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Direct synthesized graphene-like film on SiO_2: Mechanical and optical properties

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Abstract. Exploiting CVD technique for carbon deposition from C_2H_2+H_2+N_2 mixture, a graphene-like film synthesized directly on SiO_2 surface of SiO_2-Si structure was obtained. The graphene-like film was grown under thin Ni layer that is easy exfoliated from graphene-SiO_2-Si structure. Surface of the film was sufficiently smooth and reveals no winkles and holes; it has a good homogeneity and perfect adhesion to SiO_2 layer. Studying the micro-Raman spectra showed a graphene-like structure of the film; using atomic force microscopic technique, the thickness of film was determined (0.6 nm). Using spectroscopic ellipsometry and simple Cauchy model enabled us to estimate optical parameters of this graphene-like film.

Keywords: directly grown graphene on SiO_2, chemical vapor deposition, micro-Raman, AFM, spectroscopic ellipsometry.

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1. Introduction

Graphene film on dielectric structure is a basis to form Si compatible nanoelectronic devices. Nowadays, the main method to create a qualitative graphene film on a dielectric substrate is low-pressure CVD on Cu foil with following transferring the graphene film onto the dielectric substrate [1]. However, this method has several steps, which leads to pollution of the film by organic inclusions. The synthesis of graphene film directly on different dielectric layers opens wide possibilities for employment of this very promising material in silicon nano- and optoelectronics. In recent years, several methods for graphene synthesis directly on dielectric substrates were proposed: high-temperature CVD synthesis of graphene on dielectric surface via the sacrificial copper film [2]; high-temperature CVD synthesis on dielectric surface under the Ni film which was preliminary high-temperature annealed in He ambient [3]; direct CVD synthesis of nanocrystalline graphene flakes on dielectric [4]; CVD graphene film growth on dielectric surface using remote catalyzation, which includes employing floating Cu and H atoms for decomposition of the hydrocarbons [5]. The very attractive approach is direct synthesis of graphene film on dielectric under the Ni layer, since this method allows us to avoid the lithographic process on graphene film and replace them by a simple lithographic process on nickel.

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In this paper, we have presented the results on synthesis of uniform graphene film under the Ni layer on SiO_2/Si structure, without special additional annealing, which has morphological, electrical and optical properties suitable for fabrication of photoelectrical devices.

2. Experimental samples and measurement techniques

The structure of Ni-SiO_2-Si with the Ni thickness close to 110 nm and the SiO_2 thickness 420 nm was located in CVD reactor with hot walls. Heating the structure in flow of H_2(57%) + N_2(43%) gas was performed at 760 °C, and maintaining the temperature for 10 min C_2H_2 was introduced into the reactor. After that, the structure was cooled in nitrogen atmosphere during 5 min to 550 °C. The Ni films was covered by "moss" from carbon whiskers, and the Ni film with carbon whiskers was easily laminated from SiO_2-Si structure exposing the surface with dense carbon film (Fig. 1).

The surface morphology of the synthesized films was studied using optical microscopy (Axioscop 2 MAT, Carl Zeiss); surface topography and viscoelastic homogeneity of the films were investigated by Dimension 3000 NanoScope IIIa scanning probe microscope operating in the AFM tapping mode [6]. The tapping mode provides substantial reduction of contact force, improves resolution and could be used for estimation of surface homogeneity by simultaneous mapping of height and phase images (difference between phase angle of tip oscillation excitation signal and AFM tip response [7]). Chemical composition and local structure of the films were analyzed using micro-Raman spectroscopy (mRS, triple Raman spectrometer T-64000 Horiba Jobin-Yvon, equipped with electrically cooled CCD detector and excitation by the 514-nm line of an Ar-Kr ion laser). The resistivity of the films was measured using the four-probes methods with Agilent 4156C Semiconductor Analyzer. Optical constants of the deposited films were determined by spectroscopic ellipsometer M-2000 with rotating compensator from J.A. Woollam Co., Inc. in the wavelength range from 200 up to 1600 nm.

3. Results and discussion

3.1. Raman spectroscopy measurements

Raman spectra in the range of Raman shifts from 1250 to 2800 cm^{-1} measured for the studied samples are presented in Fig. 2. The clearly pronounced G band (~1600 cm^{-1}) that indicates hexagonal graphene lattice formation [8] and appearance of 2D band (~2700 cm^{-1}) that originates from the two-phonon double resonance Raman process [9], are Raman signatures of sp^2 graphitic materials [8]. The large D band (~1335 cm^{-1}) indicates the high defect densities within the as-synthesized thin films. So, we can name this film as graphene-like (GrL) material.

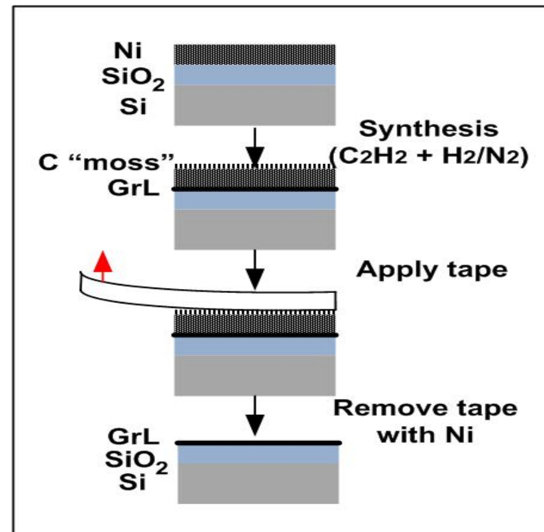

Fig. 1. Schematic description of the process, indicating the graphene-like film growth below Ni film under CVD conditions, and then removal of Ni by using the adhesive tape.

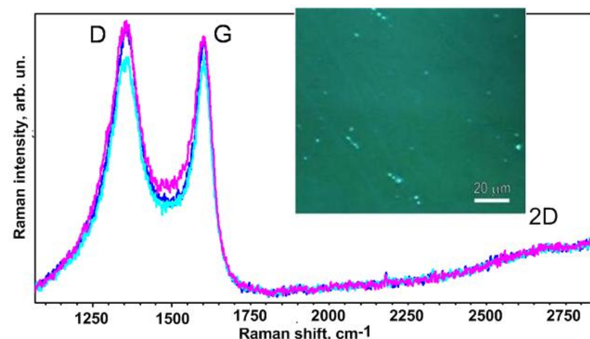

Fig. 2. Raman spectra measured in different points of the carbon film. Inset: light microscopy micrograph of the graphene-like film.

3.2. Atomic force microscopy

Surface of the film was sufficiently smooth, and optical microscopy reveals no winkles and holes (inset in Fig. 2) with the value of root mean square (RMS) surface roughness close to 0.3 nm, which was obtained from AFM measurements (Fig. 3). AFM reveals a nano-granular fine structure of film. The mean value of grain diameter equals 10 nm with the standard deviation 2 nm (note, this value over estimated due to the tip effect and could be smaller). The sharp and clear edge of film makes it possible to measure film thickness and estimate elasticity relatively to the underneath SiO_2 layer (lower-right corner of AFM image). Two maxima in the height map histogram (Fig. 3c) indicate the averaged film thickness value about 0.6 nm and phase shift histogram (Fig. 3d) maxima from softer film and stiffer substrate indicate difference 1.5°. This phase shift is constant over

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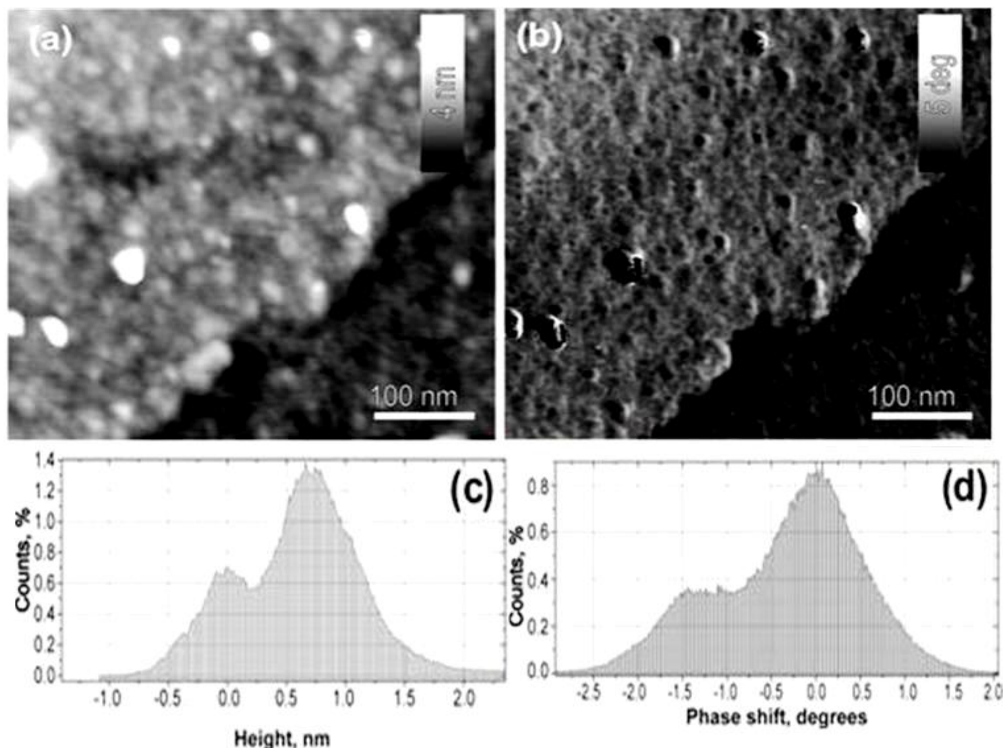

Fig. 3. Topography (a) and phase contrast (b) AFM images of the graphene-like film edge on SiO_2. Corresponding histograms of height and phase shift shown in (c) and (d).

a large area of AFM scans (not shown here), which testifies good homogeneity of film. AFM scratch test of film confirms perfect adhesion and plastic nature of film deformation under AFM tip.

Resistivity of the graphene-like film determined using the four-probes method [10] was in the range from 200 to 350 kOhm/sq. For control measurements, we used single layer CVD graphene on SiO_2 layer (385 nm thickness) fabricated by Graphene Supermarket Co [11] that showed the value of resistivity about 470 Ohm/sq., which was comparable with that of our measurements obtained on these films by using the transmission line technique [12].

3.3. Spectroscopic ellipsometry

Optical constants of the deposited film were determined using reduction of ellipsometric data to the model of a silicon substrate covered with the silicon oxide film and the deposited film with the thickness of 0.6 nm determined from AFM measurements. The bare part of the substrate was measured separately, and the thickness of silicon oxide was determined from these measurements equaled to 415.7 nm. The results of spectroscopic measuring the ellipsometric parameters for SiO_2-Si and GrL-SiO_2-Si structures are presented in Fig. 4. The presence of graphene-like film on the surface of SiO_2 layer noticeably changes the ellipsometric spectra of the structure shifting and changing the contrast of the interference structure created by silicon oxide (Fig. 4c, d).

Fixing the thickness of the GrL film to the result of AFM (0.6 nm) allows to determine optical constants of the film independently for each spectral point. Unfortunately, such a direct determination of optical constants independently for each spectral point gave no appropriate results and could not be interpreted as any regular dependence for solid material. It may be explained by strong nonlinear dependence of ellipsometric data on optical parameters of the system, so the reverse problem has multiple solutions. Also, it is produced by the standard problem of the optics of thin films, namely: measurements of only the so-called "phase" thickness instead of separate thickness and optical constants as well as strong correlation of ellipsometric data for these films [13]. So, only smooth dispersion models were applied for the data reduction. Detailed analysis and comparison of different models will be given in the forthcoming article. Here, we restricted our discussion only by general results.

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The best fitting was obtained using the simple Cauchy model describing the behavior of the refractive index. The standardly used in WVASE software Cauchy model also includes Urbach absorption, which in its definition describes exponential tail of the absorption at energies lower than the bandgap. Literal Urbach tail of the absorption index exponentially decays with wavelength, so the model has the constant $\beta > 0$, where β is the fitted coefficient in the exponent describing the dispersion. It is interesting to note that application of the standard model gave dispersionless absorption of the film. It can be understood if to remember that the absorption of graphene monolayer approaches the value $\pi\alpha$ for long wavelengths according to the model [14], where α is the fine structure constant 1/137. It requires increasing the absorption index in proportion to the wavelength $k \sim \lambda$. This behavior contradicts with the Urbach tail dependence and explains the dispersionless behavior of fitted absorption obtained with this model. However, if to lift the restriction $\beta \geq 0$ allowing β to be negative, it improves fitting. Optical constants obtained with this simplest model for the isotropic layer are shown in Fig. 5a.

In spite of weak sensitivity of ellipsometry to the transverse anisotropy [15], introduction of such an anisotropy into the model improved fitting. Results of this fitting are practically insensitive to allowing the existence of extraordinary absorption, which is rather low. Existence of the transverse absorption may be explained by ripples of graphene layers.

Approaching the constant limit in the absorption is native behavior of the Drude model, where the absorption index linearly rises with the wavelength. Combination of the Drude model with the Lorentz line was proposed for description of the optical parameters of graphene [16]. The pure Drude model gave not so satisfactory results in our case, but its accomplishing by one Lorentz line remarkably improved the situation. Again, introduction of transverse anisotropy improves fitting, however, only if the Cauchy model is used for the dispersion of the transverse optical constant. Like to the previous case, the obtained transverse absorption is rather negligible and practically does not affect the quality of fitting. It explains why the use of similar combination Drude+Lorentz for transverse constants was not successful, because this combination has

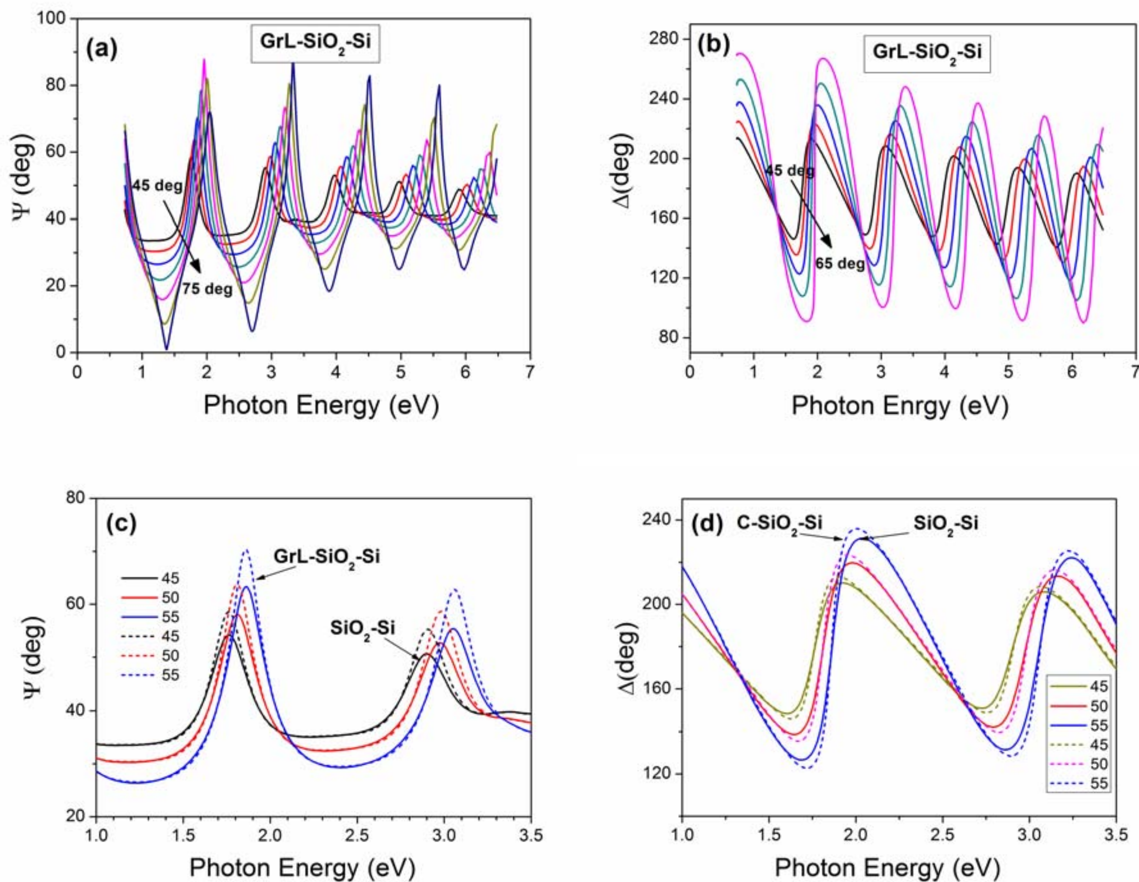

Fig. 4. Variable angle spectroscopic ellipsometry of graphene-like film on SiO_2-Si substrate: (a) Ψ and (b) Δ spectra for different angles of incidence θ measured on a graphene-like film; (c) Ψ and (d) Δ spectra measured at θ = 45°, 50° and 55° for the bare substrate and the substrate with a graphene-like layer.

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intrinsic noticeable absorption. It is worth to note that the obtained spectral position of the Lorentz line is about 4 eV, which is close to the value reported in [14]. However, in spite of more physical achievement of approaching the constant value for absorption and position of the Lorentz oscillator in this model, discrepancy of the fitting and experimental data is a bit larger in these cases than for the analogous Cauchy models.

Fig. 5a presents the results of modeling the optical constants k and n for our graphene-like film. The obtained results show that n changes from 2.1 to 2.6, and k is about 2.25 in the wavelength range from 400 up to 1000 nm. If to compare these values with those for graphene, which lie usually within the regions from 2.5 to 2.8 for n and from 1.2 to 1.8 for k [14, 17], we can see that in our case k is a bit higher than that of graphene layer. Unfortunately, preparation of the GrL layer on silicon substrate makes it impossible to directly measure the transmission for confirming it, so only modeling the absorption of our layer on the base of obtained parameters is possible. It is necessary to note that the result of measuring the phase thickness for thin films, fixing the thickness at some reasonable value (0.3…1 nm) gives corresponding scaling for obtained optical constants. However, it does not practically change calculated from these data transmission of this free standing film with fixed thickness. For the case of the Drude+Lorentz model, the transmission approaches the value 0.97, what is a bit lower that $\pi\alpha \approx 0.977$ [14, 17]. The calculated spectra reproduce minimum in the transmission in the region 4…4.5 eV reported earlier [14, 17]. It is not surprising for the Drude+Lorentz model, where additional Lorentz resonance is situated in that spectral range, but this minimum is reproduced by even Cauchy model with parameters shown in Fig. 5a. It is explained by the fact that due to film boundaries transmission of thin films is defined not by the absorption index but the imaginary part of the dielectric function divided by the wavelength [18, 19], which in our case demonstrates necessary minimum. It is easy to show that after account of the interference in the layer with boundaries the transmittance of a thin freely suspended film is described by the expression $|T|^2 \approx 1 - 4\pi n k \frac{d}{\lambda}$, where n is the refraction index of the material (real), *i.e.*, is described by the imaginary part of the dielectric function $\varepsilon'' = 2nk$ [18, 19]. It is this dependence that creates the minimum in transmittance for smooth behavior of both refraction and absorption indices shown in Fig. 5b. Modeled for absorption of a slab with the thickness 0.335 nm of a continuous material and $(1-|T|^2)$ for free standing layer with calculated optical constants is shown in Fig. 5b. Reflectivity of such a film may be omitted as it is the value of the second order of magnitude according of the small parameter d/λ. Together with those curves, the dependences k/λ and ε''/λ are shown by dash lines, too. The discrepancy is explained by the use of exact expressions for the absorption and transmission.

Thus, we can conclude that absorbance in our GrL film is lower than in graphene in deep IR part.

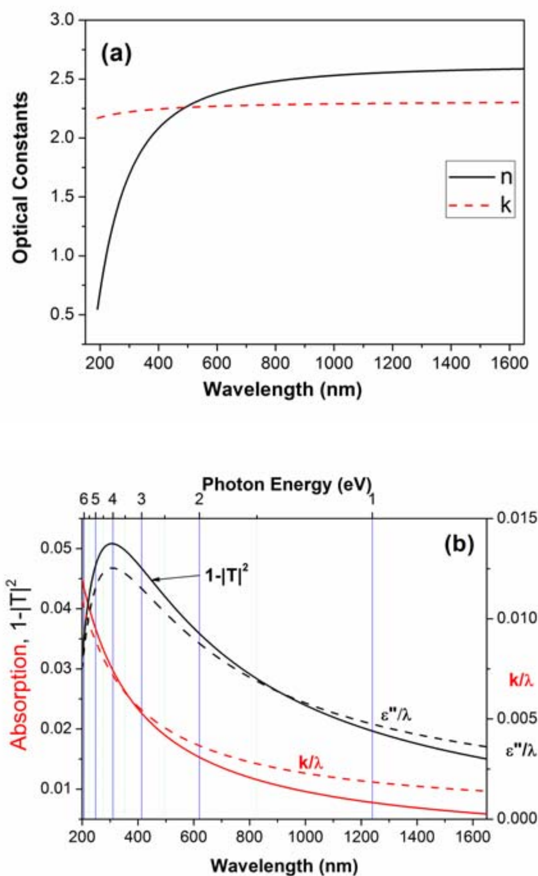

Fig. 5. Reconstructed optical constants (a) and absorption (b) of the graphene-like film.

4. Conclusions

Using a simple CVD technique and Ni-SiO_2-Si structure, the graphene-like film with thickness about 0.6 nm was directly synthesized on SiO_2 surface. The synthesized film has a good surface morphology and homogeneity but reinforced defectiveness, which results in increased resistance, but light absorption is a bit lower than that in the graphene single layer film. However, the films fabricated using this simple technique can be useful for photosensors operating in a wide range of wavelengths.

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