Chemically modified diamond surfaces
for chemical sensor application
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Recently, semiconducting diamond has attractive attention in the field of chemical and bio device application due to its material properties such as wide potential window, biocompatibility, and chemical/ physical stability. Utilizing these advantages, diamond nano-scale biosensor operates in a human body are expected. Up to now, diamond FETs operates in the electrolyte solutions have been realized [1] and sensitivity/insensitivity of halogen ions and pH are researched in detail [2]. One of the important techniques for realization of biomolecular diamond sensors is the development of the various functional surfaces. Terminating by various atoms or molecules on diamond surfaces shows various significant properties. Hydrogen-terminated diamond shows p-type surface conductivity without doping impurities, which is suitable as the channel of FETs. This surface also shows positive charge, negative electron affinity (NEA) and hydrophobic properties. On the other hand, insulating, negative charge, positive electron affinity (PEA) and hydrophilic properties are obtained by oxygen-terminated diamond. Fluorine-terminated diamond shows super hydrophobic surface with negative surface potential, which makes a sharp contrast with amino group terminated diamond. Amino group terminated diamond shows positive potential and hydrophilic properties. In addition, this surface easily immobilize biomoleculers.

	Hydrogen	Oxygen	Fluorine	Amino group
Potential	Positive	Negative	Negative	Positive
NEA/ PEA	NEA	PEA	—	—
Conductance	○	×	×	—
Properties	Hydrophobic	Hydrophilic	Super hydrophobic	Hydrophilic

Table.1 Properties of diamond surfaces terminated by various atoms.

In this study, we tried to modify the H-terminated polycrystalline diamond surface to F and NH_2 utilizing microwave plasma. H-terminated polycrystalline diamonds are deposited by microwave plasma assisted CVD system. The polycrystalline diamonds are exposed to the C_3F_8 or N_2/H_2 mixed plasma to obtain the F- or NH_2-terminated surface. After this treatment both type of substrates show high resistivity more than 1 GΩ/sq by Van der Pauw measurement.

Figure 1 shows the XPS spectra of N_2/H_2 and C3F8 plasma exposed polycrystalline diamonds. Very sharp C1s peaks are detected at 285.0 eV for both substrates. N1s (399.2 eV) and F1s (686.1 eV) peaks are observed in N_2/H_2 plasma and C3F8 plasma exposed diamonds, respectively. O1s peak is observed only for N_2/H_2 plasma treated diamond. This oxygen is due to the surface contamination of water, because the NH_2 terminated diamond is hydrophilic surface in contrast to the hydrophobic surface of F-terminated diamond.

Patterned NH_2 terminated area in F- terminated surface is also realized using metal mask. Figure 2 shows the differences of water adsorption on NH_2 and F-terminated diamond surface. Adsorption of water or organic solvent is never observed on F-terminated surface. On the other hand adsorption of water is clearly observed on NH_2 terminated diamond area. In order to determine the NH_2 termination, Cy5 fluorescence reactive dye (500nM) is also utilized. Figure 3 shows the fluorescent microscopic image of the patterned diamond surface. Clear contrast between NH_2 and F-terminated area is observed. Utilizing this technique, nano-scale patterning of NH_2 terminated surface will be realized. We have already realized nano-scale diamond FETs and solution gate FETs. Accordingly, nano-scale diamond biomolecular sensor is expected to orchestrate these diamond technologies.

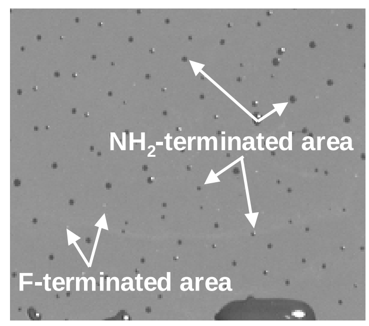

Fig. 2 Adsorption of water on NH_2 terminated diamond surface

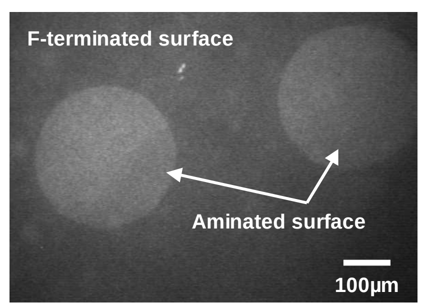

Fig.3. Fluorescent microscopic image of patterned diamond surface.

References
[1] H. Kawarada et al. Phys. Status. Solidi. A 185 (2001) 79.
[2] K. Song et al. Appl. Phys. Lett. 81 (2002) accepted.

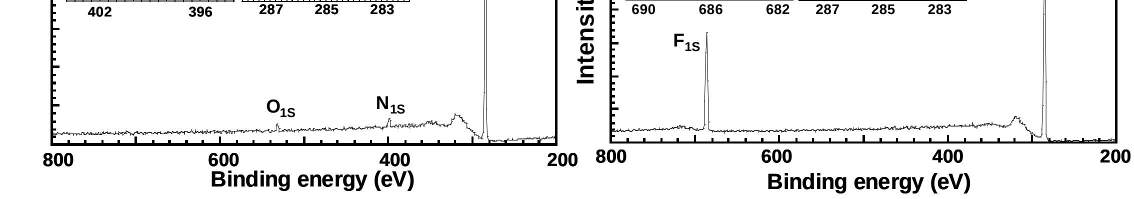

Fig. 1 XPS spectra of diamonds by (a) N_2/H_2 plasma treatment and (b) C_3F_8 plasma treatment.