Topography and electro-optic properties of graphene layers measured by correlation of optical interference contrast, atomic force, and back scattered electron microscopy

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Abstract

It is investigated, how optical interference contrast microscopy and atomic force microscopy (AFM) can serve as complementary techniques to EM in visualization, in profiling, and in measurement of conductivity of graphene on conductive and isolating substrates.

Monochromatic bright field microscopy can indicate the number of graphene layers and thickness if the graphene is on a thin optically resonant film [1,2,3]. Frequently used is a 300 nm SiO_2-layer on silicon. The method has not enough thickness resolution to resolve graphene on samples without resonant layer, e.g. on native SiO_2-layer (typical 2 nm thickness) on silicon, or on a GaAs substrate [4]. By contrast graphene on GaAs is resolved by imaging ellipsometry [5], because ellipsometry by definition is phase sensitive. Besides imaging ellipsometry spatial light interference microscopy (SLIM) [6], white light interferometry (WLI) [7] and total interference contrast (TIC) [8] are another phase sensitive methods for optical graphene profilometry.

In TIC one obtains interference between two slightly shifted optical waves carrying image information of a graphene flake (fig. 1a). The phase shift of both beams is measured by the fringe shift and is normalized on the fringe to fringe period. Just as in ellipsometry, by means of the optical model, the phase shift can be converted into height or other optical parameters of the materials of layers and substrate. TIC has some advantages with respect to WLI: TIC does not require expensive Mireau-objectives; TIC can use standard microscope objectives, which offer higher numerical aperture and higher lateral resolution; Mechanical stabilization of the interferometric paths is not required in TIC. The phase profile is recorded across one flake of graphene displayed in Fig. 1(a), in which the existence of mono- and bilayer is verified by Raman spectroscopy. We obtain all typical graphene features such as strong G mode at 1580cm-1 and the presence of a 2D peak (around 2700cm-1, fig.1c), which shape and position allows determination of the layer number [9,10,11]. The corresponding Raman traces taken at these parts of the flake are reproduced in fig. 1c. Especially the intensity ratio I(2D)/I(G) between the 2D peak and the G peak as well as the different shapes of the 2D peak are typical fingerprints of mono- and bilayer graphene in positions 'ML' and 'BL' in fig. 1a. The phase is measured along the marked black line (fig.1a) across the graphene flake. The height profile in fig.1b. is obtained as a result of fitting the measured phase with the modelled phase point by point along the cross section. In the optical model we assumed thickness 300 nm of SiO_2 layer, and for graphene refractive index n = 2.0 and extinction k = 0.5, where n and k were obtained from the dielectric constants ε_1 and ε_2 measured by ellipsometry on a sample like ours [5]. Our measured height of graphene 0.35 nm (fig.1b) is in agreement with the expected value [12].

In order to study the effect of different substrates on the properties of graphene, another flake, in this case a thicker layer stack of graphene on silicon with only 2 nm native SiO_2, was investigated by correlative microscopy of TIC and the in-situ SEM/AFM combination. By means of a suitable bias voltage on the filtering grid in front of the energy selective backscatter detector, the height variation across the graphene layers (fig.2a) is resolved: Most backscattered electrons (BE) are generated within the silicon substrate and the oxide layer. The amount of those BE, which are lost in graphene, increases with the height of the graphene layers. AFM measured the height of the layer stack in positions A: 9 nm and B: 13.5 nm in vacuum. The measured heights were held constant in the optical model, from which the phase difference vs. height is calculated under variation of the complex refractive index $N \equiv n + i\,k$ of graphene (fig.2b). One is looking for the best fit of the measured phase differences in A, B, and the origin of the plot: The phase differences read from the phase profile in A: 5° and at B: 10.6° are perfect matched with N = 3.9 + 9.2 i (ε=-67+72i) for the graphene, but not as expected with the N of graphene or graphite (fig. 2b). Consequently the optical conductivity, which is proportional to the imaginary part of ε, is about 38 fold increased for the graphene layer stack on 2 nm SiO_2 film with respect to 300 nm SiO_2 film, and about 10 fold increased with respect to thick graphite. The observed increased conductivity and the strong negative real part of ε are both mathematically consistent with the dielectric Drude function, which describes a damped harmonic electron oscillation with zero eigenfrequency and nonzero effective electron mass. The conductivity $\sigma(\omega) \equiv -i\omega\varepsilon(\omega)$ associated with the Drude function represents intra-band electron transitions [13] in graphene, which add to the inter-band transitions existing in the ideal suspended graphene, which possesses zero effective electron mass and frequency independent conductivity [14]. It is plausible, that the electrons in graphene obtain their effective mass by interaction

with the silicon through the 2 nm thin SiO_2 film. We imagine, that the charge carrier of graphene is oscillating versus the lattice of silicon ions of the silicon substrate. The force decreases, in agreement with our observation, with the distance between electron and ion defined by the SiO_2 thickness. The oscillator model of the electron is a simple model of field-induced conductivity. This effect is known from FETs, where the conductivity of the channel between source and drain is field-induced by the gate voltage.

In conclusion we find, that graphene adjusts its optical reflectivity just as a chameleon on the reflectivity of its substrate. Related interaction of graphen with substrate has been observed recently [15,16].

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Figures

Fig. 1 (a) Interference contrast image and (b) height profile corresponding to the dashed line across the graphene flake, (c) Raman measurements of the mono- and bilayer part of the flake given in (a).	Fig. 2.a. SEM of graphene layer stack on conductive silicon with 2 nm native, height measured by AFM in vacuum at position A: 9.0 nm and at position B: 13.5nm	
	b. optical phase as a function of graphene layer stack height, the complex refractive index N is the model parameter adjusted, in order to fit the measured phases in positions A: 5° and B: 10.6° c. phase profile converted into height of graphene stack by the phase function (black line) in figure b.	