DOI: 10.1017/S1431927603442803
Microsc Microanal 9(Suppl 2), 2003

Hydrogen Distribution in Carbon and Silicon Specimens Studied by the Scanning Atom Probe

O. Nishikawa, T. Murakami, M. Watanabe, and M. Taniguchi

Kanazawa Institute of Technology, 7-1 Ohgigaoka, Nonoichi, Ishikawa 921-8501 Japan

nisikawa@neptune.kanazawa-it.ac.jp

It has been known that the atom probe (AP) [1] is one of the most powerful instrument to detect the hydrogen atoms bound with other atoms such as aluminum and copper [2]. However, it has been also realized that the study of carbon and silicon is hardly investigated because the fabrication of a sharp silicon and carbon tip required for the AP analysis is fairly difficult. The introduction of a scanning atom probe (SAP) [3] made possible to mass analyze a flat specimen with microprotrusions. Accordingly, the study has been extended to carbon and silicon counting the number of hydrogen atoms absorbed in these materials. Thus, the purpose of this study is to examine the relation among the structures of carbon specimens and to clarify the effect of chemical treatment of silicon.

Graphite, vitreous carbon, CVD diamond, HPHT diamond and carbon nano-tubes (CNT) were analyzed. The purities of the graphite are 99.8% and 99.99 %. One of the CNT is the bunch of multi-wall carbon nano-tubes (MWCNT) and other is rod shaped CNT made from a mixture of C_{60} and CNT [4].

Silicon specimens were fabricated by grooving a [111]-oriented silicon wafer surface in a checker board pattern forming silicon micro pyramid arrays. The depth and the width of the grooves are 10 μm and 100 μm, respectively. The grooved specimens are etched by 1 % HF and 40 % NH_4F [5].

The number of hydrogen atoms in the carbon and silicon specimens is counted by dividing the mass to charge ratio m/n into 0.1 sections and assigning each ion, Fig. 1. Although the mass spectrum is continuous due to the dissociation of C-H cluster, each divided mass peaks are assigned. The m/n of C_5^+ is 60 and the right side of this peak is formed by the dissociated C_5H^+, $C_5H_2^+$ and so on. The ions with the m/n smaller than 60 are the dissociated hydrogen after reflected in the reflectron.

All carbon specimens contain a large amount of hydrogen. The ratio of hydrogen atoms to carbon atoms H/C of various carbon specimens are listed in Table 1. Vitreous carbon contains the smallest amount of hydrogen and H/C=0.25. The number of hydrogen atoms in the surface layers of the CVD diamond grown in hydrogen gas contains the largest amount of hydrogen, H/C=2.02.

CNT exhibits the moderate H/C values in the range of 0.283 to 0.721. Although the amount of hydrogen absorbed in the MWCNT does not change by the heating at 1000 K for 10 min, a large amount of hydrogen is desorbed from the CNT rod by storing it in a vacuum chamber.

The amount of hydrogen atoms in silicon varies with the analyzed areas. While a small number of hydrogen atoms were detected from a few silicon surface areas, Fig. 2, a large amount of hydrogen is detected with carbon and oxygen from other areas of the same specimen, Fig. 3. Variation of hydrogen, carbon and oxygen with depth is listed in Table 2 and 3. Difference in the hydrogen and oxygen contents may due to the difference in the exposed crystal plane of the analyzed area formed by the grooving.

[1] E. W. Müller and S.V. Krishnaswamy, Rev. Sci. Instrum., **39** (1968) 83.
[2] O. Nishikawa, T. Yoshimura and M. Shibata, Surf. Sci., **124** (1983) 440.
[3] O. Nishikawa, Y. Ohtani, K. Maeda, M. Watanabe, and K. Tanaka, Mater. Character. **44** (2000)

29.

[4] T. Kuzumaki, Y. Takamura, H. Ichinose, and Y. Horie, Appl. Phys. Lett., 78 (2001) 3699.
[5] Y. Morita, K. Miki, and H. Tokumoto, Mat. Res. Soc. Sym. Proc., 315 (1993) 491.

Table 1. H/C of various carbon

Specimen	H/C
Fresh CNT rod	0.541
CNT rod 40 hrs later	0.283
MWCNT	0.714
Heated MWCNT	0.714
99.99 % pure graphite	0.442
Vitreous carbon	0.249
CVD diamond	1.277
HF-CVD diamond	2.018
HPHT diamond	0.857

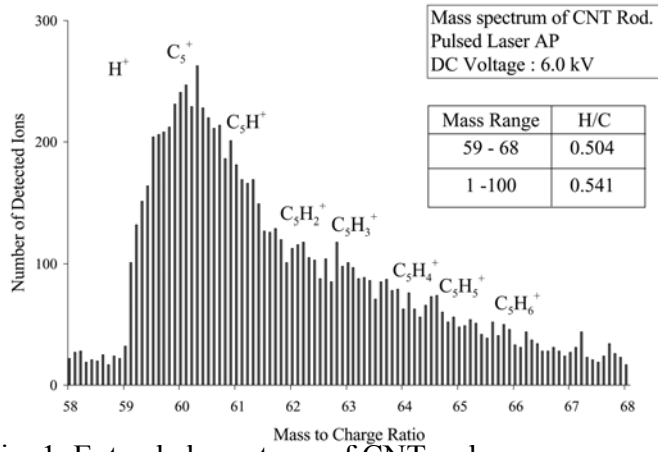

Fig. 1. Extended spectrum of CNT rod.

Table 2. Variation of H, C and O concentration with depth (Clean surface)

	HF-treated Si			NH_4F-treated Si			
	H (%)	C (%)	O (%)	Number of ions	H (%)	C (%)	O (%)
Surface Layer	24.2	14.4	0	Surface Layer 1-1000	42.8	19.7	1.20
				1001-2000	23.1	3.81	0.28
				2001-3000	20.7	0.71	0

Table 3. Variation of H, C and O concentration with depth (Relatively contaminated surface)

HF-treated Si				NH_4F-treated Si			
Number of ions	H (%)	C (%)	O (%)	Number of ions	H (%)	C (%)	O (%)
Surface layer 1-1000	42.8	19.7	1.2	Surface layer 1-2000	35.0	18.8	1.11
1001-4500	23.1	3.81	0.28	2001-3600	15.9	0.34	0.34
4501-8000	20.7	0.71	0	3601-5200	18.8	0.30	0
				5201-6800	18.8	0.31	0

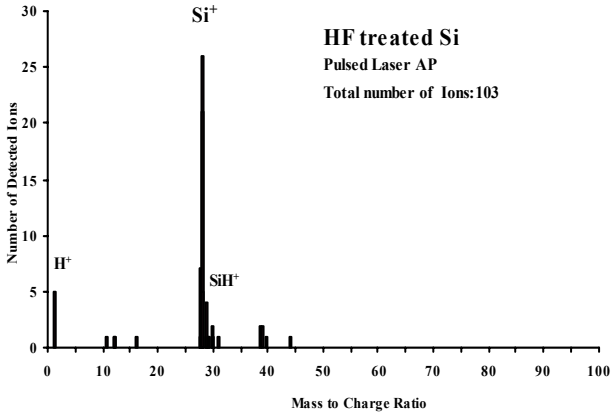

Fig. 2. Mass spectrum of clean Si.

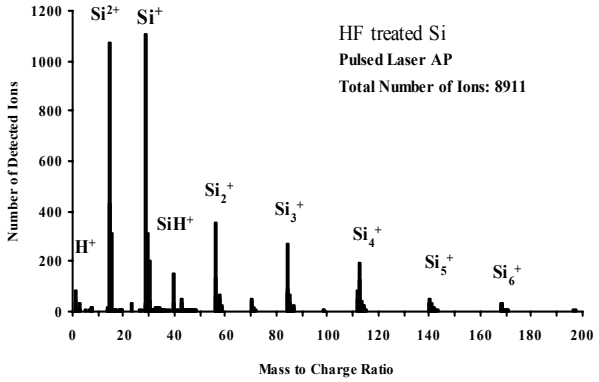

Fig. 3. Mass spectrum of relatively contaminated Si.

https://doi.org/10.1017/S1431927603442803 Published online by Cambridge University Press