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Formation of carbon nitride compounds during successive implantations in copper

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Abstract

Copper substrates are successively implanted with carbon and nitrogen ($^{13}C^+$ and $^{14}N^+$) at high fluences (5×10^{17} and 1×10^{17} at. cm^{-2}, respectively) in order to synthesize specific carbon nitride compounds. The concentration as well as the depth distribution of carbon ^{13}C and nitrogen ^{14}N are determined using non resonant nuclear reactions induced by a 1.05 MeV deuteron beam. The use of (d,p) and (d,α) reactions allows us to profile both ^{13}C and ^{14}N elements with a single and relatively rapid measurement and a quite good resolution. The bonded states of carbon and nitrogen are studied as a function of depth by X-ray photoelectron spectroscopy (XPS). The curve fitting of the C 1s and N 1s photopeaks shows that carbon and nitrogen atoms exist in different chemical states depending on the analysis depth, which correspond to specific kinds of chemical bonds. At least two characteristic C–N bonds are detected indicating that different carbon nitride compounds have been formed during the implantations.

Keywords: Carbon; Nitrogen; XPS; NRA; Implantation

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 wide band gap and high hardness and wear resistance. Indeed, some calculations predicted that α- and β-C_3N_4 would be harder than diamond [1]. A wide variety of elaboration techniques have been used such as reactive sputtering, chemical vapour deposition, pyrolysis of organic materials, laser deposition and ion implantations [2–7]. So far, whatever the technique employed, mixed phase layers are quite often obtained and it remains very difficult to achieve fully crystalline phase formation. Some studies have also shown that fullerene-like structures can be formed from nitrogen-poor CN_x phase [8]. For instance, carbon nitride systems close to the $C_{11}N_4$ stoichiometry, that present interesting mechanical properties as high compliance, have been found to be stable [9]. Although ion implantation may be one solution to synthesize these types of new compounds due to the possibility to control precisely the modifications on surface properties of materials, successive carbon and nitrogen implantations in metals have not yet succeeded in that way [10]. Nevertheless, even amorphous carbon nitride layers have suitable physical properties for the use in many tribological applications, for instance as protective coatings.

The aim of our study is to form at least homogeneous, reproducible and well characterized carbon nitride compounds by means of implantation. We performed successive implantations of ^{13}C and ^{14}N into copper at 200 °C using a 2 MV Tandetron accelerator. Then, we determined the concentration depth distributions of carbon ^{13}C and nitrogen ^{14}N using non resonant nuclear reactions (NRA) induced by a 1.05 MeV deuteron beam. To obtain information on the nature of the chemical bonds created between atoms in the carbon–nitride layer formed, we carried out XPS measurements.

2. Experimental

2.1. Materials and substrate implantation

The samples are polished polycrystalline copper substrates. Successive carbon $^{13}C^+$ and nitrogen $^{14}N^+$ implantations were

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carried out using the 2 MV ALTAIS Tandetron accelerator (Accélérateur Linéaire Tandetron pour 1'Analyse et 1'Implantation des Solides). During both implantations, the sample was maintained at 200 °C using a specific sample heater and the vacuum pressure did not exceed 10^{-5} Pa. The implantation of carbon was performed in first place. It was implanted at 400 keV with a current density of about 6 μA cm^{-2} and the final dose was 5×10^{17} at. cm^{-2} over a 5 mm × 5 mm area. The nitrogen implantation was performed at 450 keV with a current density of 4 μA cm^{-2} and the final dose was 10^{17} at. cm^{-2} (on the same area). The energies of nitrogen and carbon ions were chosen to obtain identical implantation projected ranges close to 450 nm in copper, according to SRIM code calculations [11].

2.2. *Characterization*

The concentration as well as the distribution of carbon ^{13}C and nitrogen ^{14}N were determined using non resonant nuclear reactions induced by a 1.05 MeV deuteron beam before and after the ^{14}N implantation. NRA experiments were performed using the same facilities as for the implantations (ALTAIS Tandetron accelerator). We considered the nuclear reactions ^{14}N(d,p$_0$)^{15}N, ^{14}N(d,p$_{12}$)^{15}N, ^{14}N(d,p$_3$)^{15}N, ^{14}N(d,α_1)^{12}C, and ^{13}C(d,p$_0$)^{14}C to depth profile ^{14}N and ^{13}C, and ^{12}C(d,p$_0$)^{13}C to determine the quantity of ^{12}C carbon contamination brought during implantation. Two silicon surface barrier detectors were placed at 150° and 165° relative to the incident beam to measure respectively NRA and RBS signals. A 12 μm mylar absorber foil was set in front of the NRA detector at 150° in order to stop backscattered ions and to measure α and proton energies. Since the cross sections of the nuclear reactions on ^{14}N and ^{13}C are very low, we used a large solid angle (25.7 msr) for this detector to minimize the acquisition time (about 20 min). The RBS detector was collimated (0.18 msr) to allow the detection of backscattered deuterons without any absorber foil. The α and protons emitted from nuclear reactions at low energy were also detected with a better resolution than with the NRA detector. The RBS detector was used as a monitor to determine the concentrations of nitrogen and carbon atoms implanted in the copper sample from the quantity of incident deuterons detected. The distribution homogeneity of carbon and nitrogen was controlled carrying out several measurements on the implanted area of the sample.

XPS measurements were performed to study the composition and the nature of the carbon–nitride layer 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 Kα radiation as excitation source (1486.6 eV). Nominal resolution was measured as full width at half maximum of 1.0 and 1.7 eV for core-levels and survey spectra, respectively. The argon ion gun used for sputtering was equipped with a special regulating system which enabled automated operation during long time depth profile procedures. The depth profiling conditions were the followings: raster size of about 2 mm × 2 mm, Ar$^+$ ion energy of 4 keV and sputter rates around 3 nm min^{-1}. Depth calibration was done measuring the crater depth generated by argon sputtering on the copper sample. The chemical composition was obtained from the areas of the detected XPS peaks in the C 1s, N 1s, O 1s and Cu 2p$_{3/2}$ regions, performing Shirley background subtraction and taking into account sensitivity factors for each constituent. The analyzed core-level lines were referenced with respect to the component C 1s binding energy. The peaks were analysed using mixed Gaussian–Lorentzian curves (90% of Gaussian character). 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 with the 1.05 MeV deuteron beam. Then, the formation of characteristic carbon nitrogen bonds in the implanted layer is discussed on the basis of XPS measurements.

Fig. 1 shows the experimental NRA spectrum measured at 150° after carbon and nitrogen implantations. A very intense peak is observed just below 3 MeV, which can be attributed to ^{12}C surface contamination. Around 6 MeV, the (d,p) peak corresponds to the implanted ^{13}C ions. All the other peaks are assigned to (d,p) and (d,α) reactions with ^{14}N element. From this spectrum, we determined the total concentrations and the depth distributions of ^{12}C, ^{13}C and ^{14}N elements using the SIMNRA program [12] in which specific nuclear reaction cross sections are considered and the copper sample is sliced into layers containing all the elements concerned. The simulated SIMNRA spectrum is represented in Fig. 1 and the different concentration depth distributions of ^{12}C, ^{13}C and ^{14}N calculated are shown in Fig. 2.

The ^{13}C depth distribution determined before the ^{14}N implantation is slightly narrower than the final one but both areas are identical (distributions not shown here) [13], which means that a small carbon diffusion process occurs during the nitrogen implantation. Although ^{13}C and ^{14}N concentrations correspond

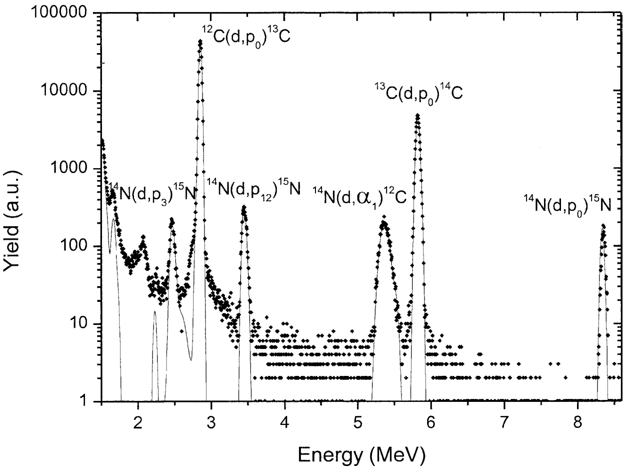

Fig. 1. Experimental and simulated NRA spectra of the copper sample implanted with ^{13}C$^+$ and ^{14}N$^+$ at 200 °C measured at 150° (NRA detector). Symbols (diamonds) and solid lines represent respectively the experimental spectrum and the simulated one with SIMNRA program.