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Enhanced optical absorption of graphene-based heat mirror with tunable spectral selectivity

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ABSTRACT

Graphene based heat mirror (i.e., graphene/Cu/graphene multilayer coating) was designed and developed to achieve enhanced optical absorption with tunable spectral selectivity. The concept of a heat mirror and a high/low/high refractive index stack was used to develop the graphene/Cu/graphene absorber and the transition from high transmittance to high absorptance was realized on quartz substrates. The thickness of the Cu layer has an important role in creating the destructive interference, for achieving high absorptance and low emittance. The refractive index of the multilayer graphene transferred on Si substrate was studied using phase-modulated spectroscopic ellipsometry. An absorptance of 0.91 and emittance of 0.22 was achieved for the SiO_2/graphene/Cu/graphene multilayer coating. For the first time, the feasibility of graphene/Cu/graphene multilayer coating for photothermal applications have been demonstrated.

1. Introduction

Graphene, a monolayer of carbon atoms in a two-dimensional honey comb lattice, with its exceptional optical and electrical properties has attracted worldwide attention since its discovery in 2004. It has been reported that monolayer graphene exhibits negligible reflectance ($R < 0.1\%$) with a transmittance (T) of 97.7% and an opacity of 2.3% in the visible wavelength range [1]. This drawback significantly affects the performance of graphene-based devices, such as broadband optical modulators [2] and photodetectors [3], as they require strong light-matter interactions. Surface plasmon polaritons generated in doped graphene promote strong light-graphene interactions in the terahertz and the far infrared regions [4]. However, in the visible and the near-infrared (NIR) range, graphene acts as lossy dielectric with wavelength-independent absorption [5]. Several possible alternatives, such as patterning of graphene into periodic arrays, attenuated total reflection configuration, and plasmonic nanostructures have been explored to enhance the optical absorption of graphene [6–15]. However, all these methods involve complicated procedures and high fabrication costs, which are undesirable for practical applications. In the present work, we have used a simple heat mirror concept to enhance the optical absorption of graphene/Cu/graphene multilayer coating ($\alpha = 0.91$). In addition, we reduced the emittance of the SiO_2 substrate by reflecting the IR radiation.

In general, absorption in thin films mainly depends on the intrinsic absorption of the material and the interference effect due to the layer thickness. As mentioned before, graphene exhibits very low intrinsic absorption, and hence, the optical absorption can be enhanced by using the interference induced absorption mechanism (i.e., destructive interference). Based on this concept, for the first time, we demonstrated the use of a simple heat-mirror to enhance the optical absorption of graphene/Cu/graphene multilayer coating. Interference induced absorption mainly depends on the refractive index and the thickness of the layers used in the coating. Destructive interference can be achieved by using a high/low/high refractive index stack with suitable layer thicknesses. A graphene-based multilayer coating (i.e., high/low/high refractive index stack) was designed and deposited on quartz and SiO_2 substrates; we demonstrate the tunable spectral selectivity (i.e., transition from antireflection coating to absorber coating) of graphene/Cu/graphene multilayer coating prepared on quartz substrates by varying the Cu layer thickness. The component layers, such as graphene and Cu were chosen suitably to achieve destructive interference in the visible region. To the best of our knowledge, this is the first report on graphene/Cu/graphene multilayer coatings for optical absorption applications. The fabrication of the graphene/Cu/graphene multilayer coating using the present method is simple and cost-effective when compared to the other methods.

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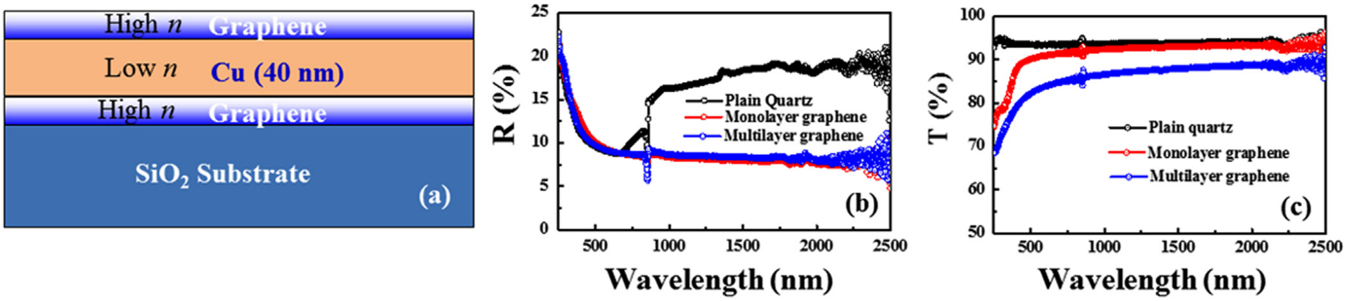

Fig. 1. (a) Schematic diagram of the graphene/Cu/graphene multilayer coating (not to scale). (b) total reflectance and (c) total transmittance of plain quartz, monolayer graphene, and multilayer graphene.

2. Experimental details

The hot-filament chemical vapor deposition (HFCVD) technique was used to grow the multilayer graphene, the details of which have been reported elsewhere [16]. Before placing the substrates (quartz and SiO_2) in the vacuum chamber, they were chemically cleaned using isopropyl alcohol and acetone. The growth process sequence of the graphene/Cu/graphene multilayer coating is shown in Fig. S1. Approximately 60 nm thick Cu layer was sputter-deposited on the SiO_2 substrate for the growth of graphene and the details of the sputtering system have been provided in our previous report [17]. The schematic diagram of the graphene/Cu/graphene multilayer coating is shown in Fig. 1a. In our previous work, the process parameters were optimized to grow monolayer, bi-layer, and multilayer graphene on Cu foils [16]. The optimized process parameters for the growth of high quality multilayer graphene were: substrate temperature − 950 °C; CH_4 and H_2 gas composition − 1:50, working pressure − 10 mbar, and growth duration – 6 min. The as-grown graphene on Cu coated quartz/SiO_2 was etched using $FeCl_3$ solution for transferring the graphene on the quartz/SiO_2 substrate. A thin Cu layer (10–40 nm) was deposited on the graphene/SiO_2 substrate. To avoid the high-temperature annealing induced effects, such as inter-diffusion between the layers and morphological changes, the top graphene layer was transferred on Cu/graphene/SiO_2 substrate. The thicknesses of the top and the bottom graphene layers were almost similar, which was confirmed by Raman spectroscopy and UV–VIS–NIR spectrophotometry. The optical constants of the multilayer graphene were measured in the wavelength range of 300–1200 nm. The structural and the optical properties of the graphene-based multilayer coating were studied using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), atomic force microscopy, optical microscopy, XFESEM, UV–VIS–NIR spectrophotometer, Fourier transform infrared spectrometer (FTIR), and phase modulated ellipsometry techniques.

The XRD patterns of the coatings were recorded using a Bruker D8 Advance X-ray diffractometer with thin film attachment, and the X-ray source was Cu K_α radiation (λ = 0.15418 nm). A DILOR-JOBIN-YVON-SPEX integrated micro-Raman spectrometer (Model Labram) was used to obtain the Raman spectra. The thickness of the Cu layer was estimated using a Carl Zeiss Supra 40VP field emission scanning electron microscope. The optical constants (refractive index (n) and extinction coefficient (k)) of multilayer graphene were measured using phase modulated spectroscopic ellipsometry (Model: UVISEL™ 460, ISA JOBIN-YVON-SPEX). A UV–VIS–NIR spectrophotometer (Perkin-Elmer, Lambda 950) and an FTIR were used to measure the reflectance of the graphene/Cu/graphene multilayer coating in the wavelength range of 0.3–25 µm. The absorptance of the coating was calculated from the reflectance data using the selected ordinates method [18]. A solar spectrum reflectometer and emissometer (Devices and Services) was used to confirm the α and the ε values.

3. Results and discussion

In the present work, multilayer graphene (i.e., 5 layers) was used to prepare the graphene-based multilayer coating. This is because, the reflectance values of the monolayer and the multilayer graphene (Fig. 1b) are almost similar (i.e., R ≅ 10%) throughout the UV–VIS–NIR region. Further, the growth of continuous monolayer graphene is difficult when compared to the multilayer graphene growth. The monolayer and the multilayer graphene grown on Cu foils were transferred on quartz substrates for the reflectance and transmittance measurements. The growth duration and the other process parameters were kept constant to grow the multilayer graphene. The presence of monolayer and multilayer graphene (i.e., I_{2D}/I_G ratio) was confirmed from the micro-Raman spectroscopy data shown in Figs. S2a and 2b, respectively (see Supporting information). The thickness of the Cu layer was calculated by measuring the growth rate and was confirmed using cross-sectional field emission scanning electron microscopy (XFESEM) studies (Fig. S2b). The multilayer graphene transferred on the quartz substrate exhibited approximately 85% T and 10% R in the UV–-VIS–NIR region (Fig. 1c). Whereas, the monolayer graphene exhibits slightly higher transmittance than the multilayer graphene.

3.1. Ellipsometric studies

To gain deeper insights about the optical properties of graphene, spectroscopic ellipsometric measurements were carried out. The experimental ψ (amplitude ratio of parallel and perpendicular components of the reflected waves) and Δ (relative phase change) spectra of multilayer graphene transferred on a Si substrate was obtained in the wavelength range of 300–800 nm. The above experimental spectra were fitted with a two-layer model. A thin Cauchy sublayer under graphene represents a spacer of water and air between the graphene layer and the substrate. The typical parameters of this layer are: thickness = 4 nm, A = 0.91, B = 13.10, C = 15.05, D = 114205.4, E = 0.81, and F = 8.17. The graphene layer was modeled using the Cauchy's formula for generating the refractive index (n) and extinction coefficient (k) spectra [19–21]. The fitting details are described in our previous work [22,23].

The theoretically generated spectra were fitted with the experimentally measured ellipsometric spectra by varying the thicknesses and the parameters of dispersion relation of every layer, to deduce the thicknesses, refractive indices, and extinction coefficients of the different layers. For the graphene layer, the Cauchy's model provided the following fitting parameters: thickness = 1.98 nm (6 layers); A = 2.5, B = 5.00, C = 5.00, D = 60000, E = 3.00, and F = 1.00. Additional details about the fitting procedure can be found elsewhere [19,20]. In brief, the measured ellipsometric spectra were fitted by minimizing the squared difference (x^2) between the measured and the calculated values of the ellipsometric parameters. The maximum number of iterations allowed was 100, and the criterion for convergence used was $\delta\chi^2$ = 0.000001.