

# Large bandgap of pressurized trilayer graphene

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**Graphene-based nanodevices have been developed rapidly and are now considered a strong contender for postsilicon electronics. However, one challenge facing graphene-based transistors is opening a sizable bandgap in graphene. The largest bandgap achieved so far is several hundred meV in bilayer graphene, but this value is still far below the threshold for practical applications. Through in situ electrical measurements, we observed a semiconducting character in compressed trilayer graphene by tuning the interlayer interaction with pressure. The optical absorption measurements demonstrate that an intrinsic bandgap of  $2.5 \pm 0.3$  eV could be achieved in such a semiconducting state, and once opened could be preserved to a few GPa. The realization of wide bandgap in compressed trilayer graphene offers opportunities in carbon-based electronic devices.**

graphene | two-dimensional materials | high pressure | electrical transport | bandgap opening

The remarkable physical properties of graphene, such as high carrier mobility, flexibility, and mechanical strength make it a wonder of materials science (1–8). For example, the very high carrier mobility of graphene of  $10,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  has promoted potential applications in high-speed integrated electronic devices. However, unlike silicon semiconductor, the main challenge for graphene-based transistors is the gapless character of graphene (9–19) that results in an impossible on/off field-effect transition and a low  $I_{\text{on}}/I_{\text{off}}$  ratio (18, 19). Considerable efforts have been made to increase the bandgap of graphene, using quantum confinement by patterning graphene in the form of a quantum dot (20), nanoribbon (21, 22), and nanomesh (23), or symmetric breaking and selective control of the carrier concentration in graphene layers by an external electric field (9–17). However, these efforts have disappointed as the maximum bandgap opening ever achieved was only several hundred meV in bilayer graphene. Promisingly, a bandgap of  $\sim 1$  eV was recently opened in nanoporous graphene (24).

Pioneering studies indicated that the electronic structure of few-layer graphene was highly sensitive to interlayer van der Waals coupling (25–27). Breaking the inversion symmetry of Bernal-stacked bilayer graphene has been shown to open a gap and the possibility of tuning the gap energy. The electronic structure of graphene can also be modified by interlayer hybridization, as exemplified in graphene/h-BN and graphene/SiC multilayers (28–32). We pursued an alternate approach of tuning the interlayer hybridization of few-layer graphene with pressure to modulate the electronic structure. The graphene sample on a different substrate has quite different pressure response (33–36). Furthermore, the behavior of graphene on a substrate at high pressure differs drastically from that of freestanding graphene (37), indicating that substrates obscure the intrinsic properties of graphene significantly.

In our study, we directly transferred the graphene sample onto a diamond surface for measurements to avoid the influence of the substrate. However, pressurizing few-layer graphene and in situ examining the change of the electronic structure, taking the electrical measurements as an example, presents many technical difficulties from preparation of defect-free graphene flakes, the

placing of microelectrodes on a tiny piece of atomic layer sample to ensure good contacts in a diamond anvil cell, and the prevention of ultrathin samples from damage under pressure. First, we developed a microwiring technique for in situ high-pressure electrical transport measurements on nanomaterials with only a few layers. A semimetal-to-semiconductor transition was observed in compressed trilayer graphene. Systematic electrical and absorption measurements provide compelling evidence that a large intrinsic bandgap of  $2.5 \pm 0.3$  eV was achieved in mechanically exfoliated Bernal-stacked trilayer graphene under compression.

## Results and Discussion

The critical experimental step is the fabrication of probing electrodes with ohmic contact that are suitable for electrical measurements on nanomaterials at high pressure. For this purpose, we used an advanced experimental technique of patterning Ti/Au film as probing electrodes on the diamond culet with an electron beam deposition method. The electrodes were then extended with platinum foils ( $\sim 2 \mu\text{m}$  in thickness) by careful hand-wiring to ensure stability under compression (Fig. 1). More experimental details on our sample preparation, transfer, and identification of the Bernal stacking order can be found in *SI Appendix*. The resistances of trilayer graphene at  $\sim 0.5$  GPa measured by two- and four-terminal electrodes were  $\sim 1.1$  k $\Omega$  and  $\sim 300 \Omega$  (*SI Appendix*, Fig. S2), respectively. These values are comparable with previously reported results (14), indicating the good quality of the graphene sheet and contacts.

The pressure response of the Bernal-stacked trilayer graphene resistance was investigated at ambient temperature (Fig. 2A).

## Significance

The remarkable physical properties of graphene make it a marvel of materials science. However, the gapless character of graphene makes it impossible to be a strong contender for postsilicon electronics. Opening a sizable bandgap in graphene is hence highly desired. We developed a microwiring technique for high-pressure electrical measurement on nanomaterials with only a few layers. Through in situ electrical and absorption studies we demonstrate that an intrinsic bandgap of 2.5 eV is achievable in compressed Bernal-stacked trilayer graphene. The realization of a wide bandgap in compressed graphene stimulates explorations for the practical application of carbon-based electronic devices.

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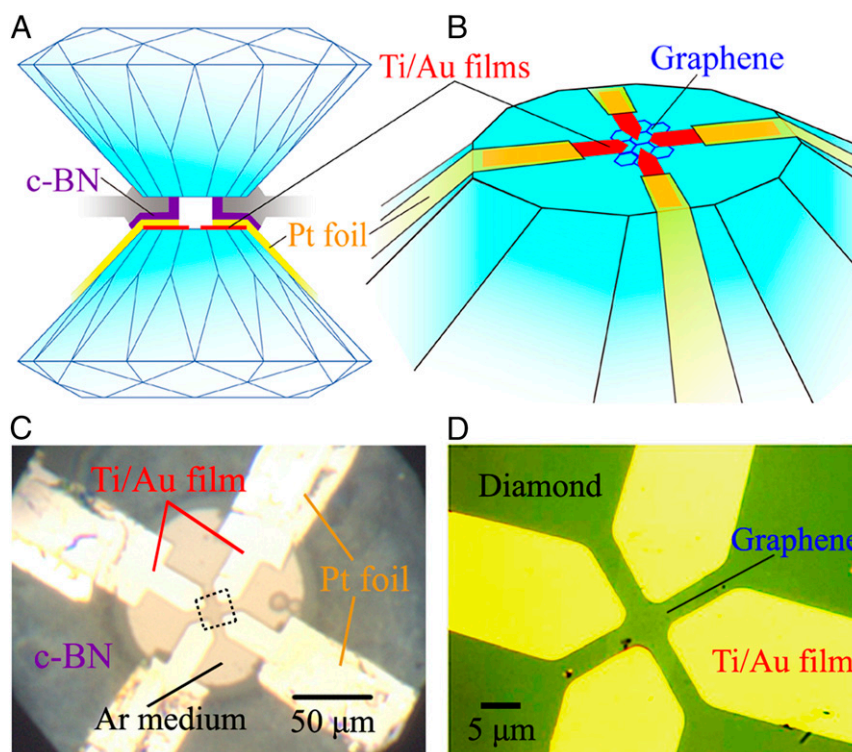
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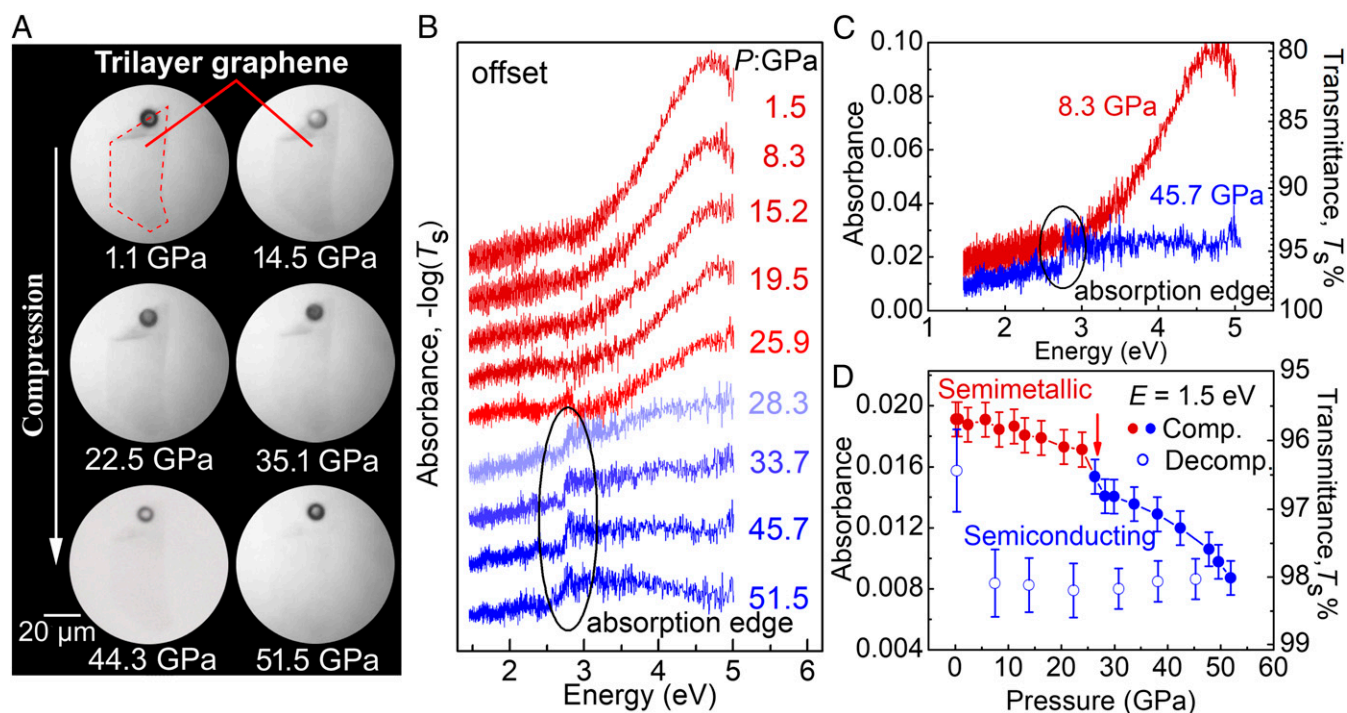
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**Fig. 4.** Bandgap opening in pressurized trilayer graphene. (A) The optical microscope image of trilayer graphene in transmission mode with a white-light source under compression. A ruby ball (black dot) was used as the pressure indicator and visual reference. (B) The optical absorbance patterns of trilayer graphene under compression. The curves are offset for clarity. (C) The absorbance of trilayer graphene at 8.3 and 45.7 GPa without offset. (D) Evolution of absorbance at a photon energy of 1.5 eV during compression and decompression.

in Fig. 4D. High-pressure Raman characterization confirms the reversible transition as well (*SI Appendix, Fig. S6*).

The UV absorbance of trilayer graphene shown in Fig. 4B drops above 28.3 GPa. A weak absorption edge starts to appear at 2.5 eV, and concomitantly the excitonic resonance peak is lost. The sharpness of the edge resembles that of an indirect gap material. However, due to the weak absorption signal of trilayer graphene under pressure, it is difficult to ascertain the nature of the gap. To this end, we adopted the Tauc plots to analyze the nature of the bandgap (42):

$$(A \cdot E)^{1/2} \sim E - E_g \text{ or } (A \cdot E)^2 \sim E - E_g, \quad [2]$$

where  $A$  and  $E$  are the absorbance and the incident energy, respectively. The analysis of experimental results reveals a bandgap of  $2.5 \pm 0.3$  eV in compressed trilayer graphene (*SI Appendix, Fig. S7*). The difference between the optical bandgap and electrical activation energy should be caused by the semimetallic/semiconducting mixed state in compressed trilayer graphene, which is supported by the simultaneously measured electrical and optical absorption results in compressed multilayer graphene (*SI Appendix, Fig. S8*). The activation energy in compressed multilayer graphene is only dozens of meV, although the multilayer graphene becomes partially transparent. Such a difference is also observed in other materials (43, 44). In the case of trilayer graphene, the semimetallic form starts to transform to a semiconducting state above 30.1 GPa but leaves a large percentage unchanged. The more conductive semimetallic state dominates the electrical properties. Hence, no sharp jump is observed in the resistance and activation energy although the bandgap of the semiconducting area is opened from 0 to  $2.5 \pm 0.3$  eV. An increasing percentage of the semiconducting state forms with further compression, resulting in a dramatic increase of resistance and activation energy with pressure. Above 59.0 GPa, a significant fraction of trilayer graphene becomes semiconducting, dominating the

electrical properties. Therefore, the resistance jumps out of the measurable range of the instrument due to the large bandgap.

Previous studies showed that strain/pressure-induced disorder could induce strong Anderson localization and further a metal-insulator transition in materials (14, 45). This type of metal-insulator transition has been observed in graphene when the resistance of graphene is over  $h/4e^2 \approx 6.45$  k $\Omega$  (45). According to electrical transport results, the semimetallic-semiconducting transition of trilayer graphene occurs at around 33.9 GPa with a sheet resistance of several hundred ohms (Fig. 24), much smaller than the resistance quantum,  $h/4e^2$ . Furthermore, the present absorption measurements, which are often less affected by the disorder, also confirm the opening of a gap. Hence, the bandgap observed here is not a consequence of the Anderson localization effect.

By comparing the pressure coefficient of the G-band frequency ( $\partial\omega_G/\partial P$ ) with that of graphite, recent Raman studies showed that a pressure-induced electron transfer occurred in alcohol-immersed monolayer and bilayer graphene, but was absent in trilayer graphene and samples immersed in argon or nitrogen (35, 36). Our Raman results show that the  $\partial\omega_G/\partial P$  of trilayer graphene is about  $4.0 \pm 0.2$  cm $^{-1}$ ·GPa $^{-1}$ , comparable with that of graphite. Thus, no electron transfer occurs between trilayer graphene and the pressure medium, and consequently the electron transfer effect does not cause the bandgap opening in compressed trilayer graphene.

Strain/stress was also applied to open a bandgap of hundreds of meV in graphene (46, 47). In our experiments, it is possible that the quasi-hydrostatic conditions after the solidification of the pressure medium at high pressure may cause strain/stress in the graphene sample. The broadening of the G band of trilayer graphene after decompression (*SI Appendix, Fig. S6*) is indicative of residual stress in trilayer graphene. However, the electrical and optical results show that trilayer graphene returns to its semimetallic state after quenching to ambient conditions although considerable residual stress remains in the sample. Furthermore, solidification of Ar and Daphne 7373 occurs at about 1 and

10 GPa, far from the semimetallic–semiconducting transition pressure of 33.9 GPa. Hence, we believe strain/stress induced by the quasi-hydrostatic conditions may affect the onset pressure of the semimetallic–semiconducting transition but does not play a key role in opening of such a large bandgap in trilayer graphene.

Recently, a diamond-like carbon film was observed in two-layer graphene followed by  $sp^2$ - $sp^3$  rehybridization through nanoindentation and compression methods (33, 34). Previous experimental and theoretical results also demonstrated that graphite transformed into an  $sp^3$ -bonded carbon phase (48–56) under cold compression, although the structure of the high-pressure phase is still controversial. In addition, the value of the bandgap opened in trilayer graphene is comparable with that of the high-pressure transparent phase of graphite (*SI Appendix, Fig. S8*). Hence, we infer that the opening of the bandgap is caused by  $sp^2$ - $sp^3$  rehybridization in pressurized trilayer graphene. Further study is needed to understand the structural evolution of trilayer graphene under compression.

In conclusion, through electrical, IR and vis-UV absorption measurements, we observed an intrinsic bandgap of  $2.5 \pm 0.3$  eV in pressurized Bernal-stacked trilayer graphene by tuning the interlayer coupling with pressure. The high-pressure semiconducting phase could be preserved to a few GPa. The achieved bandgap of

$2.5 \pm 0.3$  eV is much larger than previously reported values of several hundred meV. The bandgap of compressed trilayer graphene is larger than silicon (1.1 eV) under ambient conditions. However, the reverse engineering of fabricating a narrower gap graphene sheet is, in principle, comparatively easier. This study may stimulate explorations of practical graphene-based electronic devices.

## Materials and Methods

Trilayer graphene flakes were mechanically exfoliated from bulk graphite on  $Si/SiO_2$  surface. In situ high-pressure electrical measurements were conducted in a PPMS-9 system with a temperature range of 2–300 K. High-pressure IR absorption measurements were conducted at Beamline 1.4.3 of the Advanced Light Source, Lawrence Berkeley National Laboratory and the Infrared Lab of National Synchrotron Light Source II at Brookhaven National Laboratory. Vis-UV absorption measurements were conducted on a customized Vis-UV microscope system with a photon energy of 1.4–4.9 eV. More details about the experiments and calculations can be found in *SI Appendix*.

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