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Optical properties of nitrogen-doped graphene thin films probed by spectroscopic ellipsometry

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ABSTRACT

Nitrogen-doped graphene thin films were prepared by either chemical vapor deposition (CVD) or electrochemical exfoliation (ECE). Their optical properties were determined in the spectral region of 0.73–6.42 eV and at temperatures between 200 and 350 K by spectroscopic ellipsometry. The parameters of the dispersive structures were derived by numerical fitting of the experimental data to the stacked layer model. The optical absorption spectrum of the CVD-grown thin films is characterized by an asymmetric Fano resonance in the ultraviolet frequency region. In contrast, the line shape of the ECE-grown thin films displays less asymmetric. The excitonic resonance of the nitrogen-doped thin films is overall blue shifted by ~0.2–0.3 eV compared with that of undoped analog. We interpret these results in terms of the exothermic nature of triazine molecule adsorption due to binding to graphene's surface via electron rich nitrogen.

1. Introduction

Graphene is known as a gapless semiconductor. Opening the band gap in graphene is crucial for its applications in logic circuits and photonic devices [1,2]. Recently, doping graphene with other elements provides an effective way for achieving this goal [3–5]. For example, nitrogen atoms can be easily doped into carbon structures via forming C–N bonds due to the similarity of atomic size and five-valence-electron structure [6]. As a result, doping with nitrogen atoms allows graphene transformation into n-type semiconductor, accompanied by opening the band gap [7].

Currently, the widely used method for preparing nitrogen-doped graphene thin films involves arc charge method [8], segregation of trace amount of carbon and nitrogen in bulk metals [9], various kinds of chemical vapor deposition [10–16], and one-step method by electrochemical exfoliation [17]. Despite a rapid progress in the growth of nitrogen-doped graphene thin films, their fundamental physical properties remain poorly studied. Knowledge of charge dynamics and electron–phonon interactions is therefore very important to understand the electronic and optical properties of devices based on such thin-film structures [18–24]. Moreover, nitrogen-doped graphene has been recently proved to be an effective approach to tailor the property of graphene and greatly broaden its applications [25]. For example, nitrogen-doped graphene/CdS heterostructures show a higher photocatalytic activity than pure CdS [26]. Nitrogen-doped graphene quantum dots exhibit strong blue luminescence [27]. These results suggest the possibility to use nitrogen-doped graphene in high performance photocatalytic and biological imaging applications. Therefore, to explore the temperature dependence of optical constants of nitrogen-doped graphene is crucial to determine the threshold optical response. In this paper, we investigate the temperature dependence of the optical spectra of the graphene thin films with triazine doping using spectroscopic ellipsometry. Our goal is to understand the intrinsic mechanisms of the optical features of these materials and their temperature evolution, which are critically important for optoelectronic device applications.

2. Experimental

The undoped and nitrogen-doped graphene thin films were deposited on standard oxidized silicon substrates, i.e., SiO_2/Si, using either chemical vapor deposition (CVD) [16,28] or electrochemical exfoliation (ECE) [17]. The thickness of the oxide layer has been verified with the spectroscopic ellipsometry and determined to be about 297 nm. The surface morphology of the graphene thin films was investigated using an NT-MDT Solver P47H scanning probe microscopy. The measurements were done in tapping mode with a commercially available cantilever tip made of silicon. Fig. 1 shows the atomic force microscopy (AFM) images of four thin films. The CVD-grown films consist of single-layer graphene. In contrast, the ECE-grown films are dominated by multilayer graphene. The root-mean-square value of surface roughness for CVD-undoped, CVD-doped, ECE-undoped, and ECE-doped thin films is about 1.05, 2.08, 8.86, and 12.66 nm, respectively.

The organic molecule 1,3,5-triazine (abbreviated here as triazine) was thermally evaporated onto graphene thin films at 150 °C. Both the triazine and graphene were kept at the same temperature during

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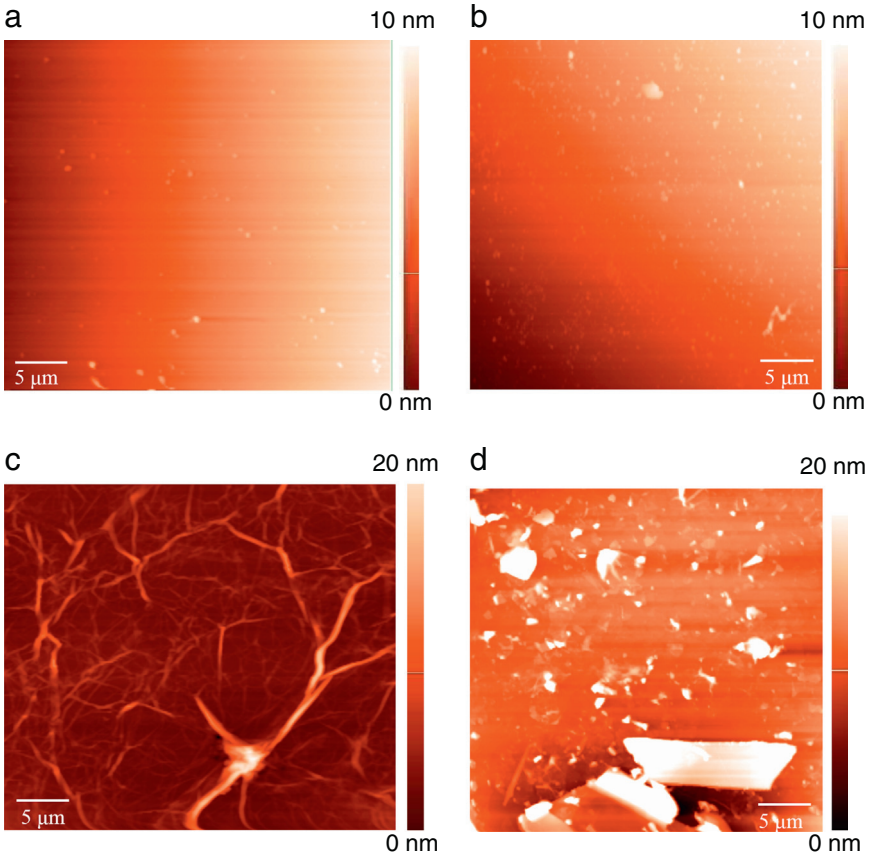

Fig. 1. AFM images of (a) CVD-undoped thin film, (b) CVD-doped thin film, (c) ECE-undoped thin film, and (d) ECE-doped thin film.

decoration. The evaporation period was around 8 h [23]. The evidence of triazine molecular decoration on graphene has been confirmed by the Raman-scattering spectroscopy [24].

Ellipsometric spectra were collected under multiple angles of incidence between 60° and 75° using a Woollam M-2000U rotating compensator multichannel spectroscopic ellipsometer over a spectral range from 0.73 to 6.42 eV. The reproducibility of the spectra was also confirmed at three different spots on the thin films using a specially designed focusing optics coupled with spectroscopic ellipsometry for the spot ($100 \times 100\ \mu m^2$) measurements. For temperature dependence measurements, the ellipsometer was equipped with a LINKAM heating/cooling vacuum stage system. Due to the 70° angle of the two stage windows, only a single angle of incidence is possible. The raw ellipsometry data Ψ and Δ are related to the complex Fresnel reflection coefficients for light polarized parallel (R_p) and perpendicular (R_s) to the plane of incidence:

$$e^{i\Delta}\tan\Psi = \frac{R_p}{R_s}. \quad (1)$$

To determine the complex dielectric response of the graphene thin films, the experimental data were processed using the stacked layer model consisting of silicon substrate/thermal silicon dioxide/thin film/surface roughness/air ambient structure. Then the error function σ was minimized in the entire spectral range:

$$\sigma^2 = \frac{1}{m}\sum_{i=1}^{m}\left[\left(\Delta_{exp}-\Delta_{calc}\right)^2 + \left(\Psi_{exp}-\Psi_{calc}\right)^2\right], \quad (2)$$

where Δ_{calc}, Ψ_{calc} and Δ_{exp}, Ψ_{exp} are, respectively, the calculated and experimental ellipsometric data and m is the number of points in the spectrum.

3. Results and discussion

Fig. 2 displays the room-temperature experimental and best-fit calculated data of the triazine-doped graphene thin films prepared by CDV and ECE. The parameters of the stacked layer model used to fit the raw ellipsometry data are listed in Table 1. The independently measured experimental data at 60° and 70° incidence angles and the modeled curves are in good agreement. It is worth noting that the values of surface roughness of four thin films are one order of magnitude smaller than those deduced from AFM measurements. This discrepancy may arise from the surface contaminations as the AFM experiments were performed on the aged thin films. The optical constants derived from the ellipsometric parameters of Ψ and Δ are shown in Fig. 3. We notice that the shapes of refractive index dispersion of the triazine-doped and undoped graphene thin films for two different prepared methods are quite similar despite a constant 5% lower level difference for the doped thin films. Optical transitions can be identified in the spectrum of resonance features that appear in the extinction coefficient, with detailed analysis shown below.

Fig. 4 shows the room-temperature optical absorption spectra of the triazine-doped graphene thin films compared with that of the undoped analog. As we can see the absorption gradually increases, manifests a sharp rise from 3 eV, reaches a maximum vale about 4.8 eV, and then shows the asymmetric line shape [29–33]. Such an asymmetry is fitted with the formula of Fano [34], $I(\omega) = I_0(q+\varepsilon)^2/(1+\varepsilon^2)$, where $\varepsilon = (\omega-\omega_0)/\gamma$, I_0 is the normalized intensity, ω_0 is the resonant (exciton) energy, γ is the effective linewidth, and q is the Fano asymmetry parameter. Our fitting curves are shown in Fig. 4. A list of fitting parameters is given in Table 2. From the results shown in Fig. 4 and the fit parameters in Table 2, three interesting optical properties in triazine-doped graphene thin films have been revealed by spectroscopic ellipsometry. First, the overall absorption profiles are similar, the observed 4.8 eV

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