Surface potential change by oxidation of the chemical vapor deposited diamond (001) surface

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Abstract. We have investigated the surface potential change accompanying the variation in diamond surface chemisorbed structures using scanning Maxwell-stress microscopy. The hydrogen chemisorbed diamond surface was prepared by a hydrogen plasma treatment following the homoepitaxial (001) diamond growth by the microwave plasma-assisted chemical vapor deposition (MPCVD). The surface chemisorbed structure was controlled by increasing the oxidized temperature in the range from 100 °C to 500 °C. The hydrogen chemisorbed diamond surface showed a minimum work function value of 4.8 eV. A thermal oxidation of the hydrogen chemisorbed diamond surface at 500 °C yielded the oxygen chemisorbed diamond surface, which showed a maximum work function value of 5.8 eV. The surface potential value, which corresponds to the surface work function value, was strongly influenced by the species of the chemisorption on the diamond surface.

1. Introduction
Diamond thin-films are very promising materials for realizing electronic and biochemical devices such as electron emitters [1], transistors, DNA chips [2] and biosensors [3]. The physico-chemical properties of diamond surfaces are key to achieving the desired properties of these devices. In order to produce high performance devices, therefore, it will be essential to control the surface physico-chemical properties of the diamond.

It has been reported that physico-chemical properties of diamond surfaces are closely related to the surface chemisorbed species on the surface. Hydrogen (H) chemisorption on a chemical vapor deposition (CVD)-grown diamond surface is well-known to be important for stabilizing diamond surface structures with sp³ hybridization [4,5]. Many reports have suggested that an H-chemisorbed structure is necessary to provide a negative electron affinity (NEA) condition on the diamond surfaces [6-9]. It was reported that the NEA condition could change to a positive electron affinity (PEA) by oxidation of the H-chemisorbed diamond surfaces. Oxidized diamond surfaces usually show characteristics completely different from those of the H-chemisorbed diamond surfaces. The unique electron affinity condition, or the surface potential, is strongly related to the chemisorbed species on diamond surfaces. The relationship between the surface chemisorption structure and the surface electrical properties, such as the surface potential of the diamond, has not been revealed yet.
In this study, changes of the surface potential associated with a change in the chemisorption from hydrogen to oxygen have been observed by scanning Maxwell-stress microscopy (SMM). For this surface characterization, an H-chemisorbed and atomically flat diamond surface was prepared by using a microwave plasma-assisted chemical vapor deposition (MPCVD) system. The degree of oxidation of the H-chemisorbed diamond surface was controlled by varying the oxidation temperature.

2. Experimental
As a substrate for this experiment, mechanically polished high-pressure and high-temperature (HPHT) synthetic boron-doped diamond (001) was used. A boron-doped homoepitaxial (001) diamond layer was grown on the substrate by a MPCVD system in the form of a cylindrically coupled microwave plasma reactor. In order to prepare H-chemisorbed surfaces, the as-grown surface was successively hydrogenated by the hydrogen plasma treatment. Surface oxidation of the H-chemisorbed diamond was carried out in a quartz reactor by using 20% oxygen diluted with nitrogen at temperatures in the range of 100-500 °C for 1 h.

The chemisorption structures of the diamond surfaces were analyzed by high-resolution monochromated X-ray photoelectron spectroscopy (XPS; VG sigma probe). The surface potentials were measured by using SMM in an ultra-high vacuum chamber [10]. Work functions were estimated using that of evaporated gold film (approximately 5.1 eV) as a reference [11].

3. Results and discussion
The relation between the oxygen core 1s (O 1s) peak intensity of the X-ray photoelectron spectra and the oxidation temperature is shown in figure 1. At oxidation temperatures below 300 °C, the intensity was constant at around zero; this temperature region was referred to as region A. In region A, the amount of chemisorbed oxygen on the surface was estimated to be slight or none; i.e., below the XPS detection limit (approximately <1%). H-chemisorption was the dominant diamond surface structure in region A, as it was in a previously reported study [5]. In the range of oxidation temperatures from 300 °C to 500 °C, the O 1s intensity increased to two different inclinations. The inclination within the range of 300 °C to 420 °C was greater than that in the range of 420 °C to 500 °C; the former inclination was referred to as region B, and the latter as region C. In region B, most of the chemisorbed hydrogen was replaced by oxygen as the oxidation temperature increased, as indicated by the greater inclination. In region C, the chemisorbed oxygen species were dominant on the diamond surface; however, the amount of chemisorbed oxygen continued to increase along with the slight increase in the inclination.

Figure 2 shows the relationship between the oxidation temperature and the surface work function of oxidized diamond surfaces. The values of the surface work function were estimated from the surface potential data measured by the SMM; the surface potential of the gold was used as a reference. The surface potential of gold was measured as 80 meV. This measured value corresponded to the previously reported surface work function of 5.1 eV [11]. The surface work function of the as-grown diamond surface is indicated in figure 2 by a dotted line. Oxidation temperatures below 300 °C corresponded to region A. Region B corresponded to a range from 300 °C to 400 °C, and temperatures from 400 °C to 500 °C corresponded to region C, as shown in figure 1. With increases in the oxidation temperature, the surface work function in region A increased slightly from 5.0 eV to 5.2 eV while no change was observed in the O1s peak intensity (figure 1). As the oxidation temperatures in region B increased (300 °C – 400 °C), the surface work function increased drastically, in contrast to the moderate effect of temperature increases in region A. In region B, a complete change in the chemisorption species on the diamond surfaces on which hydrogen was replaced by oxygen yielded similarly large changes in the surface work functions. In region C (400 °C – 500 °C), the surface work function was constant, although a slight increase in the O1s peak intensity occurred. Further oxidation produced maximum oxygen coverage; however, such a change did not effect a clear change in the surface work function.
Figure 1. The relation between the oxidation temperature and the O(1s) photoelectron intensity obtained from the X-ray photoelectron spectra.

Figure 2. The relation between the oxidation temperature and the surface work function of the oxygen-chemisorbed diamond surfaces.
Figure 3 shows the morphological and the potential images of diamond surfaces with different chemisorption structures. The upper images were obtained from the H-chemisorbed diamond surface prepared by the hydrogen plasma treatment. The lower images were from an oxygen (O)-chemisorbed diamond surface, which was oxidized at a temperature of 500 °C. The e-beam evaporated gold thin-film was deposited partially on the surface as the reference material for a comparison between the surface potentials of the H-chemisorbed diamond and that of the O-chemisorbed diamond. The left side of the images indicates the surface morphology; the gold thin-films were observed as a stepwise pattern with a 0.15 µm-thickness on the diamond surfaces. The right side of the images indicates the surface potential. The surface potential of the H-chemisorbed surface was higher than that of the gold film by +200 mV, while that of the O-chemisorbed surface was lower than that of the gold film by −500 mV. In addition, we observed that the values of surface potentials both on the H-chemisorbed and the O-chemisorbed diamond surfaces at the positions 40 µm from the boundary between the gold film and the diamond surface were 250 mV and −650 mV, respectively. These values agree with the results shown above in figure 2(b). There was a clear inverse correlation between the surface potential and the surface work function. The H-chemisorbed diamond surface showed a smaller surface work function than that of gold. In contrast, the O-chemisorbed diamond surface exhibited a surface work function larger than that of gold. The surface work function of the oxidized diamond surface was greater than that of the H-chemisorbed diamond surface.

|                | Morphology | Potential image |
|----------------|------------|-----------------|
| **(a)** Hydrogen-chemisorbed | ![Morphology](image1) | ![Potential image](image2) |
|                | ![Morphology](image3) | ![Potential image](image4) |
| **(b)** Oxygen-chemisorbed     | ![Morphology](image5) | ![Potential image](image6) |

**Figure 3.** The morphological images (left) and the potential images (right) of (a) the hydrogen-chemisorbed and (b) the oxygen-chemisorbed diamond surfaces measured by the SMM.
4. Conclusions

In order to clarify the relationship between diamond chemisorption structures and unique surface affinity conditions, variations in surface oxidation structures and in surface potentials were measured. At oxidation temperatures below 300 °C, a small change in the surface work function was observed while the oxygen core 1s peak intensity was constant at zero. Oxidation in the temperature range from 300 °C to 400 °C spread chemisorbed oxygen over the surface, and the surface work function drastically increased. In contrast, at oxidation temperatures above 400 °C, the surface work function changes were not clearly observed. The surface work functions were strongly correlated with the surface electronic states. A change of the chemisorbed species on the surface sensitively affected the surface work function.

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