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Wettability and Surface Energy of Hydrogen- and Oxygen-Terminated Diamond Films *

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The contact angle and surface energy values of diamond are systemically investigated in terms of surface treatments (hydrogen- and oxygen-terminations), structure feature (single crystal diamonds and polycrystalline diamond films), crystal orientation ((100), (111) and mixed (100)/(111) orientations), different fluids (probes of polar deionized water and nonpolar di-iodomethane). It is found that the hydrophobic/hydrophilic characteristic and surface energy values of diamond are mainly determined by the surface hydrogen/oxygen termination, and less related to the structural features and crystal orientation. Based on the contact angle values with polar water and nonpolar di-iodomethane, the surface energies of diamond are estimated to be about 43 mJ/m^2 for hydrogen-termination and about 60 mJ/m^2 for oxygen-termination. Furthermore, the varying surface roughness of diamond and fluids with different polarities examined determine the variation of contact angles as well as the surface energy values. These results would be helpful for a more detailed understanding of the surface properties of diamond films for further applications in a broad number of fields, such as optical and microwave windows, biosensors, and optoelectronic devices, etc.

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Diamond exhibits unique physical and chemical properties,[1] such as the ultra-wide band gap, chemical inertness, the highest hardness, high thermal conductivity, self-cleaning and stain resistance, and biocompatibility. These special advantages make diamond an ideal material used in the optical probes and sensors,[1,2] semiconductor devices,[1,3] and so on. The surface properties of diamond are widely investigated, since the performance of devices is usually related to its surface energy, surface conductivity and surface electrical properties.[4−6] As one considerable parameter, the wettability is characterized by the contact angle θ, which is mainly determined by surface free energy and geometric structures of the surface.[7,8] The natural diamond exhibits a moderate hydrophobicity related to the surface energy of diamond.[9] Treated by hydrogen- or oxygen-plasma, the surface wettability can change to the hydrophobic or hydrophilic state, which is related to the changes of the surface reconstruction and surface termination, as detected by Raman and XPS analysis.[10] Moreover, the contact angle values for diamond films were affected by varying surface morphologies (for example, by surface etching[11]). Especially, the polycrystalline films with nano-sized grains are favorable for realizing superhydrophobicity (with hydrogen termination) and superhydrophilicity (with oxygen termination).[12,13] In addition, for nano-diamond films, it was reported that the wettability can be adjusted by two types of *in situ* chemical vapor deposition (CVD) process of the oxygen and water vapor etching.[14] The pH of liquid droplet,[13,15] annealing in oxygen or air atmosphere, acid and alkali treatments, and electrochemical oxidation modifications[16] have been proposed to influence the wettability behaviors. However, there are a few systematic researches on the wettability properties related to the facts combining surface energy, surface termination, and morphology of diamond films.

In this Letter, the wettability property of diamond is systemically analyzed in terms of surface treatments (hydrogen- and oxygen-terminations), structural features (polycrystalline diamond films (PDFs) and single crystal diamonds (SCDs)), and crystal orientation. Two kinds of liquids of polar deionized water and nonpolar di-iodomethane are used to calculate the corresponding surface energy (γ_S value) of diamond. The relations between wettability and varying structure feature and surface modulation are investigated. It is found that the hydrophobic/hydrophilic characteristics and surface energy values of diamond are mainly determined by the surface termination, and less related to the structural features and crystal orientation.

The PDFs were deposited on polished silicon wafers by the microwave plasma CVD (MPCVD) method at frequency of 2.45 GHz with reaction mixture gases of hydrogen/methane (H_2/CH_4). Before deposition, the silicon wafers were ultrasonic treated

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in nano-diamond suspension, and then cleaned in ethanol solution and deionized water to remove the powder residue. After CVD process deposition for 36 h, the samples were cooled down to room temperature and removed from the chamber. The typical thickness for free-standing PDFs was about 150 μm. The high-temperature-high-pressure synthesized Ib (100) and (111) SCDs (size of $4 \times 4\,\mathrm{mm}^2$) after mechanically polishing were used as the substrate for the hydrogen- and oxygen-termination treatment processes. The hydrogen termination samples were obtained by hydrogen plasma in the MPCVD system at 800℃ for 30 min. To realize oxygen termination, the samples were annealed in air at low temperature of 500℃ for 30 min. For surface etched samples, a thermal oxidation process was carried out at 800℃ for 15 min in air atmosphere.

The surface morphology, structure, and surface chemical absorption states were characterized by means of scanning electron microscopy (SEM, FEI MAGELLAN-400), atomic force microscopy (AFM, Cypher ES), Raman spectroscopy (Renishaw RM-1000 inVia Raman microscope with laser excitation at 514 nm), and high-resolution x-ray photoelectron spectroscopy (XPS, ESCALAB-250Xi). The contact angles (θ) were measured by the sessile drop method using an XE-CAMC33 system. The liquid droplet with 0.5 μL was used. The surface energy was calculated by the Owen–Wendt–Rabel–Kaelble method.[17] All the contact angle tests were carried out at room temperature.

Figure 1 shows the SEM images of the PDFs samples with (100)-, (111)- and mixed (100)/(111)-orientated grains. In Fig. 1(a), the main grain crystals have square (100) top surface with an average grain size of ∼ 25 μm. In addition, some tiny polycrystalline grains with random orientation appear around the column (100) grains. For the (111)-orientated PDFs (Fig. 1(b)), the majority of grains have typical trilateral surface with a high density of growth step, and the average grain size is ∼60 μm. Figure 1(c) shows the PDF with mixed (100)/(111)-orientated grains, and the average grain size is ∼25 μm. Observed from cross-sectional SEM images of PDFs (not shown), the roughness are several micrometers for those samples.

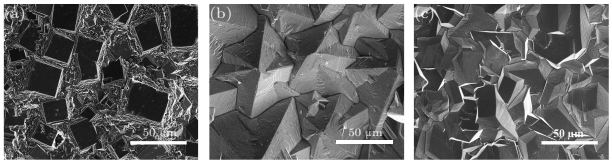

Fig. 1. SEM images of polycrystalline diamond films (PDFs) mainly consisting of (a) (100)-, (b) (111)- and (c) mixed (100)/(111)-orientated grains.

The three-dimensional micro-topography of the (100)- and (111)-orientated SCD surface appears in the AFM image (Fig. 2). Different from the cases of the PDFs in Fig. 1, both the SCD samples have smooth surface with nanometer-scale roughness. The surface of (100)-orientated SCD is relatively smoother than that of (111)-orientated SCD.

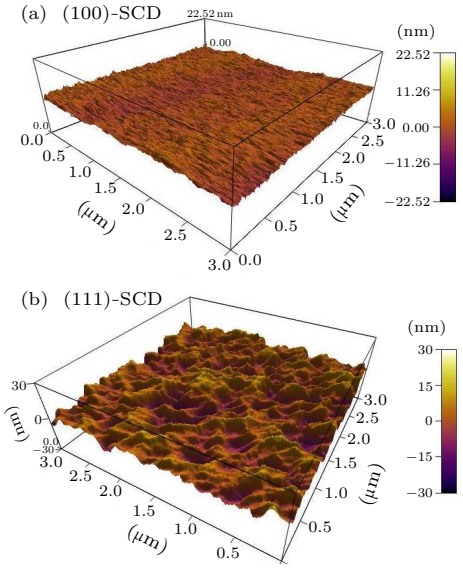

Fig. 2. AFM images of the mechanically polished surfaces of (a) (100)- and (b) (111)-orientated single crystal diamonds (SCDs).

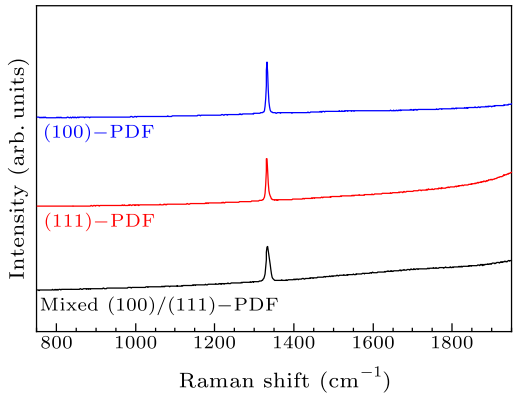

Fig. 3. Raman spectra of the polycrystalline diamond films (PDFs) mainly consisting of (100)-, (111)-, and mixed (100)/(111)-orientated grains.

The Raman spectra for PDFs (Fig. 3) reveal the typical peak at 1332 cm^{-1} related to the intrinsic zone-centre phonon of diamond,[18] while the peaks from other non-diamond phases are not detected, meaning that the CVD diamond films have high quality. To analyze the components of surface, the XPS test was performed for the (100)-orientated SCD sample with hydrogenation and oxygenation terminations as an example, as shown in Fig. 4. In the energy spectrum, the two obvious peaks at 285 eV and 532 eV correspond to C 1*s* and O 1*s*, respectively. The O 1*s* peak appearing for hydrogen-terminated samples is weak, which is related to the absorption of oxygen in air.[19] The intensity of the O 1*s* peak for the oxygen-terminated sample after thermal oxygen treatment enhances significantly, and the corresponding O 1*s*/C 1*s* ratio is

much larger than that for the hydrogen-terminated one, which denotes that the oxygen termination has been successfully modified.

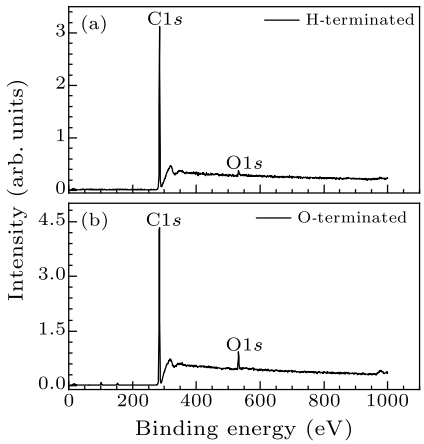

Fig. 4. XPS spectra of single crystal diamonds (SCDs) with (a) hydrogen- and (b) oxygen-termination surfaces.

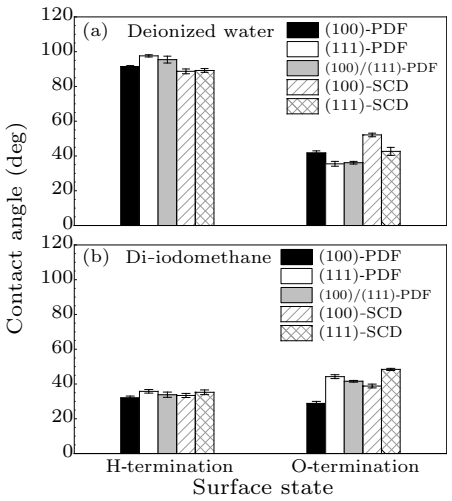

Fig. 5. Contact angle θ of various diamond samples (labeled in the insets) examined with liquid droplets of (a) deionized water and (b) di-iodomethane.

The measurements of the contact angles (θ) with two kinds of liquids (deionized water and di-iodomethane) are plotted in Fig. 5. For each sample, the average contact angle value was obtained by five independent measurements, and the measured error range is estimated to be within $\pm 2°$. When the deionized water is used as the probe liquid, the examined contact angle values (θ) of the hydrogen-terminated PDF samples with different orientations are 91°–98°, and those for hydrogen-terminated SCDs are ∼89° (Fig. 5(a)). This reveals that either hydrogenated PDFs or SCDs have hydrophobic property. For the oxidized diamonds, the θ values of PDFs are 35°–42°, and those of SCDs are 43°–52°, showing the hydrophilic property for both PDFs and SCDs. There is a significant difference in the contact angle values between hydrogen-terminated and oxygen-terminated diamond films. Compared with the natural diamond with weak hydrophobic property,[9] it denotes that the surface termination strongly determines the varying contact angles and wettability prosperity. In detail, the θ values of the SCD and PDF samples are slightly different, since the PDF has relatively larger roughness than that of SCD, as shown in Figs. 1 and 2. Note that the θ values nearly do not show an obvious relationship to the crystal orientations of (100), (111) or mixed (100)/(111), which is consistent with the previous results.[5,12,20] It is concluded that the hydrophobic/hydrophilic characteristics of diamond are mainly determined by the surface hydrogen/oxygen termination.

In addition to polar deionized water, the nonpolar liquid of di-iodomethane is proposed as a probe to study the wettability property on various diamond surfaces (Fig. 5(b)). The θ values are 32°–36° (29°–48°) for hydrogenated (oxygenated) diamond films, suggesting that hydrogen/oxygen termination has no obvious influence on the contact angles for di-iodomethane. In contrast to water with polarity, the wettability property of nonpolar liquid on diamond surface shows a hydrophilic feature nearly independent of surface termination, crystal orientation, SCD or PDF.

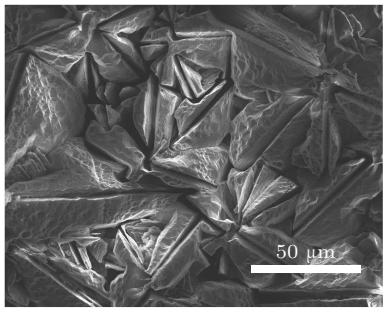

Fig. 6. SEM image of the polycrystalline diamond film (PDF) mainly consisting of (111)-orientated grains after thermal treatment at 800℃ in air.

To further investigate the influence of surface morphology on wettability of diamond, a further oxygen etching process at high temperature (800℃) was performed on a (111)-PDF to increase the surface roughness. The SEM image in Fig. 6 shows that a serious etching phenomenon occurs on the surface. The grooves (pits) appearing on both boundaries and surfaces of grains effectively enhance the roughness of the films. For the as-etched sample, the contact angle for the polar deionized water increases from hydrophobic 97° (before thermally etching treatment) to 117° with hydrogenation surface, and interestingly, the contact angle of the oxygenation surface becomes zero, namely a super-hydrophilic phenomenon is realized. With the liquid droplet of nonpolar di-iodomethane, the contact angles for both the hydrogenated and oxygenated samples after thermal etching are zero (named as superhy-

drophilicity). The realization of superhydrophilicity (O-termination surface) and enhanced hydrophobicity (H-termination surface) can be attributed to the additional grooves (pits) appearing on the as-treated surface of PDF. It is thus concluded that the wettability of diamond films can be efficiently modulated by combining surface termination and more rough morphology.

Surface energy (γ_S) is an important parameter determining surface property of diamond. There is no direct method of measuring the free energy of solid surfaces under ambient conditions, an indirect method starts with Youngs' moduli[21] for liquid, solid and vapor in equilibrium,

$$\gamma_S = \gamma_{SL} + \gamma_L \cos\theta, \tag{1}$$

where γ_S is the solid surface/vapor energy (tension), γ_{SL} is the solid-liquid interfacial tension (energy), γ_L is the vapor/liquid tension, and θ is the contact angle between a liquid drop and the solid surface. Equation (1) is rigorous for liquid, solid and vapor in equilibrium with a force balance. Here, it can also be considered as an energy balance because an interfacial tension of force per unit length is equivalent to an energy per unit area.[22]

The surface energy is obtained by the Owen–Wendt–Rabel–Kaelble method as follows:[17]

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\sqrt{\gamma_S^D \cdot \gamma_L^D} - 2\sqrt{\gamma_S^P \cdot \gamma_L^P} \tag{2}$$

where γ^D and γ^P are the dispersion and polarity tension, respectively. The superscripts D and P denote the dispersive and polar contribution to the corresponding interfacial tension. Additionally, the surface tension is composed of an independently dispersive and polar force, as expressed by

$$\gamma_{S/L} = \gamma_{S/L}^D + \gamma_{S/L}^P. \tag{3}$$

According to the Owen–Wendt–Rabel–Kaelble equation, the parameters of two probes of polar and nonpolar liquids are required to be examined for the calculations. Thus, the polar deionized water and nonpolar di-iodomethane are selected in this work. The surface energies for the polar deionized water (nonpolar di-iodomethane) used in the calculations are as follows:[20] surface energy γ_L, dispersion γ_L^D and polar γ_L^P are 72.8 mJ/m^2 (50.8 mJ/m^2), 21.8 mJ/m^2 (50.8 mJ/m^2) and 51.0 mJ/m^2 (0 mJ/m^2), respectively.

For diamonds with varying surface structures and modifications, based on the measured θ values and Eqs. (1)–(3), the calculated γ_S, γ_S^D and γ_S^P values are obtained and summarized in Table 1. The calculated surface energy γ_S of hydrogen-terminated PDFs is about 43 mJ/m^2, similar to the datum of hydrogen-terminated SCD (about 42 mJ/m^2). For oxygen-terminated PDFs and SCDs, the γ_S values are about 60 mJ/m^2 and 51–55 mJ/m^2, respectively, which are slightly larger than those for the cases of hydrogenated surfaces. Consequently, the crystal orientation of diamond has less effect on its surface energy, while the surface functional modification plays an important role in determining the surface energy. Additionally, the enhancement of the surface roughness could increase the surface energy to a certain extent, as for the case of surface-etched PDFs (∼66 mJ/m^2 for H-termination and ∼75 mJ/m^2 for O-termination).

It is found that the contact angle is related to the polarity of liquid droplets (Fig. 5). Since the hydrogen (oxygen) terminated diamond exhibits a negative (positive) electron affinity,[23] the dipole of water molecules would be parallel to hydrophobic surface and perpendiculars to hydrophilic surface.[10] It is thus possible to obtain a weak (strong) interaction with water on the hydrogen (oxygen) terminated diamond surface, leading to a large (small) contact angle (Fig. 5(a)). For the nonpolar di-iodomethane, the interactions between liquid molecules on either hydrogenated or oxygenated diamond surface are similar, and then the contact angles are not significantly affected by the electronic properties of the diamond surface (Fig. 5(b)).

Table 1. Surface energy (γ_S), dispersion (γ_S^D), and polar (γ_S^P) components of various diamond samples with H and O terminations.

Samples	Termination	γ_S (mJ/m^2)	γ_S^D (mJ/m^2)	γ_S^P (mJ/m^2)
(100)-PDF	H-	43.951	43.515	0.436
	O-	59.346	32.691	26.655
(111)-PDF	H-	43.303	43.288	0.015
	O-	60.633	24.521	36.112
(100)/(111)-PDF	H-	43.815	43.730	0.085
	O-	60.573	25.958	34.615
(100)-SCD	H-	42.925	41.968	0.957
	O-	51.590	29.981	21.610
(111)-SCD	H-	42.077	41.124	0.953
	O-	55.686	23.334	32.352
Surface-etched (111)-PDF	H-	66.265	60.855	5.410
	O-	75.023	35.010	40.013

In conclusion, we have investigated the wettability property and surface energy of diamond films, related to the surface termination (hydrogenation and oxygenation) and structure features of both polycrystalline and single crystal diamonds. The variation of wettability property of polar and nonpolar liquid droplets examined is dependent on diamond surface termination and the polarity of the droplets. The calculated surface energies of the diamonds with various features are mainly determined by the functional modification on the surface rather than their intrinsic structures. These results suggest that as an important functional material, diamonds with controlled wettability property are suitable to meet the requirements in practical applications working under various ambient conditions.

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