Depth profiling of carbon and nitrogen in copper using nuclear reactions

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Abstract

Simultaneous implantations of ^{12}C and ^{15}N were performed into copper using the non deviated beam line of a 2 MV Tandetron accelerator. The atomic composition of the implanted layer was measured using appropriate nuclear reactions with a 1.05 MeV deuteron beam. $^{12}C(d,p_0)^{13}C$ and $^{15}N(d,\alpha_0)^{13}C$ nuclear reactions were used to depth profile simultaneously ^{12}C and ^{15}N and to determine the relative contribution of multi-ionised ^{12}C and ^{15}N ions to the carbon and nitrogen distribution. We also used the narrow resonance at 429 keV of the $^{15}N(p,\alpha\gamma)^{12}C$ nuclear reaction to check the validity of our results . The depth distributions obtained with this resonant nuclear reaction confirmed that (d,p) and (d,α) reactions are well suited to profile both carbon and nitrogen elements with a quite good resolution. Moreover, using these reactions makes possible to profile ^{12}C and ^{15}N atoms with a single and relatively rapid measurement.

PACS codes : 25.40.Ny, 25.45.De, 29.30.Ep

Keywords : depth profiling, ^{15}N, NRA, RNRA, $^{15}N(d,\alpha_0)^{13}C$, $^{15}N(p,\alpha\gamma)^{12}C$

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1. Introduction

In recent years, the synthesis of crystalline carbon nitride C_3N_4 has been extensively investigated due to its highly interesting mechanical properties. Indeed, some calculations predicted that several structures as β-C_3N_4 would be harder than diamond [1]. So far, whatever the technique employed, mixed phase layers are quite often obtained and it remains very difficult to achieve fully crystalline phase formation [2-4]. Among these techniques, ion implantation may be an interesting solution, even if successive carbon and nitrogen implantations in metals have not yet been conclusive [5].

In this work, we performed different types of implantations with carbon ^{12}C and nitrogen ^{15}N ions into copper samples. Then, we determined the depth distributions of ^{12}C and ^{15}N using $^{12}C(d,p_0)^{13}C$ and $^{15}N(d,\alpha_0)^{13}C$ nuclear reactions with a 1.05 MeV deuteron beam. We also compared the ^{15}N implantation depth profiles determined by this NRA method with the ones obtained using the resonant $^{15}N(p,\alpha\gamma)^{12}C$ nuclear reaction [6].

2. Experimental

The samples were polished polycrystalline copper substrates. Two types of implantations were carried out with our 2 MV Tandetron accelerator (ALTAÏS[1]); a successive nitrogen $^{15}N^+$ and $^{15}N^{2+}$ implantation on a deflected beam line (first implantation), and a simultaneous multi-ionised ^{12}C and ^{15}N implantation on a non deflected beam line (second implantation). To perform these implantations, CN^- anions were produced by a Cs sputter ion source and injected in the low energy part of the Tandetron accelerator. After passing through the gas exchange channel, a large variety of C^{n+} and N^{q+} ions were produced leading to different energies for carbon and nitrogen ions (Table1) in the non deviated beam line. During both implantations, the samples were maintained at room temperature and the vacuum

[1] Accélérateur Linéaire Tandetron pour l'Analyse et l'Implantation des Solides

pressure did not exceed 10^{-5} Pa. The terminal voltage of the accelerator was fixed at 400 kV for all the implantations. In the first implantation, the nitrogen $^{15}N^{2+}$ was implanted in first place. The corresponding energy was 1050 keV with a current density of 3 µA.cm^{-2} and the final dose was 10^{17} at.cm^{-2} over a 5×5 mm^2 area. The nitrogen $^{15}N^{+}$ implantation was performed on the same target spot with an energy of 648 keV and a current density of 6 µA.cm^{-2}. The final dose was 2×10^{17} at.cm^{-2}. The energies of $^{15}N^{+}$ and $^{15}N^{2+}$ ions corresponded to implantation projected ranges respectively close to 580 and 820 nm in copper, according to SRIM2003 code calculations (Table 1) [7]. During the second implantation performed on the non deviated beam line of the accelerator, the current density was measured around 20 µA.cm^{-2} and the total final dose (including C and N ions) was estimated at 10^{18} at.cm^{-2}.

The depth distribution of nitrogen ^{15}N in the first implantation and the ones of carbon ^{12}C and nitrogen ^{15}N in the second implantation were determined with resonant (RNRA) and non resonant (NRA) nuclear reactions using the same facilities as for the implantations. For NRA analyses, ^{15}N and ^{12}C atoms were depth profiled using $^{15}N(d,\alpha_0)^{13}C$ and $^{12}C(d,p_0)^{13}C$ nuclear reactions with a 1.05 MeV deuteron beam. Two silicon surface barrier detectors were fixed at 150° and 165° relative to the incident beam to measure respectively NRA and RBS signals. A 12 µm mylar absorber foil was placed in front of the NRA detector (25.7 msr) to stop backscattered ions and to measure energetic α and proton particles. The RBS detector was collimated (0.18 msr) to allow the detection of backscattered deuterons without any absorber foil. The RBS detector was used as a monitor to determine the quantity of incident deuterons during the measurements. For RNRA analyses, we considered the very narrow resonance at 429 keV (width of 120 eV) of the $^{15}N(p,\alpha\gamma)^{12}C$ nuclear reaction [6]. A NaI scintillation detector was used to detect the gamma radiation emitted at 4.43 MeV by the nuclear reaction. The ^{15}N depth profiling was carried out by varying the energy of the incident

proton beam from 420 to 700 keV with 2 keV steps. A chromium nitride sample with a well defined atomic composition was used as a reference for the determination of absolute concentrations.

3. Results and discussion

Fig. 1a and 1b show the experimental NRA spectra measured at 150° for the first and the second implantation. A very intense peak is observed in both spectra just below 3 MeV, which can be attributed to ^{12}C surface contamination in the first implantation and to a mixing between surface contamination and implanted ^{12}C ions in the second one. The peak detected around 4 MeV corresponds to the (d,α) reaction with the implanted ^{15}N ions. Another peak below 6 MeV is assigned to the (d,p) reaction with ^{13}C isotopes. We can observe that all the peaks are broader for the second implantation where multi-ionised ions with different energies are implanted (Table 1). From these spectra, we determined the total concentrations and the depth distributions of ^{12}C and ^{15}N elements using the SIMNRA program [8]. The simulated SIMNRA spectra are presented in Fig. 1 and the different calculated depth profiles of ^{12}C and ^{15}N are shown in Fig. 2 and Fig. 3.

In the first implantation, the total nitrogen concentration calculated from the curve area in Fig. 2a (2.5×10^{17} at.cm^{-2}) corresponds well to the expected one. The corresponding ^{12}C depth distribution is not reported here as ^{12}C presence is mainly due to a 50 nm thick surface contamination layer occurring during ion implantation (carbon build-up phenomenon [9]). The experimental distribution maxima, respectively close to 600 and 860 nm for $^{15}N^{+}$ and $^{15}N^{2+}$ ions, correspond well with the projected ranges calculated with SRIM2003 program (Table 1). In the second implantation, several distributions are observed around a main peak which corresponds to $^{15}N^{+}$ implanted ions. From the comparison with the distribution obtained in the first implantation and from the SRIM2003 calculated projected ranges

(table 1), we can attribute the first shoulder around 300 nm to neutral ^{15}N implanted atoms and the 3 other ones at 880, 1020 and 1200 nm to respectively $^{15}N^{2+}$, $^{15}N^{3+}$, and $^{15}N^{4+}$ implanted ions. A ^{15}N surface peak is also detected, which can be explained by a diffusion process of nitrogen during the implantation.

Then, we used the resonance at 429 keV of the $^{15}N(p,\alpha\gamma)^{12}C$ nuclear reaction to confirm the validity of the results obtained by NRA for both implantations. The ^{15}N depth distributions obtained by RNRA are shown in Fig.2. The NRA ^{15}N depth profiles are relatively close to the RNRA ones, and the contributions of different multi-ionised carbon and nitrogen ions are clearly revealed by both techniques. Although we have not estimated the exact depth resolution of the NRA method used in our experiments, the RNRA results confirm that (d,α) nuclear reactions are well suited to profile nitrogen elements with a quite good resolution. In Fig. 3 are shown the depth profiles of nitrogen and carbon ions determined by the NRA method for the second implantation. A very thin ^{12}C contamination layer (< 2 nm), characteristic of the carbon build-up phenomenon, is detected [9]. This carbon layer is not visible in the Fig. 3 due to too small scales. As for the ^{15}N depth profile, a shoulder attributed to neutral ^{12}C implanted species, is detected before the main peak (corresponding to $^{12}C^{+}$ ions), but only one is observed for deeper ranges. It indicates that only very small quantities of $^{12}C^{3+}$ and $^{12}C^{4+}$ ions are present in the implantation ion beam. This was confirmed measuring the different intensities of multi-ionised carbon ion beam on a deviated beam line of the accelerator. We can also remark that the nitrogen and carbon total concentrations simultaneously implanted on the non deviated line are quite equal, which is interesting for the purpose of forming carbon nitride compounds close to the C_3N_4 stoichiometry.

4. Conclusion

We showed that $^{12}C(d,p_0)^{13}C$ and $^{15}N(d,\alpha_0)^{13}C$ nuclear reactions are well suited to profile both carbon and nitrogen elements in a single and relatively rapid measurement and with a quite good resolution. After a simultaneous carbon and nitrogen implantation, we were able to distinguish the relative contributions of multi-ionised elements to the total depth profiles. Moreover, the distributions of nitrogen ^{15}N obtained by RNRA, using the $^{15}N(p,\alpha\gamma)^{12}C$ reaction, were very close to the ones determined by NRA. The strong correlation in shape and in concentration between the ^{15}N and ^{12}C depth profiles suggests that carbon nitrides close to the C_3N_4 stoichiometry may be synthesized in copper.

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Tables

Table 1: Energies of implantation and experimental (R_{exp}) and calculated (R_{SRIM}) projected ranges of ^{12}C and ^{15}N ion depth distributions in copper for a terminal voltage of 400 kV on our Tandetron accelerator.

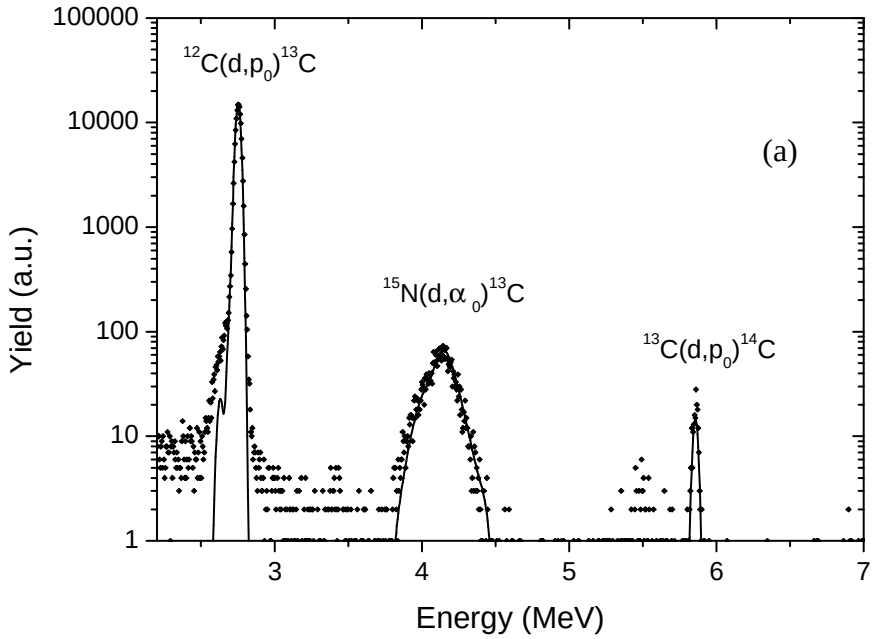
	E (keV)	R_{SRIM} (nm)	R_{exp} (nm) 1st implantation	R_{exp} (nm) 2nd implantation
C	195	240	-	300
C^+	600	585	-	600
C^{2+}	1000	840	-	880
N	243	250	-	300
N^+	648	580	600	600
N^{2+}	1050	820	860	880
N^{3+}	1450	1000	-	1020
N^{4+}	1860	1180	-	1200

Figure captions

Figure 1: Experimental (dots) and simulated (solid lines) NRA spectra at 150° of the copper sample implanted at room temperature with (a) $^{15}N^{+}$ and $^{15}N^{2+}$ (1^{st} implantation) and (b) $^{12}C^{n+}$ and $^{15}N^{p+}$ (2^{nd} implantation on the non deviated beam line).

Figure 2: Depth distributions of ^{15}N ions determined from SIMNRA simulations (open squares) and from RNRA measurements (solid lines) for the copper samples implanted with (a) $^{15}N^{+}$ and $^{15}N^{2+}$ (1^{st} implantation) and (b) $^{12}C^{n+}$ and $^{15}N^{p+}$ (2^{nd} implantation on the non deviated beam line).

Figure 3: Depth distributions of ^{12}C (filled triangles) and ^{15}N (open squares) ions determined from SIMNRA simulations for the copper sample implanted on the non deviated beam line (2^{nd} implantation).



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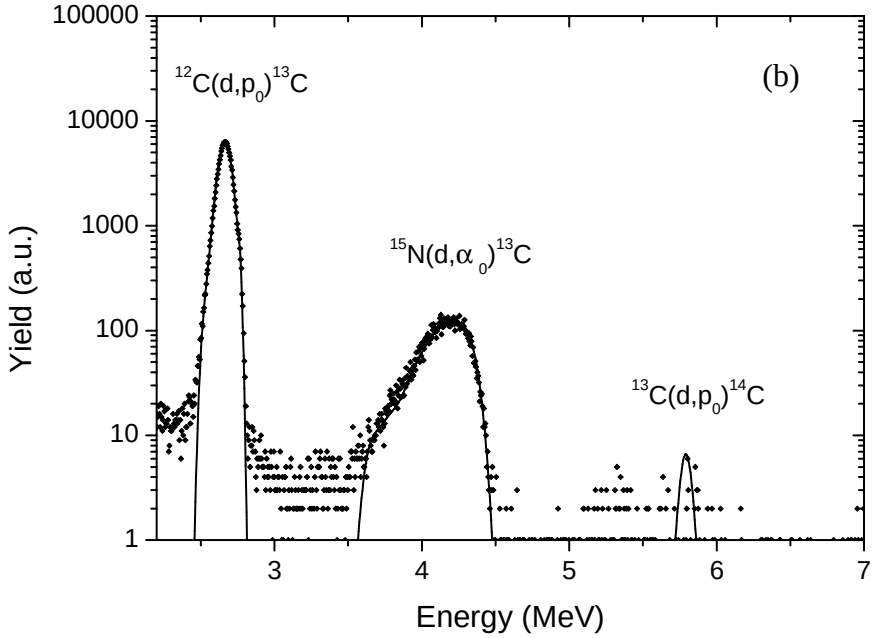

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176 Figure 1

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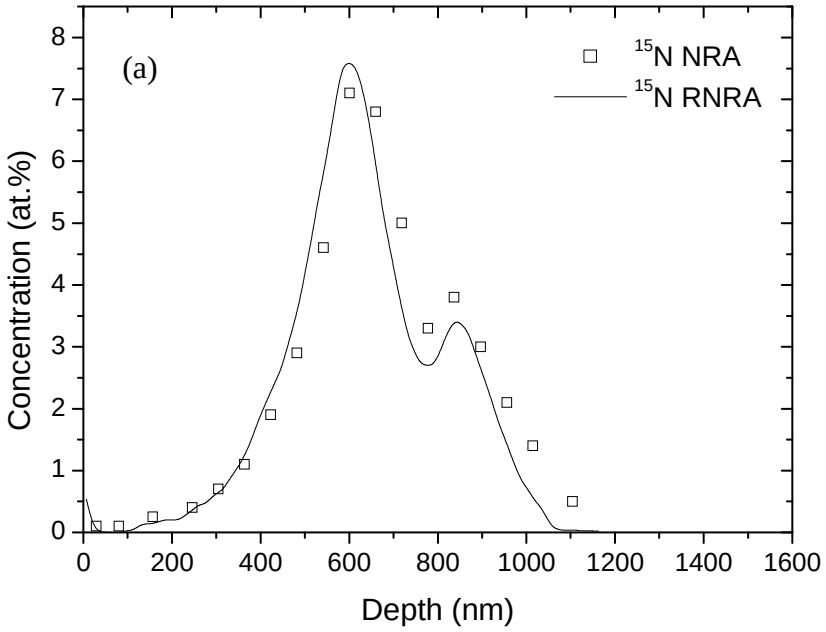

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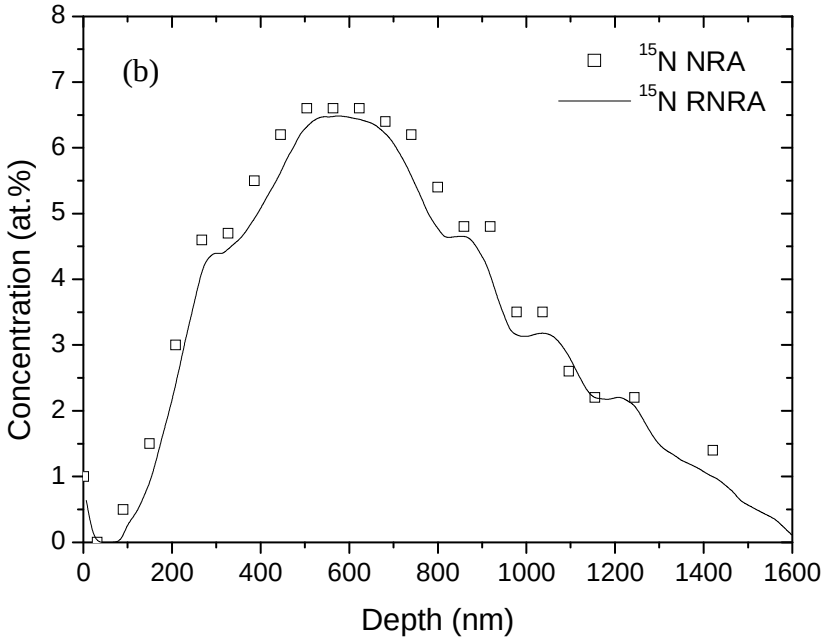

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181 Figure 2

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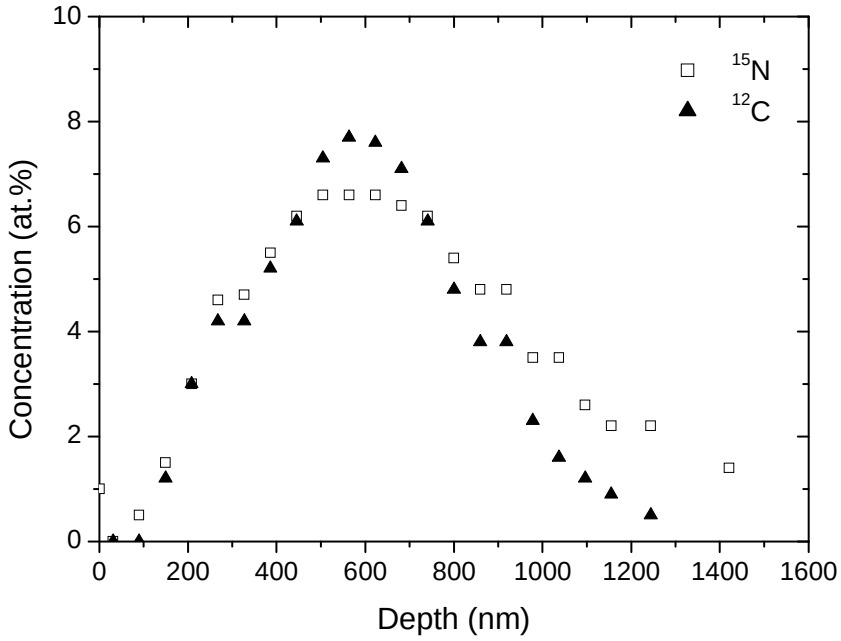

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185 Figure 3

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