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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 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

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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.

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

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.

Fig. 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 Kokkoris et al. [9], Pellegrino et al. [10] and 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 Fig. 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 Fig. 2 (a) and (b) respectively. A carbon surface contamination of about 20 nm is clearly observed in Fig. 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 Fig. 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

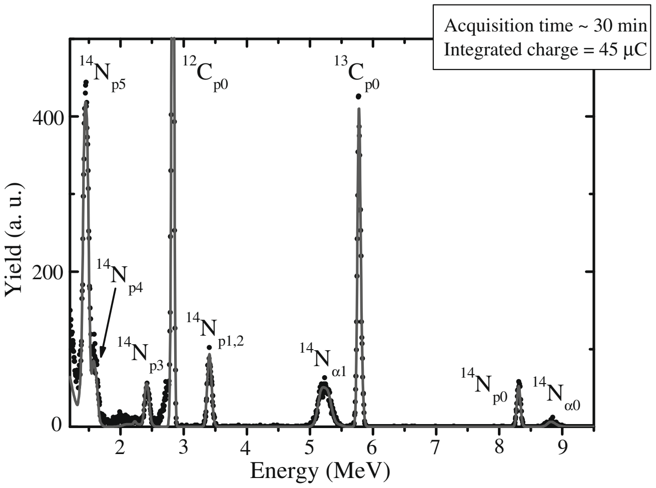

Fig. 1. Experimental and simulated NRA spectra recorded at 150° (NRA detector) for the copper sample simultaneously implanted with ^{13}C and ^{14}N at 250 °C. Symbols represent the experimental spectrum and black line represents the simulation realized with SIMNRA code. Notations of C and N peaks are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

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