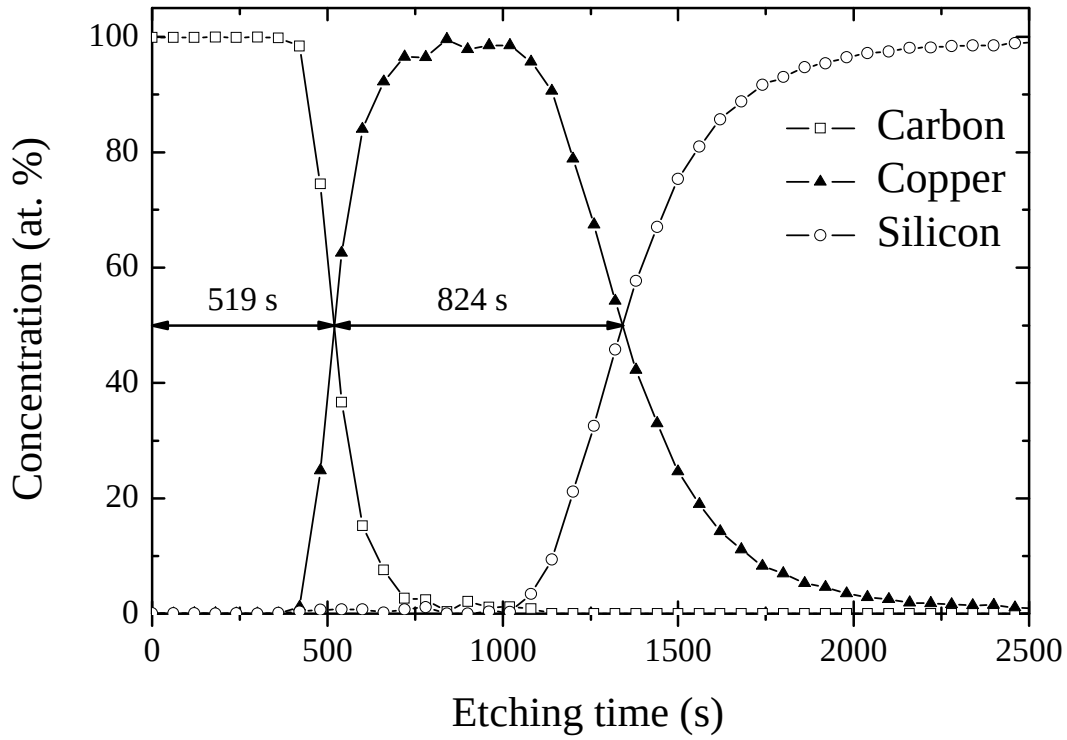

Figure 3

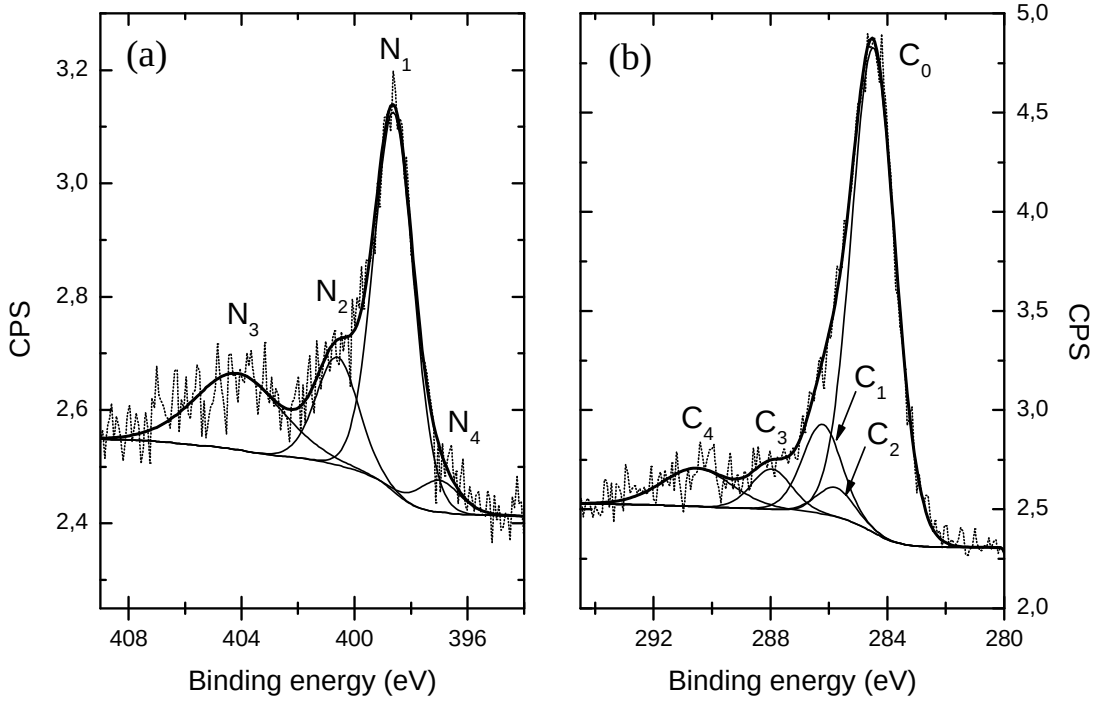

Figure 4