Comparison of Various Methods for Transferring Graphene and Few Layer Graphene Grown by Chemical Vapor Deposition to an Insulating SiO₂/Si Substrate

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Submitted September 12, 2013; accepted for publication September 27, 2013

Abstract—The objective of this study is to compare the results of transferring graphene and few layer graphene (FLG) up to 5 nm thick, grown by chemical vapor deposition (CVD) at a reduced pressure to a SiO₂/Si substrate using four different polymer films. The chosen transfer methods are based on the most promising (according to published data) materials: polymethyl methacrylate, polydimethylsiloxane, thermoscotch, and polycarbonate. It is shown that the most promising transfer method (minimum resistance and maximum carrier mobility) lies in the use of polycarbonate thin films with their dissolution in chloroform. In this case, the following parameters are steadily obtained: the graphene and FLG resistance is 250–900 Ω/□ and the carrier mobility is 900–2500 cm²/(V s).

DOI: 10.1134/S1063782614060049

1. INTRODUCTION

Since its discovery, graphene as a one-atom-thick material has attracted considerable attention due to hopes for new physical phenomena, the appearance of new functionalities and new design solutions in developing devices on its basis. The studies of graphene have confirmed these hopes to a large extent (see, e.g., [1]). However, in turning to the practical applications of graphene, it was unexpectedly found that device structures based on multigraphene a few nanometers thick have even more interesting properties than graphene itself in many cases [2–4]. Therefore, it is of interest to fabricate not only graphene, but also multigraphene layers a few nanometers thick. Currently, the application of the CVD (chemical vapor deposition) method to produce graphene and multigraphene on copper substrates allows the growth of both ordinary polycrystalline films [5, 6] and individual large graphene domains up to 5 mm in size [7] or large domains incorporated into a polycrystalline matrix [8]. The further application of graphene requires its transfer from a metal substrate to an insulating substrate. It should be noted that the transfer method, in particular, controls to a large extent the parameters of the fabricated layers. At present, various transfer methods have been proposed, which are being improved with time to obtain, as a result, chemically purer graphene [9–12]. In this study, CVD modes applied to polycrystalline graphene and few layer graphene growth on copper substrates are found. Methods for transferring the grown films to SiO₂/Si insulating substrates with a SiO₂ thickness of 300 nm providing the highest carrier mobility are compared. Transfer methods using polymethyl methacrylate (PMMA), polydimethylsiloxane (PDMS), thermoscotch (scotch whose adhesion varies upon heating), and polycarbonate (poly(bisphenol-A-carbonate)) are compared. It is shown that the most promising transfer method (minimum resistance and maximum carrier mobility) lies in the use of polycarbonate thin films. In this case, films with sheet resistances of 600–950 Ω/□ and carrier mobilities of 1000–2500 cm²/(V s) are obtained. A scheme is proposed, making it possible to transfer relatively large graphene or multigraphene areas to SiO₂/Si substrates, which includes such technological stages as electrochemical separation of the polycarbonate film with graphene from the copper substrate, film clamping to a new substrate using stamp lithography equipment, and subsequent polycarbonate dissolution in chloroform.

2. EXPERIMENTAL

As growth substrates, copper foil (Alfa Aesar Co.) 25 μm thick with a purity of 99.999% was used. Before growth, the foil was chemically treated in a 5% HCl:H₂O solution to remove the oxide, and 20–40-min preannealing was performed at a temperature of
1000–1050°C in an Ar + H₂ atmosphere. The H₂ content in the gas mixture was 10%. This annealing appreciably decreased the surface relief of the copper foil and caused the formation of domains (single-crystal grains) within it. The surface-relief measurements using atomic-force microscopy (AFM) yielded ~10 nm per square 5 μm² in area; the grain sizes reached 10–150 μm.

Graphene and multigraphene were grown by CVD at temperatures of 1000 and 1050°C, a pressure of 7.2 Torr, and a total gas-flow rate (Ar, H₂, CH₄) of 50 L/h. Graphene films were grown using a gas mixture with the volume fractions CH₄:H₂:Ar = 1:1.3:4. The growth time was the main parameter varied from 5 to 20 min. To provide good adhesion, graphene was transferred to a SiO₂/Si substrate using Eitre6 Nanoimprinter Obducat stamp nanolithography equipment.

Raman-scattering (RS) measurements were performed at room temperature using the excitation radiation of an argon ion laser with a wavelength of 514.5 nm (2.41 eV). The laser-beam power was maintained at a level of 2–3 mW to avoid sample annealing by the laser.

The current–voltage (I–V) characteristics were measured using a Keithley picoammeter (model 6485); two silver paste contacts to the films and an additional contact to the silicon substrate were formed. To characterize the grown films, the volume resistivity ρ (Ω cm) and the sheet resistance ρ* = RW/L (Ω/□) (R is the measured resistance of the grown film, W and L are the film width and length) were calculated. The transfer I–V characteristics of a field-effect transistor whose gate was a silicon substrate were used to calculate the carrier mobilities μ by a well-known formula for the linear portion of the I_DS(V_G) characteristics similarly to that for ordinary semiconductor field-effect transistors,

$$\mu = \frac{L}{C_g W V_{DS}} \frac{\Delta I_{DS}}{\Delta V_G}$$

where C_g is the specific capacity of the gate insulator, V_{DS} is the drain–source voltage, ΔI_{DS} and ΔV_G are the changes in the drain current and gate voltage, respectively.

3. RESULTS AND DISCUSSION

3.1. Graphene and FLG Growth by Chemical Vapor Deposition

The RS spectra of FLG films on copper substrates, grown in various times are shown in Fig. 1a. The baseline bend is associated with copper-substrate oxidation. Attention should be paid to the absence of the defect-related peak D (1350 cm⁻¹) in the spectra. The peak position and width point to the high quality of the grown FLG film. The additional oxidation of FLG on the copper substrate upon exposure to ultraviolet illumination [13] allowed domain-wall visualization. The characteristic domain size was 3–10 μm.

3.2. FLG Transfer to the SiO₂/Si Substrate

More detailed diagnostics of the grown films is possible only after their transfer to the insulating SiO₂/Si substrate. It is clear that the transfer technology will control in many respects the properties of the transferred film; therefore, the most interesting and promising approaches known from publications were tested, on the basis of which an original transfer method was developed. In general, grown graphene is transferred using various polymer films applied to it. Then the copper substrate is etched away or is electrochemically separated. Finally, the polymer film with the graphene is placed onto the required substrate and the film is removed in some way from the graphene.