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Workfunction variation across surface of an H-terminated diamond film measured using Kelvin probe force microscopy

J.H. Lay [a,*], K.M. O'Donnell [b], P.W. May [c]

[a] Bristol Centre for Functional Nanomaterials, University of Bristol, Tyndall Avenue, Bristol BS8 1FD, United Kingdom
[b] Centre for Nanoscience and Quantum Information, University of Bristol, Tyndall Avenue, Bristol BS8 1FD, United Kingdom
[c] Department of Chemistry, University of Bristol, Bristol BS8 1TS, United Kingdom

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ABSTRACT

With the ability to image both topography and contact potential difference simultaneously, Kelvin probe force microscopy (KPM) is an effective tool for the electrical characterisation of diamond surfaces. In this work we measure variations in contact potential difference across the surfaces of boron-doped diamond films in order to investigate work function variations caused by surface features. Significantly, we demonstrate work function variations in excess of 300 mV across the surfaces of two differently prepared diamond films. Variations of this magnitude may have implications for the use of diamond in a number of electronic applications.

1. Introduction

A great amount of interest has developed in the potential uses of diamond as an electronic material due to a combination of extreme mechanical properties twinned with favourable electronic properties such as high electron and hole mobilities, large band gap and low dielectric constant [1]. The biological compatibility and chemical stability of diamond have also led to interest in the potential of diamond as a biological sensor or template. Successful integration of diamond in the fields of micro- and nanoelectronics requires an understanding not only of the electrical properties of the bulk, but also of the electrical properties on micro- and nanometre length scales. This is particularly true for devices utilising surface transfer doping such as ion-sensitive FETs [2], as the electrical properties depend critically on how molecular adsorbate levels align with the diamond levels.

A suitable candidate technique for the electrical characterisation of diamond surfaces is Kelvin probe force microscopy (KPM) [1], a non-contact scanning probe technique capable of measuring contact potential difference and surface topography simultaneously. Apart from showing local variation in work function indicative of defects [3], adsorbates [4] or compositional differences [5], the contact potential image can be used locate dopants [6] and dynamic charge-trapping behaviour [7]. In ultra-high vacuum, KPM can operate in either amplitude modulation or frequency modulation mode [8]. Amplitude modulation KPM (AM-KPM) is an overtone-oscillation-based technique, whereby an AC voltage tuned to the first overtone of the cantilever resonant frequency is applied to the cantilever such that it oscillates in two modes. The contact potential difference (CPD) between the probe tip and a given point on the surface of a specimen can be measured by applying an additional DC voltage component to the tip and using a lock-in amplifier to adjust this component until the second resonant oscillation is at a minimum, at which point the DC voltage is equal in magnitude to the contact potential. As the tip scans along a surface, a lock-in amplifier is used to continuously track the applied DC voltage component to the CPD using feedback from the behaviour of the cantilever. The feedback loop enables contact potential to be measured at each point in a single scan. The theoretical energy resolution of the technique is dependent on the Q-factor of the cantilever used, though many other factors influence the accuracy of measurements made using KPM [9].

AM-KPM has previously been used to characterise diamond surfaces in a number of ways. Szunerits et al. [10] report KPM images of a polished boron-doped diamond surface in argon atmosphere, showing variations in contact potential of approximately 20 mV, attributed to either changes in dopant concentration or surface adsorbates. Separate studies made by Tachiki et al. [11] and Salvadori et al. [12] demonstrated the use of KPM to observe differently terminated regions across a diamond surface. In these two studies, variations in potential of 100 and 95 mV, respectively, were measured across the interface between hydrogen-terminated and oxygen-terminated regions. Given that the electron affinity and work function of oxygenated and hydrogenated surfaces are known from photoemission studies to be very different [13], the small contact potential difference is surprising. In addition to measurement of 80 mV potential variation across terminations, Rezek et al. [14] reported the variation in contact potential difference as a function of illumination using a spotlight, showing potential variations of

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* Corresponding author.
E-mail address: Joshua.Lay@bris.ac.uk (J.H. Lay).

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the order of 200 mV from dark to light. A possible issue with KPM of diamond surfaces in air is that the hydrophilic nature of the oxygen-terminated surface may give rise to a potential-masking effect caused by adsorbed water molecules on the surface of the material [15]. Therefore ultra-high vacuum (UHV) conditions are essential for reliable results. Under UHV conditions, Pakes et al. [4] reported variations in contact potential of 25 mV across a hydrogen-terminated diamond surface attributed to variation in surface orientation due to anisotropic plasma etching.

For AM-KPM it has been previously reported [3] that electric fields originating from the body of the cantilever rather than the tip can introduce a lateral averaging effect on contact potential readings. When using the amplitude modulation technique it is also beneficial to understand the potential effects that topographical features and gradients may have on any potential readings obtained. For example, when the tip encounters steep gradients it may overshoot, leading to retraction of the tip from the surface causing cross talk between topographic and electronic measurement; resulting in a shadowing effect on the contact potential reading. In this work, we present Kelvin probe force microscopy of diamond surfaces in UHV, demonstrating the effect of a number of surface features on the contact potential of the surface.

2. Methods

2.1. Chemical vapour deposition (CVD)

Two boron-doped diamond films (B1, B2) were deposited onto 10 × 10 mm single crystal Si (1 0 0) substrates using microwave plasma CVD. Prior to deposition, the substrates were manually abraded with 1–3 μm diamond powder in order to provide a seed layer for diamond growth. Both films were deposited for 90 min at a substrate temperature of ~850 °C using a gas mixture of $Ar/H_2/CH_4/B_2H_6$, yielding diamond films approximately 3 microns thick. The Ar, H_2 and B_2H_6 flow rates were constant at 500, 40, and 0.1 sccm, respectively, while the CH_4 flow rate was either 15 sccm (sample B1) or 30 sccm (sample B2). The films were grown under a pressure of 150 Torr and microwave power of 1.0 kW. Preparation in this way yields electrically conducting, microcrystalline, faceted diamond films with hydrogen-terminated surfaces. Both film surfaces were viewed using a JEOL 7600 field emission scanning electron microscope.

2.2. Kelvin probe force microscopy

Both diamond specimens were sonicated in isopropyl alcohol prior to being analysed using an Omicron UHV VT AFM scanning probe microscope. Once inside the vacuum chamber, both specimens were annealed to 400 °C in order to remove any surface contaminants that may have accumulated after the films were deposited. KPM was performed in amplitude modulation mode using Nanosensors PPP-EFM Si cantilevers with a Pt/Ir conductive tip coating.

3. Results and discussion

3.1. Scanning electron microscopy

Figure 1a and b demonstrate the surface appearance of both diamond specimens. Both figures show that a range of grain orientations are present of the surface of each sample. It can be observed from Figure 1a that the majority of grains in specimen B1 are no larger than 1 μm in diameter, with grains appearing to contain few defects. In contrast, specimen B2 contains larger grains of diameter no more than 2 μm and a much higher defect density. The different structures of the two films are caused by the different methane flow rates used during the growth process. Figure 1b shows a number of structures with a pentagonal appearance. These structures are known as twin quintuplets and are formed by multiple twinning induced by the presence of $\Sigma 3$ grain boundaries [16].

3.2. Kelvin probe force microscopy

Figure 2 shows a twin quintuplet found on the surface of specimen B2, obtained using amplitude modulation KPM. The topographic map in Figure 2a shows that the surface height varies by approximately 500 nm within the scanned region, with at least four different diamond grains evident. The pentagonal shape situated slightly to the left of centre is a twin quintuplet with diameter ~500 nm. Figure 2b is a map of contact potential difference obtained for the same scan area. It should be noted that in this map a more negative contact potential refers to a greater work function, because the work function, Φ, is calculated using the following equation:

$$\Phi_{\text{surface}} = \Phi_{\text{tip}} - V_{\text{cp}}$$

where Φ_{surface} is the work function of the surface in question, Φ_{tip} is the work function of the cantilever tip and V_{cp} is the contact potential difference measured between tip and sample. With the above equation taken into account, the very top of the twin quintuplet is clearly defined in the potential map by a pentagonal outline representing a greater work function than the majority of the feature. Indeed, in a number of cases it appears that facet edges are well defined by an increase in apparent work function. The df image in Figure 2d shows that topographic crosstalk is unlikely at the facet edges since there is no specific contrast solely related to the edges. For example, the lower edge of the pentagon is effectively invisible

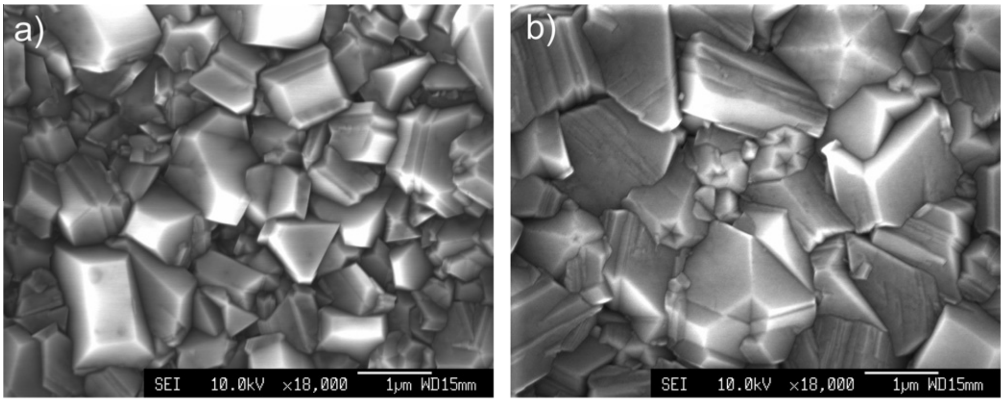

Figure 1. Scanning electron micrographs of specimen B1 (a) and specimen B2 (b).

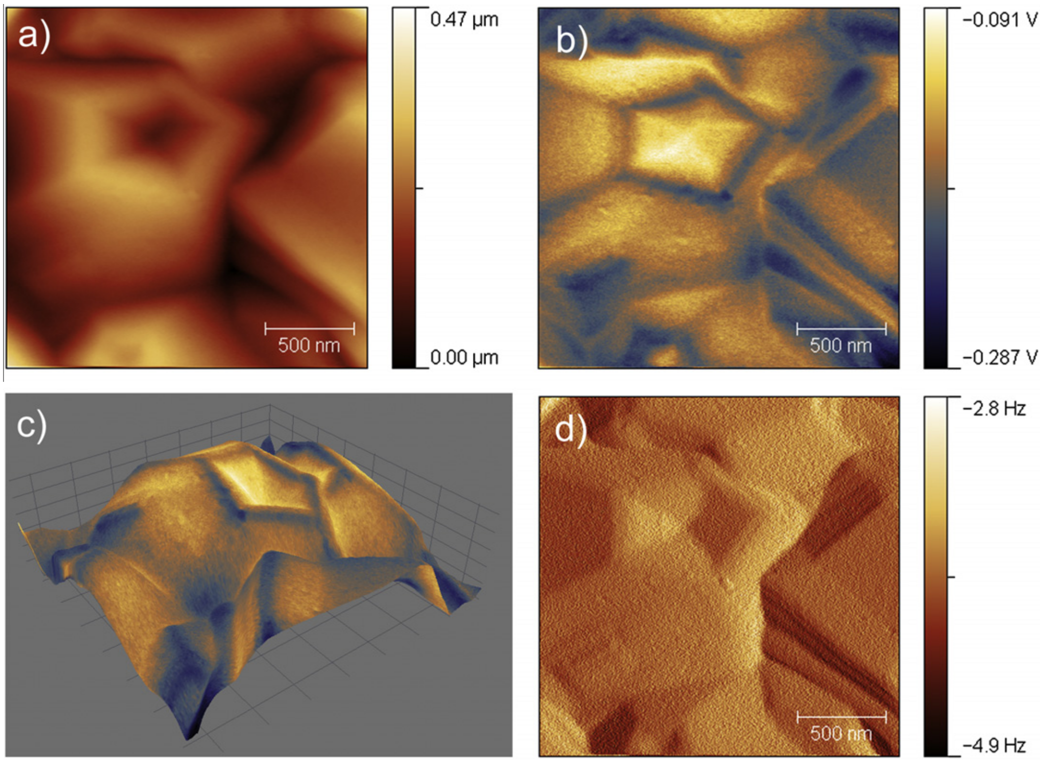

Figure 2. Images of specimen B2 obtained using KPM, (a) surface topography map, (b) contact potential difference map, (c) three-dimensional topographic map overlaid with contact potential map, and (d) df (frequency shift) image.

in the df image, but shows significant contrast in the contact potential image. The df contrast relates instead to the slope of the facets relative to the scan direction.

Figure 3 shows an area on the surface of specimen B1, and includes a line profile taken through a section of this area to show the variations in contact potential measured along the indicated path. This demonstrates the effect of crystal orientation on work function by showing that a single grain surface has a uniform work function at least 100 mV lower than the remainder of the scan area. Crystal orientation, however, is not the only factor affecting the work function of the surface; with evidence of this shown in Figure 3. Analysis of height-distribution data associated with Figure 2b reveals that the average work function of the internal faces of the quintuplet surface is ~40 mV lower than the average work function of its external faces. Although small relative to variations measured elsewhere on the surface, this 40 mV difference in potential is significant due to all measured faces being of the {1 1 1} orientation [17]; suggesting that additional factors other than crystal orientation have contributed to the difference in surface work function between the twinned faces. With this considered, it is possible that the evident difference in work function is caused by localised pinning of the Fermi level, as has been previously reported by Rezek and Nebel [18].

An important outcome of the experiments presented in this work is the measurement of large variations in work function across a hydrogen terminated diamond surface. An example of this is shown in Figure 3, where an area denoted by the number ‘2’ on the surface of the diamond film has caused a local increase in work function of approximately 200 mV. Given that the area in question appears to be situated on the surface of a larger grain, this area is unlikely to be a diamond grain and is more probably a surface defect. Due to the cleaning process and annealing treatment used prior to imaging, it is also very unlikely that this area deposited onto the surface after the growth process. For the above reasons it is thought that the region is a graphitic defect deposited towards the end of the CVD process. The presence of other such defects is suggested in the SEM image of the specimen in Figure 1a, where a number of dark, rounded shapes can be seen on the surface of a (1 0 0) facet (bottom left corner of image). The measured work function increase of 350 mV from bright grain surface to defect is also consistent with the assignment of the defect to graphitic carbon, as the work function of hydrogen-terminated boron-doped diamond (1 1 1) is reported to be 4.2 eV [19] with the work function of graphite reported as 4.6–4.7 eV [20].

Other than the potential shift measured across what is likely to be a diamond–graphite interface, large potential shifts of over 100 mV have been measured across the surface of the H-terminated diamond surface also (demonstrated in Figure 3b). Potential shifts of up to 200 mV are also measured across the surface of specimen B2, as shown in Figure 2b. Sharp potential contrast is observed at step edges and boundaries in particular, giving the topography of the surface strong definition. As mentioned earlier, variations measured across the twin quintuplet surface suggest that factors other than crystal orientation may also affect the surface work function. Given the experimental conditions and heat treatment used, it is possible but unlikely that surface adsorbates are responsible for additional variation in contact potential. Pinning of the Fermi level at grain boundaries and local variation in dopant concentration are two possible causes of the measured potential variations. Previous measurements of diamond surfaces using KPM such as those performed by Pakes et al. [4], have not yielded such high variations in work function. In the above case variations of 25 mV are attributed to variations in surface orientation caused by anisotropic plasma etching. Other studies performed in ambient conditions [11,12,14] instead of UHV demonstrate variations of 100 mV or less when scanning across the boundary between oxygen- and

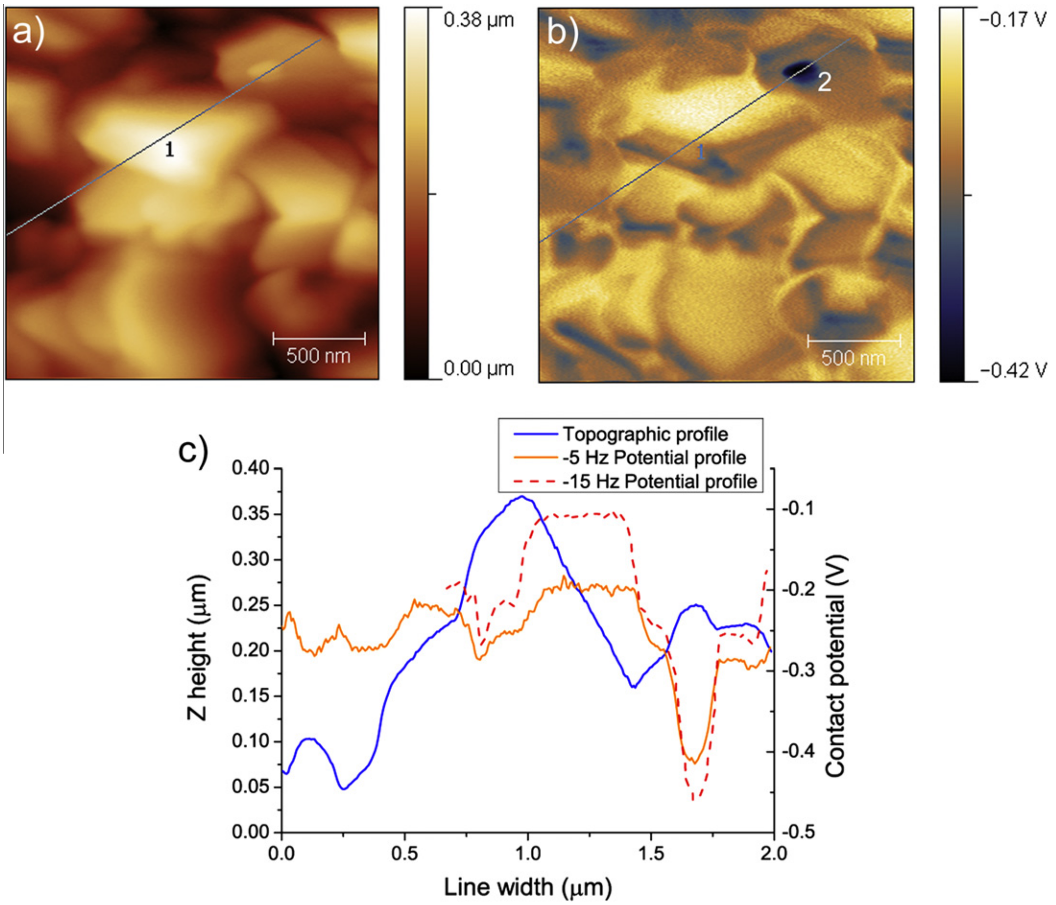

Figure 3. Images of specimen B1 obtained using KPM, (a) surface topography map, (b) contact potential difference map with '2' representing a possible graphitic feature on the diamond surface, (c) line profiles corresponding to line 1 in (a) and (b), demonstrating variations in contact potential across the surface of the specimen.

hydrogen-terminated regions. When we consider that variations of higher magnitudes were measured in this work across a solely hydrogen-terminated surface, it becomes clear that more sensitive measurements are possible when using UHV. This is likely to be because there are no additional influences, such as surface dipoles caused by water molecules, affecting potential measurement when using UHV conditions.

4. Conclusions

KPM has been successfully employed under UHV conditions to measure variations in work function across two boron-doped diamond surfaces. The results found in this work show potential variations as large as 350 mV across an annealed CVD grown diamond surface. Although some of the steep variations observed appear to be caused by the presence of graphitic material, the dependence of work function on the local crystal structure of the surface is also demonstrated. The observed variations caused by neither crystal orientation nor crystal phase may be caused by other factors such as localised dopant concentration. The large potential variations measured across diamond films not subjected to specific surface treatments should be considered before use in applications utilising the surface electronic properties of the material.

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References

[1] J.M.R. Weaver, D.W. Abraham, J. Vac. Sci. Technol. B. 9 (1991) 1559.
[2] B. Rezek, D. Shin, H. Watanabe, C.E. Nebel, Sens. Actuat. B. 122 (2007) 596.
[3] Y. Rosenwaks, R. Shikler, Th. Glatzel, S. Sadewasser, Phys. Rev. B. 70 (2004) 085320.
[4] C.I. Pakes, D. Hoxley, J.R. Rabeau, M.T. Edmonds, R. Kalish, S. Prawer, Appl. Phys. Lett. 95 (2009) 123108.
[5] H. Hoppe, T. Glatzel, M. Niggemann, A. Hinsch, M.Ch. Lux-Steiner, N.S. Sariciftci, Nano Lett. 5 (2005) 269.
[6] M. Ligowski, D. Moraru, M. Anwar, T. Mizuno, R. Jablonski, M. Tabe, Appl. Phys. Lett. 93 (2008) 142101.
[7] E. Verveniotis, J. Cermak, A. Kromka, B. Rezek, Phys. Status Solidi B 246 (2009) 2798.
[8] Th. Glatzel, S. Sadewasser, M.Ch. Lux-Steiner, Appl. Surf. Sci. 210 (2003) 84.
[9] U. Zerweck, C. Loppacher, T. Otto, S. Grafstorm, L.M. Eng, Phys. Rev. B 71 (2005) 125424.
[10] S. Szunerits et al., J. Phys. Chem. B 110 (2006) 23888.
[11] M. Tachiki et al., Surf. Sci. 581 (2005) 207.
[12] M.C. Salvadori, W.W.R. Araujo, F.S. Teixeira, M. Cattani, A. Pasquarelli, E.M. Oks, I.G. Brown, Diam. Relat. Mater. 19 (2010) 324.
[13] F. Maier, J. Ristein, L. Ley, Phys. Rev. B. 64 (2001) 165411.
[14] B. Rezek, C. Saurer, C.E. Nebel, M. Stutzmann, Appl. Phys. Lett. 82 (2003) 2266.
[15] H. Sugimura, Y. Ishida, K. Hayashi, O. Takai, N. Nakagiri, Appl. Phys. Lett. 80 (2002) 1459.
[16] D. Shechtman, J. Mater. Sci. 41 (2006) 7720.
[17] H. Sawada, H. Ichinose, Diam. Relat. Mater. 14 (2005) 109.
[18] B. Rezek, C.E. Nebel, Diam. Relat. Mater. 14 (2005) 466.
[19] L. Diederich, O.M. Kuttel, P. Aebi, L. Schlapbach, Surf. Sci. 418 (1998) 219.
[20] S. Suzuki, C. Bower, Y. Watanabe, O. Zhou, Appl. Phys. Lett. 76 (2000) 4007.