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Etch free graphene transfer to polymers☆

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ABSTRACT

Graphene transfer is critical for successful graphene-device integration. Even though multiple transfer approaches have been developed, an optimal solution is still not available. In this paper, we demonstrate dry transfer of graphene transfer Cu foil to polystyrene using mild heat and pressure. Two different printing systems are evaluated: a wafer bonder and a more cost-effective heat press. Chemical, morphological, structural and electrical characterization of the samples before and after transfer is performed. The results suggest that differences in the operation of the printing devices can be correlated to uniformity of transferred graphene. Regardless of the printing approach the surface resistivity of the polymer was decreased by 16 orders of magnitude.

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1. Introduction

The outstanding electrical, optical, mechanical and thermal properties of graphene, combined with its chemical stability, low gas permeability and flexibility are the reason for extensive research exploring the use of graphene in organic electronic applications. Some of the applications include organic light emitting devices (OLED), organic solar cells, touch screens, memory devices, and smart windows [1–4]. Critically, these applications require significant development in methods both for the large-scale synthesis and transfer of graphene [5]. Further fine-tuning of graphene chemical and electrical properties, depending on the application, is needed as well. This is particularly true in the production of next-generation flexible, foldable and wearable devices that require the integration of graphene with polymers. Direct graphene growth onto a polymer substrate has not yet been demonstrated and thus graphene–polymer integration depends on graphene transfer. Prior attempts used sacrificial polymer layers [6] and thermal release tape [7] to stabilize graphene while the growth substrate (e.g. Cu foil) was etched away. However, the subsequent removal of these support materials can be incomplete and additional cleaning steps are needed. Organic solvents and thermal annealing approaches work well for inorganic materials but are incompatible with most polymers. Thus, alternative routes are needed.

We recently reported an etch-free method for graphene transfer [8]. In this approach, the surface of the polymer substrate was modified using a two step approach: plasma surface functionalization followed by the deposition of a N-ethylamino-4-azidotetrafluorobenzoate coating. Independently, graphene was grown on a Cu foil growth substrate using chemical vapor deposition. To transfer the graphene, both substrates were placed in a Nanoimprinter (Nanonex NX 2000) heated to 150 °C and pressurized to 500 psi (3.44 MPa). While effective, these systems are not widely available. Here, we explored two lower cost printing machines that operate at atmospheric pressure. Chemical, morphological, structural and electrical analysis of the polymer surfaces before and after graphene transfer showed that the amount of force and its distribution over the graphene/Cu foil/polymer during print are essential for uniform graphene transfer.

2. Materials and methods

2.1. Materials

Polystyrene films (thickness of ~250 μm) were purchased from Tekra. Typical sample size was approximately $1 \times 1\ \text{cm}^2$. N-ethylamino-4-azidotetrafluorobenzoate (TFPA) was synthesized as described in Ref. [8]. Graphene was grown via chemical vapor deposition on a copper foil [9].

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2.2. Methods

2.2.1. Graphene transfer to polystyrene

Polystyrene was exposed to a pulsed, electron beam-generated plasmas produced in a carbon dioxide background at a pressure of 90 mTorr for 1 min at 10% duty factor. Then, the polymer was dip-coated in a solution of 4 mM N-ethylamino-4-azidotetrafluorobenzoate (TFPA-NH_2) in methanol for 2 h. The TFPA coated polymer was placed in contact with graphene/Cu foil and transferred under heat (150 °C) and a range of applied forces. Two very different printing machines are used: 1) EVG 501 wafer bonding system and 2) a commercially available heat press (Panther Press) typically used for clothing. To transfer with the wafer bonder, the chamber was held at atmospheric pressure, the loading and unloading were performed at 70 °C, and the bonding was performed at 150 °C for 30 min for all experiments. With the heat press, the top surface was heated to 150 °C for 30 min. In the final step, the polymer substrate with attached graphene was separated from the metal foil.

2.2.2. Raman spectroscopy and micro-Raman maps

Raman spectra were acquired using a Renishaw inVia Raman microscope with a constant power of 20 mW and exposure time of 20 s. Micro-Raman maps were collected on two custom-built systems. The microRaman map of the wafer bonded sample was collected using a 514 nm excitation laser that was provided by a Coherent Innova 90-5 Argon-Ion laser. It was focused on the sample through a 100×, 0.75 NA objective on a Mitutoyo microscope. The laser power at the sample surface was measured to be ~8 mW. The Raman scattered light was then collected through the objective and focused onto a thermoelectrically cooled, Ocean Optics QE65000 spectrometer via a 200 lm optical fiber with an acquisition time of 20 s. The map of the heat press bonded sample was obtained using a 488 nm laser that was focused on the sample through a 100×, 0.65 NA microscope objective. The Raman scattered photons were dispersed in a half-meter Acton Sp-2500 spectrometer and detected using CCD Princeton instrument array (Spec-10:400BR back-thinned, deep-depleted array).

2.2.3. Hall effect measurements

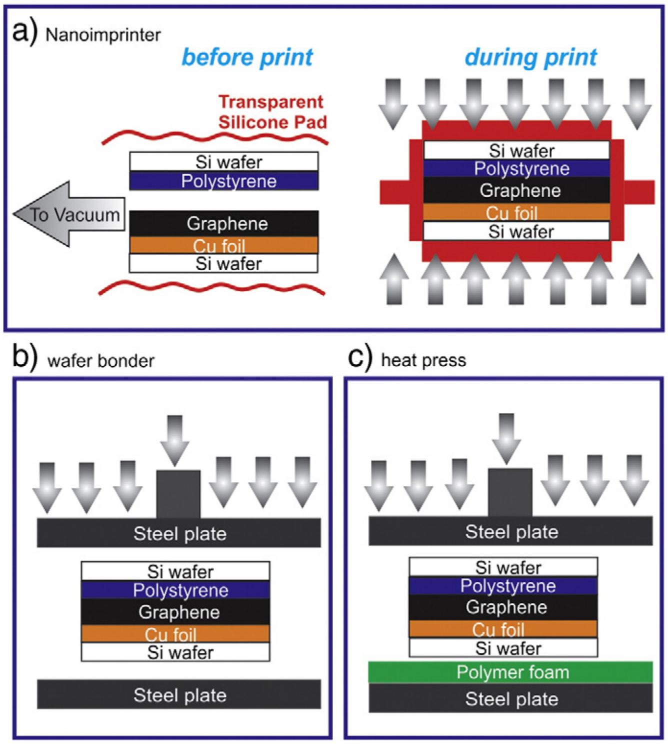
Hall effect mobility and carrier density measurements were carried out at 300 K using copper pressure clips in van der Pauw configuration. The clips were used as probe contacts over areas of 0.5×0.5 mm^2. The currents used for the measurements were 1 and 50 μA, while the magnetic field was approximately 2 kG.

2.2.4. Atomic force microscopy

The polymer surface morphology was studied at various scales using an atomic force microscope (Nanoscope III, Veeco Metrology, Santa Barbara, CA) operated in tapping mode. Surface images were obtained from 5 μm × 5 μm scans using resolution of 256 × 256 pixels; z scale was 3 μm. The scan rate was 1.5 Hz. For a quantitative evaluation of the topography changes, root-mean square roughness was calculated from the surface height data z_i using $R_q = \left[\frac{1}{N}\sum_{i=1}^{N}|z_i - \bar{z}|^2\right]^{1/2}$, where $\bar{z}$ is the mean height.

2.2.5. X-ray photoelectron spectroscopy

Surface elemental and chemical state analyses were performed on a K-Alpha spectrometer (Thermo Scientific, Al-Kα X-ray source, 1486.6 eV, spot size of 400 μm). Analyzer pass energies of 200 eV were used for elemental survey spectra. K-Alpha's charge compensation system was used during the analysis.



Scheme 1. Schematic of printing configuration in (a) Nanoimprinter; (b) wafer bonder and (c) heat press.

3. Results and discussion

A systematic study of the effect of applied force on graphene transfer was conducted using a wafer bonding tool. The applied force over sample surface area of approximately 1 cm^2 was varied from 0 to 500 N (0 to 5 MPa). The initial experiments used a force of 350 N (3.5 MPa) in an effort to replicate previous printing conditions of 3.44 MPa in the Nanoimprinter; however the transfer was unsuccessful and the polymer film was highly deformed. This may result from differences in the printing arrangement (Schematic 1). In the Nanoimprinter (Schematic 1a), the polystyrene film and Gr/Cu foil are positioned between two Si wafers within silicone pads, then vacuum is applied between the silicon pads. To achieve the pressure of 3.44 MPa, the space outside the pads was backfilled with nitrogen. This gas pressure mechanism differs substantially from the mechanical force mechanism of the wafer bonder (Schematic 1b), where the substrates are positioned between Si wafers inside two stainless steel plates and the force is applied via computer control. Notably, higher force up to 500 N did not improve transfer. The applied force was then lowered, with test prints at 150, 100, and 50 N until a successful print was ultimately observed at 25 N (250 kPa). Further lowering of applied force to 5, 1, and 0 N did not yield graphene transfer, suggesting a small but finite load is required to achieve good conformal contact between the polymer and the graphene/Cu foil. The success of low pressure transfer suggested utilization of a commercially available heat press to simplify the process and significantly reduce equipment cost. The heat press (Schematic 1c)

Table 1
Elemental composition of untreated and modified polystyrene in every step of sample preparation: plasma treated and azide coated polystyrene (PS before print) and PS after print.

Sample	C1s	O1s	N1s	F1s
Untreated PS	97	3	0	0
Plasma-treated PS	81	19	0	0
PS H before print	83	11	3	3
PS H after print	87	10	1	2