

Towards controlled graphene properties: Direct synthesis on dielectrics and Tuning via stress

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Interest in graphene since its isolation in 2004 has rapidly escalated. It has been described as nature's thinnest elastic material and its exceptional mechanical and electronic properties make it an extremely exciting material. Within the realm of electronics, it is its one atoms thickness, planar geometry, high current-carrying capacity and thermal conductivity and potential to open a gap when existing as a narrow ribbon that hold particular promise. These features make it ideally suited for further miniaturizing electronics to form ultra-small devices and components for future semiconductor technology.

In order for graphene to realize its potential in electronics various obstacles need to be overcome. One of the more important aspects is its actual synthesis. Various routes exist to synthesize graphene; however, most are not best suited for integration into current silicon technology. The primary routes are through graphite exfoliation, epitaxial graphene, graphene oxide and chemical vapor deposition. Most of these routes require the graphene to be transferred onto a dielectric or, as in the case of SiC, require high temperatures. To use graphene as the basis of field-effect transistors at room temperature one needs to modify graphene's semi-metallic nature so as to open a band gap. When existing as narrow strips (nanoribbons) quantum confinement effects lead to band gap formation. Most band gap engineering routes use multiple lithographic steps to fabricate a graphene device. This leads to contamination and disorder to the flake. Dry lithography-free techniques can help, nonetheless technical difficulties still remain. Another approach is chemical modification, for example, graphene oxide in which hydroxyl and other chemical groups attach to graphene. Although the technique is able to lift the degeneracy of the π band at the Fermi level of graphene, it is difficult to control its electronic properties and avoid defect formation.

A more attractive route to control graphene's properties is through mechanical strain engineering which modifies graphene's geometrical structures. For example, substrate-induced sublattice symmetry breaking in epitaxially grown graphene can give rise to energy gaps; scanning tunneling microscopic studies show evidence for strain-induced spatial modulations in the local conductance of graphene on SiO₂; strain with triangular symmetry induces strong gauge field that effectively act as a uniform magnetic field exceeding 10 T. However most of these experiments are based on graphene layers with fixed static strain. Thus, new techniques allowing for *strain on demand* are quite important in order to intentionally tune and understand the interplay between geometry and electronic properties of graphene.

Uniaxial strain on graphene has been experimentally controlled by bending graphene on a plastic substrate, and using Raman spectroscopy to probe its phonons. However, this bending-substrate geometry is not practical for many experiments. Moreover, uniaxial strain moves the relative positions of the Dirac cones and induces a significant influence in the intervalley double-resonance processes. Thus, biaxial strain, which ensures a planar-substrate geometry and avoids complicate perturbations to the Dirac cones, would be more suited to control the graphene's properties.

Recently we developed a method by utilizing a piezoelectric substrate to control the properties of micro-/nanostructures. [1-2] The same approach has been successfully applied to the strain engineering of single layer graphenes (SLG). [3] We use a 300 μm [Pb(Mg_{1/3}Nb_{2/3})O₃]_{0.72} - [PbTiO₃]_{0.28} (PMN-PT) substrate overgrown with a thin (~20 nm) epitaxial layer of La_{0.7}Sr_{0.3}MnO₃ (LSMO) acting as top contact, see Fig. 1. The backside is coated with gold. A bias voltage V applied to the PMN-PT results in an out-of-plane electric field F which leads to an in-plane strain ϵ_{\parallel} . After the deposition of a 1 μm -thick SiO₂

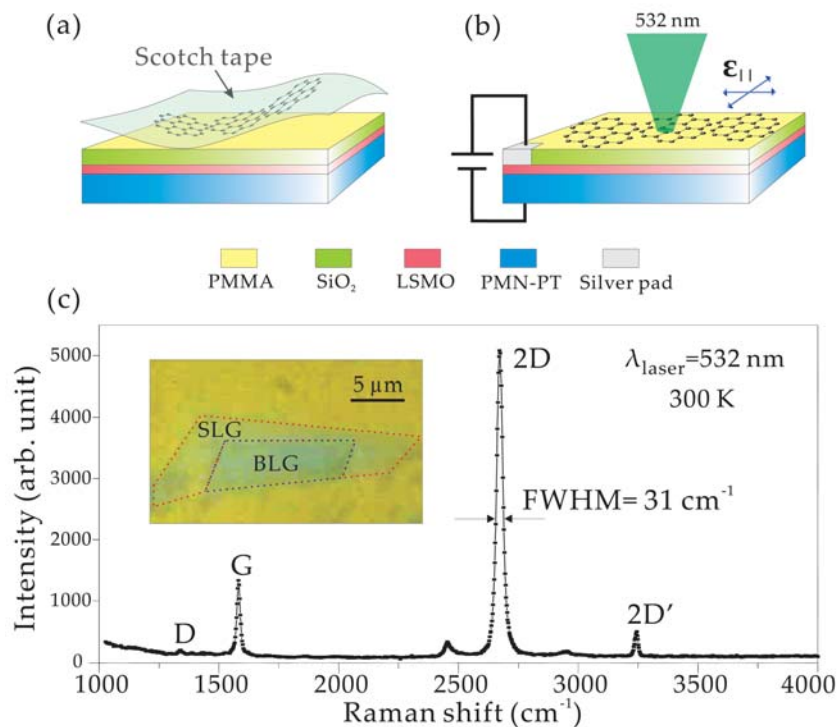


Fig. 1: (a) Mechanical cleavage technique with a scotch tape is used to fabricate graphene which is then transferred, using a thin layer of PMMA as glue, onto a SiO₂/LSMO covered PMN-PT substrate. (b) Schematic drawing of the electro-mechanical device used to apply in-plane biaxial strain to the graphene. (c) Typical Raman spectrum (measured at 300 K) of SLG that is transferred onto a piezoelectric substrate. The inset is an optical microscopy image of the SLG as well as of a BLG (bilayer graphene), indicating the good optical contrast.

layer, the substrate is spin-coated with a 60 nm-thick PMMA (polymethyl methacrylate) layer. We fabricate the graphene samples from highly ordered pyrolytic graphite (HOPG) by mechanical cleavage with the scotch tape technique. The tape is then placed onto the substrate followed by a baking process at 120 °C for 10 min [Fig. 1(a)]. The glue-like PMMA layer becomes solid and the graphene layers are transferred onto the piezoelectric actuator [Fig. 1(b)]. The thickness of the interfacial SiO₂/PMMA layers has been carefully optimized to visualize the SLGs under an optical microscope.

Figure 1(c) shows the typical Raman spectrum (measured at 300 K) of a SLG after transfer onto the piezoelectric substrate. The characteristic Raman features are the so-called *D*, *G*, *2D*, and *2D'* peaks, which locate at 1339 cm⁻¹, 1581 cm⁻¹, 2671 cm⁻¹, and 3245 cm⁻¹, respectively. Many of the measurements on graphene need to be performed at low temperature. The advantage of using PMN-PT crystal is that it is capable of exerting either compressive or tensile stresses at very low temperature. Figure 2(a) presents the color-coded intensity map of the Raman peaks of one SLG sample as a function of the voltage *V* applied to the PMN-PT actuator (measured at 15 K). *V* is swept several times between -550 ~ *V* and 1100 ~ *V* with steps of 20 ~ *V*, to demonstrate the reversibility of the strain tuning technique. The maximum voltage is only limited by our power supply, in fact, with a thinner PMN-PT substrate it is possible to achieve the same out-of-plane electric field *F* (therefore, the same in-plane strain ε_{||} with much smaller voltage. For *V* < 0 the graphene experiences an in-plane tension (T) and the Raman peaks show roughly a linear shift to lower frequency, as reported before. In-plane compression (C) on the graphene is also feasible with this piezoelectric actuator, just by applying a positive voltage *V* > 0 to the substrate. From Fig. 2(a) we do not see any hysteresis over multiple compressing/stretching cycles.

The Grüneisen parameters describe the strain sensitivity of the phonon frequencies, and are thus an important fundamental set of parameters for graphene. There have been

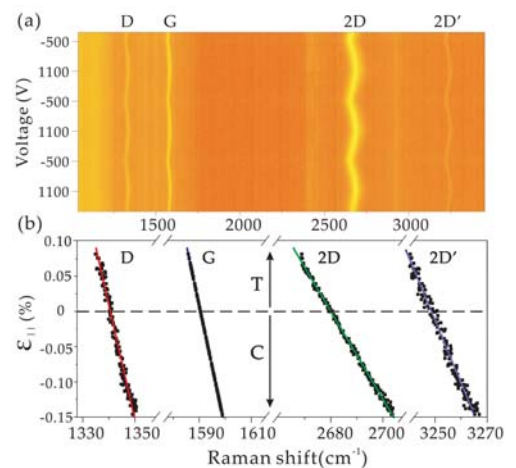


Fig. 2: (a) Color-coded intensity map of the Raman peaks of one SLG sample as a function of the voltage applied to the PMN-PT actuator. The Raman spectra measured at different strain are fully reproducible over multiple compressing/stretching cycles without hysteresis (b) *D*, *G* and *2D* peaks plotted as a function of the biaxial strain ε_{||}, the solid lines are linear fits. Both tensile strain (T) and compressive strain (C) are feasible with the piezoelectric actuator.

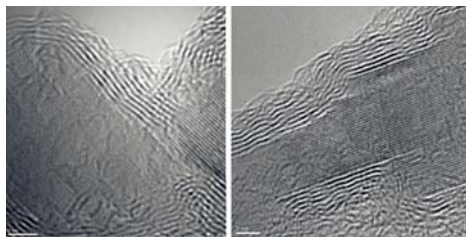


Fig. 3: Multilayer graphene synthesized over MgO from cyclohexane at 775 °C and 100 mbar. The attachment of graphene layers to the (100) oxide step edges can be observed.

several attempts to measure the Grüneisen parameters under uniaxial strain or hydrostatic strain. As discussed before the D , and $2D$ peaks are zone-boundary phonons activated by intervalley double resonances, the relative movement of the Dirac cones changes the phonon wave vector we are probing. Therefore, it would be more suitable to measure the D mode Grüneisen parameter under biaxial strain. After the strain calibration by the movement of G mode,[3] we can plot the strain-dependent shifts of all Raman peaks in Fig. 2(b). All peaks show smooth and linear shifts with biaxial strain, indicating that neither slippage nor corrugation of the graphene occurs during the experiment. Linear fits of all data (under either compressive or tensile strain) yield the Grüneisen parameters $\gamma_D=1.8$, $\gamma_D=2.30$, $\gamma_{2D}=2.98$, and $\gamma_{2D'}=1.73$. Our results are in good agreement with values derived from first-principles calculations for graphene, and experimental values for carbon materials under hydrostatic pressure (for example, carbon fibers and graphite), suggesting that graphene has similar strain dependencies of the Raman frequencies with graphite. There are some differences between our results and the values derived from uniaxial experiments, which might be explained by the reasons stated above. In the experiments we found different strain sensitivities of the D mode and its overtone $2D$ mode, i.e., different Grüneisen parameters. This peculiar phenomenon has been theoretically predicted for two-dimensional graphite. Our experimental studies [3] suggest that the defect-activated D mode is in fact associated with intervalley double-resonance scattering with two different phonon processes. The inelastic scattering by a phonon and the elastic scattering by a defect can happen at reversed time sequences, thus involving phonons with different wavevectors. The $2D$ mode, however, does not need defects for its activation and only involves the elastic scattering process. The linewidth analysis of the D and $2D$ modes at different applied strain supports this conclusion.[3]

Although we have shown the potential of graphene strain engineering via piezoelectric actuation there exists a technical drawback, similar to the for graphene based FETs, namely the need to transfer the material onto the piezoelectric material (or gate dielectric in the case of FETs). Transferring graphene generally leads to damage and impurity deposition which can adversely affect its performance. For example the PMMA gluing layer in aforementioned technique can be a drawback when performing STM analysis. Thus, the fabrication of graphene devices with atomically uniform dielectrics which can provide a uniform electric field and/or uniform stress induction across the active region is attractive. To this end we are developing thermal CVD techniques to deposit graphene directly on dielectrics at temperatures below 500°C. In Fig. 3, a variety of micrographs are seen which show we are able to grow graphene flakes on the surface of magnesium oxide and tune the growth from single to multi layers. The multi layers shown in the overview of Fig. 3(a) are grown from cyclohexane at 775°C and 100 mbar. With these conditions, the reaction stops when the catalyst is fully encapsulated by graphitic layers. We found that the number of layers can increase up to nine. In Fig. 3(c) we highlight the closely spaced parallel lattice fringes of the crystals are those of (100) planes on top of which there is epitaxial graphitic carbon. Furthermore, as indicated by the arrow, the multilayers are ubiquitously anchored into step edges on the (100) surfaces. We propose that, similar to observations in silicon carbide growth, these step sites initiate the growth of graphitic layers. We argue that these step sites are not only nucleation sites, but also growth sites because growth appears to stop once the particle is fully encapsulated. In this regard, this work corroborates previous studies suggesting the cooperative role of oxide supports in the growth of multiwalled carbon nanotubes. We also investigated zirconium oxide to further elucidate the atomic surface structure required for graphitic synthesis on oxides. This catalyst has recently been extensively explored for the synthesis of carbon nanotubes. In our case, the synthesis of graphitic layers is performed on nanocrystallites which following the reaction are in the baddeleyite form and the graphitic layers are anchored on a face with (020) at its surface normal.

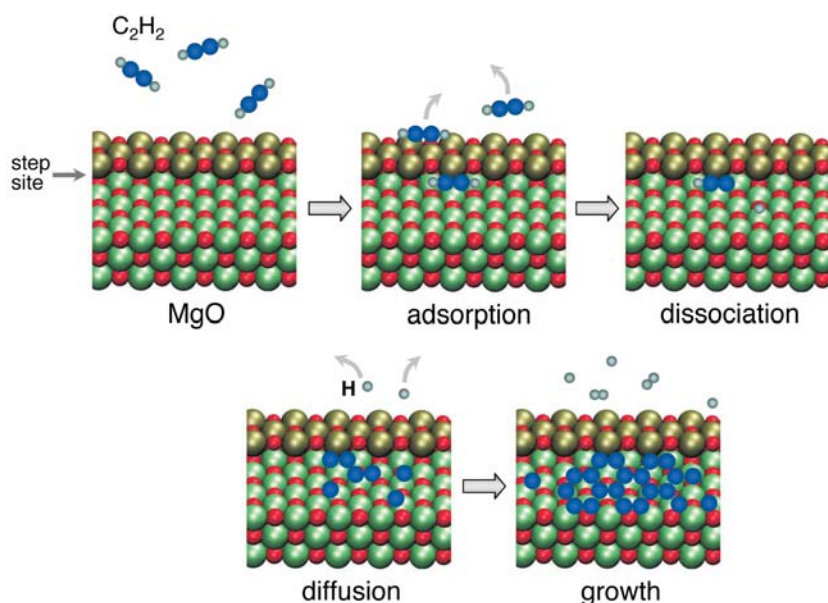


Fig. 4: Proposed growth processes for graphene at step sites on oxides. C_2H_2 is preferentially adsorbed at step sites, where it dissociates, thereafter H diffuses away and finally carbon addition leads to graphene growth. (Blue = carbon, gray = hydrogen, red = oxygen, green/gold = Mg).

Preliminary first principles density functional theory investigations using MgO (100) surfaces with step sites as a model system for oxides show acetylene does not easily adsorb on the surface but does so more readily at steps sites. More over, acetylene dissociation on the surface is shown to be endothermic whilst at a step site the process is exothermic. Complimentary diffusion studies show a diffusion barrier of ca. 0.38 eV for C and 0.2 eV for H over an oxygen atom on the MgO (100) surface. This points to C remaining on the surface whilst H simply flies away. We propose a graphene formation mechanism involving four distinct sub-process; the adsorption of the carbon feedstock molecules on the substrate surface, dissociation of hydrogen from the precursor, surface diffusion and addition of carbon atoms to the network. These sub-processes are shown in Fig. 4.

Conclusions

In conclusion we have achieved several milestones towards the controllable modification of the graphene properties. First, we demonstrate that tunable modification of the graphene Raman modes can be realized by applying external biaxial strains. The experiment utilizes a newly developed piezoelectric actuator-based technique. The key mechanical characteristics of graphene, i.e., the Grüneisen parameters, are studied under biaxial strain. Combining graphene with the piezoelectric actuator promises new opportunities to study and control the strain-related behaviors of graphene, such as the ballistic conductance, the basal-plane hydrogenation, and the thermal conductivity, with unprecedented details. Second, we are aiming at the direct synthesis of graphene on dielectric substrates, which could avoid the use of PMMA gluing layer and provide a uniform electric field and/or uniform stress induction across the active region. Regards the thermal CVD investigations, our experimental and theoretical data indicate high K dielectrics have potential for the catalytic formation of graphene via thermal CVD at temperatures below 500°C.

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[2] F. Ding *et al.*, *Phys. Rev. Lett.* **104**, 067405 (2010).

[3] F. Ding *et al.*, *Nano Letter* **10**, 3453 (2010)

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