

# SURFACE MODIFICATION OF PYROLYTIC GRAPHITE BY USING NITROGEN LOW-ENERGY ION IMPLANTATION

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## Introduction

Nitrogen ion implantation is one of the methods for the introduction of nitrogen into carbon materials and expected to obtain the interesting properties such that  $\beta$ -C<sub>3</sub>N<sub>4</sub> (Liu and Cohen 1985) and/or nitrogen substituted graphite (Santos and Alvarez 1988) have. Using the ions with the energy lower than 1 keV for the implantation, the penetration of the ion occurs preferentially within the skin region. It is expected, therefore, to form an amorphous carbon nitride on the surface within several nm in depth. But, the introduction process and the properties of the modified layer were not fully clarified because of its thinness. The authors have analyzed previously the surface of a highly oriented pyrolytic graphite (HOPG) implanted with nitrogen ion (Hamamura *et.al.* 2006). It was found that the ion implantation results in the generation of defects on the basal plane and the introduction of nitrogen containing species corresponding to nitrile, amine, and hetero cyclic compounds such as pyridine. The dependence of the formation of the species on the ion energy and dose was reported.

To clarify the nitrogen introduction process, however, the reliability of the thickness of the modified layer formed by the low energy ion implantation was not enough, because the thickness was roughly calculated using the data of angle resolved X ray photoelectron spectroscopy (ARXPS). In the report, to increase the reliability for the depth profile, the thickness was calculated using the data from the measurements of Raman spectroscopy.

## Experiment

The sample was ZYB grade HOPG of NT-MDT, being 6 × 12 × 1.7 mm in size. To obtain a clean basal plane, the surface was peeled off using adhesive tape. Before the irradiation, the chamber was evacuated to less than 1.0 × 10<sup>-4</sup> Pa. The gas used was nitrogen with 99.999% in purity. The ion gun used was Varian #981-2043 which was an electron impact type. The irradiation was carried out under the pressure at 1.3 × 10<sup>-2</sup> Pa. The substrate was at room temperature. The incident angle of the ion beam to the surface was 90 deg. The acceleration energy was varied between 100 eV and 1 keV. The ion dose was 1.0 × 10<sup>17</sup> cm<sup>-2</sup> corresponding to a saturation of nitrogen incorporation into HOPG. The Raman spectroscope used was HORIBA Jobin Yvon T-64000. The spot size of the laser beam was 1μm and the excited wavelength was 514.5 nm.

**Figure 1** shows a first order Raman spectrum of the irradiated sample. The spectrum was separated into three peaks as follows: A G-peak at ~1580 cm<sup>-1</sup> is due to the E<sub>2g</sub> mode of HOPG substrate, a D-peak at ~1360 cm<sup>-1</sup> is attributed to a disorder of the structure, and a broad peak around 1550 cm<sup>-1</sup> is due to a structure of the modified layer. The broad peak is usually detected in an amorphous carbon (a-C) structure such as diamondlike carbon (Watanabe *et.al.* 1993).

**Figure 2** shows a schema of Raman spectroscopy. The incident beam and Raman light were scattered in the sample skin as a function of the depth  $z$ . The measured intensity  $I^c$  is given by

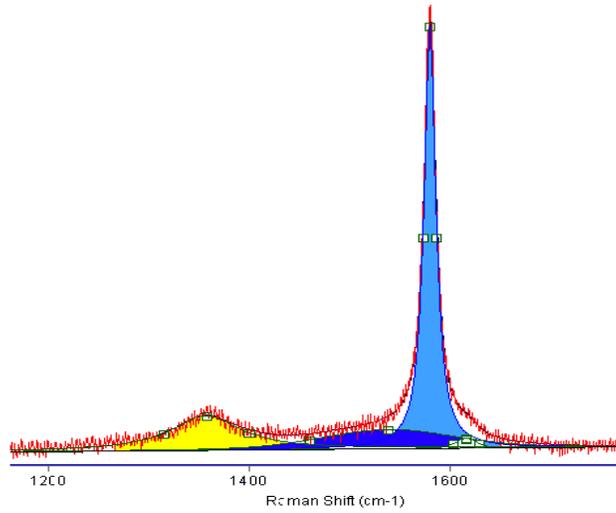
$$I^c(t, \nu) = \int_0^t I^c(z, \nu) dz = I_\infty^c(\nu) \left[ 1 - \exp\left(-\frac{2t}{\lambda_c}\right) \right], \quad (1)$$

where  $\lambda_c$  is the optical mean free path of Raman light in the modified layer,  $t$  is the thickness of modified layer,  $\nu$  is the wave number corresponding to Raman shift and  $I_\infty^c$  is the saturated value of  $I^c$  (Scharf and Singer 2003).

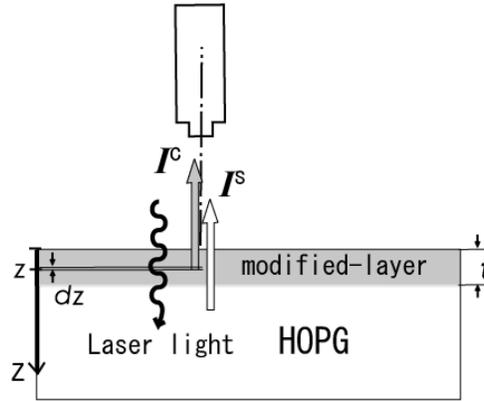
In the case of  $t \gg \lambda_c$ , the intensity of the peak from the modified layer becomes  $I_\infty^c$ . The thickness as a function of  $\nu$ ,  $t(\nu)$ , is given by

$$t(\nu) = \left( \frac{\lambda_c}{2} \right) \ln \left[ \frac{I_\infty^c(\nu)}{I_\infty^c(\nu) - I^c(\nu)} \right]. \quad (2)$$

The intensity of an amorphous carbon nitride film of about 1.0 μm in thickness on the SKD11, which was prepared by means of a magnetron sputtering, was substituted for  $I_\infty^c$ .



**Figure 1.** Raman spectrum of irradiated HOPG surface



**Figure 2.** Schema of Raman spectroscopy

**Figure 3** shows peak intensities of the G-peak and a-C peak versus acceleration energy of the ion. Increasing the energy, the intensity of the G-peak from the substrate decreased and that of the a-C peak increased. According to an increase of the energy corresponds to an increase of the thickness, the results agree with those of Sharf and Singer (2003). Substituting the a-C peak intensities in the equation (2), the thickness dependence on the acceleration energy is estimated for the  $\lambda_c$  values of 100, 130, 180 nm (**Figure 4**). The thickness of the modified layer formed by the acceleration energy of 100 eV is about 0.7 times in comparison with that of 1 keV, independent of the value of  $\lambda_c$ . **Figure 5** shows depth profiles of nitrogen atom in the sample irradiated with the energy of 100 eV and 1 keV estimated from ARXPS. The introduction depth of nitrogen atom was estimated about 4.5 nm for the irradiation at 100 eV and about 5nm at 1 keV. The two depth values are rather close. According to the previous report (Hamamura *et.al.* 2006), for the irradiated profile at 100 eV, it was suggested that the shallow region about 1 nm from the surface was damaged preferentially by the ion bombardment. The a-C peak of the Raman spectrum is not attributed to the damaged layer. Therefore, the substantial thickness should be deduced to 3.5 nm by subtraction of the damage layer of 1 nm from 4.5 nm at 100 eV. The value is 0.7 times in comparison with the thickness of the modified layer formed by the irradiation of 1 keV. The ratio agrees with the value obtained by the data (**Figure 4**).

Curve fitting of the dependence of the thickness on the acceleration energy was performed by varying  $\lambda_c$  (**Equation (2)**). The calculation carried out using the estimated thicknesses of about 3.5 nm for the irradiation at 100 eV and 5 nm at 1keV.  $\lambda_c$  was estimated to be about 130 nm from the curve fitting.. The value is that between  $\lambda_c$  of a-C film and a-CH film. The present results suggest that the structure of the modified layer is assumed to be a-C or a-CH including nitrogen.

The projected range  $R_p$  of the ion in HOPG was calculated by SRIM. The values of  $R_p$  thus obtained are 0.8 nm and 3 nm in the case of the ion energy of 100 eV and 1 keV, respectively.

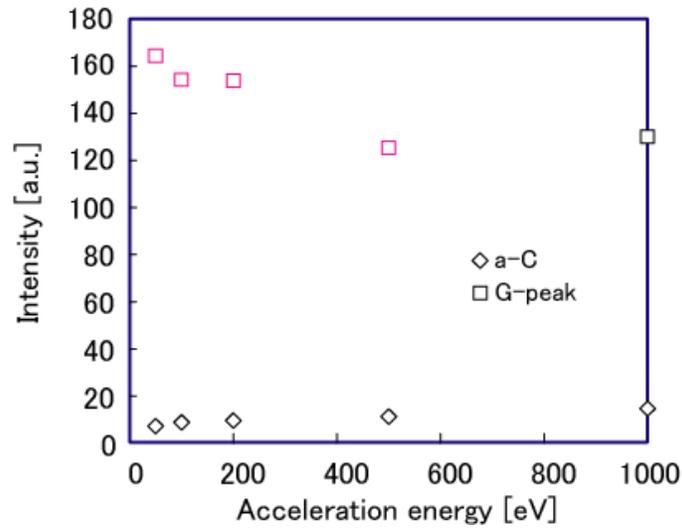


Figure 3. a-C peak Raman intensity vs. acceleration energy

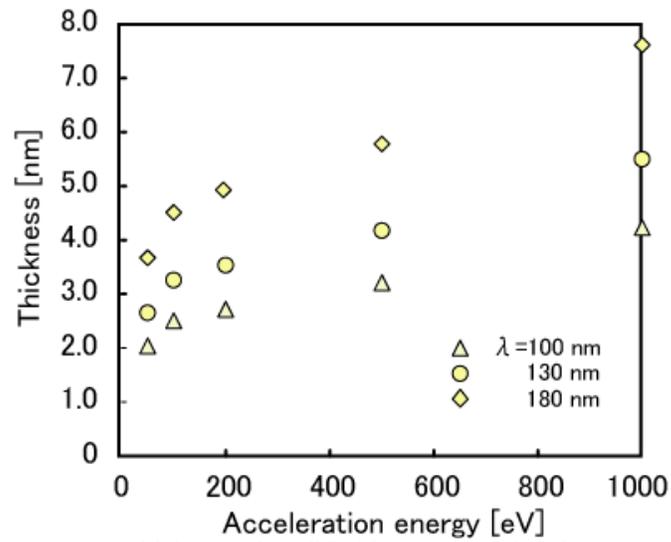


Figure 4. Thickness of modified layer vs. acceleration energy

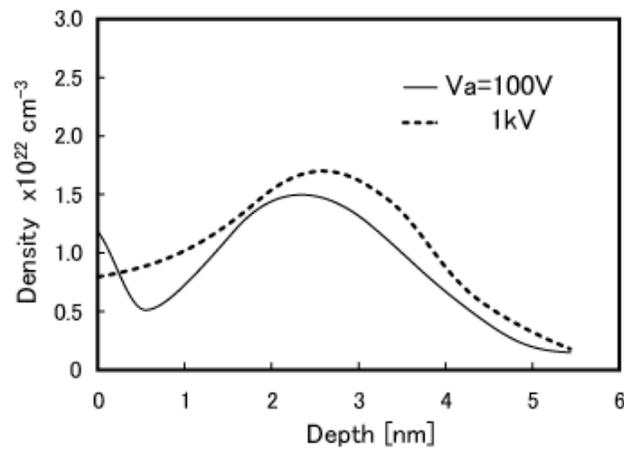


Figure 5. Depth profile of nitrogen atom (Hamamura *et.al.* 2006)

These values are less than the thicknesses for respective ion energies estimated by ARXPS and Raman spectroscopy. The analysis depth of ARXPS depends on the photoelectron inelastic mean free path, which is given as a function of the density and the number of valence electrons in the equation proposed by Ashley (1980). Assumed the density of  $3.9 \text{ gcm}^{-3}$  in the equation, the thickness estimated by ARXPS is changed to be 3nm. But, the density is not adequate to the a-C or a-CH including nitrogen.

By the way, the penetration depth by the diffusion depends not on the ion energy but on the density of introduced nitrogen atoms in the sample. The modified layer formed by diffusion process of nitrogen atom is due to exist deeper than  $R_p$  in the sample. The thickness of the modified layer estimated by the data of ARXPS and Raman spectroscopy were deeper than the value of  $R_p$  calculated by SRIM. Therefore, the layer formed by the diffusion process is deduced to exist in 2-3 nm below the implanted depth in the sample. As the results, for the implantation with the energy of low energy region, it is confirmed that the introduction of nitrogen atom was occurred by the diffusion process addition to the ion implantation process.

## Summary

Low energy nitrogen ion implantation was performed onto HOPG surface. To clarify the dependence of nitrogen introduction process on the acceleration energy, the thickness of the modified layer was estimated by using the data of Raman spectrum. According to the data from the ARXPS and Raman spectra, the thickness of the modified layer was evaluated to be about 3.5 nm and about 5 nm in the case of the ion energy of 100 eV and 1 keV, respectively. The optical mean free path in Raman spectroscopic analysis in the modified layer was evaluated to be about 130 nm. The result indicates that the modified layer consisted mainly of nitrogen a-C or a-CH structure.

## Acknowledgement

The authors are grateful to Dr. Y.Sakamoto and Mr. Y.Yasuda for their technical supports.

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