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Formation of Graphene Island on Si (100) Substrate Prepared by Simple-Spray Method: Morphological and Optical Analyses

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Abstract. We study morphology and optical properties of graphene. A graphene on Si (100) substrate has been successfully prepared by the simple-spray method. The heat treatment of 150°C was performed during the deposition to assist the distribution of graphene on Si (100) substrate. We revealed that the graphene was well distributed with an island structure was observed. The real part and imaginary part of the refractive index of the graphene island were presented. Furthermore, the optical analysis revealed that the UV absorption was observed in our system. The results shown here would provide a good understanding of the graphene island properties, which potential for the optoelectronic-based application. In any case, our proposed method would reduce the complexity of the production of graphene with the inexpensive and simple procedure.

Keywords: Graphene island, Si (100) substrate, simple-spray method, UV absorption

1. Introduction

Graphene is one of an allotropes of carbon with an sp^2 bond of carbon and hexagonal crystal structure [1]. Graphene is a zero-band-gap semimetal which is one of most promising two-dimensional materials for future optoelectronics, sensors, and nanoelectronics applications due to its attractive optical transparency (97.7%) [2], electrical conductivity (with charge mobility of 2.5×10^6 cm^2 V^{-1} s^{-1}) [3], thermal conductivity (5×10^3 W m^{-1} K^{-1}) [4] and mechanical properties (with Young's modulus of 1.0 TPa) [5]. Today, monolayer and few-layer graphene (FLG) have been produced by several methods, including chemical vapor deposition (CVD) [6], thermal annealing [7], unzipping carbon nanotubes (CNTs) [8], solvothermal [9], electrochemical [10], thermal decomposition [11], ball-milling exfoliation [12], calcination [13], irradiation of highly charged ions [14], epitaxial growth [15], mechanical exfoliation [16], liquid-phase exfoliation [17], and thermal exfoliation[18]. However, these production methods are still under improved. Among, several graphene production methods, CVD is the promising method for large-scale production due to obtaining high-quality graphene [19]. However, CVD is a high-cost method and needs a careful preparation procedure.

In this study, we propose graphene growth by the simple-spray method. Graphene has been successfully produced by reducing graphene oxide (GO) using the spray method [20-22]. However, the additional solvents, such as ethanol, *N*-methyl-2-pyrrolidone (NMP), *N*,*N*-dimethylformamide (DMF), are needed to prepare the GO solution [23]. Here, we focus on the morphological and optical properties of the graphene obtained from the simple-spray method. Our method would simplify graphene production with an inexpensive and short procedure. The morphological and optical analyses of our sample would provide a good understanding of the formation of graphene island and its optical characteristics, which is a basis for developing optoelectronic-based graphene applications.

2. Methods

Graphene island was produced by the simple-spray method; spray generator: ultrasonic frequency (1 GHz), power driver: 2.9 W, nozzle: 700 hole with diameter of ~300 nm. Graphene precursor was prepared from a solution containing graphite powder and ethanol. The precursor has deposited on Si (100) substrate, which was cleaned by using ethanol, acetone, and DI water, respectively. The spray was performed at the spray distance of 4 cm for 5 min. Heat treatment at a temperature 150^{o}C was performed during the deposition to assist the formation of graphene on Si (100) substrate.

Surface morphology of the sample was characterized by scanning electron microscopy (SEM) FEI: INSPECT S50. The optical properties of the sample, including refractive index and optical absorption, were studied by spectroscopic ellipsometry Micropack: Spec-EI 2000 at an incident angle of 70^o and polarization angle of 45^o. Refractive index of the sample was determined by constructing optical model and optical fitting using Equation 1 [24].

$$\rho = \frac{r_p}{r_s} = \tan \Psi .\ \exp\left(i\Delta\right) \tag{1}$$

with ρ is the reflectivity, r_p/r_s is the reflectivity ratio of p- and s-polarized light waves, Ψ is the amplitude ratio, Δ is the phase difference. The refractive index and optical absorption of the sample are determined by fitting using Equation 2-4.

$$r_p = \frac{n_t \cos\theta_i - n_i \cos\theta_t}{n_t \cos\theta_i + n_i \cos\theta_t} \text{ and } r_s = \frac{n_i \cos\theta_i - n_t \cos\theta_t}{n_i \cos\theta_i + n_t \cos\theta_t} \tag{2}$$

$$N \equiv n - ik \tag{3}$$

$$\alpha = \frac{4\pi k}{\lambda} \tag{4}$$

with N is the complex refractive index, n and k are the real part and the imaginary part refractive index, α and λ are the absorption coefficient and the wavelength of light source. Indices of i and t represent incident and transmission conditions.

3. Results and Discussion

Figure 1 presents an SEM image of graphene on Si (100) substrate prepared by the simple-spray method. The result reveals that graphene was distributed in an island shape, which is composed of few-layer graphene (FLG). The graphene island showing the transparent appearance with the wrinkle, was observed. Previously, the presence of wrinkles was associated with the existence of carboxyl (-COOH) and hydroxyl (-OH) groups in graphene [25]. In addition, the growth condition contributed to the presence of wrinkles. The use of short heating time provides insufficient time for the formation of a perfect graphene layer on the substrate [26]. Furthermore, high magnification SEM image confirms two types of structures, including graphene island (above) and cluster structure (below), which is distributed on the entire substrate surface. Here, the cluster structure was attributed to the existence of a carbon cluster formed during spray deposition process. We infer that the formation of graphene island was conducted by the diffusion and precipitation of carbon. Other studies reported on the formation of the graphene layer from the carbon cluster grown by another deposition method [26, 27].

Figure 2 illustrates graphene growth by using the simple-spray method. Here, the mist, contain carbon and ethanol, is deposited on the substrate surface by the sprayer. A heat treatment is performed during the deposition to eliminate the solution phase and assist the diffusion/distribution of carbon on substrate surface. During the process, carbon precipitated, forming carbon cluster, and subsequently forms a graphene island.

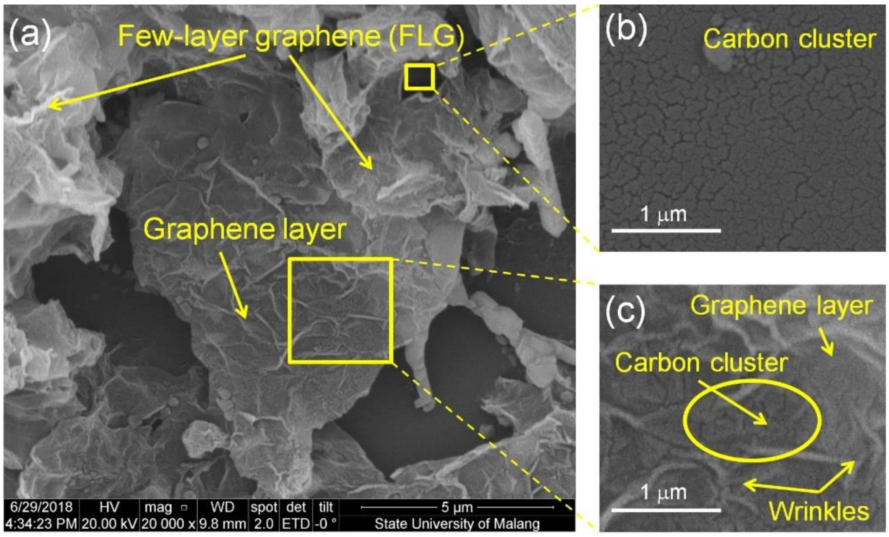

Figure 1. Surface morphology of graphene island ZnO prepared by the simple-spray method, with graphene island is comprised of few layers of graphene (a), High magnification of carbon the cluster on Si (100) substrate (b), and formation of a graphene layer on carbon cluster (c).

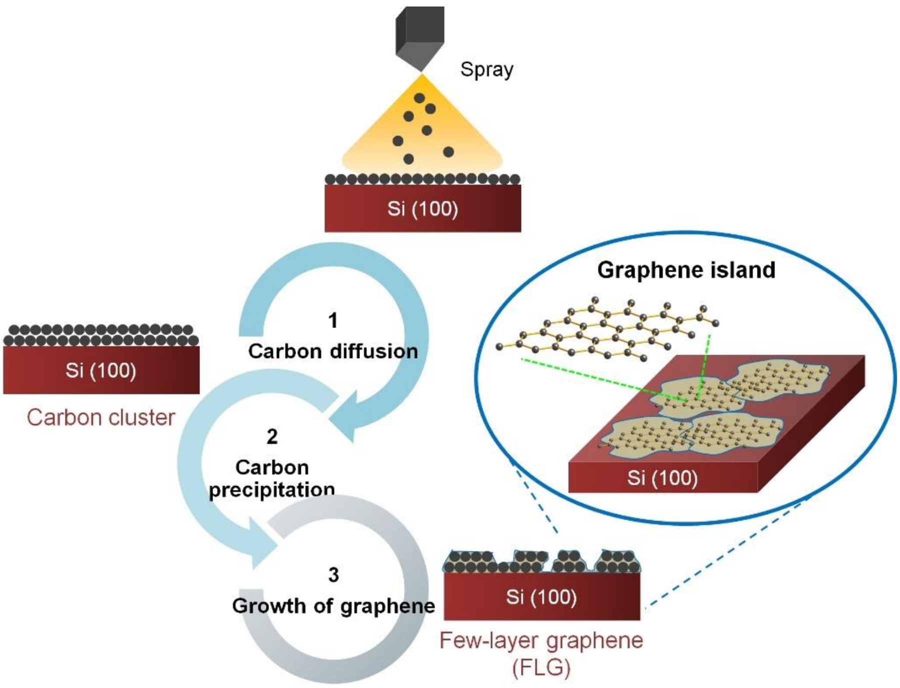

Figure 2. Schematic diagram of the formation of graphene island prepared by the simple-spray method.

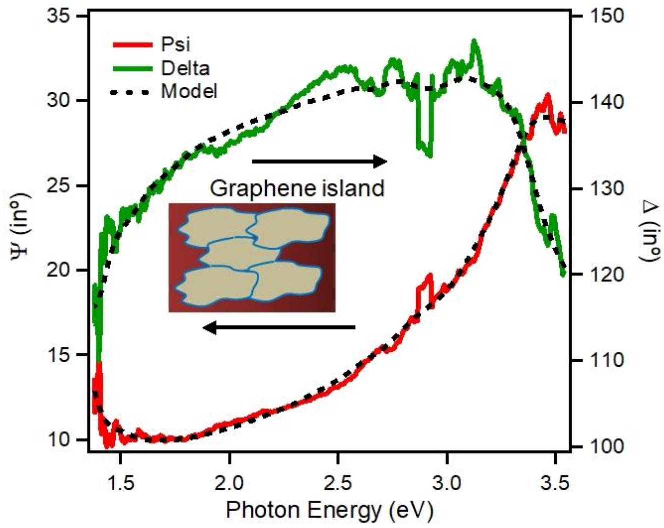

Figure 3. Best fitting amplitude ratio and phase difference of graphene island obtained from spectroscopic ellipsometry.

Figure 3 presents amplitude ratio (Ψ) and phase different (Δ) spectra of graphene island. An instrument fingerprint is noted at energy of 2.9 eV. The ripple curves of both spectra indicate a non-uniformity distribution of graphene, which is contributed by island distribution and wrinkles structure. The thick layer of the materials is indicated by the existence of few oscillators at lower energy [24, 28, 29]. The absence of oscillator (line-like characteristic) in Ψ and Δ spectra indicates that the graphene has a thin layer. The thickness of the graphene island is obtained by using spectroscopic ellipsometry analysis with a value of 37 nm. The thin layer of graphene will imply the light pass through easily the graphene, in other words, it has high transparency.

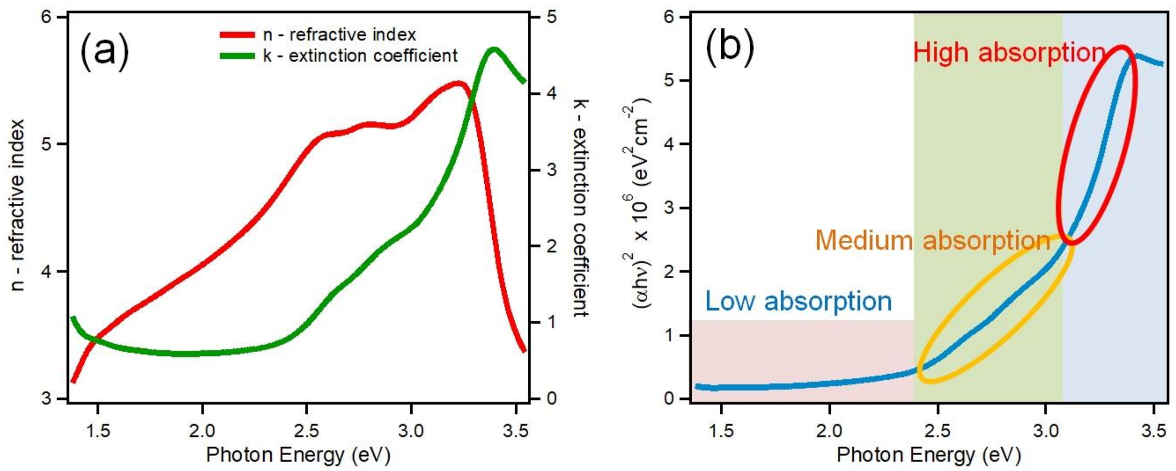

Figure 4. Real part- and imaginary part-refractive index (a) and absorption of graphene island (b).

In order to study the optical properties of graphene island, a complex refractive index analysis of graphene island was presented. Figure 4 (a) shows the characteristic of a real part- and imaginary part-refractive index of the sample, which shows the similar profile with a previous report [27]. The real part-refractive index indicates the phase velocity, which determines the refractive index value of material (n), while imaginary part-refractive index indicates the attenuation coefficient/extinction coefficient (k). The graphene island shows normal dispersion from 1.3 – 3.1 eV, where the refractive index tends to increase with increasing photon energy. This result is attributed to the transparent characteristic of graphene island. The refractive index of graphene island significantly decreases at a photon energy of ~3.3 eV accompanied by increasing of extinction coefficient with a maximum value at ~3.4 – 3.5 eV. At this region, the increase of extinction coefficient indicates the increase of optical absorption of graphene island. Furthermore, the absorption spectra are presented to give a good understanding of optical properties of graphene island. Figure 4 (b) shows that graphene island has wide range absorption in observed photon energy of 1.3 – 3.5 eV, with low absorption at 1.3 – 2.4 eV, medium absorption at 2.4 – 3.1 eV, and high UV absorption at 3.1 – 3.5 eV (~5.3×10^6 eV^2 cm^{-2}). This condition makes graphene island have a potential condition for developing solar harvesting devices and other optoelectronic applications.

4. Conclusion

The inexpensive and simple procedure of graphene growth has been proposed. The graphene island has been successfully produced from thermal-assisted carbon cluster deposited by the simple-spray method. The graphene island is arranged by few-layer graphene (FLG) with island thickness of 37 nm. The graphene has transparent characteristic at photon energy range of 1.3 – 3.1 eV and wide range absorption from IR to UV range. The wide range optical absorption with high UV absorption will give a good condition for developing wide-range optoelectronic applications, especially for solar harvesting devices.

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