Structural and electrical properties of carbon ion implanted ultrananocrystalline diamond films*

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ABSTRACT: We have investigated the structural and electrical properties of carbon ion implanted ultrananocrystalline diamond (UNCD) films. The impedance spectroscopy measurements show that impedance value of diamond grains is relatively stable, while that of grain boundaries (R_b) dramatically increases after C^+ implantation and decreases as annealing temperature (T_a) increases from 650 to 1000 °C. This means that C^+ implantation has more significant impact on the conductivity of grain boundaries (GBs). Conductive atomic force microscopy results evidence that the number of conductive sites increases in GB regions at T_a above 900 °C, which is originated from the formation of nanographitic phase confirmed by high resolution transmission electronic microscopy. Visible Raman spectra show that resistive trans-polyacetylene oligomers desorb from GBs at T_a above 900 °C, which also results

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in the lower R_b values of samples C12900 and C121000. With T_a increasing to 1000 °C, diamond grains become smaller with longer GBs modified by more ordered nanographitic phase, supplying more conductive sites and lower value of R_b .

Keywords: UNCD; C ion implantation; annealing; electrical properties

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1. Introduction

Diamond films have many excellent properties such as high hardness, good chemical stability and high thermal conductivity.^[1-3] Ultrananocrystalline diamond (UNCD) film is a unique form of carbon, in which 3-5 nm sized diamond grains are surrounded by amorphous carbon matrix. The UNCD films have applications where high conductivities are required, including electrochemical electrodes,^[4-6] field emission,^[7] heterostructures.^[8,9] Much work has been paid to improve the conductivity of UNCD films. It has been reported that nitrogen-doped UNCD films exhibit n-type conduction with an enhanced electrical conductivity, which is attributed to increased sp^2 bonds at grain boundaries (GBs).^[10, 11] Phosphorous and oxygen ion implantation were used to increase the conductivity of nanocrystalline diamond grains and amorphous carbon GBs, which improved the n-type Hall mobility of UNCD films.^[12,13] The hybrid structure of ultrananocrystalline diamond and graphene nanoribbons promoted high mobility n-type conductivity in oxygen ion implanted UNCD films.^[14] Lithium ion implantation induced the formation of electron trap centers inside diamond grains, whereas post-annealing healed the defects and converted amorphous carbon phase into nanographite, forming conduction channels

for the effective transport of electrons.^[7]

Amorphous carbon in the GBs is a common existed component in UNCD films, whose electrical properties were reported to be not sufficiently high and, therefore, limited the applications of UNCD films.^[15] It is believed that the conversion of amorphous carbon to a conducting graphitic phase along the GBs enhance the efficiency for transporting electrons on the surface and hence improved the conductivity for UNCD films.^[16, 17] It was also reported that copper^[18] and gold^[19] ion implantation and annealing promoted the electrical properties of UNCD films by decreasing the amorphous carbon content and even inducing the nanographitic phase in GBs. This suggests that it is effective to improve the electrical properties by modifying the structure and component of amorphous carbon GBs. Carbon ions are not the dopant for diamond grains but prefer to make the amorphous carbon GBs more ordered to enhance its conductive mobility value. High dose C^+ ion implantation (10^{15} cm^{-2}) and annealing was reported to result in the crystallization of graphite phase that was not transformed from amorphous carbon in UNCD films and degrade the field emission properties.^[20] Here we implanted lower dose of C^+ to regulate the microstructure of UNCD films especially in GBs to improve their electrical properties. High resolution transmission electronic microscopy (HRTEM) and visible Raman spectroscopy were used to characterize the microstructure of the films after ion implantation and annealing. The conductive atomic force microscopy (AFM) was used to provide the images of conductive capacities on different parts of the UNCD films. Impedance spectroscopy (IS) was performed to distinguish the conductivity

contributions from diamond grains and GBs.

The results show that the impedance resistance of GBs dramatically increases after C^+ implantation, while it is effectively reduced as T_a increases from 650-1000 °C. The impedance of diamond grains is relatively stable. This suggests that C^+ implantation has a greater impact on the impedance of GBs than diamond grains. When T_a is above 900 °C, the number of conductive sites increases markedly in the GB region of UNCD films due to the formation of nanographitic phase, which is responsible for the reduced impedance resistance of GBs.

2. Experimental details

UNCD films were deposited by using a hot filament chemical vapor deposition (HFCVD) system on single crystal silicon (111) wafers. The carbon source was acetone, the volume ratio between acetone and hydrogen was 1-2% with the total gas flow 200 ml/min, the working pressure in the reaction chamber was 0.5-1.4 kPa, and the temperature of the substrate was about 850 °C. The thickness of as-deposited UNCD was about 5 μm with a growth rate of 1.5 $\mu\text{m/h}$. C^+ implantation was performed on as-deposited UNCD films with implantation energy of 90 keV and a dose of 10^{12} cm^{-2} . For room-temperature implantations, there is a universal critical damage density, $10^{22} \text{ vacancies/cm}^3$, which, when exceeded, will result in the complete graphitization of heavily damaged diamond crystals upon annealing.^[21] It was shown that 10^{12} cm^{-2} of C^+ implantation at room temperature was far below the critical dose ($2\text{-}3 \times 10^{15} \text{ cm}^{-2}$).^[22] The implantation profile has been determined by the Stopping and Range of Ions in Matters (SRIM-2013) software. The C ions were

implanted into diamond with an ion average range of 121 nm, creating 10^{19} vacancies/cm³ at meantime. The implanted samples were annealed at 500, 650, 725, 800, 900 and 1000 °C for 30 min with the pressure of 4000 Pa (80% N₂ and 20% O₂), named as C12500, C12650, C12725, C12800, C12900 and C121000, respectively. The annealing at 900 °C for 30 min was performed on as-deposited UNCD film (sample 900-A) to distinguish the effects of C⁺ implantation and annealing on the electrical properties of UNCD films.

High resolution transmission electronic microscopy (HRTEM) was used to characterize the microstructure of the films by using Tecnai G2 F30 S-Twin produced by Philips-FEI. Visible Raman spectroscopy measurements with 514 nm excitation wavelength (JobinYvon, Labor Raman HR-800) were performed on samples at room temperature. Conductive AFM and scanning kelvin microscopy (SKM) were carried out in Scanning Probe Microscope (SPM) Solver P47 (NT-MDT, Russia) under ambient conditions.

Ti (500 nm)/Au (300 nm) contacts were made on SPC-350 magnetron sputtering system and then annealed in vacuum under 450 °C for 20 min. The diameter of the electrode is 2 mm. I-V measurements taken on the samples at room temperature show that ohmic-contact is formed. The impedance properties of samples were determined using Autolab potentiostat-galvanostat connected with a four-probe station covering the frequency range 0.01Hz to 10 MHz. Impedance spectroscopy has been deployed to study the electrical properties of single crystal diamond and polycrystalline diamond. This technique involves the measurement of real and imaginary components

of films impedance as a function of both frequency and temperature. The impedance as a complex number, can be defined as

$$Z = Z' - jZ'', \quad (1)$$

where the real part refers to the resistance contributions and the imaginary part to the capacitive. In a typical impedance spectroscopic analysis, the impedance is measured as a function of frequency, and the real component plotted against the imaginary component as the change of frequency. These so-called “Cole-Cole” plots may then reveal different semicircular responses for each RC component of the film.^[23]

Theoretically, a double resistance-capacitance (RC) parallel model in series could be used to simulate the electrical conduction of diamond films contributed from uniformly distributed diamond grains and GBs, as illustrated in Fig. 1. The resistance between the electrode and diamond films will be taken into account during practical measurements, here defined as R_e . Here the symbols R_g , R_b , C_g , C_b represent the resistance of diamond grains and boundaries, and capacitance of diamond grains and boundaries, respectively. Each parallel RC equivalent circuit model fits each Cole-Cole semicircle accurately. The fitting procedure used here is the same as the one described by Kleitz and Kennedy and allows the determination of resistance and relaxation frequencies with a good precision.^[24]

The complex impedance can be expressed as:

$$Z' = R_e + \frac{R_g}{1 + \omega^2 R_g^2 C_g^2} + \frac{R_b}{1 + \omega^2 R_b^2 C_b^2} \quad (2)$$

$$Z'' = \frac{\omega R_g^2 C_g}{1 + \omega^2 R_g^2 C_g^2} + \frac{\omega R_b^2 C_b}{1 + \omega^2 R_b^2 C_b^2} \quad (3)$$

when plotted in the complex plane, Z' versus Z'' takes the forms of two semicircles in which the contributions of diamond grains and GBs are easily identified, hence the electrical conduction paths of the bulk material can be studied separately.

3. Results and discussion

I-V measurements were carried out every time to make sure that ohmic contacts formed between the electrodes and UNCD films before the IS measurements. Fig. 2 shows that Cole-Cole plots of samples and Si substrate, in which the Cole-Cole plot of Si substrate is too tiny to be clearly observed, so it is enlarged in the inset of Fig. 2(a). One semicircle is observed in the Cole-Cole plot of Si substrate, and the impedance value is lower than 1 k Ω , which is 1-2 orders of magnitude lower than those of annealed samples, implying that the Cole-Cole plots of samples mainly represent the electrical properties of UNCD films. The Cole-Cole plots of all samples can be fitted as two semicircles, indicating that two components contribute to the conductivity. The total impedance value of as-deposited sample is the lowest in these samples, around 28 k Ω . It increases to 62 k Ω in sample C12500 and 121 k Ω in sample C12650. It is noted that the semicircular response in sample C12725 is accompanied by an additional semicircle which extends to low frequencies, in which low frequency response is incomplete and measured as an arc due to the limited measuring range. Despite all this, the total impedance value of sample C12725 is estimated to be higher than that of sample C12500 but lower than that of sample C12650.

Fig. 2(b) shows the Cole-Cole plots of samples 900-A, C12800, C12900 and C121000. The total impedance value of sample 900-A is about 8 k Ω , and it increases

to 47 k Ω in sample C12800. As T_a increases above 800 °C, it decreases to 29 and 32 k Ω in samples C12900 and C121000, respectively. The impedance value of sample 900-A is found to be much lower than that of sample C12900, indicating that IS measurements effectively reflect the role of C^+ implantation in the electrical properties of UNCD films despite that the ion implanted layer is thin compared to the thickness of the UNCD films. The total impedance of sample 900-A is found to be lower than that of as-deposited sample, suggesting that annealing prefers to decrease the impedance of UNCD films.

The resistance and capacitance values were extracted according to the equivalent circuit model and listed in Table 1 to understand the responses quantitatively. It is observed that the semicircular response at low frequency displays a capacitance value in the range of 0.2-9 nF, whereas the high frequency region has a capacitance of 70-110 pF. It is well-established for polycrystalline materials that capacitance values in picofarad levels arise from the contribution of crystal grains, while nanofarad level responses are attributed to GBs.^[25] It is therefore clear that both nanocrystalline diamond grains and GBs in UNCD films contribute to the electrical characteristics being measured.

The R_e values listed in Table 1 remain in the range of 1.4-1.7 k Ω except sample C12650 (because the electrodes on sample C12650 were deposited by vacuum evaporation method), which means that the ohmic contact is stable in these samples and provides good testing conditions for IS measurements. It is observed that the R_g value of as-deposited sample is 25.9 k Ω , and it significantly decreases to 4.5 k Ω in

sample 900-A. This implies that 900 °C annealing decreases the resistance of diamond grains in UNCD films. It is also noted that the R_g value of sample C12900 is 19.5 k Ω , much higher than that of sample 900-A, but lower than that of as-deposited sample. In C^+ -implanted samples, the R_g values decrease from 33.4 to 18.9 k Ω as T_a increases from 500 to 725 °C. When T_a is above 800 °C, the R_g values are 27.3, 19.5 and 23.6 k Ω in samples C12800, C12900 and C121000, respectively. C^+ implantation is found to increase the R_g value of UNCD films, which is not so dependent on annealing temperature.

It is observed that the R_b value of sample 900-A is 2.2 k Ω , slightly higher than 1.4 k Ω in as-deposited sample. The R_b value of sample C12500 is 26 k Ω and dramatically increases to 97.4 k Ω in sample C12650. It starts to decrease with T_a further increasing and finally reaches 6.6 k Ω in sample C121000. These R_b values are higher than that of as-deposited sample, meaning that C^+ implantation increases the impedance of GBs even though it is effectively reduced by annealing.

The IS results show that the contribution of diamond grains in the conductivity is increased after C^+ implantation and annealing. The dramatically increased R_b values of C^+ -implanted samples decrease with T_a increasing from 650-1000 °C, while the R_g values remain stable, indicating that C^+ implantation has a greater impact on the impedance of GBs. Lower R_b values of samples C12900 and C121000 illustrates that the GB regions are more conductive than C^+ -implanted samples annealed at lower T_a .

To observe the conductive behaviour in a microscopic scale, conductive-AFM and SKM were carried out. The Pt-coated Si cantilever with the tip curvature radius of

~ 35 nm was used to obtain surface height relief in tapping mode. The sample-probe gap $\Delta = 100$ nm was used during SKM measurements. For each sample, the measurements were repeated in 5 arbitrary chosen $3 \times 3 \mu\text{m}^2$ regions. Fig. 3 shows the surface height relief and local conductance of samples C12725, C12900 and C121000. The surface height relief graphs show that the most probable relief height of samples increases as T_a increases, indicating that the exposed area of nanoclusters become more obvious at higher T_a . It is noted from the local conductance maps that the samples become more conductive as T_a increases. The most conductive areas in sample C12725 are scattered in the film while they become continuous in samples C12900 and C121000, indicating that more conductive sites appear in these two samples. Combining with the IS results, we find that the R_g values of these three samples increase with increasing T_a , while R_b values decrease as T_a increases, indicating that the conductive sites appeared at high T_a mainly locate at the GBs region.

Fig. 4(a) shows the conductance histograms of samples C12725, C12900 and C121000, which also exhibits that annealing at 900 °C and 1000 °C leads to ~ 10 times higher conductance in the range of 100-500 nS compared to the sample annealed at 725 °C, which evidences the increasing number of conductive sites. Fig. 4(b) shows the contact potential histograms of samples C12725, C12900 and C121000. It is observed that the contact potential of samples increases with T_a increasing, implying the loss of negative electron affinity at higher T_a .^[26] It is probably because of the

absence of H-termination of nanocrystalline diamond grains when T_d is above 800 °C. [27-29]

The increasing numbers of conductive sites in samples C12900 and C121000 indicates the microstructure changes in GB regions. To understand the origination of these highly conductive GBs, we carried out HRTEM measurements to characterize the microstructure of samples C12900 and C121000. During the TEM specimen preparation, the Si substrate was firstly removed and the UNCD film closing to the Si side was further removed by Argon ion milling, leaving the surface area (ion implantation region) for observation. Figs. 5(a) and (b) show the low magnification TEM images of samples C12900 and C121000 with the selected area electron diffraction (SAED) patterns shown in the insets, respectively. The SAED patterns of both samples contain diffraction rings corresponding to (111), (200) and (311) lattice planes of diamond, which indicates diamond grains are the main content in films. The grains are around ~5-10 nm and they are uniformly distributed in sample C12900, while they become smaller in sample C121000, leaving more GB paths along the diamond grains.

Fig. 5(c) shows the high magnification TEM images of sample C12900 with Fourier-transformed (FT) diffractogram corresponding to the entire image (FT₀), area 1 (FT₁) and area 2 (FT₂). The FT₀ image in Fig. 5(c) shows a ring with many spots and a central diffuse ring, which represents the information of diamond grains and GBs in sample C12900. The central diffuse ring in FT₁ pattern of area 1 is inversely transformed to get an insight view of GB microstructure, as shown in Fig. 5(c₁). The

curved fringes with the spacing of ~ 0.35 nm are observed in Fig. 5(c₁), pointing to the (0002) planes of graphitic structure, which indicates that nanographitic phase forms in the GBs of sample C12900. The diffraction points in FT₂ pattern is also inversely transformed in Fig. 5(c₂), which shows a lattice structure with the spacing of ~ 0.21 nm, reflecting the ordering of the (111) planes of diamond. Notably, a diffused spot is observed in FT₂ image, which implies that amorphous carbon exists in sample C12900. It is thus clear that the spots in the diamond lattice ring of FT₀ image represent nanocrystalline diamond grains in different orientations. The nanographitic phase existing in the GBs is less ordered than diamond phase since no spot is observed in the graphite corresponding ring. It is found that the spots deviate from the lattice ring in a small degree, probably due to the diamond lattice damage caused by ion implantation.

Fig. 5(d) shows the high magnification TEM images of sample C121000 with Fourier-transformed (FT) diffractogram corresponding to the entire image (FT₀), area 1 (FT₁) and area 2 (FT₂). The densities of spots in diamond ring of FT₀ image is higher than that of sample C12900, and the central ring corresponding to the graphite is thinner, which evidences the smaller size of diamond grains and more ordered graphitic phase in sample C121000. The inversely transformed structures in Figs. 5(d₁) and (d₂) also show the ordering of (0002) plane graphite and (111) plane diamond, respectively. The center area of FT₂ image in Fig. 5(d) is much darker than that in Fig. 5(c), which means that the content of amorphous carbon is much lower in sample C121000. These HRTEM results confirm that diamond grains are the main content in

the films, and nanographitic phase and some amorphous carbon phase exists in GBs of samples C12900 and C121000. More ordered nanographitic phase and more GB paths along smaller diamond grains exist in sample C121000 than that in sample C12900, which is in agreement with the lower R_b value for sample C121000. It is concluded that the conductive sites observed in Figs. 3(d) and (f) are mainly formed by nanographitic phase and they give attributions to low impedance GBs.

To further investigate the microstructure changes of GBs in C^+ -implanted samples, the visible Raman spectra in the range of 800-2000 cm^{-1} for as-deposited sample, sample 900-A and C^+ -implanted films are shown in Fig. 6(a). The Raman spectra of UNCD films can be fitted well with six Gaussian-Lorentzian peaks. The peaks at 1550-1570 and 1340 cm^{-1} , respectively, correspond to G-band and D-band.^[30] The peak at 1332 cm^{-1} arises from diamond,^[31] while the peak at 1200 cm^{-1} is related to amorphous sp^3 carbon.^[32] In addition, two peaks at 1140-1190 (ω_1 peak) and 1480 cm^{-1} (ω_3 peak), respectively, have been ascribed to the bending and stretching vibrations of trans-polyacetylene (TPA) situated at the GBs of UNCD films.^[33]

Fig. 6(b) shows the I_D/I_G values (intensity ratio of D band to G band) as a function of T_a from the fitted peaks in Fig. 6(a). It is observed that the I_D/I_G value of as-deposited sample is the highest (1.07) and decreases after 900 °C annealing (0.96). It becomes lower in the T_a range of 500-800 °C (0.91-0.93) and then increases at higher T_a (~1.05) in C^+ -implanted samples, indicating that the size of sp^2 -bonded carbon located at GBs decreases at 500-800 °C and then increases at 900-1000 °C.^{[34,}

^{35]} This is consistent with the results that nanographitic phase forms conductive sites

in sample C12900 and C121000. Fig. 6(c) shows the dependences of full width at half maximum (FWHM) values of ω_1 and ω_3 peaks on T_a . The FWHM values of ω_1 and ω_3 peaks keep stable when T_a is lower than 900 °C and increase at above temperature. The $I_{\text{TPA}}/I_{\text{sum}}$ values of samples annealed at 500-725 °C (15.0-15.5 %) are slightly higher than that of as-deposited sample (14.75 %) and then become lower in sample C12800 (14.6 %), while they dramatically decrease in samples C12900 (11.8 %) and C121000 (9.6 %), as shown in Fig. 6(d). This implies that the TPA oligomers in GBs start to desorb when T_a is higher than 800 °C, which is in agreement with the contact potential result. TPA chains, as one of the π -conjugated polymers, are nonconductive without dopants.^[36] It was reported that more TPA dangling bonds in UNCD films led to high sheet resistance.^[37] After 1000 °C annealing, it is observed that both the FWHM values of ω_1 and ω_3 peaks increase and the $I_{\text{TPA}}/I_{\text{sum}}$ value dramatically decreases, which agrees with the result that R_b value of sample C121000 is lower than that of sample C12900.

IS results show that R_g value is relatively stable in the conductivity while R_b value dramatically increases after C^+ implantation, which indicates that the contribution of diamond grains is increased after ion implantation. The R_b values gradually decrease as T_a increases from 650-1000 °C, which means that C^+ implantation has a greater impact on GBs than on diamond grains. It is evidenced by IS and AFM results that the number of conductive sites in GBs increases as T_a increases from 725 to 1000 °C. HRTEM and AFM results evidence that the number of conductive sites in GBs increases at T_a higher than 900 °C due to the formation of

nanographitic phase. Visible Raman and HRTEM results also show that the nanographitic phase is more ordered in sample C121000 than that in sample C12900, which forms more conductive sites and leads to the lower R_b value of sample C121000.

4. Conclusion

In conclusion, C^+ implantation dramatically increases the impedance resistance of GBs, which is effectively reduced as T_a increases from 650-1000 °C. In these processes, the impedance resistance of diamond grains is relatively stable. This suggests that C^+ implantation has a greater impact on the impedance of GBs than that of diamond grains. Conductive atomic force microscopy results evidence that the number of conductive sites in GBs dramatically increases when T_a is above 900 °C due to the formation of nanographitic phase confirmed by HRTEM microscopy. Visible Raman and HRTEM results show that the nanographitic phase is more ordered in sample C121000 than that in sample C12900, which further decreases the R_b value of sample C121000.

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Table 1 Resistance and capacitances value of as-deposited sample, sample 900-A and

 C^+ -implanted samples

Sample	R_e (k Ω)	R_g (k Ω)	C_g (pF)	R_b (k Ω)	C_b (nF)
As-deposited	1.4	25.9	71.4	1.4	2.2
900-A	1.5	4.5	105.0	2.2	7.5
C12500	1.5	33.4	74.3	26.0	1.2
C12650	0.2	23.7	94.8	97.4	0.2
C12725	1.7	18.9	77.5	51.4	9.4
C12800	1.5	27.3	86.3	17.7	0.5
C12900	1.6	19.5	89.9	8.1	3.7
C121000	1.6	23.6	98.9	6.6	2.1

Figure captions

Fig. 1(a) Schematic diagram of the electrical measurement across the film. (b) Equivalent circuit for the electrical response of a UNCD sample with contributions from diamond grains (g) and grain boundaries (b), and the electrode interface (e).

Fig. 2 The characteristic Cole-Cole plots measured for (a) as-deposited sample, Si substrate, samples C12500, C12650, and C12725, and (b) samples 900-A, C12800, C12900, and C121000.

Fig. 3 The surface height relief of samples C12725 (a), C12900 (c) and C121000 (e) and the local conductance of samples C12725 (b), C12900 (d) and C121000 (f) at $U=2$ V, respectively.

Fig. 4 (a) Conductance histograms and (b) contact potential histograms of samples C12725, C12900 and C121000 from conductive-AFM measurements.

Fig. 5 Low magnification TEM images with the selected area electron diffraction (SAED) pattern in the insets of sample (a) C12900 and (b) C121000. (c) High magnification TEM image of sample C12900 with Fourier-transformed (FT) diffractogram corresponding to the entire image (FT₀), area1 (FT₁) and area 2 (FT₂) in the inset. (c₁) and (c₂) show the inversely transformed structures of graphite ring and diamond diffraction points in area 1 and area 2, respectively. (d) High magnification TEM image of sample C121000 with FT diffractogram corresponding to the entire image (FT₀), area 1 (FT₁) and area 2 (FT₂) in the inset. (d₁) and (d₂) show the inversely transformed structures of graphite ring and diamond diffraction points in

area 1 and area 2, respectively.

Fig. 6 (a) Visible Raman spectra of C^+ -implanted samples and as-deposited sample. (b) Dependences of I_D/I_G values on annealing temperatures (T_a). (c) Dependences of FWHM values of ω_1 and ω_3 peaks on T_a . (d) Dependences of I_{TPA}/I_{sum} values on T_a .

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6