

Sustainability of Carbon Nanocomposites Under High Temperature and Pressure

C-nanocomposites for space engineering applications

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Abstract-In this article we explored the sustainability of carbon nanocomposite material under high temperature and pressure shock waves developed in an air ambience. The changes in the morphology, crystal structure and electrical properties of carbon nanostructures are discussed by comparing with untreated structures. After shock wave treatment, we have noticed two typical modifications such as weight-loss in the deposited material and formation of diamond nanoparticles. However, the impact of shock wave is limited to the carbon nanoparticles those are residing on the top-surface of the films. Degrade in the overall quality of treated films and increase in their electrical resistance has been noticed.

Keywords- Carbon Nanostructures; Thermal Protection Systems; Space Engineering Applications; High Enthalpy Shock Wave; Thermal Stability

I. INTRODUCTION

The carbon nanostructures including nanotubes [1], nanorods [2], nanoparticles [3], etc. have received considerable attention due to their size dependent thermal stability and phase transformation [4]. As the size of carbon particles reduces to nanoscales, the phase transformation from graphite to diamond occurs even at low temperature and pressure [5]. Besides this, finite-size effects have remarkable consequences on other material properties including bulk module, dielectric constants and optical excitation energies as compared to bulk. In general, the graphitic nanomaterials possess excellent mechanical, thermal and electrical properties, excellent dimensional stability and excellent optical properties [6]. In recent years, carbon has been well adopted in aerospace engineering as an ablative layer or thermal protection layer/system (TPS) material for space shuttles (SS) particularly at nose cones and wing leading edges. This is due to its high adsorbability of heat fluxes and emissivity (~ 0.8 - 0.98) of byproducts as steam into space along with its low density (1568 kg m^{-3}), high specific heat ($\sim 0.71 \text{ J gK}^{-1}$), high thermal conductivity ($\sim 90 \text{ W mK}^{-1}$) and high melting point ($\sim 3800 \text{ K}$) [7]. It can also form multi-oxide components composed of a refractory crystalline oxides (skins) and glass components (amorphous). However, thorough investigations on these by-products are necessary in view of their increase of demand in space engineering. However, till today there has been no systematic report on the physical behavior of carbon nano-composites particularly nanoparticles under high temperatures and pressures. Thus, we have initiated systematic investigations on carbon nanoparticles and the observed preliminary results are reported in this article. Here, the films of graphitic carbon nanoparticles (GCNPs) were developed using homebuilt spray technique and exposed them under high enthalpy shock tube in an air ambient. One of the most important ideas here is that estimation of phase and structural stability along with chemical composition of GCNPs layers under high pressure and temperature since these structures absorb thermal energy by undergoing changes of shape and phase when they are subjected to shock wave.

II. EXPERIMENTAL PROCEDURE

The deposition of layers of graphitic carbon nanoparticles using homebuilt spray system, shock wave treatment in high enthalpy shock tube and characterization techniques adopted for the analysis of untreated and treated layers are described below in two sub-sections.

A. GNP Films Preparation and Shock Treatment

Thick films of graphitic carbon nanoparticles have been deposited on 3 mm thick aluminum substrates using a simple spray method by spraying the NPs dispersed solution. In a typical process, the films were prepared at a substrate temperature of 523 K by using high pure nitrogen gas as a carrier gas. Initially, 100 mg of GCNPs powder was dissolved in a mixed solution of deionized water and methanol (10:1). Further, the NPs dispersed solution was transferred to spray reservoir and sprayed sequentially on to pre-heated substrates by passing nitrogen gas with a pressure of 150 kPa. Here, the solution was sprayed for 2 s and maintained a gap between successive sprays of around 10 s in order to reach the substrate temperature to a fixed value and the total area of deposition was about $1.5 \times 1.5 \text{ cm}^2$.

The as-deposited GCNPs films were exposed to high enthalpy shock wave in free piston shock tube (FPST), as shown in Fig. 1. The detailed working principle and experimental procedure of FPST has been reported elsewhere [8, 9]. In brief, the samples were exposed to shock wave in an air ambience, a test gas, by driving 20 kg cylindrical piston in a compression tube for the duration of 2 ms. Here, the piston was driven in the compression tube filled with 100 kPa helium by a high pressure nitrogen gas of around 1.8 MPa and the experiment was carried out at a typical pressure of 12 kPa.

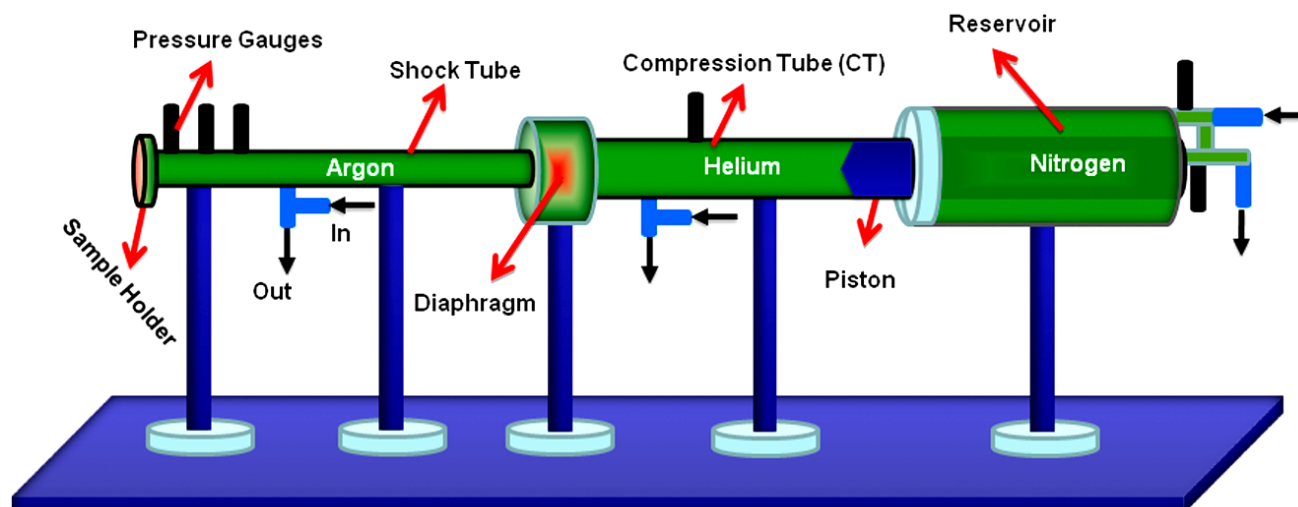


Fig. 1 Schematic diagram of FPST used for the shock wave treatment of GNPs

B. Characterizations

The untreated and shock wave treated GCNPs films were examined with various advanced analytical techniques. The crystal structure of the films was examined using transmission electron microscope (TEM), high-resolution TEM (HRTEM) and selected area electron diffraction (SAED). The composition of the films was estimated using energy dispersive X-ray spectroscopy (EDS) attached with scanning TEM (STEM). The surface morphology of the GCNPs films was investigated using FESEM and TEM. The surface roughness of the films has been roughly estimated using non-contact optical profiler. The quality of the films along with their optical behavior was studied using confocal micro Raman with the help of 514.5 nm laser and mono-cathodoluminescence (CL) attached with FESEM. The electrical properties of the structures were also measured using probe station attached with semiconductor parameter analyzer at room temperature by using silver (Ag) as Ohmic contacts.

III. RESULTS AND DISCUSSION

The parameters like temperature, pressure, velocity of the shock wave and Mack number in the shock tube are found to be 11,000 K, 6 MPa, 2.3 km/s, and ~ 7 , respectively. Further, the loss in GCNPs material is calculated by measuring the sample weight before shock and after shock, and it is found to be 19 mg and loss per unit area per kPa pressure is of about 0.7 mg. The observed loss in the deposited material is majorly attributed to the pressure and temperature evolved in the shock tube and might be occurred in different ways including the ejection, evaporation (sublimation) and/or melting of material due to high pressure shock wave and high temperature, etc. As compared to untreated GCNPs films (10 μm), the shock treated films under air ambience showed low micro-level surface roughness of about 4 μm .

A. Surface Morphology

The surface morphology of the as-deposited and shock wave treated GCNPs films has been studied by FESEM and the recorded images at higher magnifications are shown in Fig. 2(a, c). The surface of as-deposited GCNPs films contains slightly aggregated NPs, which have smooth and spherical surface. The evaluated surface diameter of the NPs is varied between 50 and 350 nm. The surface morphology of the shock treated GCNPs films remains as nearly same as untreated films. However, a few of the GCNPs on the surface of treated films are brighter than that of others (represented by red circle in Fig. 2c). Furthermore, these brighter NPs have slightly different surface morphology (rough surface with irregular shape, which has been clearly noticed from TEM analyses of shock treated GCNPs films) than that of GCNPs. These NPs on the surface of GCNPs, probably belong to diamond NPs (DNPs), were developed through the phase conversion of graphite as diamond under high temperature and pressure. However, the presence of bright DNPs only just on the top surface of GCNPs films clearly emphasized that the impact of shock wave is only limited to the surface layer of GCNPs films. The diameter of shock wave treated GCNPs is varied between 100 and 400 nm. It emphasised that apart from the formation of DNPs, the dimensions of GCNPs also varied with shock wave treatment. The observed results such as loss in material, reduction in surface roughness, and formation of DNPs reveal that upon shock wave treatment, the GCNPs films experience layer by layer ablation through various chemical kinetics and thereby release variety of byproducts in the form of gases such as oxides, nitrides, etc. (investigations on gases released at the time of shock treatment are in progress) and also change their phase from graphite to diamond.

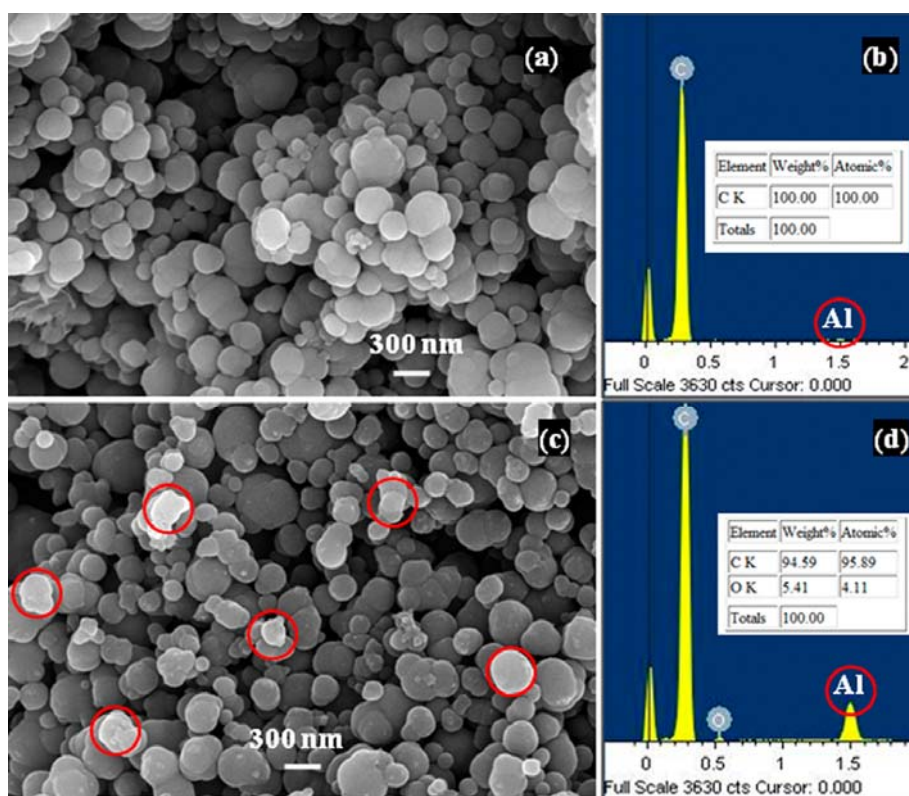


Fig. 2 (a, b) FESEM image and EDAX profile of as-deposited and (c, d) FESEM and EDAX profile of shock wave treated GCNP films

B. Crystal Structure

The XRD profiles of untreated and treated GCNPs films show (Fig. 3) that the untreated GCNPs films contain nanoparticles that are uniquely oriented along the (001) planes since the diffracted peaks observed at 24.46° and 43.36° are belonging to (002) and (101) orientations of graphite [10, 11]. However, the shock wave treated GCNPs films exhibited an additional peak at 33.1° , which belongs to (110) plane of diamond [12]. Other than these peaks, a dominant broad peak observed at 17.7° belongs to Al_2O_3 phase formed on the Al substrate. As compared to the untreated films, the graphite peak intensities of treated films are low mainly due to the loss of material on the substrate, and also formation of low-quality or amorphous carbon related NPs. In order to explore the crystal structure and structural modifications in shock wave treated GCNPs and confirm the above results, low-dimensional structural analyses have been carried out by TEM, HRTEM and SAED techniques.

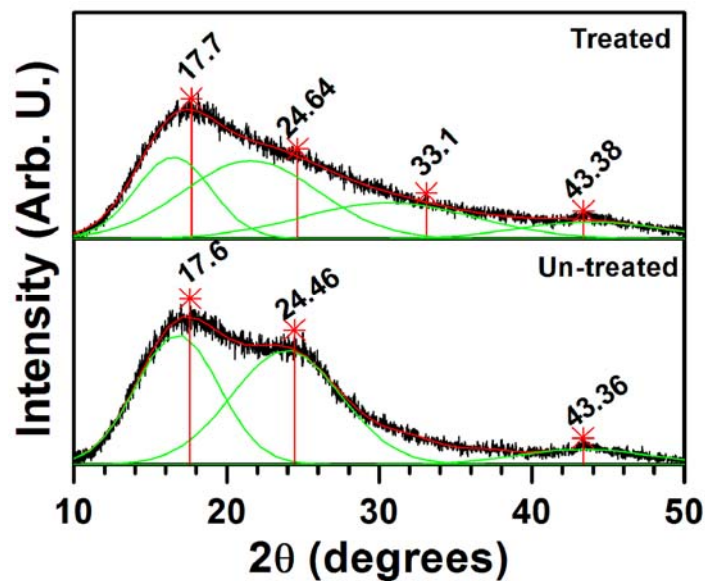


Fig. 3 XRD profiles of as-deposited and shock wave treated GCNPs

The HRTEM image of as-deposited GCNPs is shown in Fig. 4a and its TEM, fast Fourier transform (FFT) and SAED images are showed as insets of Fig. 4a. TEM analysis (top left inset of Fig. 4a) clearly reveals that the as-deposited GCNPs are slightly aggregated and all of them have smooth surfaces and also confirm their dimensions as same as observed in FESEM studies. The

blurred and mixed standing-waves like HRTEM fringes of GCNP show that the as-deposited GCNPs are slightly poor in crystallinity. The spreading of these lattice-fringes all over the NP demonstrates that these GCNPs are completely crystallized structures. The FFT image (bottom left inset of Fig. 4a), taken from Fig. 4a, reveals that these GCNPs are hexagonal graphitic carbon structures (two distinguishable points belong to (002) and (004) planes) and preferentially oriented along the $\langle 001 \rangle$ direction [13]. The SAED studies on GCNP (right inset of Fig. 4a) confirm the above results since the evaluated d-spacing values of three continuous diffraction rings are found to be 0.338, 0.167, and 0.112 nm, respectively. Further, the HRTEM analysis on two segregated GCNPs shows that the lattice fringes at their interfaces are well connected with certain order of interactions. It implies that the interface between aggregated GCNPs is also crystallized and probably free from interfacial defects. Moreover, this type of interactions probably leads to form cross-linked GCNPs chains/domains.

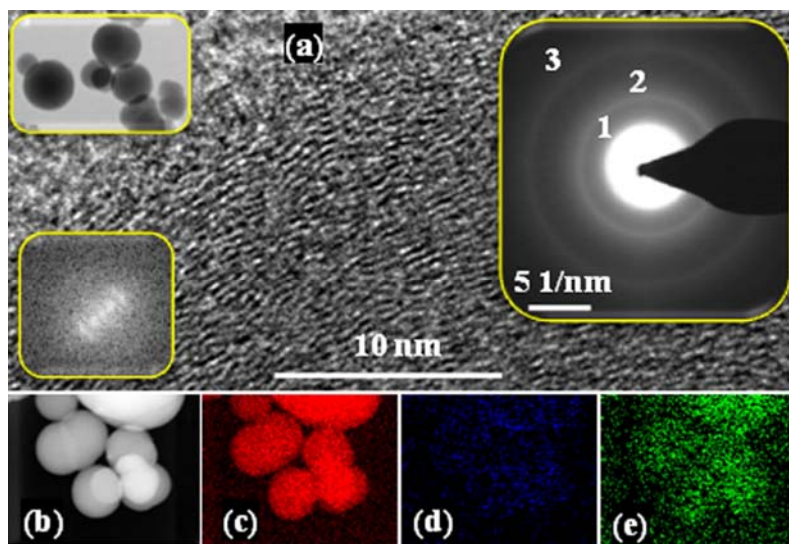


Fig. 4 (a) HRTEM (inset left-top: TEM, left-right: FFT, and right: SAED images), (b) STEM images of as-deposited GCNPs and (c), (d) and (e) are elemental mappings of carbon, aluminium and oxygen, respectively

HRTEM images of shock wave treated GCNPs are shown in Fig. 5a, and their TEM and FFT images are shown as insets of the same image. TEM image of shock wave treated GCNP (top left inset of Fig. 5a) represents a group of NPs. The HRTEM image taken from an appropriate place consists of well organized and clearly distinguishable concentric circular lattice fringes with continuous crests and troughs along its diameter. From the FFT analysis of HRTEM image (left-bottom inset of Fig. 5a) it has been seen that these lattice-fringes are expanded along the $\langle 001 \rangle$ direction and are clearly belonging to graphitic-carbon. It indicates that the crystal structure of GCNPs remain as hexagonal even after shock wave treatment. However, part of the shock wave treated GCNPs consist of nearly similar structural features as observed in untreated GCNPs films (Fig. 6b) along with thick amorphous layer covered on them. These results clearly emphasized that upon shock wave treatment only a few of the NPs residing on the surface of GCNPs are becoming more crystalline and other NPs remain as same.

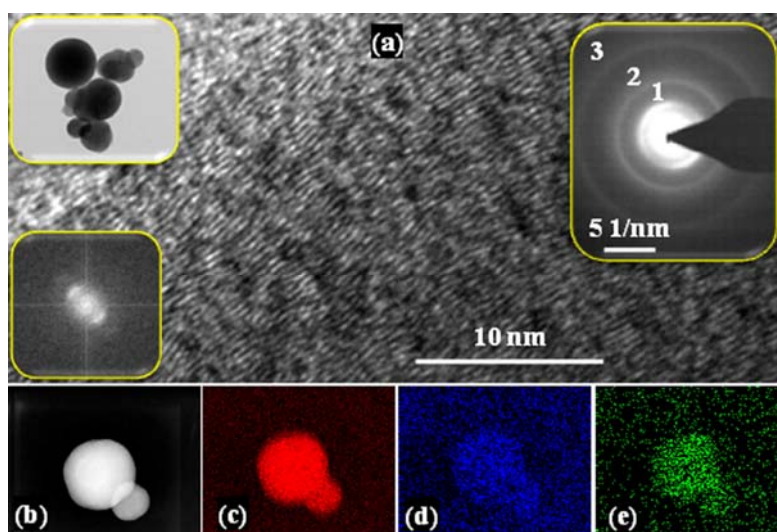


Fig. 5 (a) HRTEM (inset left-top: TEM, left-right: FFT, and right: SAED images), (b) STEM images of shock wave treated GCNPs and (c), (d) and (e) are elemental mappings of carbon, aluminium and oxygen, respectively

In case of DNPs, the structures clearly consist of highly crystalline lattice fringes (Fig. 6c). It has been further confirmed by SAED analysis, which is shown in Fig. 6d. From this figure, we can notice two sets of diffraction spots along with three diffraction rings. The evaluated d-spacing values between diagonal spots are found to be ~ 0.2544 nm (std. 0.2522 nm). It clearly

indicates that the newly formed single crystalline NPs belong to cubic diamond structure and have (110) plane as preferential orientation. As usual, the diffracted rings belong to graphitic carbon nanoparticles, as observed above. Thus, highly crystalline hexagonal graphite and cubic diamond crystal structures are uniquely oriented along the (001) and (110) planes, respectively. From these results, it can be understood that upon shock wave treatment, the formation of DNPs and improvement in the crystallinity of few GCNPs have been taken place exclusively on the surface of GCNPs films.

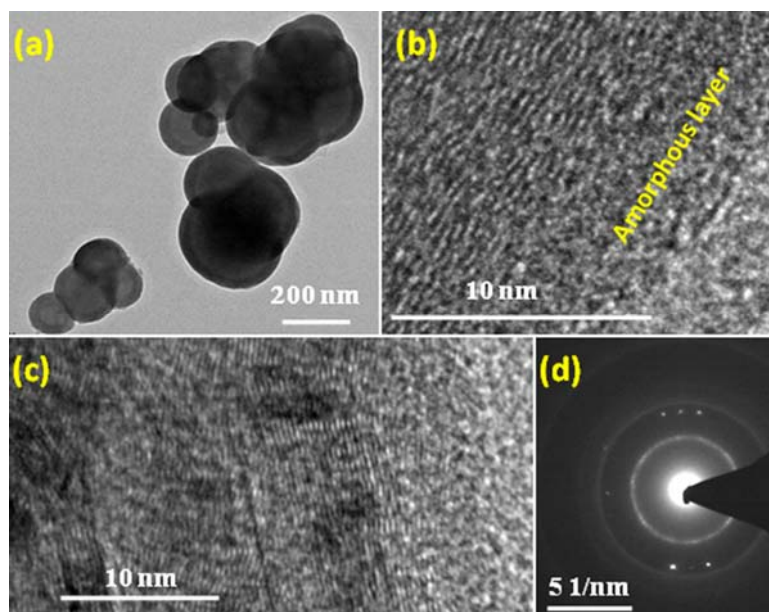


Fig. 6 (a) TEM image of GCNPs after shock treatment, (b) HRTEM image amorphous covered GCNP (c) HRTEM image of DNP and (d) its SAED image

C. Chemical Composition

The chemical composition of the as-deposited and shock treated films were examined using EDAX attached with FESEM and shown in Fig. 2(b, d). It shows that the untreated GCNPs films consist of purely carbon, whereas the shock wave treated films contain small amount of oxygen (4.11 atomic %) along with carbon. However, both untreated and treated GCNPs films exhibit Al peak, which is attributed to the substrate. In order to justify these results and thereby reveal the existing compound(s), we examined the as-deposited and shock wave treated GCNPs with EDS and STEM attached with TEM. The EDS analysis reveals that the as-deposited GCNPs themselves contain small amounts of oxygen and aluminium (Al) particularly on the surface of NPs along with carbon, whereas, the shock wave treated samples contain slightly more Al and oxygen along with carbon. The presence of all these elements (C, Al and O) can be clearly noticed from the elemental mapping of the as-deposited and shock wave treated GCNPs shown in Fig. 4(b-e) and Fig. 5(b-e). Based on these results it can be understood that at the time of deposition of GCNPs films itself, a small amount of aluminium oxide layer probably deposited on the surfaces of few initial layers of GCNPs, which are in contact with the surface of substrate. Further, upon shock treatment under high pressure and temperature in air ambience, the amounts of Al and O are slightly increased probably due to evaporation of Al from substrate and thereby, formation of Al-O or Al-C compounds by reacting with the traces of oxygen and also with GCNPs. However, the overall changes in chemical composition of GCNPs films are marginal.

D. Cathodoluminescence (CL) Properties

The CL spectra of as-deposited and shock wave treated films are shown in Fig. 7. The untreated GCNPs films exhibited a broad CL spectrum between 250 and 800 nm, whereas the shock wave treated GCNPs films showed slightly sharp peak along with a fine and small peak at 695 nm. From the broad CL spectrum of GCNPs films, we have noticed three distinguishable emission peaks centred at the wavelengths of 380 (3.26 eV), 415 (2.99 eV), and 510 nm (2.43 eV), whereas peaks related to shock wave treated films belong to 412 (3.01 eV), 432 (2.87 eV), and 695 nm (1.78 eV). The second and third peaks i.e. 415 and 510 nm, of untreated GCNPs films probably originate from the second nearest interband transitions in disordered and ordered GCNP structures, respectively since the disordered nanostructures generally exhibit higher forbidden gaps than that of ordered structures [14]. The first peak emitted at 3.26 eV belongs to defects states including surface reconstructions, dislocations and surface defects, present in the surface of graphitic NPs since the electrons from these defect states will be contributed for the electron-hole recombination [15]. However, newly raised emission peaks in the CL spectrum of treated GCNPs films at 2.87 and 1.78 eV belong to interband transition in diamond and smallest GCNPs, respectively [16, 17]. Similar results have been observed by Fabisiak et al. in hydrogenated amorphous carbon deposited at various substrate temperatures. While increasing substrate temperature from room temperatures to 400°C, they observed a decrease in the photoluminescence intensity and explained based on the distribution of the density of states within the mobility gap [18]. These CL analyses also reveal the existence of DNPs in shock wave treated the GCNPs films in the presence of air and further, the degradation in the quality of GCNPs.

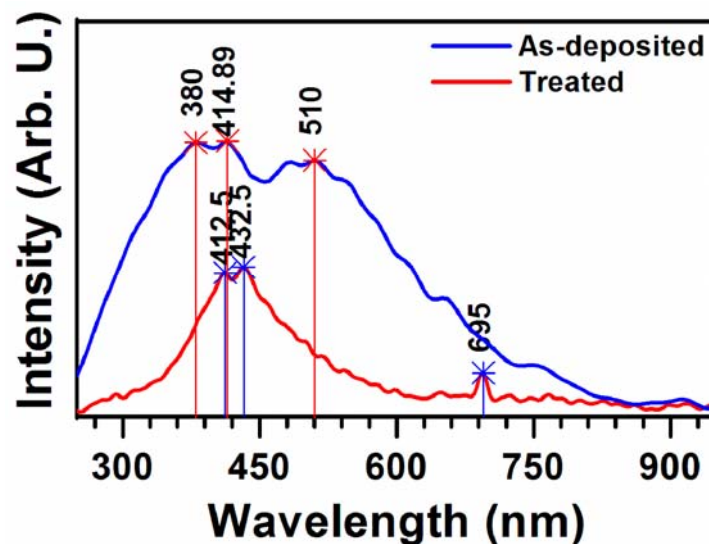


Fig. 7 Mono CL spectra of as-deposited and shock wave treated GNPs

E. Raman Studies

The Raman spectra of as-deposited and shock wave treated GCNPs films are shown in Fig. 8. The first-order Raman spectrum of GCNPs films exhibited only two distinguishable sharp peaks, which are centred at the frequencies of 1359 and 1587 cm^{-1} . The first peak belongs to A_{1g} mode of disordered (D-line) GCNPs and the second peak belongs to the Raman active E_{2g} mode of ordered (G-line) GCNPs [19]. It indicates that the as-deposited GCNPs films exclusively composed of GCNPs^[19] and have sp^2 hybridized C-C bonds in the form of hexagonal aromatic rings [20]. The presence of disorder and order structures in the as-deposited GCNPs films is consistent with the data observed in TEM analysis. Further, the intensities of G and D lines are nearly similar, which reveals that the untreated GNPs consist equal amounts of ordered and disordered structures. On the other hand, the shock wave treated GCNPs films in air ambience exhibited one lower frequency peak centred at 656 cm^{-1} along with previous peaks as observed in as-deposited GCNPs films, which belongs to band stretching mode of Al-O [21]. However, we could not notice any peak related to DNPs (it could be around 1332 cm^{-1}) [13] probably due to low density of DNPs and/or low intensity peak which could be hindered under the peak of 1358 cm^{-1} .

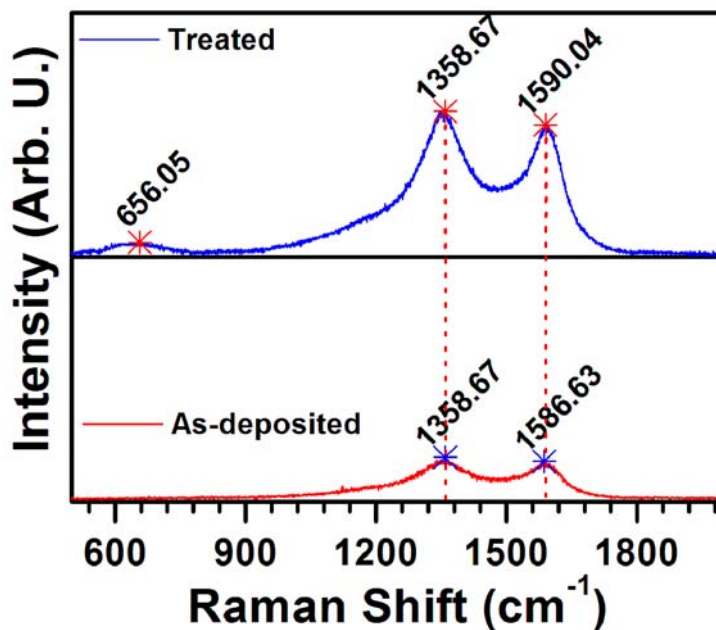


Fig. 8 Raman spectra of as-deposited and shock wave treated GCNPs.

As compared to the deposited films, the peak positions of D- and G-lines of treated films are unchanged and however, their intensities drastically increased with shock wave treatment. Further, the sharpness of both the peaks and area under them also increased. These results indicate that the shock wave treatment of GCNPs films under an air atmosphere strongly enhance both the structures i.e. disordered and ordered structures of GCNPs. However, careful analyses of these D and G-peaks reveal that upon shock wave treatment the enhancement in the disorderedness of GCNPs films is slightly higher than that of orderedness since the full width at half maximum (FWHM) value and height of D-peak as compared to G-peak is abruptly decreased for shock

wave treated GCNPs films. These can be noticed from Table 1, which represents the data evaluated from deconvolution of Raman spectra of untreated and treated GCNPs films by Gaussian curve fit. Further, upon shock wave treatment the intensity ratio (I_D/I_G) of these peaks is slightly increased from 1.07 to 1.11. These results, therefore, emphasize that upon shock wave treatment the as-deposited GCNPs become more disordered structures.

TABLE I DATA EVALUATED FROM RAMAN SPECTRA OF UNTREATED AND TREATED GNP FILMS BY GAUSSIAN CURVE FIT

Untreated GCNPs films:				
Peak	Area	Center (cm^{-1})	FWHM (cm^{-1})	Height
D	20089	1357.8	193.34	82.902
G	9347.8	1586.4	92.421	80.701
Treated GCNPs films:				
D	32103	1356.9	93.399	274.25
G	32103	1356.9	93.399	274.25

F. Electrical Properties

The current-voltage (I-V) characteristic plot of the as-deposited and shock wave treated GCNPs films are shown in Fig. 9. These measurements were carried out at room temperature by probe station attached with semiconductor analyzer using silver (Ag) paste as Ohmic contacts. The resistance of the films has been calculated from the inverse slope of the I-V curves. The as-deposited GCNPs films exhibited an electrical sheet resistance of $11 \Omega/\text{cm}^2$, whereas the treated films showed slightly high resistance of $50 \Omega/\text{cm}^2$. Similar behaviour has been observed from the shock wave treated GCNPs films under an inert atmosphere i.e. argon ambient [22]. Thus, the presence of high resistance in shock wave treated GNP films is probably attributed to the presence of low-quality nanostructures and high resistive diamond particles, amorphous compounds, as well as decrease in film thickness.

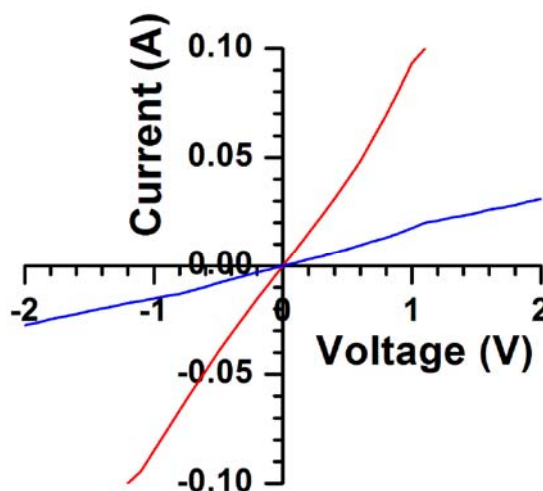


Fig. 9 Current-voltage plots of (red) as-deposited and (blue) shock wave treated GNP films

IV. CONCLUSIONS

GCNPs films deposited on aluminium substrates have been exposed to high enthalpy shock wave in the presence of air and analyzed with advanced analytical techniques in order to understand the impact of shock wave on their physical properties including weight loss, change in crystalline quality, morphological, chemical and optical properties, and electrical properties. The observed results are summarized below.

The impact of shock wave on GCNPs films is exclusively limited to the surface particles present on the GCNPs films and the weight loss of deposited material per unit area is found to be 19 mg. The morphology of the shock wave treated GCNPs films is slightly changed as compared to untreated films, and nanostructures like diamond nanoparticle, are formed. The formation of DNPs on the surface of GCNPs films is confirmed by XRD, TEM, and CL studies. The shock wave treated films contain small traces of aluminium and oxygen in the form of byproducts probably due to air ambience and substrate.

Though the loss in material is considerably high, these preliminary results strongly promote the adoptability of GCNPs in the development of re-entry space shuttles. Upon shock wave treatment we have noticed DNPs and degradation in the quality of GCNPs films. However, in order to understand the behavior of carbon nanoparticles under different temperatures and partial

pressures of air in depth, similar experiments will be carried out under the same shock tube and tried to explore the chemical kinetics and sustainability of these nanostructured films.

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