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Low temperature boron doped diamond

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Low temperature boron doped diamond (LT-BDD) film deposited under 600 °C (460 °C minimum) has been reported. Study reveals that the deposition temperature and boron dopant cause nanocrystalline diamond (NCD) instead of ultrananocrystalline diamond (UNCD). Unlike conventional NCD, LT-BDD has faster renucleation rate, which ensures a low surface roughness (approximately 10 nm at 0.6 μm thickness). The overall characteristics of LT-BDD are mixed with the characteristics of conventional NCD and UNCD. Raman spectrum and electrochemical characterization prove that the quality of LT-BDD is similar to those grown under 650-900 °C. LT-BDD enables diamond applications on microelectromechanical systems, bio- and optical technologies. © 2013 AIP Publishing LLC.

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Chemical vapor deposition (CVD) generated diamond brings natural diamonds’ high hardness, high chemical inertness, and low friction into many industrial applications. Conductive or semi-conductive diamond, doped by boron, nitrogen and phosphorus enhances its applications in electronics, especially in electrochemical technologies. Diamond deposition usually requires a “normal temperature” between 650 and 900 °C to ensure diamond film quality and to provide an acceptable deposition rate. These high temperatures can easily destroy or significantly damage biosensors, complementary metal–oxide–semiconductor (CMOS), photonic or optical devices when diamond is integrated with them. In general, for lower deposition temperatures, more materials can be integrated with diamond with wider diamond market applications. In practice, a diamond film deposited at a temperature lower than 600 °C can be defined as low temperature diamond, above which many device and material properties are subject to significant alteration. For example, the Curie point of quartz crystal microbalances for biosensors is 573 °C, and the anneal point of BK-7 a typical optical glass is 600 °C. One of the thermal budget limits for low stand-by power, 0.25 μm foundry CMOS devices is 475 °C for 0.5 h. Indeed, the lower the deposition temperature, the more applications of diamond can be explored. While non-doping deposition has been achieved at low temperature, low temperature boron doped diamond (LT-BDD) was rarely reported. The tetrahedral atomic structure of diamond is so stubborn that dopant atoms of the approximate size of carbon atoms, such as boron, have difficulty in adjustment of the diamond lattice to accommodate their substitution for carbon. To date, the authors have not seen any published work on LT-BDD with promising deposition rates and high film quality, which is the subject of this paper.

LT-BDD film synthesis begins with a substrate seeding step with commonly used seeding processes such as surface scratching with diamond abrasives or agitating the substrate in seed slurry, which produces a high density of diamond seed sites, usually in the order of 10⁸–10¹⁵/cm², on the substrate to encourage rapid and uniform diamond film deposition. The substrate can be elemental or compound materials, such as silicon, silicon dioxide (SiO₂), quartz, glass, nitride, and silicon carbide, and refractory metals, such as niobium, tantalum, and tungsten. Diamond synthesis utilizes a hot-filament chemical vapor deposition (HFCVD) process with a methane (CH₄) and hydrogen (H₂) gas mixture; however, unlike a conventional CVD diamond recipe with a very low CH₄/H₂ ratio, e.g., <3%, we use a so-called “Non-inert gas ultrananocrystalline diamond (UNCD) recipe” distinguished from conventional argon-rich UNCD recipes, with CH₄/H₂ ratio ≥5%. We found that this type of gas chemistry does not reject boron at low temperature to form doped diamond, instead of forming non-diamond substance, such as graphite. Trimethylboron (TMB, i.e., B(CH₃)₃) is used as a source of boron dopant, with a Boron/Carbon (B/C) ratio in a range from 1500 ppm to 5000 ppm. With this type of recipe, we achieved LT-BDD under temperature between 460 and 600 °C. The following study is focused on performance of the diamond deposited under the lowest temperature, approximately at 460 °C. The deposition temperature is measured by a thermocouple intimately touching the backside of the wafer to be coated.

A thickness of 700 nm (measured by Filmetrics F20) LT-BDD film was achieved after a 20-h deposition, so the average deposition rate is ~35 nm/h. The measured resistivity of the film on SiO₂ wafers was in a range of 0.02–0.09 Ω·cm, measured by a four-point probe resistivity meter (Pro 4, Lucas Labs, with Keithley digital multimeter). The stress of the film ranged from 250 to 600 MPa compressive, measured by a (Veeco Flexus 2320) stress measurement tool. Fig. 1(a) shows a top view scanning electron microscopy (SEM) image of a LT-BDD film with 100 nm thickness. It can be seen that LT-BDD tends to form nanocrystalline diamond (NCD), although the recipe parameters are based on the UNCD recipe for normal temperature deposition. Such a result is interesting and controversial as previous reports show that NCD can only be generated under conditions of low CH₄/H₂ ratio, <3%. It indicates that the two changed conditions, i.e., boron doping and low temperature together cause the film to form NCD instead of UNCD. We observed that a film with a similar recipe but deposited at a temperature of 700 °C was

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characterized as doped UNCD, and a film with a similar recipe deposited at the same low temperature (460°C), but without TMB input, was also observed to deposit as UNCD as shown in Fig. 1(b). The NCD character of LT-BDD is also confirmed by the Raman spectra presented below. Our explanation is that under low temperature, the reaction \((\text{CH}_x + \text{H} \rightarrow \text{CH}_4)\) opposite to the generation of diamond precursors becomes more significant than that under normal temperature condition. At the same time, bonding with boron atoms also consumes some \(\text{CH}_x\) precursors, so the possibility of re-nucleation becomes lesser, which causes grain size larger than that of UNCD. However, more data of the grain size and morphology versus boron concentration and versus deposition temperature are needed to support this explanation.

Figs. 1(a) and 1(c) are SEM images of LT-BDD with 100 nm and 600 nm thickness, respectively. It can be seen that as the film thickens, the grain size of the film increases in a very slow manner, from \(\sim 50\) nm to \(\sim 100\) nm on average. For UNCD, re-nucleation rate is much greater than the growing rate of existing grains, so its grain size and roughness almost do not increase; for conventional NCD, re-nucleation rate is much slower than the growing rate of existing grains, so grain size and roughness increase quickly; for LT-BDD, re-nucleation rate is comparable with and just slightly lower than the growing rate of existing grains, so its overall grain size increases very slowly. Optical profilometry (WyKo 3300) revealed that the root means square (RMS) roughness of the LT-BDD film increased from 8.5 nm at 80 nm-thick to only 11.2 nm at 600 nm-thick. Among NCD films, such a number is the smoothest according to the authors’ literature study, in which it is comparable to that of UNCD. Smooth diamond surfaces are extremely important for applications in tribology and biology, and are most compatible for semiconductor process applications.

The Raman spectrum of LT-BDD shown in Fig. 2(a) exhibits a broad peak at 1220 cm\(^{-1}\) and 460 cm\(^{-1}\), both of which are reported for boron doped polycrystalline diamond synthesis, indicating that the diamond deposited under these low temperatures is heavily boron doped NCD. The peak at 1220 cm\(^{-1}\) should represent the combined peak of single optical phonons caused by the incorporation of boron in the diamond lattice, representing a carrier concentration \(>10^{19}/\text{cm}^3\), or a \(\text{B}/\text{C}\) ratio \(>400\) ppm. Weak peaks at 1332 cm\(^{-1}\) and 1550 cm\(^{-1}\) suggest very high doping level in the diamond and a low \(sp^2\) graphite content in this type of NCD. In contrast, the Raman spectrum of low temperature non-doped diamond shown in Fig. 2(b), indicates a typical UNCD signature, defined by abundant \(sp^2\) forms of carbon at the grain boundary, including disputable peaks of the \(v1\) and \(v3\) modes of transpolyacetylene (1150 cm\(^{-1}\) and 1450 cm\(^{-1}\)), D-bond carbon (1360 cm\(^{-1}\)), and G peak of disordered carbon (1560 cm\(^{-1}\)). It once again suggests that boron doping causes grains larger than UNCD at low temperature (the Raman spectrum of normal temperature boron doped UNCD is not shown here but will be discussed in detail in another publication).
Electrochemical properties of LT-BDD and NT-BDD (normal temperature boron doped diamond) were evaluated using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) before and after electrochemical pretreatment (ECP) (Fig. 3). All electrochemical experiments were carried out with an Autolab potentiostat (PGSTAT 302 N, Metrohm USA) in a three-electrode setup using a Saturated Calomel Electrode (SCE, Accumet, New Hampshire, USA) as reference and Pt coil (Alfa Aesar) counter electrode. The electrode surfaces were cleaned with ECP pretreatment (ECP) (Fig. 3). All electrochemical experiments were carried out in a solution of 5 mM Fe(CN)6 3/4+ - redox couple in 0.01M phosphate buffer. Cyclic voltammograms were recorded between −0.5 V and +1.5 V, 250mV/s, in 0.1M H2SO4 to achieve stable electrochemical signals. The BDD electrode was used as the working electrode. Cyclic voltammograms were recorded between −1.0 V and +1.0 V vs. SCE with a 100mV/s scan rate. The EIS spectra were recorded between 0.1 Hz and 100 kHz at 10 mV ac signal amplitude (rms value) at Open Circuit Potential of +0.18 V. All measurements were carried out in a solution of 5 mM Fe(CN)6 3/4+ - redox couple in 0.01M phosphate buffer.

Cyclic voltammograms showed a quasi-reversible behavior with a separation in reduction-oxidation “redox” peak potential (∆E p) of ~400 mV for both LT- and NT-BDD (Figs. 3(a) and 3(b)). Previous EIS studies showed that the surface of NT-BDD consists of grain and grain boundary configuration. Grains consist of sp3 bonded carbon atoms and grain boundaries are formed by sp2 bonded carbon atoms. This chemical and structural distinction between grain and grain boundaries gives rise to morphological variation on the electrode surface. Thus, the overall surface can be rendered as chemically heterogeneous. Characterization of LT-BDD film using EIS technique showed interesting properties. The BDD experimental data were fitted to an equivalent circuit model \[ R(C[QR]) \], and capacitance (C), resistance (R) and constant phase element (CPE) are the circuit elements. Interestingly, same circuit fitted well to both NT- and LT-BDD films, but the values of the circuit elements varied. This fitting of the same circuit made it possible to compare the properties of both the films. Table I shows values of the circuit elements \( R, C, Q, N, R \) for the LT- and NT-BDDs before and after ECP. We attributed capacitive element of the circuit to grains and CPE to grain boundaries. The rational for doing so is physically smooth surface of grains which may be the origin of a surface with a single time constant and thus capacitive behavior. Generally, it is considered that a majority of boron dopants reside on the grain boundaries making the surface of grain boundaries chemically more heterogeneous than that of grains. This may be responsible for time constant dispersion and thus corresponds to CPE element of the circuit. The impedance due to CPE is given as \( Z(\omega) = 1/(j\omega)^N \), where \( \omega \) is the angular frequency of the AC signal, and \( C \) is the measured capacitance. The overall value of capacitance for both as-deposited NT- and LT-BDD is of the order of \( \mu F \). Such low capacitance shows that both NT-BDD and LT-BDD correspond to material with a low dielectric constant. However, the capacitance of grains from the value of \( C \) for LT-BDD is ~10 times more than that of NT-BDD after the ECP process. This indicates that the dielectric constant of NT-BDD is 10 times lower than that of LT-BDD. Therefore, by growing diamond at low temperature we found a method to increase the dielectric constant of BDD. The impedance due to CPE is given as \( Z(\omega) = 1/(j\omega)^NQ \), where \( \omega \) is the angular frequency of applied AC signal, \( Q \) is measured CPE, and \( N \) is a constant. The \( N \) value \( (0 < N < 1) \) is a good indicator of electrode surface heterogeneities. For \( N \) value that is close 1 implies a homogenous surface and a value of 0.4-0.6 implies a heterogeneous surface. From Table I, it is clear that the impedance due to CPE for both LT- and NT-BDD remained almost same. Thus, temperature variation in the growth process of both the diamond films does not contribute to a significant change in value of CPE corresponding to grain boundaries. If the circuit elements are true indicator of the surface properties, then it raises an interesting question: Why the temperature variation does not cause significant change in the impedance of CPE due to grain boundaries? Further, the real part of impedance \( (Z_{Re}) \) for LT- and NT-BDD does not show any significant change in the values. Generally, for an electrochemical cell, the current is given by following relationship:

\[ I = I_0 \sin(\omega t + \phi), \]

\[ I_0 \] is the amplitude of current signal, \( \omega \) is the angular frequency, and \( \phi \) is phase, and voltage is given as

\[ V = V_0 \sin(\omega t), \]

and the impedance is given as
considered like a pure resistor, and is simply given as
\[ Z(\omega) = Z_0 \exp(i\phi) \rightarrow Z_{Re} = Z_0 \cos(\phi), \quad Z_{Im} = Z_0 \sin(\phi). \] (3)

From Bode phase plot (Fig. 4), it is clear that the phase varies between 2° and almost 10° for the entire frequency spectrum for both the films. Since, \( \cos(2) \) to \( \cos(10) \) varies between 0.99 and 0.98 and \( \sin (2) \) to \( \sin (10) \) varies between 0.03 and 0.17, the contribution from the imaginary part to the overall impedance can be neglected. \( Z_{Re} \cong Z_{Im} \), and \( Z(\omega) = Z_0 = Z_{Re} \) for entire frequency range.

Thus, for both LT- and NT-BDD, impedance can be considered like a pure resistor, and is simply given as
\[ Z(\omega) = Z_{Re} = Z_0 = R. \] The impedance measured at highest frequency (100 kHz) is that of solution resistance because high frequency AC signal is like that of a fast short duration pulse, and it cannot perturb the system significantly. Therefore, the main contribution to the impedance is due to solution resistance. Whereas, impedance measured at low frequency consists of contribution from electrode surface and solution resistance. Therefore, if the contribution from imaginary part of impedance is negligible, then the impedance of real part at lowest frequency minus the solution resistance is equal to the resistance of the electrode surface \( (R = Z_{Re} (0.1 \text{Hz}) - R_s). \) For NT, \( R = 158 \Omega \), and for LT, \( R = 161 \Omega \), and these values clearly show that surface resistance of electrode for both the films has remained constant.

Finally, we witness that by growing BDD at LT we observe significant reduction in the capacitive impedance of the grains of BDD, whereas the overall surface conductivity of the film and CPE of grain boundaries was found to be same as that of NT-BDD. The data clearly show that high quality diamond can be grown at low temperature without appreciable change in the overall film conductivity.

In conclusion, we produced and studied the boron doped diamond film deposited under low temperature (~600°C, 460°C minimum up to date of report). LT-BDD exhibits properties between conventional UNCD and NCD. Low temperature and boron dopant seem two essential conditions to form the diamond with grain size larger than UNCD. Compared with conventional NCD, LT-BDD film shows high renucleation rate during the deposition which results in a surface with extremely low roughness, in the order of 10 nm RMS. The roughness increases very slowly along with the film thickness, which is similar to that of UNCD film growth. This insignificant dependence of roughness to film thickness could be very valuable for microfabrication, such as device patterning, bonding, and integrating. The Raman and electrochemical studies confirm that the film quality and performance of LT-BDD are similar to those of NT-BDD. With further process optimization, LT-BDD deposited under a temperature lower than 400°C can be expected.