

APPLICATION NOTE

Graphene and Graphene Oxide

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ABSTRACT

Graphene and graphene oxide layers are localized and characterized on different substrate materials by means of the spectroscopic imaging ellipsometer nanofilm ep3se. The thickness and the dispersion functions of the refractive index n and of the extinction k of a few μm -wide layers are obtained. The results of imaging ellipsometry agree with the results obtained by the combination of AFM and confocal microscopy within the error margins. By contrast to the latter methods the measurement time is much shorter with imaging ellipsometry.

Introduction

Graphene is one two-dimensional layer of the three-dimensional graphite. The interest in graphene is supported by the remarkable electronic properties of this material and potential electronic applications. It exhibits high crystal quality, ballistic transport of electrons on a submicron scale (even under ambient conditions) and its charge carriers accurately mimic massless Dirac fermions. Graphene samples currently used in experiments are usually fabricated by micromechanical cleavage of graphite, i.e. slicing this strongly layered material by gently rubbing it against another surface. Although graphene is probably produced every time one uses a pencil, it is extremely difficult to find small graphene crystallites in the 'haystack' of millions of thicker graphitic flakes which appear during the cleavage. In fact, modern visualization techniques (including atomic-force, scanning tunneling and electron microscopies) have difficulties in finding graphene because of their extremely low throughput at the required atomic resolution or the absence of clear signatures distinguishing atomic monolayers from thicker flakes. Even Raman microscopy, which recently proved itself as a powerful tool for distinguishing graphene monolayers, has not yet been automated to allow search for graphene crystallites. Moreover, the differences between two layers and a few layers of graphene sheets are not obvious in Raman spectra.

Although atomic force microscopy (AFM) measurement is the most direct way to identify the thickness of graphene, the method has a very slow throughput and may also cause damage to the crystal lattice during measurement. Furthermore, the interpretation of the obtained thickness values is hard to interpret, due to adsorbents on the sheet under ambient conditions^[1].

Until now, the only way to isolate graphene is to cleave graphite on top of an oxidized Si wafer and then carefully scan its surface in an optical microscope^[2]. Thin flakes are sufficiently transparent to add to an optical path, which changes their interference color with respect to an empty wafer. Contrast spectra and contrast images on SiO_2 or Si_3N_4 or PMMA films can be used to determine the number and optical properties of graphene layers^[2,3]. The same inspection method applies to layers of graphene oxide, which is a

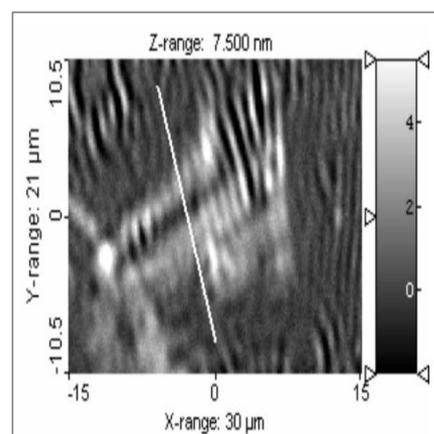


Fig. 1: Thickness map of graphene layer on GaAs substrate, calculated in a few seconds from the Delta map in fig. 5.

material that can be exfoliated to form stable colloidal suspensions in water. At an appropriate concentration, evaporation of droplets of such a colloidal suspension on a surface yields individual graphene oxide layers. This material draws a great attention as a filler of nano-composites as well as a paper-like material. As an alternative for graphene a few layers or even one single layer of graphene oxide is promising. In this application note it is demonstrated, how thickness, refractive index and extinction of graphene oxide are measured by imaging spectroscopic ellipsometry on a single layer of graphene oxide on $\text{Si}_3\text{N}_4/\text{SiO}_2/\text{Si}$ -substrate^[4]. After that we apply this technique to few layers of graphene on GaAs-substrate^[5].

METHODS AND MATERIALS

Samples

1. single layer of graphene oxide on thick film of Si_3N_4 on Si wafer substrate
2. few layers of graphene on GaAs wafer

Instrumentation

Spectroscopic Imaging Ellipsometer EP3SE, filter set with ± 20 nm bandwidth, 5 x and 50 x objectives

Tasks

- Quick search for layers of graphene and graphene oxide.
- Identification of the layered material through its refractive index and extinction
- Measurement of thickness of the layers

Steps of Evaluation

- Record ellipsometric contrast images to identify sheets of graphene and graphene oxide.
- Set regions of interest (ROIs) on the sheet and on the environment. Record spectra of ellipsometric observables Delta/Psi as average over each ROI. Fit the spectra, and obtain the thickness, refractive index, and extinction of the sheet as free fit parameters.
- For high resolution small scale inspection record Delta/Psi maps and obtain one map of thickness of the sheet.

MEASUREMENTS

Graphene Oxide

The sheets of graphene and graphene oxide are easily found in the real time contrast image of the nanofilm_ep3 (fig. 2 and 3). The spectrum of Psi (fig. 4) on graphene oxide has been recorded as mean value of the four ellipsometric zones in order to provide the best accuracy. The spectrum is fitted based on a simple optical model, which contains one optically isotropic layer of graphene oxide on the substrate. The substrate underneath graphene oxide has films of Si_3N_4 and natural SiO_2 on a silicon wafer. One spectrum is recorded on the substrate next to the graphene oxide sheet. Out of the fit of the spectrum one obtains the thickness of both films of Si_3N_4 69.39 ± 0.04 nm and SiO_2 2.4 ± 0.3 nm. Those parameters are kept constant in the model, when the spectrum of ROI 0 fig. 2 on the single graphene oxide layer is fitted for thickness, refractive index and extinction of graphene oxide. The results are compared with measurements by atomic force microscopy (AFM) and confocal microscopy (CM) in tab.1.

Graphene

Spectra of Delta and Psi were recorded in the ROIs of fig. 3 on graphene sheets on a GaAs-substrate. The spectra of ROIs 0 and 2 located on the bare GaAs were fitted for the

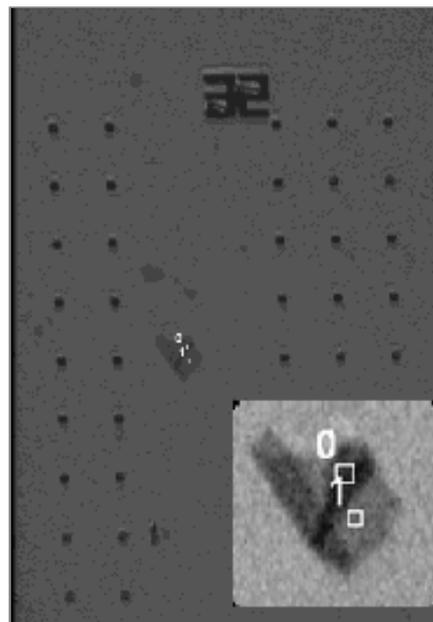


Fig. 2: Ellipsometric micrograph taken at a wavelength of 517 nm with regions of interest (ROIs), over which Delta and Psi are integrated. 5 x objective, 0.8 mm x 1.2 mm field of view of large image. The inset is a magnification of the GO sheet, size 50 μm x 50 μm . Marked rectangles are regions of interest, over which Psi is integrated. The area noted by '0' is on top of the triple layer and the area noted by '1' is a single layer.

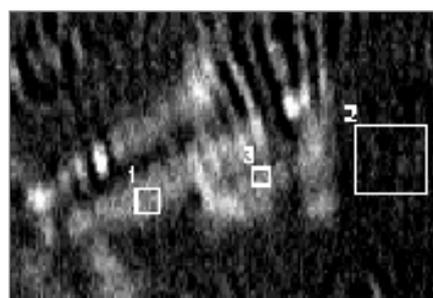


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dispersion functions of refractive index $n(\lambda)$ and extinction $k(\lambda)$. Those functions were then used to fit the spectra of ROIs 1 and 3 on graphene for thickness, refractive index and extinction^[5]. In order to obtain the thickness profile with high lateral resolution (fig.6), one microscopic map of Delta was recorded (fig.5) and converted into the map of thickness of the graphene layer (fig. 1). The obtained refractive index and extinction^[5] were kept constant for the conversion from Delta into thickness. If the optical parameters should vary over the graphene sheet, it would be an option of the nanofilm_ep3 to record and fit a spectrum of maps of Delta and Psi. The spectrum of maps would be fitted by the same optical model, which was used to fit the spectra of the ROIs. In that way, maps of refractive index, extinction, and thickness can be obtained.

Results

Let us compare the imaging spectroscopic ellipsometry with FM and CM: The AFM must measure the thickness, in order to enable to obtain the refractive index and extinction from the CM, because the CM alone has not enough accuracy to measure all three parameters, thickness, refractive index, and extinction independently from each other. The combination of AFM and CM on the same graphene oxide sheet requires a mechanism for localisation of the sheet in the measured spots of both devices. By contrast such a mechanism is not required with an imaging ellipsometer. The nanofilm_ep3 measures optical properties and thickness profiles and maps within a view minutes. By contrast to AFM, imaging ellipsometry is quick and non-destructive.

The agreement of the results of both methods on graphene oxide in tab.1 is within the error margins. We have applied the imaging spectroscopic ellipsometry also on several graphene sheets on different substrates. It is investigated how universal the extinction and refractive index of graphene is^[5].

Conclusion

With the imaging spectroscopic ellipsometer EP3SE one can measure the dispersion functions of refractive index and extinction, and the film thickness of graphene and graphene oxide. The measurement with the nanofilm_ep3 is quicker than alternative methods, i.e. the combination of AFM and CM, or the combination of an optical microscope with AFM/SNOM and Raman-spectroscopy. And the nanofilm_ep3 is also cheaper.

References

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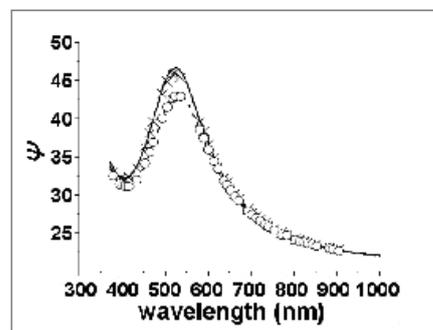


Fig.4: Spectra of Psi at 60° angle of incidence as a function of wavelength, recorded on thermally treated single layer of graphene oxide in ROI 1 of fig. 1, measured Psi of substrate (x), material (o), and fitted Psi (solid line), taken from [4].

Material	ROI	Method	Thickness [nm]	refractive index n	Extinction k
graphene oxide	1	Imaging spectr. ellipsometry	1.3 ± 0.3	1.9 ± 0.2	0.48 ± 0.07
graphene oxide	1	AFM/Confocal Microscopy	1.3	1.8	0.45

Fig.4: Spectra of Psi at 60° angle of incidence as a function of wavelength, recorded on thermally treated single layer of graphene oxide in ROI 1 of fig. 1, measured Psi of substrate (x), material (o), and fitted Psi (solid line), taken from [4].

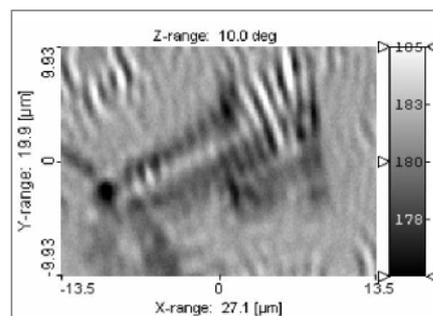


Fig.5: Detail of the Delta map obtained at 502 nm wavelength and 50° angle of incidence for the field of view given in fig. 3 on the graphene layer on GaAs wafer, recorded in one minute.