Fluorinated graphene oxide, nanocrystalline diamond multilayer thin films for optical and electromagnetic limiting applications

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1 Introduction

Although several protective coating materials exist today, there are limitations in which they are designed and in operation for a specific environment. Functionality of these protective coatings under extreme conditions has always been a challenge, as it is difficult to achieve a single reliable solution. Some of the limitations of protective coatings that need to overcome are surface oxidation, mismatch of thermal expansion coefficients, corrosion, and poor mechanical strength. In most defense and space applications, there is a need for electromagnetic (EM) radiation absorbing materials that can simultaneously withstand high temperatures, corrosion, and chemical exposure [1].

Carbon-based materials are perceived as interesting EM radiation absorption materials [2]. Two-dimensional (2D) materials such as graphene and its derivatives like graphene oxide (GO), reduced graphene oxide (rGO), and fluorinated graphene oxide (FGO) are gaining increased attention as potential microwave absorbers due to their large surface area, and superior electronic, mechanical and thermal properties [3–8]. By the fluorination of GO, C-F covalent bonds are formed. These bonds give rise to the electronegative property in FGO to increase polarity and high dielectric loss factor [9, 10]. Apart from the superior properties of graphene, FGO has additional material properties such as hydrophobicity or amphiphobicity, high thermal conductivity, increased oxidation and thermal stability, and high absorption of optical and microwave energies [6, 11, 12]. These properties open new possibilities to use FGO for a broad range of applications including: as optical limiters and attenuators for lasers and electromagnetic (EM) radiation. Several applications of FGO

as an optical limiter have already been reported in the literature [13, 14].

Chemical vapor deposited (CVD) diamond is also well known for its excellent material properties such as high thermal conductivity (five times that of copper), optical transparency through most of the optical spectrum, extreme hardness, high Young's modulus, chemical inertness, and radiation hardness [15]. This makes diamond an ideal protective coating material for extreme conditions that include high temperatures, chemical and radiation environments, e.g., as in space and defense applications. With developments in several CVD processes such as hot filament CVD (HF-CVD) [16, 17], and microwave plasma CVD [18], it is now possible to grow uniform polycrystalline diamond thin films on nearly any substrate, even at lower substrate temperatures. The thickness and grain size can be controlled by varying the growth parameters such as the temperature, pressure, and gas flows of the precursors. With the controlled growth of diamond thin films, varying grain sizes, thicknesses and crystallinity, realization of several devices and coatings is now possible: e.g., Schottky diodes [19], field effect transistors (FETs) [20], metal oxide semiconductor (MOS) capacitors [21], infrared (IR) sensors [22], electron field emitters [23], detectors for high energy physics; IR windows, protective coatings [24–27], micro lenses [28], etc.

In the current work, we study properties of the unique combination of the two extreme materials, FGO and diamond, as multilayer protective coating for extreme conditions. The large surface area of FGO attenuates the incoming EM energy that gets converted to thermal energy which can be effectively dissipated through the diamond thin film making the multilayer composite layer operate as a protective coating for extreme conditions. A quick and effective method of processing FGO from GO using Capacitively Coupled Plasma (CCP)-Reactive ion etching (RIE) plasma fluorination process is developed in this study. The FGO is processed on nanocrystalline diamond (NCD) films grown over crystalline silicon (Si) and amorphous fused silica (FS) substrates. The Contact angle

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measurements, Raman spectroscopy and atomic force microscopy (AFM) are used to characterize the NCD films, GO and FGO films at different stages of processing. The synthesized FGO/NCD multilayer composite on both the Si and FS substrates are subjected to EM absorption tests for further study. The choice of using Si and FS substrates was made to demonstrate FGO/NCD multilayers on both optically opaque and transparent substrates, with different dielectric constants, to study the impact on both substrates. The multilayer FGO/NCD on FS substrate can act both as an optical limiter and EM absorption material where optical transparency is a requirement.

Prior to the NCD deposition, a nucleation pretreatment on Si and FS substrates was performed through seeding process by sonication using a nanodiamond suspension in methanol for 20 min. The wafers were subsequently rinsed in acetone, methanol, and isopropanol. A detailed process of the seeding processes can be found elsewhere [16]. The HFCVD process was used to grow NCD films on 4" Si and FS substrates at AKHAN Semiconductor Inc. Tungsten filaments with a diameter of 0.63 mm were heated to 2000–2400°C by applying a DC bias voltage. The substrates were placed 10–20 mm below the filaments. The deposition of NCD is comprised of a three-step process that includes carburization of the filaments, nucleation, and growth. NCD synthesis by HFCVD is well known, where detailed setup and growth process are discussed in detail [13, 14].

Commercially obtained GO aqueous solution was spin coated onto the NCD/Si and NCD/FS substrates to obtain GO/NCD multilayers. The substrates were coated at a spin speed of 2000 RPM for 1 min and then baked at 100°C for 1 min. To incorporate fluorine into the GO layers, an Oxford CCP-RIE plasma fluorination process was used. CHF₃ and CF₄ gases were flowed at 45 and 15 sccm, respectively, for 5 min at a 30 mTorr chamber pressure and with an applied power of 50 W and a DC bias of 100 V.

Surface characterization of the NCD, GO, and the FGO film structures was carried out by AFM in tapping mode and contact angle measurements, and Raman spectroscopy using a 532 nm laser. All the measurements were conducted subsequently after each process step. The morphologies of the structures and the contact angle measurements can be seen in Fig. 3, with clear changes to surface structure and associated

hydrophilicity/hydrophobicity. The thickness and surface roughness of the deposited films at all stages of the NCD growth, GO and FGO fabrication processes were determined by AFM and ellipsometry. The thickness of the GO and FGO layers was close to 10 nm, which is estimated to be 10–14 layers [29]. For the contact angle measurements, single liquid analysis using deionized water was performed using a controlled drop height and software analysis. A cross-sectional schematic of the structure is shown in Fig. 1. AFM images (in tapping mode) of NCD on Si, NCD on FS and FGO on Si, and FS substrates can be seen in Fig. 2.

Furthermore, EM testing was performed to measure relative electromagnetic loss in the 2 GHz to 8 GHz band at SportOn International (USA), Santa Clara in an isolation chamber to minimize the effect of background energy on the results. The test setup includes a signal generator, two horn antennas, a spectrum analyzer, and a foam block to hold the sample under test. The test setup can be seen in Fig. 5. The foam block was as big as the horn antenna emitter, with one of the sides covered in conductive tape. A hole of 0.6 in. in diameter was made, which is smaller than the wafer size. With a reference blank sample of Si (no coating) mounted to the foam block, the block was positioned in front of one of the horn antennas. The second antenna was oriented to radiate the sample. One of the horn antennas was driven with a continuous wave signal from 2 GHz to 8 GHz in 0.25 GHz steps. The signal strength received at the second antenna was recorded. The blank Si sample was replaced with NCD/Si sample. The change in received signal strength from the reference blank sample to the signal strength received with the NCD/Si sample was recorded. The diamond only sample was replaced with the FGO/NCD/Si sample and the signal was again swept from 2 GHz to 8 GHz in 0.25 GHz steps. The change in received signal strength from the reference blank to the signal strength received with the diamond and FGO coated sample was recorded. The same experiment is repeated for NCD/FS and FGO/NCD/FS samples.

2 Results and discussion

The synthesized NCD films have uniform coverage without pin holes and grain size between 200 and 300 nm as seen from

Fig. 1 Schematic of the FGO/nanocrystalline diamond thin film on silicon/fused silica substrate showing the FGO with different functional groups. The FGO is of few layers with 10 nm in thickness, NCD is 100 nm and the Si/FS substrate of 200 μ m in thickness

Fig. 2 AFM images of (a) NCD/Si, (b) NCD/FS, (c) FGO/NCD/Si substrate, and (d) FGO/NCD/FS substrate

the atomic force microscopy (AFM) images in Fig. 2a–b. The thickness of the films is close to 100 nm as measured by ellipsometry and the films are strongly adhered to the substrate. The RMS surface roughness is around 30–40 nm. The contact angles for NCD, GO/NCD and FGO/NCD surfaces are 76.8°, 44.7° and 102.2°, respectively. The as grown NCD films are hydrophobic due to the presence of H_2 in the plasma. However, after the deposition of GO, the surface became hydrophilic. With the fluorination of the GO surface, the surface returned to hydrophobic with a contact angle of 102.2°. Fluorination makes the surface more hydrophobic giving rise to large contact angles. The FGO exhibits amphiphobicity, where the contact angle is above 90°. This agrees with the contact angle measurements on FGO by A. Matkhar et al.

[14]. Higher degree of hydrophobicity can be attributed to the replacement of hydroxy molecules with fluorine, reducing the wettability of the surface sheet (Fig. 3).

From the Raman characterization plots in Fig. 4, the D and G peaks of the diamond signature can be seen on both the substrates [20]. The plots obtained from FGO/NCD/Si and FGO/NCD/FS can be seen in Fig. 4. The Raman plots for NCD, GO and FGO on Si, and NCD, GO and FGO on FS are shown in Figs. 4a and b, respectively. The D peak for NCD is at 1335 cm^{-1} and for G is at 1540 cm^{-1} . The peak observed at 1450 cm^{-1} represents the CH bonds [30]. The Raman spectra for FGO and diamond has been overlapped due to similar D and G peaks of FGO and diamond. The D and G peaks for GO on Si are around 1337 cm^{-1} and 1567

Fig. 3 Contact angle images of (a) NCD/Si, (b) GO/NCD/Si and (c) FGO/NCD/Si, corresponding to water drop contact angles of 70.8, 44.7, and 102.2, respectively

Fig. 4 Raman plots of thin film NCD, GO and FGO on Si substrate, (left), and NCD, NCD/GO and NCD/FGO on fused silica substrate (right)

cm^{-1} , respectively and D and G peaks of FGO are at 1339 cm^{-1} and 1560 cm^{-1} respectively. Furthermore, the D and G peaks of GO and FGO on FS substrate are at 1333 cm^{-1} and 1555 cm^{-1} and 1335 cm^{-1} and 1560 cm^{-1} , respectively. The slight differences in the peaks of GO and FGO on both the substrates could be substrate-dependent due to the grain boundaries and surface roughness of NCD films. The I_D/I_G for GO and FGO on both the substrates did not change much indicating that the layer thickness did not have any impact due to fluorination. However, the change in the peaks D and G indicate the change in the functionalization groups. The fluorination replaces the C-H and C-O bonds to C-F and the time of fluorination also influences the amount of fluorination [31]. The shift in G peak also indicates the defects induced due to the fluorination process and the increase in the electronegativity. The peaks at 1450 cm^{-1} observed in the GO and FGO films are due to the NCD film lying underneath. A detailed Raman study using UV would distinguish the carbon signatures.

The process of deriving FGO from GO can be extended for use in processing large area films beyond 4-in. wafers. The method has been optimized for large area substrates. The thickness of the FGO films was measured to be 10 nm, which is close to the GO film thickness. This implies that etching of the GO films is limited to fluorine/hydroxy molecular exchange, with limited carbon etching using the plasma fluorination process. The fluorine atoms are covalently bonded to the GO films. The fluorination of GO can occur due to the substitution of hydrogen atoms in C-H and O-H bonds, as well as oxygen atoms in oxygen-containing groups [31]. The CF_4/CHF_3 controlled etching of oxide in Si and SiO_2 structures has been shown previously, and fluorine is well known to be not etch reactive with carbon films [32]. The hydrophobicity also indicates that fluorine atoms have indeed been incorporated into the GO films as was seen in the previous reports, where the Raman transition from GO to FGO and associated contact angle changes are due to the presence of fluorine atoms at nearly all carbon inlets/outlets, qualitatively and quantitatively in agreement with those reports [12]. The thermal expansion coefficients of FGO and diamond are low with negligible

lattice mismatch. This also makes the NCD/FGO multilayer a great candidate for operation at high temperatures.

In the process of EM wave attenuation, EM power is depleted and gets converted to thermal energy. The presence of different polar functional groups, the material thickness and the electric and magnetic dipoles of the materials influence the absorption phenomenon of the radiation [33]. The FGO/NCD thickness of 110 nm on Si and FS substrates of 200 μm . Although most of the absorption is due to the FGO/NCD layers, the substrate also influences the absorption due to its dielectric constant. By varying the thickness of both FGO and NCD layers, the absorption can be changed. The EM test plots showing the reflection loss (RL) can be seen in Fig. 5. The maximum RL of FGO/NCD/Si is -13 dB at 7.7 GHz and of FGO/NCD/FS is -18 dB at 5.2 GHz . The difference in the RL values and the frequency of the maximum RL can be attributed to the substrates due to the change in their dielectric constants.

The reflection loss (RL) of an absorber material is calculated by [33]:

$$RL \text{ (dB)} = 20 \log \left| \frac{Z_{in} - 1}{Z_{in} + 1} \right|$$

Where, Z_{in} represents the input characteristic impedance and is given by:

$$Z_{in} = \sqrt{\mu_r/\epsilon_r} \tanh \left[j \left(2\pi \mathcal{F}^d / c \right) \sqrt{\mu_r \epsilon_r} \right]$$

Here, $\mathcal{F}$ is the matching frequency, d is the thickness of the absorbing material, c is the velocity of light, μ_r is the permeability and ϵ_r is the permittivity of the absorbers.

The RL is dependent on the thickness of the absorption layers. Several studies on the RL in EM absorption materials can be found, where the thickness and the material impact the RL [34]. FGO and diamond are both electronegative materials and hence the absorption is strong even when the thickness is in the nanometers range. With the increase in the thickness of both FGO and NCD, the RL can be increased. Additionally, by modifying the amount of GO fluorination, the surface

Fig. 5 The EM test setup comprising of two Horn antennas acting as transmitter and receivers, which are connected to the RF power amplifier, RF signal generator and spectrum analyzer. The test sample

is placed in between the transmitter and the receiver antennas (*left*). The plots of reflection loss Vs Frequency of silicon and fused silica substrates are shown (*right*)

properties can be modified. This is evident in the shift of G peaks in GO and FGO from Raman analysis in Fig. 3. The shift indicates increase in electronegativity due to the induction of dipoles that arise from the addition of C-F atoms into the lattice. The dipoles impact the EM absorbing properties. This in turn can be utilized to obtain maximum absorption at a particular frequency. A more detailed testing with different coating thicknesses, with different incident powers and frequencies is for further study.

3 Conclusion

The current study is a demonstration of combining two extreme materials with extraordinary material properties, opening a new window for unique applications in optics and electro optic devices and coatings. We have successfully coated the diamond surfaces with FGO by spin coat dispersion and plasma fluorination. The role of the protective composite on the surface of Si and FS was compared with the respective non-protected substrate types. Extreme EM absorption was obtained with a FGO/NCD composite on Si and FS substrates with RL of -13 dB at 7.7 GHz and -18 dB at 5.2 GHz, respectively. The difference in the surface morphology was pronounced when comparison was performed with a graphene oxide and intrinsic surface, where the amphiphobicity was readily evident through dramatic changes to the contact angle measurement. The presented FGO diamond composite protection method with some tunability of EM absorption is fully scalable and can be realized on the commercial level. FGO processed diamond surfaces could also be used for MOS or CMOS semiconductor device applications,

as well as, selectivity sensors, biological applications and anti-corrosion coatings.

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