Surface conductivity change by oxidation of the homoepitaxially grown diamond (100) surface

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Abstract. We have investigated the electrical conductivity change that occurs by oxidation of a homoepitaxially grown diamond (100) surface. For this purpose, atomically flat diamond (100) surfaces homoepitaxially grown by a microwave plasma-assisted chemical vapor deposition (MPCVD) were prepared. It is well-known that a CVD-grown diamond surface is a hydrogen-chemisorbed structure. Surface chemisorbed structures of diamond can be controlled by oxidation in air at temperatures from 25 °C up to 350 °C. The degree of oxygen-chemisorption on the diamond surfaces was analyzed by X-ray photoelectron spectroscopy (XPS). The electrical resistivity (or conductivity) of the diamond surfaces was measured at room temperature under nitrogen flow by using the van der Pauw four-probe system. The surface resistivity of diamond was drastically increased at 300-350 °C, a temperature range corresponding to the beginning point of surface oxidation of a diamond analyzed by the XPS.

1. Introduction

Diamond has a wide band gap of 5.5 V and is generally known as a highly insulating material [1]. The surface of natural diamonds such as a precious stone and in polished form as a jewel has an oxygen (O)-chemisorbed structure. On the other hand, the surface of diamonds grown by the chemical vapor deposition (CVD) method, which can produce high quality films for practical use, has a hydrogen (H)-chemisorbed structure. It is well-known that the CVD-diamond surface can be stabilized as an H-chemisorbed structure with sp³ hybridization [2,3]. It has been reported that hydrogenated diamonds exhibit surface electrical conductivity [4,5], and that a sub-surface hole accumulation layer in these diamonds is responsible for this phenomenon [6,7]. We previously reported that the H-chemisorption of the diamond surface gradually changed to O-chemisorption by surface oxidation based on chemical reactions at a temperature range of 300-350 °C [2,3]. The relationship between the change in the chemisorbed structures on the diamond surface and the surface conductivity has not yet been elucidated. The surfaces of diamonds to be studied should be smooth. A polished diamond surface is usually very rough due to its hardness. An annealing treatment can change the diamond surface into a graphitic structure. A high quality diamond homoepitaxy by CVD yields an atomically smooth diamond surface [8].

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In this paper, we showed that the change in the electrical conductivity of the CVD diamond surface in a flow of dry air varied with the oxidation temperature. For this study of the surface, we first prepared atomically flat diamond (100) surfaces by applying high quality diamond homoepitaxy to polished diamond surfaces. The diamond surfaces were measured by atomic force microscopy (AFM) to determine their surface smoothness. The as-grown diamond surfaces were terminated with chemisorbed hydrogen. The surface bond termination was controlled from hydrogen to oxygen by thermal oxidation in a range from room temperature to around 350 °C. We discuss the relationship between the change in the surface resistivity (or conductivity) and the change in the chemisorbed structure of the homoepitaxial diamond (100) surface.

2. Experimental

A mechanically polished high-pressure and high-temperature (HPHT) synthetic single crystal diamond (100) that was 2 mm square and 0.5 mm thick was used as a substrate. In order to prepare an atomically flat diamond surface, a homoepitaxial (100) layer was grown on the substrate by the MPCVD system. A cylindrically coupled microwave plasma reactor was used for the diamond growth. As a reactant gas, methane (CH₄) diluted with hydrogen (H₂) was used. The CH₄ concentration was 1% in the gas phase. The reaction pressure was 50 Torr, and the total flow rate was 500 cm³min⁻¹. The substrate temperature was maintained at around 800 °C, as measured by an optical emission pyrometer. The incident microwave power was 800 W. In order to produce the H-chemisorbed structure on the diamond surface, the as-grown surface was hydrogenated by H₂ plasma treatment in series. The homoepitaxial diamond surfaces were measured by AFM (SII; SPI3700-SPA300 system) to determine their surface smoothness. The Rms values of surface roughness were calculated for a measured area 1 µm-square on the diamond surface.

The surface bond termination from hydrogen to oxygen was controlled by thermal oxidation in a range from room temperature to 350 °C. The oxidation was performed by a flow of dry air (20% oxygen (O₂) in nitrogen (N₂) balance) under atmospheric pressure for 30 min. The chemisorption structures of the diamond surfaces were analyzed by high-resolution monochromated X-ray photoelectron spectroscopy (XPS; VG sigma probe). The surface resistivity of the diamond was measured at room temperature under N₂ flow by the van der Pauw method using four gold (Au)-coated probes.

3. Results and discussion

Typical AFM images and the Rms values of polished HPHT diamond (100) substrates and those of homoepitaxial grown diamond (100) surfaces on the substrates are shown in figures 1 and 2, respectively. The polished diamond surfaces (before homoepitaxy) were very rough, with Rms values in the range of approximately 50 nm (see figure 1). On the other hand, most of the homoepitaxial diamond surfaces grown by MPCVD had very small Rms values in the range of approximately 10 nm (see figure 2). Seven of the samples had atomically smooth surfaces with Rms values of less than 1 nm. These results indicate that we successfully obtained atomically flat diamond surfaces for the surface study of the homoepitaxial diamond layer on polished diamond substrates. For the surface conduction measurements, we used the seven diamond samples with atomically flat surfaces, which are shown enclosed within the circle in figure 2(b).

Figure 3 shows the oxidation temperature dependence of the surface resistivity. In the case of oxidation temperatures below 300 °C, the surface resistivity was constant at around 1x10⁴-3x10⁵ ohm/sq. The 300°C oxidation resulted in a drastic increase of the surface resistivity of some measured diamonds. A surface resistivity >10¹¹ ohm/sq indicates that the surface resistivity was too high to measure. In all measured samples, the surface resistivity was sharply increased by the oxidation at temperatures in the range from 300 °C to 350 °C.
As shown in figure 4, the XPS analysis of the diamond surfaces revealed that an H-chemisorbed diamond surface did not change at oxidation temperatures below 300 °C; oxygen started to chemisorb onto the diamond surface at oxidation temperatures of 300 °C and over. The observed change in the surface resistivity was strongly related to the change of the chemisorption state. We previously reported that the H-chemisorbed diamond surface could be easily oxidized at a temperature range of 300-350 °C. The O-chemisorbed surface structure includes two types of bonding structures: a ketone and an ether [2,3]. From these experimental results, it is clear that the surface conductivity disappeared immediately with a change in the chemisorbed species from hydrogen to oxygen.
4. Conclusions
The surface conductivity change varied with variation in the diamond (100) surface. We measured chemisorbed species with increasing oxidation temperatures in a range from 25 °C to around 350 °C. An atomically smooth diamond (100) surface and a hydrogen-chemisorbed surface were simultaneously prepared by homoepitaxial growth with the microwave plasma-assisted chemical vapor deposition method. The surface conductivity disappeared at oxidation temperatures of 300-350 °C, in which temperature range the surface chemisorbed species changed from hydrogen to oxygen. We have elucidated the relationship between the change in the surface chemisorbed species and the surface conductivity of a homoepitaxial diamond (100). Based on our experimental results, hydrogen chemisorption on the diamond surface was necessary and sufficient for the appearance of surface conductivity.

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