Surface Oxygen Adsorption and Electric Property of Hydrogen-Terminated Single Crystal Diamonds by UV/ozone Treatment *

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Surface terminations of diamond play an important role in determining the electric properties of diamond-based electronic devices. We report an ultraviolet/ozone (UV/ozone) treatment process on hydrogen-terminated single crystal diamond (H-diamond) to modulate the carrier behavior related to varying oxygen adsorption on surfaces. By UV/ozone treatments, the induced oxygen radicals are chemically adsorbed on the H-terminated diamond and replace the original adsorbed H, which is analyzed by x-ray photoelectron spectroscopy. The concentration of oxygen adsorbed on surface increases from ∼3% to ∼8% with increasing the ozone treatment time from 20 s to 600 s. It is further confirmed by examining the wettability properties of the varying diamond surfaces, where the hydrophobic for H-termination transfers to hydrophilic for partly O-termination. Hall effect measurements show that the resistance (hole mobility) of the UV/ozone-treated H-diamond continuously increases (decrease) by two orders of magnitude with increasing UV/ozone treatment time from 20 s to 600 s. The results reveal that UV/ozone treatment becomes an efficient method to modulate the surface electrical properties of H-diamonds for further investigating the oxygenation effect on two-dimensional hole gas based diamond devices applied in some extreme environments.

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Among the as-known materials in nature, diamond is an extremely functional material with unique and excellent properties of wide bandgap, high thermal conductivity, high electron and hole mobility, high breakdown voltage, superhardness, chemical inertness, biocompatibility, etc.[1–3] Diamond has been widely applied in high frequency and high power electronic devices. For semiconductor and electronic devices, high performance n-type and p-type doping are required, however, the doping-level for diamond is “asymmetry" between p- and n-type dopants, i.e., deep donors versus shallow acceptor.[1–4] The p-type diamond with a relatively shallow acceptor level of 0.37 eV is performed by boron doping, and boron concentration can be easily modulated on a large scale. However, it is still a challenge to realize n-type diamond with shallow donor level, although phosphor is a representative candidate donor in diamond (donor level of 0.57 eV) and an ultraviolet diamond p–n junction has been constructed.[5] For high frequent power electronic devices, two-dimensional electron gas is generally proposed for the designation,[6] however, diamond-based devices cannot be achieved due to the limit of shallow donor for n-type characteristics. Alternatively, two-dimensional hole gas (2DHG) from the hydrogenated diamond (H-diamond) surface is widely proposed in electronic devices, though it has dense hole density of $\sim 10^{13}\,\mathrm{cm}^{-2}$ with mobility of $\sim 10^{2}\,\mathrm{cm}^{2}\cdot\mathrm{V}^{-1}\cdot\mathrm{s}$.[2,4,7,8] The conductivity of the 2DHG is not absolutely ascribed to the H adsorption, additional H_3O^+ and OH^- ions from water layer in air might be required as acceptors forming an electron sink for the subsurface hole accumulation on the surface.[9] Metal oxides (e.g., Al_2O_3) substitute the traditional acceptor on the surface giving long-time and thermal stability, and consequently, these metal oxides can be used as an insulator for field effect applications.[5,10,11] It is known that for diamond, oxygen treatment (e.g., oxygen plasma,[12] thermal oxygen heating, oxygen ion implantation,[13] and ultraviolet (UV)-oxygen[14,15]) is a conventional method to modulate the bulk or surface electrical properties. Among those methods, the UV/ozone oxygenation performed at room temperature is proposed as a moderate and highly efficient process. On the other hand, ozone treatment is a convenient way to keep the insulation between electrodes of diamond devices without introducing structure damage and contaminations. UV/ozone treatment has been widely applied in diamond related fields, however, there are a few reports on varying oxygen concentration by changing the UV/ozone treatment time to affect the surface electrical properties of H-diamond, especially for hydrogenated single crystal diamonds.

In this work, by UV/ozone treatment process, an enhanced oxygen adsorption occurs on the hydrogen-terminated single crystal diamond surface, and the oxygen concentration varies with increasing the treatment time. The wettability of diamond surface transfers from hydrophobic for H-termination diamond to hydrophilic for partial O-termination. Furthermore, Hall effect measurements indicate that the oxygen-treated surface shows p-type conduction, and the resistance (Hall mobility) increases (decreases) at high

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oxygen concentrations. The results reveal that by UV/ozone treatment, the structure modification and properties of H-diamond have been modulated related to oxygen adsorption, which would determine the performance of novel designed 2DHG devices.

The samples were prepared as follows. The mechanically polished high-temperature-high-pressure synthesized (100) Ib single crystal diamond (size of $3 \times 3 \times 0.5\,\text{mm}^3$) was selected as a seed substrate for H-diamond deposition. Prior to the deposition process, the substrates were boiled in a mixture of H_2SO_4 and HNO_3 at 300 ℃ for three hours to remove the non-diamond phase carbonaceous materials and various contaminations, and then they were cleaned by ultrasound in an acetone solution for 30 min. The as-treated seeds were put into a microwave plasma chemical vapor deposition system (MPCVD, 6 kW at 2.45 GHz) to deposit a thin homoepitaxial layer. The growth parameters for the H-diamond layer are as follows: deposition temperature 900–930 °C, flow rates of gases $H_2/CH_4 = 500/0.5$ in sccm, and reaction pressure 100 torr. The low CH_4 concentration in the feed gas with respect to that of H_2 (CH_4/H_2 ratio of 1000 ppm) is proposed to realize full covered H-termination of the as-deposited diamond layer. The thickness of the samples is about 100 nm with a deposition rate of 50 nm/h. Ti/Au electrodes with Ohmic contacts were deposited by a sputtering process on the four corners of H-diamond surface. Subsequently, the H-terminated samples were put into a UV/ozone treatment chamber (BZZS250 GF-TC) equipped with 300 W power UV lamp having emissions at 185 and 254 nm for ozone treatment for times of 20, 30, 60, 180, 360, and 600 s. The H-diamond surfaces before and after ozone treatment are characterized by means of atomic force microscopy (AFM, Cypher ES), high-resolution x-ray photoelectron spectroscopy (XPS, ESCALAB-250Xi). The contact angles (θ) were measured with the sessile drop method by an XE-CAMC33 system using a liquid droplet in a volume of 0.5 μL. Hall effect measurements were performed by the van der Pauw method (Lakshore 8400 Hall system). All experiments were carried out at room temperature.

The surface morphologies of H-diamond epitaxial layers before and after UV/ozone treatment were examined by AFM (not shown). For the as-deposited H-diamond, the atomically smooth surface is presented implying high quality homoepitaxial growth under the optimized condition. After treatment by UV/ozone, the smooth surface is maintained, meaning that there is little damage appearing on the surface.

The surface adsorption of oxygen dependent on UV/ozone treatment time was detected by XPS spectroscopy, as shown in Fig. 1. In a wide range of binding energy (Fig. 1(a)), the signals of O 1s examined for the H-diamond samples treated by UV/ozone at 0, 20, 30, 60, 180, 360 and 600 s are presented. In the insets of Fig. 1(a), the C 1s and O 1s signals are centered at 285.7 eV and 532.1 eV, respectively, the latter is correlated to oxygen bonded to the diamond surface identified as C=O.[12,16] In general, the stronger intensity of the O 1s peak corresponds to the more oxygen chemical adsorption on diamond surface. Taking the relative sensitivity factor (RSF) into account, the adsorbed oxygen concentration was calculated from the ratio of intensity area of the O 1s to C 1s signals, plotted in Fig. 1(b) as a function of ozone treatment time. For the as-grown H-diamond film, the weak O 1s peak appears to be related to the absorption of oxygen in air, where the oxygen content estimated is ∼2.3%, meaning that the surface is clean. Evidently, treating by UV/ozone, the oxygen content on diamond surface increased sharply in a short treatment time from 3.2% for 20 s to 6.1% for 60 s. With continuously increasing the treatment time to 600 s, the oxygen content slowly increases up to 7.9%. It is reasonable that under UV/ozone treatment, more chemically adsorbed oxygen atoms replace the original H atoms on the surface of single crystal diamond.

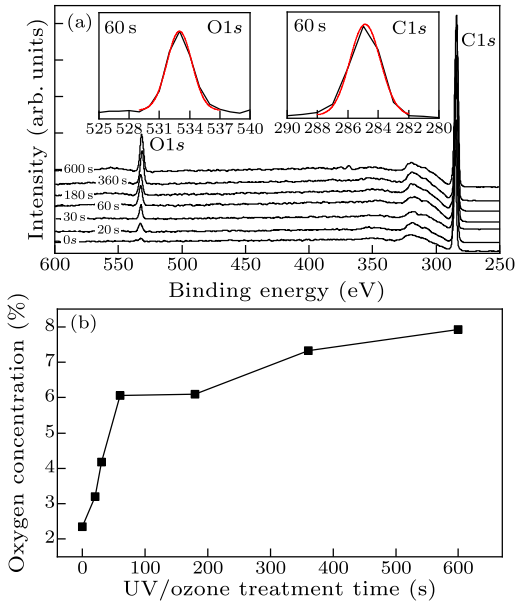

Fig. 1. (a) XPS spectra of scan over a wide range of binding energy of the H-diamond surfaces before (0 s) and after treated by UV/ozone for 20–600 s. The insets are the high-resolution scans of O 1s and C 1s of the surface treated for 60 s. (b) The content of adsorbed oxygen on diamond surface as a function of UV/ozone treatment time.

On H-diamond surface, besides the adsorbed H atoms, the other radicals (such as H_3O^+, OH^-, HCO_3^-) are presented when the H-diamond is exposed in air, which is ascribed to an electrochemical process in a cover water layer with exchanged electrons to the surface.[9,17] For a UV/ozone process, under UV irradiation, the O_2 in air is excited and converted to ozone of O_3 (by 185 nm line), and a part of O_3 molecules are broken up by 254 nm line into O_2 molecules and singlet atomic oxygen (^1O). These reactive oxygen specials easily react with the surface carbons forming C=O bonds on diamond surface and efficiently replace the

original H, OH^- radicals.[18] During the oxidation process, O_3 plays a crucial role in realizing more oxygen absorption rather than that of O_2 and ^1O.[15] With continuously increasing the UV/ozone treatment time, more oxygen specials generate and further cover the diamond surface, as demonstrated by XPS (Fig. 1) and the following wettability examinations (Fig. 2).

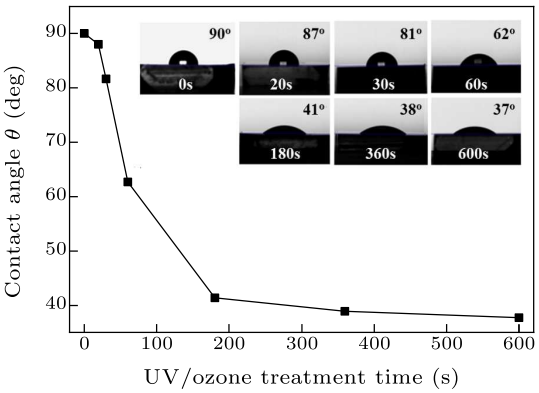

Fig. 2. Variation of contact angle for the UV/ozone treated H-diamond as a function of treatment time. The insets are the photographs of water droplets on the surfaces treated by UV/ozone for different times.

Wettability property of the UV/ozone treated surface reflects the state of oxygen adsorption. Observed from Fig. 2, the contact angle of the full H-termination diamond is ∼90°, and then sharply decreases from ∼87° to ∼41° with increasing the UV/ozone treatment time in a short time-scale from 20 s to 180 s, and finally, it becomes saturation at about ∼37° for further treatment. The saturated contact angles are larger than those for UV/ozone treated ultrananocrystalline diamonds (having a small contact angle of ∼10° at ∼8% oxygen content),[15] due to the significant differences in surface structure and morphology.[19,20] It is known that the diamond with H-termination (O-termination) is hydrophobic (hydrophilic) with a contact angle region of 90°–160° (0°–90°), which can be further modulated by introducing some special rough surface designs.[19–22] For single crystal diamonds with smooth surface, hydrogenation or oxygenation plays a key role in determining its wettability, i.e., the hydrogenated (oxygenated) surface has a contact angle of about 90° (40°–50°).[19] Interestingly, in this work, by varying the ozone treatment time in minutes or seconds, the contact angels are gradually varied, indicating that the concentration ratio of the adsorbed hydrogen and oxygen can be adjusted sensitively relating to the treatment time, which is in accordance with the XPS results stated above. UV/ozone treatment thus provides a suitable method for more precise and moderate modulating of the concentration of oxygen termination on diamond surface, with respect to the other methods of oxygen-plasma or high temperature thermal treatment in air.

It is known that the H-diamond is a p-type semiconductor having 2DHG characteristics near the surface, and nearly full surface coverage of C–H bonds is a necessary condition.[7,10,23] Surface adsorbates or insulation films on H-diamond, processing unoccupied orbitals[23] or negative charges[24] forming electric field, are needed to produce holes. On the other hand, the insulating adsorbates may damage the p-type characteristic and/or conductivity of H-diamond. For example, chemical oxidation process was applied using an acid mixture heated at high temperatures (∼300°C), resulting in surface termination with full oxygen in place of original hydrogen, and the conductive H-diamond becomes insulated.[1–3] As mentioned above, the UV/ozone treatment is a suitable method to precisely modulate the concentration of oxygen termination on diamond surface, it is expected to affect the electronic property of H-diamond surface related to the oxygen adsorption with varying contents. The electric properties including resistance and Hall mobility are tested by Hall effect measurements. All the samples show positive Hall coefficients, confirming that the conduction is p-type.

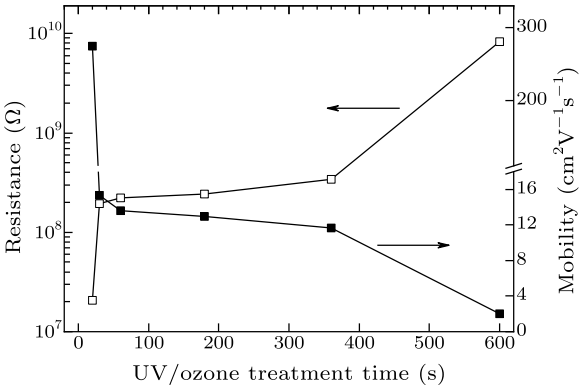

Fig. 3. Resistance and Hall mobility of the UV/ozone treated H-terminated diamonds as a function of treatment time.

Figure 3 shows the time-dependent electrical resistance and Hall mobility of the samples under UV/zone treatments. The resistance increases rapidly by one order of magnitude for 30 s treatment ($1.9 \times 10^8\,\Omega$) with respect to that for 20 s ($2.0 \times 10^7\,\Omega$), and then the resistance increases slowly with further treatment from 30 s to 360 s. With further increasing the treatment time to 600 s, the resistance of $8.2 \times 10^9\,\Omega$ is around 24 times that treated for 360 s ($3.4 \times 10^8\,\Omega$). The resistance of the films treated for a long time (>10 min) was so high that we could not perform Hall measurements. On the contrary, the corresponding Hall mobility shows an opposite trend with respect to the case of resistance. Hall mobility decreases sharply 18 times within 10 s from $274.3\,cm^2{\cdot}V^{-1}{\cdot}s^{-1}$ for 20 s treatment to $15.3\,cm^2{\cdot}V^{-1}{\cdot}s^{-1}$ for 30 s, and subsequently, following a slow decrease with the increase of treatment time to $2.0\,cm^2{\cdot}V^{-1}{\cdot}s^{-1}$ for 600 s by two orders of magnitude. The variation tendency of the electric properties is consistent with the above results of XPS and wettability. It is further confirmed

that under UV/ozone with increasing treatment time, more chemically adsorbed O atoms replace the original H atoms on H-diamond, leading to the decrease of Hall mobility, and consequently, the electric behavior is modulated from p-type semiconductor to insulator.

In conclusion, the surface adsorption and properties of hydrogenated (100) single crystal diamond treated by UV/ozone are investigated systematically. The increased concentration of oxygen adsorption on H-diamond surface with the increase of ozone treatment time was demonstrated by the examinations of XPS, wettability and Hall effect measurements. The generated O_3 under UV irradiation efficiently enhances the O atom adsorption partially instead of original H atoms. The concentration of oxygen adsorbed chemically on diamond can be precisely controlled by adjusting ozone treatment time in seconds. The properties of wettability and electrical conductivity of H- and O-diamond are modulated by changing oxygen content under ozone treatment. These results suggest that UV/ozone process is a suitable tool to highly efficiently determine surface properties of diamond crystals working in practical applications.

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