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Temperature-induced strain release via *rugae* on the nanometer and micrometer scale in graphene monolayer

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ABSTRACT

Wrinkles are one possible *rugae* phase that can be observed in two-dimensional crystals. Those topographic features, with dimensions ranging from nanometers to micrometers, can be identified in single-layer graphene transferred onto various substrates. When the temperature of the sample is varied, the different thermal expansion coefficients of graphene and its supporting substrate lead to reconstruction of the graphene's topography, which results in spatially inhomogeneous strain and doping. Using Raman spectral mapping, we investigated in situ the temperature dependence (50–300 K) of topographic features in a graphene monolayer grown by chemical vapor deposition (CVD) and transferred onto a Si/SiO_2 substrate. We find that the temperature-induced strain follows the temperature variation of the cubic lattice parameter of the Si substrate. Furthermore, the temperature-induced strain has an unambiguous relation to the topographic reconstruction of the graphene monolayer. We focused on the behavior of two types of *rugae*: 1) large wrinkles with dimensions that are larger than the laser spot size and can be traced directly and 2) nanoscale wrinkles and ripples, which can be identified by changes in the parameters of the principal Raman active bands of the graphene monolayer. In addition, we observed that temperature-induced reconstructions are accompanied by local variation of doping.

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1. Introduction

It is well known that strain can be induced in a thin film during growth due to the interaction between the film and its substrate [1]. Most often, strain is induced by temperature effects related to the different thermal expansion coefficients (TECs) of two materials. It can also occur due to imperfect fit between the lattice parameters of the substrate and the film. During the growth of two-dimensional (2D) materials, which can be considered monolayer films, these effects should be taken into account. Several authors [2,3] have shown that lack of fit between the lattice parameters creates strain in single-layer graphene grown on SiC.

The influence of the different TECs of graphene and the substrate can be observed during the post-growth cooling of graphene grown on Cu [4] or Ni [5] foil using chemical vapor deposition (CVD) or during thermal strain engineering of wrinkles in graphene on Cu [6] or Ir [7].

The metal substrate contracts more while cooling down [8] than graphene [9], which results in overabundance of the graphene and formation of *rugae*. Typical *rugae* include large wrinkles, ripples, creases, folds, ridges, crinkles and crumples. Depending on the growth conditions, *rugae* can be observed at the nanometer and/or micrometer scale [10]. *Rugae* with a length/width aspect ratio (significantly) larger than one that can reach lengths up to many micrometers are called wrinkles. Wrinkles are formed when graphene undergoes in-plane compressive deformation during CVD growth or transfer. This deformation can also be applied during an experiment [11]. On the other hand, *rugae* with a length/width aspect ratio near 1 and dimensions smaller than 10 nm are called ripples. They act as out-of-plane deformations stabilizing the 2D graphene against thermal fluctuations, interaction with the rough surface of the substrate, and defects in the graphene's crystal structure [12]. *Rugae* formations also help avoid strain in the graphene layer; therefore, the strain in the *rugae* is expected to be very low.

Induced strain is not the only factor governing the shape of wrinkles; it acts in combination with the actual boundary conditions,

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such as the edges of a graphene flake [13,14], the grain boundaries of graphene [15], defects [16], or other wrinkles [14]. All these factors determine how *rugae* behave when strain is applied to them.

Additional *rugae* can develop during growth due to replication of the substrate topography [17] or during the transfer process [18,19]. After transferring the graphene to the Si/SiO_2 substrate, *rugae* are still present and can be easily imaged. For example, using atomic force microscopy (AFM) or scanning electron microscopy (SEM), different types of *rugae* can be observed on the micrometer or nanometer scale (see (a) and (b) in Fig. 1).

As shown recently, the TECs of graphene and the Si/SiO_2 substrate are different and have opposite signs [20]. Therefore, the graphene will contract or expand when the sample is heated or cooled, respectively [13,20–22]. Obviously, variations in strain are induced when graphene on a Si/SiO_2 substrate is annealed at a high temperature or cooled to liquid helium temperature.

The effects of temperature were also observed in graphene grown on an Ir(111) single crystal using low energy electron diffraction (LEED) [7] and grazing incidence x-ray diffraction (GIXD) [23]. These experiments show that graphene on Ir(111) is under strain when the temperature varied between 10 and 1300 K and shows temperature-dependent hysteresis. Furthermore, recent investigations of strain in isotopically labeled double-layer graphene revealed that spatial variation of temperature-induced strain is not homogeneously distributed between the top and the bottom layers [24].

Although *rugae* are usually present in graphene grown using CVD, relatively little is known about changes in the electronic band structure of graphene caused by the formation of topographic corrugations. As the effective gauge field follows the local curvature of the graphene, *rugae* can significantly modify the electronic properties of graphene. For example, Zhu et al. [4] investigated electrical resistivity along and across a wrinkle and concluded that there is a significant relationship between the topography and electronic properties of graphene. Obviously, *rugae* are closely related to the reactivity of a graphene layer as the local curvature of the graphene promotes chemical functionalization [25]. Some studies employing scanning tunneling microscopy (STM) [26,27] have suggested that so-called pseudo-magnetic fields could be observed on the wrinkles that form during post-growth cooling.

Recently, using magneto-Raman spectroscopy, Neumann et al. [30] showed that strain variations on the micrometer and nanometer scale can be identified. On the micrometer scale, induced strain variations can be easily observed on spatially resolved Raman maps as the resolution of the technique is comparable to the size of the wrinkles. However, strain variations on the nanometer scale, which are significantly smaller than the laser spot size, can be identified by the line width of the 2D mode of graphene.

In our work, we examine the temperature behavior of two border fractions of a CVD-grown graphene monolayer using Raman spectral mapping. The first fraction is referred to as 'flat' and corresponds to the regions in which the graphene is well adhered to the substrate. The second fraction is referred to as 'wrinkled' and corresponds to the area of the graphene in which topographic corrugations are induced either by growth or the transfer process. Raman spectral mapping allows us to address the relation between strain release and changes in doping caused by topographic variations induced by heating or cooling of a large ($25 \times 25\ \mu m^2$) graphene monolayer without influencing the behavior of the induced topographic corrugations during measurement.

2. Materials and methods

2.1. Growth of the graphene monolayer

The graphene samples were synthesized using CVD as reported previously [31]. Copper foil was heated to 1273 K and annealed for 20 min under a flow of 50 standard cubic centimeters per minute (sccm) of H_2. Then copper foil was exposed to 30 sccm of CH_4 and 50 sccm of H_2 for 20 min, whereafter the copper foil was cooled to room temperature. The grown graphene was then transferred onto a clean Si/SiO_2 substrate using poly(methyl methacrylate) (PMMA) according to procedures reported previously [32]. Residual PMMA resist was removed by thermal annealing at 798 K for 2 h in an Ar/H_2 atmosphere. Gold markers were created on the graphene layer using optical lithography, a Cr (5 nm)/Au (50 nm) layer was sputtered, and then lift-off was performed. Residual resist was removed by thermal annealing at 798 K for 2 h in an Ar/H_2 atmosphere.

2.2. Characterization of the topography

The topography of the graphene monolayer was studied using AFM and SEM. AFM images were measured using a Bruker Dimension Icon with ScanAsyst-Air silicon nitride probes. Measurements were performed in the PeakForce tapping mode with a peak force setpoint of approximately 1 nN. SEM images were acquired using an HR-SEM Hitachi S4800 scanning electron microscope with an acceleration voltage of 5 kV.

2.3. Low-temperature Raman spectromicroscopy

Temperature-dependent (50–300 K) in situ Raman spectral mapping was used to study spatial variations in temperature-induced strain and doping. The contribution of the wrinkled and flat areas was decoupled.

To perform the experiment, the sample was fixed on a low-temperature confocal Raman microscope insert (attoRAMAN, attocube) placed in a Physical Property Measurement System (PPMS, Quantum Design). The sample space was flushed several times with He gas, after which the sample space was evacuated to 5 mbar. The Raman spectra were acquired using a WITec Alpha300 spectrometer with 2.33 eV (532 nm) laser excitation, a laser spot size of approximately 500 nm, a 100× objective (with a numerical aperture of 0.82), and a lateral resolution of 500 nm. The sample was then cooled from 300 K to 50 K, and a Raman map of approximately the same sample area ($25 \times 25\ \mu m^2$) was acquired every 50 K, with lateral steps of 500 nm or 1000 nm in both directions. The accumulation time of each spectrum was 26 s.

The intensity (I), Raman shift (ω), full width at half maximum (FWHM), and ratio of Lorentzian to Gaussian components of the peaks were determined by fitting pseudo-Voigt peak functions to the spectra. To account for wrinkles, we assumed that doping and strain were bimodally distributed [33].

We fit the principal Raman active bands of graphene to pseudo-Voigt peak functions as follows: the D mode was fit with a single pseudo-Voigt line shape, the G mode was fit with three pseudo-Voigt line shapes (G_1, G_2, and D′), and the 2D mode was fit with two pseudo-Voigt line shapes ($2D_1$, and $2D_2$). The G_1 and $2D_1$ components account for the global behavior of the graphene layer, and the G_2 and $2D_2$ components account for local variations in strain and doping in the laser spot area [33]. Finally, we use the G_1 and $2D_1$ components to calculate strain and doping in the graphene monolayer.

3. Results and discussion

3.1. Basic characterization

The topography of the graphene monolayer was first inspected using AFM and SEM. The typical appearance of wrinkles at different scales is shown in Fig. 1a and 1b. Two structures with typical

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