Fragmentation and structural transitions of few-layer graphene under high shear stress

Cite as: Appl. Phys. Lett. 118, 213101 (2021); doi: 10.1063/5.0049592
Submitted: 6 March 2021 · Accepted: 23 April 2021 · Published Online: 24 May 2021

Mingzhi Yuan,1 Resta A. Susilo,1,a) Shujia Li,1 Jiajia Feng,1 Vicente Benavides,2,5 Jian Chen,4 Alexander V. Soldatov,1,5,6,b) and Bin Chen1,b)

AFFILIATIONS
1 Center for High Pressure Science and Technology Advanced Research, Shanghai 201203, China
2 Department of Engineering Sciences and Mathematics, Luleå University of Technology, SE-97187 Luleå, Sweden
3 Department of Materials Science, Saarland University, Campus D3.3, D661-23 Saarbrücken, Germany
4 Department of Physics, Southern University of Science and Technology, Shenzhen, Guangdong 518055, China
5 Center for High Pressure Science (CHIPS), State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao, Hebei 066004, China
6 Department of Physics, Harvard University, Cambridge, Massachusetts 02138, USA

a) Present address: Department of Physics, Pohang University of Science and Technology, Pohang 37673, Korea.

b) Authors to whom correspondence should be addressed: alexander.soldatov@ysu.edu.cn and chenbin@hpstar.ac.cn

ABSTRACT
A key factor that determines the mechanical and electrical performance of graphene-based materials and devices is how graphene behaves under extreme conditions, yet the response of few-layer graphene to high shear stress has not been investigated experimentally. Here we applied high pressure and shear to graphene powder using a rotational diamond anvil cell and studied the recovered sample with multiple means of characterization. Sustaining high pressure and shear, graphene breaks into nanometer-long clusters with generation of large number of defects. At a certain stress level, it transforms to amorphous state and carbon onions. The reduction of infrared reflectivity in the severely sheared phase indicates the decrease in conductivity. Our results unveil the shear sensitive nature of graphene, point out the effects of shear on its physical properties, and provide a potential method to manipulate this promising material.

Graphene has been in the focus of materials research for over a decade due to the superior physical properties it exhibits. The attractive properties of graphene such as high mobility, stability, and thermal conductivity have made it a promising material in novel microelectronic systems. Moreover, the mechanical behavior of graphene has been investigated by both experiments and theoretical simulations.1 It was reported that graphene has the Young’s modulus and intrinsic strength up to 1 TPa and 130 GPa, respectively, which made it the strongest material ever measured.1 Reinforcement of mechanical properties including fracture toughness and flexural modulus has been demonstrated in the graphene-incorporated composites.1 In order to develop the application of graphene as nanomechanical material, it is important to understand how it behaves under extreme mechanical conditions, especially under high shear stress. It is believed that the properties of graphene and other carbon-based materials are significantly affected by structure, morphology, and defects, which could be dramatically altered by mechanical manipulations.8–11 Recently, attention has been drawn to the shear sensitivity of carbon materials.10–11 The transformation to diamond from glassy carbon and graphite was found to be thermodynamically favored with the application of shear. As to graphene, the occurrence of shear-induced diamonization has been predicted by molecular dynamics simulations,1 while the effect of high shear stress on graphene has not been sufficiently studied by experimental work.

In this work, high pressure and shear were applied on graphene powders and the recovered samples were studied using Raman spectroscopy, transmission electron microscope (TEM), and infrared (IR) spectroscopy. Shear-driven defect generation and fragmentation of graphene under high pressure were revealed. Nanographene, amorphous, and carbon onions were observed as the products of graphene suffered from extensive shear. The decrease in IR reflectivity indicated the decrease in transport properties of the sheared material. Our results demonstrate the fragmentation and the subsequent transformations of graphene under high shear stress, point out its potential...
influence on physical properties, and provide a deeper insight into the limitation of devices based on this strongest material.

The high pressure and shear were applied to the sample using the rotational diamond anvil cell (rDAC, Fig. S1).16,17 The diameter of the anvil culets was 300 μm. To emphasize the effect of shear stress, relatively large sample chambers (~270 μm in diameter) were drilled in the pre-indentated steel gaskets. Graphene powders (XF NANO) with the thickness of 5–8 layers and sheet size of 3–5 μm were loaded into the chamber without pressure-transmitting medium. The pressure was estimated based from the Raman shift of stressed diamond anvil.18

The Renishaw inVia Raman system with a 532 nm excitation laser was used in the collection of all Raman spectra. Three runs of the experiments were conducted. In the first two runs, the samples were pre-compressed to ~16 GPa followed by rotation by 225° of one of the diamond anvils while the exerted axial force was kept constant. After the rotation, the pressure in the center of the culet rose to ~32 GPa while the pressures at the edge remained almost unchanged. In the third run, the sample was pre-compressed to ~15 GPa and one of the anvils was rotated by 45°. The pressure increased to ~19 GPa after rotation. The increase in pressure gradient suggested that the samples were under tremendous friction shear stress caused by the radial flow during the rotation and thickness reduction.19–21

A Raman mapping was conducted on one of the recovered samples after shear by 225° to examine the spatial homogeneity of the spectra [Fig. 1(a)]. The spectra exhibit high heterogeneity across the sample chamber. Using the intensity filter at 1450 cm\(^{-1}\) with which the spatial distribution of the spectra can be clearly observed, three regions (A, B, and C) could be distinguished. The intensity at 1450 cm\(^{-1}\) in the spectra goes through a “low-high-low” evolution with the increase in distance to the center of sample chamber. Representative spectra in A, B, and C regions suggest that the recovered sample contains three major structural states with very different features [Fig. 1(b)]. In region A, the spectrum is similar to the one from the original sample, with a typical G-band at 1580 cm\(^{-1}\) and a minor D-band at 1352 cm\(^{-1}\). In region B, the peaks broad significantly, and the intensity around 1450–1470 cm\(^{-1}\), also known as the peak position of fullerene-like carbon (“F-band”), increases. The high intensities of F-band and the peak at ~1200 cm\(^{-1}\) indicate the high density of pentagon and heptagon (h-band) defect in the material, respectively.22 Eventually, at the periphery of the sample chamber, region C, the F-band becomes weak, while the intensity of D-band grow to a level that is comparable to the G-band intensity.

These results indicated that irreversible, systematic transitions occurred in the sample and the produced material structure varied depending on its distance to the rotational center of the diamond anvil. In the central area of the chamber (region A), where the maximum normal pressure in this experiment was applied, the graphene survived due to the lack of shear stress. In the medium region (B), the increased and uniform shear stress smashed the graphene into nano clusters with the Raman feature that is similar with nanographene and amorphous carbon. In the periphery area of the chamber (C), where potential sliding between surfaces, interaction with the metal gasket and other complicated mechanical conditions were dominating, the graphene remained in relatively big particle sizes, with highly concentrated structural defects. The estimated \(L_0\) (coherent Raman scattering size) using the fitted spectra (Fig. S2, Table S1–S5) from A, B, and C are 25, 2–3, and 10 nm, respectively,22 confirming the fragmentation behavior of graphene powders under different combinations of normal and shear stress.

We can use the results of Raman spectra peak fitting for qualitative estimation of nanographene vs amorphous phase contents in different regions of the sample via an integral intensity factor, \(R_{GA}\) (see supplementary material for definition). The \(R_{GA}\) for regions A and C is about 80% (Table S5) that demonstrates the nanographene phase is a dominant structural component. Region A and C belong to the Stage I in Ferrari and Robertson’s three stages of amorphization trajectory.

![Graphene powder Raman mapping](image_url)

**FIG. 1.** (a) Raman mapping of graphene powders recovered from high pressure and shear. Step size: 3 × 3 μm\(^2\). Three regions with different intensities at 1450 cm\(^{-1}\) are defined as A, B, and C. The dashed lines are guides for the eye. The white straight lines indicate the positions where the spectra in Figs. 2(a) and 2(b) were obtained. The inset shows an optical image of the sample before pressure was released. (b) Representative Raman spectra collected in A, B, and C regions. The spectrum of the pristine graphene powders was included for comparison.
for disordered carbon.\textsuperscript{23,24} The difference in these regions primarily comes from the defect density in the nanographene phase. The peak area ratio (AD/AG) that is proportional to the number of defects in graphene is substantially higher in region C compared to that in region A that is a result of much higher shear stress exerted in the region C, far from the sample center region A. On the contrary, for region B, RGA/\textsuperscript{C24} \textapprox 55\% that implies almost equal content of nanographene vs amorphous phase and extremely high defect concentration (AD/AG = 1.25, Table S5).

To track the evolution of the spectra, a linear Raman scan with higher spectra quality along the radius of the sample chamber was conducted. Overlapped spectra from positions across the boundaries between A, B and C (marked in Fig. 1) highlight gradual changes in the graphene powders through 10–30 \textmu m ranges [Figs. 2(a) and 2(b)]. The intensity ratios of D-band and F-band to G-band (ID/IG and IF/IG) extracted from the linear scan suggest an “order-disorder-order” transition in the sample with the increase in the distance to the center of sample chamber [Figs. 2(c) and 2(d)]. One should notice that the increase in ID/IG at positions near the center is sharper than IF/IG, with the reach of a stable value (IF/IG = 0.85) in about 30 \textmu m and stabilizes at \textapprox 0.7. This indicates that with the increase in radius (shear), the accumulation of defect in graphene is accompanied and followed by breaking down of the 2D sheets. The fragmentation of material starts together with defect generation under minor shear and lasts even after the defect is saturated. Finally, the graphene reaches a lower in-plane size limit at the mechanical condition of this experiment. At the edge of the sample chamber, the ID/IG climbs to an abnormally high level before it drops, which could be related to the increase in the clusters size (Table S5, supplementary material) as well as the complicated stress state near the metal gasket. The result of linear Raman scan on another sample sheared by 225° is similar to the mapped sample, suggesting good reproducibility of the experimental data.

TEM characterizations further revealed informative microstructure of the recovered sample. The lamellae for TEM observation were lifted from regions A and B in the sample in Fig. 1(a) and the edge part of the sample sheared by 45° using a focused ion beam system (FEI Versa 3D), and TEM images were obtained using an FEI TECNAI G²S-TWIN field emission electron microscope. Figure 3(a) shows the high-resolution TEM (HRTEM) image of the recovered graphene in the central area of the sample chamber. The measured interlayer spacing is around 0.34 nm. Although bending and folding of graphene films were observed, the straight and intact graphene layers agreed with the results from Raman spectra, suggesting that normal stress simply had limited influence on the sample. From the position corresponding to region B, the graphene powders were laminated due to the uniaxial compression and relatively uniform shear, and electron diffraction shows preferred orientation of the lattice in the material [Fig. 3(b) and inset]. HRTEM image of this region demonstrates the significant loss of long-range order, revealing the curling and fragmentation of graphene sheets under high shear stress [Fig. 3(c)]. Graphene clusters with the size at nanometer level were observed as the product of this severe mechanical treatment. Interestingly, in the lamella extracted from the edge area of a sample recovered from 15 GPa and 45° of the
rotation, amorphous carbon and carbon onions could be found [Fig. 3(d)]. This highlighted the appealing effect of shear, resulting rich and complicated structural and morphological transitions in the graphene powders system.

In order to investigate the physical property of the graphene powders after fragmentation and transition, IR reflectivity was measured on the sample recovered from 16 GPa and 225°C of the rotation. A Fourier transform IR spectrometer (Bruker VERTEX 70v) was coupled to a microscope (Bruker HYPERION 3000) to perform the IR microspectroscopy. A gold foil was used as the calibrant. Nineteen spectra were captured across the sample chamber to compare the reflectivity of the material sustained different level of shear stress. Compared to the high IR reflectivity from the metallic graphene in the center, the low frequency reflectivity decreases at the edge of the sample chamber in both horizontal and vertical direction of the sample plane [Fig. 4]. To better understand the reflectivity data, the spectra were fitted using a multi-component Drude–Lorentz (D–L) model that consists of a Drude peak and two Lorentz peaks. The fitted curves are shown as solid lines in Fig. 4. The optical conductivities were then calculated from the fitted IR reflectivity curves by using Kramers–Kronig constrained variational dielectric analysis as shown in Fig. S3 in supplementary material. It can be seen that the optical conductivities of the edge parts are significantly reduced compared to that of the central ones. This indicates that the edge part of the recovered sample has significantly lower carrier densities and thus can be said to be less-metallic than the pristine graphene. The observed defect concentration and loss of long-range ordering in the sheared material could be the underlying reason.

The sp² to sp³ transition or diamondization of graphene under hydrostatic compression has been revealed by in situ Raman spectroscopy, resistance measurement, and x-ray diffraction, but it was found to be reversible after relaxation when pressure was released.9,25,26 In contrast, the diamond phase transited from graphite under shear could
be preserved to ambient condition,\cite{Lee2008, Zhang2014} and the diamondization of graphene under shear was also predicted theoretically.\cite{Kim2011} This makes the rDAC experiments a hopeful approach to synthesize the long pursued “diamondene,” the atomically thin diamond. However, in our experiment, although the indentation (ring crack) of the anvil culets (Fig. S4) and the decrease in optical conductivity supported the formation of super-hard phases\cite{Chatterjee2012, Porwal2013} and concentration of sp$^3$ bonding in the sheared material, neither cubic nor hexagonal diamond phase could be found in the recovered sample. With current observations, the potential graphene-diamond transition under shear was still reversible and to break down the graphene sheets. The thermodynamic stability of diamondene was not enhanced by shear treatment.

Due to the geometry of rDAC, it is straightforward to have the impression that the shear stress is in proportion to the distance to the rotational center, while the real stress state is much more complicated because of the sliding between surfaces\cite{Batsanov2012, Batsanov2013} and deformation of gasket. With finite element method modeling, distribution of normal and shear stresses, sample thickness, plastic strain, and more details can be estimated in the rDAC.\cite{V. I. Levitas and O. M. Zarechnyy2014, Fei2011} Furthermore, the recent establishment of delicate stress sensors of N–V color centers in diamond anvils has made it possible to experimentally measure all six stress components under high pressure, thus paving the way for the quantitative study of shear sensitivity of graphene.\cite{Song2019, Gao2019, Paul2016}

In conclusion, the shear-induced defect generation, fragmentation, together with the structural and morphological transitions of graphene powders were demonstrated by Raman spectroscopy and TEM characterizations. IR reflectivity measurements indicated that the electrical conductivity could reduce significantly in the sheared material. Our results highlight the shear sensitivity of graphene under high pressure despite its extraordinary mechanical properties, such as high Young’s modulus and intrinsic strength. The fragile and unstable nature of graphene should be taken into consideration while it is expected to enhance the performance in materials and devices. In the next steps, advanced theoretical calculations and experimental stress calibrations in diamond anvil cells could be applied to estimate the normal and shear stress threshold of the described behaviors of graphene in our work, thus providing deeper understandings of this important yet rarely investigated phenomenon. On the other hand, the potential of rDAC in producing various structures in carbon systems, especially disordered ones, should be noted. Unlike most of the mechanical manipulations presented, shear induces irreversible structural and morphological transitions, which could be an essential factor in bandgap engineering of graphene and the fabrication of diamondene.

See the supplementary material for the geometry of rDAC. Raman spectra analysis, optical reflectivity data, and photomicrograph of anvils after experiments.

M.Y. thanks Lingkong Zhang and Kexin Sun for helpful discussions and Yanping Yang for technical support. This work was supported by the National Natural Science Foundation of China (NSFC) under Grant No. U1530402.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

REFERENCES