Simultaneous depth profiling of the ^{12}C and ^{13}C elements in different samples using (d,p) reactions.

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Abstract

Nuclear reactions (d,p) are often used to perform depth profiling of light elements in solids. In particular, protons coming from $^{12}\text{C}(\text{d},\text{p}_0)^{13}\text{C}$ and $^{13}\text{C}(\text{d},\text{p}_0)^{14}\text{C}$ reactions are emitted at very different energies. Consequently these two reactions can be used to depth profile ^{12}C and ^{13}C simultaneously. Nevertheless the cross section of $^{13}\text{C}(\text{d},\text{p}_0)^{14}\text{C}$ reaction is ten times smaller than the $^{12}\text{C}(\text{d},\text{p}_0)^{13}\text{C}$ one. So, the geometry of detection must be judiciously chosen in order to depth profile these two elements with a high sensitivity and good resolution.

In the framework of this study we have performed 400 keV ^{13}C ions implantation into polished copper substrates at different temperatures and implanted doses with a 2 MV Tandem accelerator. Using the reactions described above, we have studied the evolution of ^{13}C depth profile as a function of implanted doses and temperature. We have also determined the origine of surface contamination that appears during the implantation process.

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1. Introduction

Since 1985 and the fullerene C₆₀ discovery [1], there has been an intensive effort driven by the scientific community to study the so-called novel carbon nanostructures (fullerenes, nanotubes, carbon onions). At present there are numerous techniques allowing to synthesize carbon onions [2-5]. One of them developed by T. Cabioch et al. in the early 1990s uses high dose carbon ion implantation into hot substrates (like copper or silver) [4,6-9]. Recently the same team has been shown by successive ¹³C and ¹²C low energy implantation into silver that depth distribution of implanted carbon has a Gaussian-like shape and there is no preferential carbon diffusion towards the surface during the implantation process [10].

In this paper, we study high energy implantation of ¹³C into copper and we try to explain the depth distributions observed as a function of implanted dose and temperature. On the other hand, it is well known that build-up of Carbon occurs during ion implantation. This phenomenon is directly related to residual vacuum and implantation parameters and we try to show that it is responsible to the surface contamination observed on the implanted samples. We optimized the detector geometry in order to depth profile ¹²C and ¹³C with high sensitivity and good resolution by using nuclear reactions induced by deuteron.

2. Experimental details

Polished copper substrates were fixed into a furnace mounted in an implantation chamber to perform different ¹³C⁺ ions implantations at different temperatures (200, 370 and 600 °C). Each one was performed in residual pressure less than 7 · 10⁻⁴ Pa. ¹³C⁺ ions of 400 keV were produced by ALTAÏS¹ the 2MV Tandatron accelerator installed at LARN (Namur). About 4 hours of implantation was necessary to obtain an average dose of 5 · 10¹⁷ at.

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cm^{-2} on a rectangular surface ($5 \times 6 \text{ mm}^2$) with ion beam intensity of about $1.6 \mu\text{A}$. Due to the fact that the beam was not homogenous, we are able to measure the areal density at different places on the implanted specimens using the reactions described below.

In order to characterize the implanted samples in one measurement, we used non resonant nuclear reactions (NRA) induced by 1.050 MeV deuteron beam ($1 \times 1 \text{ mm}^2$). Two silicon surface barrier detectors were mounted at 135° and 165° relative to the incident beam. The NRA detector at 135° measured protons emitted by $^{12}\text{C}(\text{d},\text{p}_0)^{13}\text{C}$ and $^{13}\text{C}(\text{d},\text{p}_0)^{14}\text{C}$ reactions. A $12\mu\text{m}$ MylarTM absorber foil was placed in front of the detector to stop the intense flow of backscattered ions. Since the cross section of the $^{13}\text{C}(\text{d},\text{p}_0)^{14}\text{C}$ is ten times lower (about 3 mb sr^{-1}) [11] than the cross section of $^{12}\text{C}(\text{d},\text{p}_0)^{13}\text{C}$ [12-14], we have chosen to use a large solid angle (25.7 msr) in order to obtain a good statistic while limiting the acquisition time to about 10 minutes. The RBS detector placed at 165° was collimated with a very small solid angle (0.18 msr) in order to detect backscattered deuterons flow without any absorber. The backscattered deuterons on copper were used as a monitor to measure incident particles [15]. Each of the three samples was measured in five different places in order to evaluate the non uniformity of carbon beam irradiation. The acquisition time for each measurement was monitored by integrating the current beam to obtain an accumulated charge of $15 \mu\text{C}$.

3. Results

The measurements were realized at different places on each sample and show that the implanted dose varied in a wide range (from $2 \cdot 10^{17}$ to $16.3 \cdot 10^{17} \text{ at. cm}^{-2}$) according to the position on the irradiated zone. These doses were calculated by simulation of the experimental spectra with the SIMNRA code [16]. As indicated in the previous section, the average

implanted dose is $5 \cdot 10^{17} \text{ }^{13}\text{C cm}^{-2}$ and we have performed reactions to reveal the non-uniformity which is not the first objective of this paper.

Figure 1 shows typical experimental NRA spectra of copper samples implanted with ^{13}C at various temperatures recorded in the NRA detector. The $^{12}\text{C}_{\text{p}_0}$ at 2.9 MeV and the $^{13}\text{C}_{\text{p}_0}$ at 5.9 MeV are due to nuclear reactions $^{12}\text{C}(\text{d},\text{p}_0)^{13}\text{C}$ and $^{13}\text{C}(\text{d},\text{p}_0)^{14}\text{C}$ respectively. We have adopted the same identification for the reactions induced by deuterons (i.e. $^{16}\text{O}_{\text{p}_0}$ as nuclear reaction $^{16}\text{O}(\text{d},\text{p}_0)^{17}\text{O}$). We can observe that the intensity of the $^{13}\text{C}_{\text{p}_0}$ peak is proportional to the implanted dose. The shape of this peak is wider for the sample implanted at high temperature (Fig. 1a). This effect due to diffusion phenomenon during implantation will be discussed later.

The intensity of the $^{12}\text{C}_{\text{p}_0}$ peak reveals the build-up phenomenon during the implantation. At temperature lower than 370°C (Fig. 1b and 1c) we can observe a very intense contribution of ^{12}C at the surface while ^{12}C contamination is strongly reduced when the implantation temperature is 600°C (Fig. 1a). As it can be seen on Figure 1, a shoulder at low energy of the $^{12}\text{C}_{\text{p}_0}$ peak reveals the high sensitivity of this reaction. We can measure the areal density of ^{12}C in the bulk of the implanted samples.

At low energy ($< 2.5 \text{ MeV}$) the spectra for the high temperature (600°C) and the low temperatures (200°C and 370°C) are completely different. We can observe on figure 1a the peaks $^{16}\text{O}_{\text{p}_0}$ and $^{16}\text{O}_{\text{p}_1}$, due to the presence of oxygen, at 2.2 and 1.35 MeV respectively. The sensitivity of these reactions is limited by an interference with the $^{13}\text{C}(\text{d},\alpha_0)^{11}\text{B}$. In order to simulate the spectra at low energies, the cross section of this reaction already measured by Marion et al. [17] for energies higher than 1 MeV should be measured at lower energies.

4. Discussion

Figure 2 shows the depth distributions of ^{12}C , ^{13}C and ^{16}O . The concentration of samples has been sliced into layers containing all concerned elements, which are represented by the different points. The surface contribution ($^{12}\text{C}_{\text{surf}}$) is clearly observed in figure 2b and the areal density of ^{12}C has been calculated and reported in Table 1. This surface contribution is due to build-up of ^{12}C during the implantation. The sample implanted at 600°C contains the lowest ^{12}C contamination. This effect is explained by the dependence of the sputtering yield to the temperature. As the implantation temperature is increasing, the sputtering yield is also increasing [18,19].

At medium implantation temperature (370°C) the ^{13}C depth profiles show a Gaussian shape (Fig. 3). The projected range increases with the implanted dose. The experimental and theoretical projected ranges, calculated with SRIM code [20], are reported in Table 2. The theoretical R_p values have been calculated for a target composition corresponding to the half maximum of carbon contents (4th column in Table 2). It is clearly seen in table 2 that the agreement between experimental and calculated values is very good.

The ^{13}C depth profile at high temperature (600°C) shows a dissymmetrical distribution (Fig. 2a) which is correlated to the ^{12}C depth distribution (Fig. 2b). The wide distribution of ^{13}C is explained by diffusion process during implantation. This effect should be confirmed with a theoretical model like TRIDYN code [21] adapted to take into account the diffusion process. The correlation between ^{13}C and $^{12}\text{C}_{\text{bulk}}$ distribution is also explained by diffusion of ^{12}C during the implantation process.

Moreover, the oxygen depth distribution of the high implantation temperature is correlated to ^{13}C depth distribution. This effect should also be confirm when $^{13}\text{C}(\text{d},\alpha_0)^{11}\text{B}$ will be measured at low energies.

5. Conclusion

We have developed an ideal geometry of detection in order to analyse simultaneously ^{12}C , ^{13}C and ^{16}O by using nuclear reactions induced by deuteron. Two detectors were used to perform these measurements. The first detector positioned in RBS geometry was used as a monitor and the second one placed in NRA geometry showed a large solid angle to depth profile ^{12}C , ^{13}C and ^{16}O simultaneously. Depth profiling of ^{12}C reveals a surface contamination due to ^{12}C build-up during implantation process and small bulk component which is correlated with ^{13}C depth distribution. The sensitivity of the $^{12}\text{C}(\text{d},\text{p}_0)^{13}\text{C}$ nuclear reaction allows to detect 0.1 at. % of ^{12}C . At low implantation temperature ($< 370^\circ\text{C}$), the ^{13}C depth profiles show a Gaussian shape with $(R_p)_{\text{exp}}$ close to theoretical range $(R_p)_{\text{th}}$ calculated with SRIM code. For high temperature of implantation (600°C), the ^{13}C depth profile shows a diffusion process.

Finally we were able to make obvious that only first $1000 \cdot 10^{15}$ at. cm^{-2} samples are weakly oxidized as long as implantation temperature is maintained below 370°C . On the other hand oxidation is ten times higher for implantation realized at 600°C . Moreover ^{16}O depth profile seems to be correlated to ^{13}C depth distribution. In order to measure precisely oxygen, the cross section of $^{13}\text{C}(\text{d},\alpha_0)^{11}\text{B}$ nuclear reaction should be measured for projectiles energies below 1 MeV.

6. References

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Figure 2 – J. L. Colaax et al.

Figure 3 – J. L. Colaux et al.

Figure 1: Experimental NRA spectra of copper samples implanted with $^{13}\text{C}^+$ at various temperatures and fluences (6.1 to $16.3 \cdot 10^{17}$ at. cm^{-2}) recorded in the NRA detector. Symbols represent the experimental spectra and the black lines represent simulations realized with SIMNRA code.

Figure 2: Depth distributions of (a) ^{13}C , (b) ^{12}C and (c) ^{16}O for $400 \text{ keV } ^{13}\text{C}^+$ implantations into copper performed at different temperatures and for various fluences (6.1 to $16.3 \cdot 10^{17}$ at. cm^{-2}).

Figure 3: Depth distributions of ^{13}C for 400 keV ion implantation into copper performed at 370°C with various fluences (2.0 to $15.4 \cdot 10^{17}$ at. cm^{-2}).

Table 1

Equivalent thickness (expressed in 10^{15} at. cm^{-2}) of different components of implanted samples according to SIMNRA simulations.

		Sample implanted at 200° C	Sample implanted at 370° C	Sample implanted at 600° C
Implanted dose	^{13}C	$6.1 \cdot 10^2$	$15.4 \cdot 10^2$	$16.3 \cdot 10^2$
(10^{15} at. cm^{-2})	$^{12}\text{C}_{\text{surf.}}$	275	138	18

Table 2

Comparison between $(R_P)_{\text{exp}}$ and $(R_P)_{\text{th}}$ as function of implanted dose. The 4th column indicates the composition of the target used to calculate the $(R_P)_{\text{th}}$ with the SRIM code.

Dose (10^{17} at. cm^{-2})	$[^{13}\text{C}]^{\text{max}}$ % at.	$(R_P)_{\text{exp}}$ (10^{15} at. cm^{-2})	Composition of target	$(R_P)_{\text{th}}$ (10^{15} at. cm^{-2})
15.4	40	4300	$\text{C}_{0.200}\text{Cu}_{0.800}$	4140
6.8	23	4040	$\text{C}_{0.115}\text{Cu}_{0.885}$	3930
5.8	17	4020	$\text{C}_{0.085}\text{Cu}_{0.915}$	3950
5.0	15	3960	$\text{C}_{0.075}\text{Cu}_{0.925}$	3880
2.0	6.5	3940	$\text{C}_{0.032}\text{Cu}_{0.968}$	3810