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Formation of wrinkles on graphene induced by nanoparticles: Atomic force microscopy study

B. Pacakova [a, b], J. Vejpravova [a, *], A. Repko [b, c], A. Mantlikova [a], M. Kalbac [d]

[a] Institute of Physics CAS, v.v.i., Na Slovance 2, 182 21, Prague 8, Czech Republic
[b] Charles University in Prague, Faculty of Mathematics and Physics, Ke Karlovu 3, 121 16, Prague 2, Czech Republic
[c] Charles University in Prague, Faculty of Science, Albertov 6, 128 43, Prague 2, Czech Republic
[d] J. Heyrovsky Institute of Physical Chemistry CAS, v.v.i., Dolejskova 3, 182 23, Prague 8, Czech Republic

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ABSTRACT

Wrinkles in monolayer graphene (GN) affect the GN electronic and transport properties. Defined network of wrinkles can be reached by placing the GN on a substrate decorated with nanoparticles (NPs). In order to explain mechanism behind the topographically induced changes of the electronic structure of the GN and to correlate it with the wrinkling, correct description of the GN morphology is of high demand. We propose a methodology based on advanced analysis of atomic force microscopy (AFM) images, which enables determination of the contact/delamination of the GN from the substrate and correlation of the NP density with the character of the wrinkling. Also the relevance of detection of the NPs hidden beneath the GN layer is discussed. The study was carried out on the samples of the GN transferred on the top of SiO_2/Si substrate decorated with metal-oxide NPs with nominal diameter of 6 and 10 nm. The NP density varied in the range of ~20–450 NPs/μm^2. The projected area of wrinkles increased linearly with the increasing NP density, independently on the NP diameter.

1. Introduction

Creation of wrinkles is a property of any constrained thin sheet [1–5], self-similar hierarchy of wrinkling is established both for a thin fabric as well as suspended graphene (GN) [1]. Moreover, GN itself is intrinsically non-flat [6,7], because ideal 2D flat crystals are unstable to thermal fluctuations [6–8]. If the GN is transferred to the substrate, the wrinkles naturally created on as-grown layer are either released or preserved, depending on the morphology of underlying substrate and topography of supported GN which differs from intrinsic corrugations in the free standing layer [2,7,9–11].

In order to develop the GN with distinct level of wrinkles (means to influence density of wrinkles, percentage of the GN layer covered with wrinkles, height of wrinkles, mean orientation of wrinkles and others), two approaches were already presented in the literature: transfer of the GN on elastic substrate [12] or on decorated substrates, covered either with the 50 nm SiO_2 NPs [13,14] or nanopillars of varying height and curvature of the top of pillars in a range of tens-hundreds of nm [15–17].

Wrinkling phenomena in GN appeared to be interesting for several reasons. At first, electronic and transport properties known for non-perturbed GN [18,19] are affected by presence of corrugations [20–24]. The scattering of the charge carriers is influenced by any topographical inhomogeneity in the GN layer [25,26] and is manifested for example as decreased and/or fluctuating carrier mobility and charge density [23,27,28] or creation of electron-hole puddles [20,25,29,30]. Formation of wrinkles, more specifically delamination of the GN from substrate is connected with the doping of the GN layer from the substrate [14,31,32]. Delaminated parts of the GN are the wrinkles themselves, but for the supported GN, smooth parts of the GN among the wrinkles can be also elevated above the substrate. Hence doping can be affected in desired way when the well-defined part of the GN is wrinkled and delaminated [14,32].

Finally, creation of wrinkles is connected with the introduction of the shear strain into the GN layer [4,14,33,34] and hence induced change of the electronic properties of GN [15,24,35–41]. It was reported that for specific strain symmetries (three-axial, C_{3v}), the local potential centers are formed in the GN layers [42,43]. Strain can be induced both into the flat part of the GN

* Corresponding author.
E-mail address: vejpravo@fzu.cz (J. Vejpravova).

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(wrinkles propagating in three different directions can induce such three-axial strain [36,37]) and GN parts directly capping the supporting nanoparticles (NPs) [13]. The consequence of creation of local potential center is the postulation of existence of the so-called "pseudofields" [42,43]. As far the necessity of existence of short-range potential for modification of the magnetoresistance of graphene was reported [44], GN supported by the NPs also seems to be good candidate for examination of this phenomena. Fundamental understanding of the topographical properties of wrinkled GN and their relation to electronic structure is important to assign the underlying mechanism.

In our work, we systematically studied morphology and wrinkling hierarchy of the GN layer covering the substrate decorated with the metal-oxide NPs. The main advantage of the metal-oxide NPs in comparison to metallic NPs is their resistance against annealing, which is required during transfer of the GN. The charge transfer and potential plasmon interactions are also minimized. Such GN covered metal-oxide NP decorated substrates can be used for studies of the transport phenomena in GN due to induced wrinkles only, which would not be possible if the metal NPs were used instead.

We prepared eleven samples of the CVD-grown GN transferred on the Si/SiO_2 substrates decorated with the 6 and 10 nm metal-oxide NPs with surface density within a range of 20–450 NPs/μm^2 and demonstrated that defined wrinkling of the GN can be reached by changing the NP surface density.

We present here the statistical analysis and data processing of the Atomic Force Microscopy (AFM) images of wrinkled GN on decorated substrates and specify relation between creation of wrinkles and the density of the NPs on the substrate. It is shown that delamination of the GN from substrate and preferential orientation of wrinkles can be determined just with the use of the AFM. Relevance of detection of the NPs beneath the GN is also discussed.

2. Material and methods

2.1. Preparation of the GN@NPs samples

The samples of GN supported by the NPs were prepared by spin-coating of the available NP dispersions with varying concentration on the substrates and subsequent transfer [45] of the CVD grown GN layer [46,47] on the top. Two batches of the samples were prepared, first batch (Batch 1) with use of the $CoFe_2O_4$ NPs with the nominal diameter ~ 6 nm prepared by Repko et al. [48] (the GN_1-GN_6 samples), second batch (Batch 2) with the γ-Fe_2O_3 NPs with the nominal diameter of 10 nm prepared by Salas et al. [49] (GN_7-GN_11 samples).

The $CoFe_2O_4$ NPs were originally prepared by the hydrothermal procedure in oleic acid–water–pentanol system described in Ref. [48], modified by DMSA to get hydrophilic solutions of the NPs. γ-Fe_2O_3 NPs were prepared by the thermal decomposition of iron organic precursor ($Fe(acac)_3$) [49], hydrophobic NPs were then dispersed in hexane. In preparation of both batches of samples, the 30 μl of the NP dispersions of different concentrations were dropped on the $SiO_2/Si(100)$ substrate and spun at 2500 rmp for 50 s. The first batch of the samples was exposed to 15 min annealing at 300 °C in air prior to the GN transfer, second batch was annealed after transfer of GN. GN was prepared by the CVD growth on the copper foil by process reported in Ref. [47] and subsequently transferred to decorated substrates with use of the PMMA [45]. The GN_1 and GN_7 samples were not used for further studies of the induced wrinkling because of the impossibility of reliable analysis.

2.2. Atomic Force Microscopy (AFM)

The AFM images were captured at ambient conditions with the Veeco Multimode V microscope equipped with the JV scanner, with the resolution of 1024 lines. Fresh RFESP probe (k = 3 N/m, f_0 = 75 kHz, nominal tip radius = 8 nm) by Bruker was used for each sample, preserving the wear of the tip comparable. All images were captured in the standard tapping mode in order to minimize force acting on the GN layer. The scan rate was 0.8 Hz. The amplitude setpoint was chosen as near to the free amplitude as was possible. Several images of decorated substrates as well as the GN layer were captured, with the maximum image size of 25 μm^2. The captured images were processed afterwards in the Gwyddion software [50] by 1st or 2nd order flattening and scars correction. The root-mean square roughness [51,52], σ_p of the bare substrates, decorated substrates, smooth and wrinkled parts of the GN layer were determined.

The objects on the surface (both the NPs on substrate and wrinkles on the GN layer) were located by height and slope threshold masking method [50,53,54], setting the threshold height and slope for each image individually. Masking of selected objects/regions on substrate enables to evaluate properties of masked and unmasked parts of the image separately.

Grain analysis of masked images (Gwyddion) was used to determine the number of the NPs in the image of decorated substrate of defined area. Then the surface NP density, ρ_{NP} was calculated. The histograms of equivalent disk radius, r_{eq} were created for localized NPs, distributions of the r_{eq} values were refined with the log-normal distribution function. Mean diameter of the NPs for each individual sample was determined. Moreover, the maximum heights of the individual NPs, z^{NP} were collected, refinement of resulting histograms with the log-normal distribution function provided mean height of the NP, z_m^{NP}. The (x, y) coordinates of each single localized NP were used to calculate the mean interparticle distance, d_{real}^{mean} by the triangulation method [55]. The triangulation method was implemented in the Matlab code for simulations of the random distribution of the NPs in defined area (see section 2.3.).

For the images of the GN layers, the value of the masked projected area attributed to wrinkles, A_{wr} was determined for each image.

In further analysis, we used basic property of the AFM image, which is an array of pixels with the (x, y, z) coordinates. It is easy to collect the z coordinates for whole image and to create the height histogram (z-histogram) for whole image as well as masked and unmasked regions separately. z-histograms were created both for decorated substrates and the GN layers. Images of the GN layer used for creation of z-histograms were chosen to always contain at least small rupture in the GN in order to "see" the substrate beneath and set the zero height of the image as the minimum height of the substrate. z-histograms of whole images and images with excluded masked regions were constructed in order to specify the heights attributed to the objects (NPs or wrinkles) and the flat parts of images (substrate, smooth parts of the GN).

The height-height autocorrelation functions (HHCF) both of decorated substrate as well as compact GN layer were generated for each individual sample, obtained curves were compared with the Gaussian HHCF [52,56].

Two-dimensional fast Fourier transformation (2D FFT) was applied to images of compact GN layers in order to determine the sharp edges at the image and hence identify local symmetry of the wrinkles and their preferential orientation.

In order to locate the NPs beneath the GN, the analysis of phase images was done. Areas of the images with elevated phase values were attributed to the NPs. Particle search was done by the threshold masking method. Details are summarized in the