



Adhesion energy of as-grown graphene on copper foil with a blister test



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ABSTRACT

Interfacial adhesion energy between as-grown graphene and its growth substrate reveals the nature of bonding, as well as provides insights for large-scale roll-to-roll graphene transfer. In this study, a novel sample preparation scheme was developed and a unique quasi-static blister test was performed to measure the adhesion energy between as-grown graphene and its copper foil substrate. The copper foil was treated with acetic acid for 4 h, 24 h and 48 h prior to graphene growth. The corresponding adhesion energy was determined to be $0.74 \pm 0.13 \text{ J/m}^2$, $1.10 \pm 0.16 \text{ J/m}^2$, and $1.53 \pm 0.11 \text{ J/m}^2$, respectively. Longer exposures to acetic acid led to rougher copper foil surfaces, and thus higher adhesion energy. This trend is in contrast to that for transferred graphene, which has been found to have weaker adhesion to rougher substrates. The experimental results from this study suggest that the interaction between as-grown graphene and its seed layer was mainly due to van der Waals, instead of covalent or ionic bonds and that surface roughness of the growth substrate could be a significant factor in determining the as-grown graphene adhesion energy.

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1. Introduction

Chemical vapor deposition (CVD) on metal catalytic substrates, e.g., copper and nickel foil, is widely used for synthesizing large-scale graphene films for future flexible electronics applications [1–6]. CVD graphene must be transferred from its metallic growth substrate to a target where functional devices will be built. In the past, graphene transfer had been achieved by etching away the metallic growth substrate with a copper etchant solution, e.g. iron nitrate [7,8]. More cost-effective methods were recently proposed where the as-grown graphene was delaminated with an electrochemical or a direct dry-peeling technique [9–13]. Dry-peeling was also proposed in transferring other large area 2D materials including MoS₂ and bismuth to a polymer target [14,15]. Therefore, understanding and characterizing the adhesion energy of as-grown 2D materials such as graphene to its growth substrate is a critical step for understanding the nature of adhesion and for developing a

successful transfer process, especially for large-scale roll-to-roll production.

Adhesion energy of *transferred* graphene on various substrates has been reported; however, little has been done to investigate the adhesion energy of *as-grown* CVD graphene on its native metal growth substrate. To date, adhesion energy measurements for as-grown graphene are primarily accomplished with dry peeling using a double cantilever beam sample. Yoon et al. first conducted such a test and reported an adhesion energy of $0.72 \pm 0.07 \text{ J m}^{-2}$ for as-grown graphene on copper film [11]. In a similar test, Na et al. discovered a rate-dependent effect with a graphene on copper foil sample and found that the adhesion energy was 6.0 J m^{-2} [12]. In a related development, the adhesion energy of as-grown graphene on copper film was reported as $1.54 \pm 0.07 \text{ J m}^{-2}$ [13]. The adhesion energy of as-grown graphene was also measured with a nano-scratch technique, where a lateral force was applied at the graphene-metal interface [16]. The interfacial adhesion energy was determined to be 12.8 J m^{-2} on copper and 72.7 J m^{-2} on nickel. Such high values may indicate possible covalent bonding of graphene to nickel and partial ionic bonding to copper, but are more likely due to extensive plastic deformation of metal in the scratching process.

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The large discrepancy among reported adhesion energy values of as-grown graphene necessitates further investigation using an alternative approach. As a standard testing procedure for interfacial adhesion energy between a film and a rigid substrate, the blister test with water as the loading medium ensures a quasi-static delamination process when volume is increased at a low and constant rate [17–23]. Blister tests have been used to investigate the adhesion energy of transferred graphene on silicon wafer and copper substrates [24–27]. Koenig et al. reported an interfacial adhesion energy of $0.45 \pm 0.02 \text{ J m}^{-2}$ for exfoliated monolayer graphene and $0.31 \pm 0.03 \text{ J m}^{-2}$ for multilayer graphene of 2–5 layers on a silicon oxide substrate using a blister test [24]. A follow-up study by Boddeti et al. produced an interfacial energy measurement of 0.24 J m^{-2} between transferred graphene and silicon oxide [25]. Cao et al. developed a modified plate theory to account for the residual stress and rotational stiffness of CVD-grown graphene transferred to copper film, and reported an adhesion energy value of 0.51 J m^{-2} [26]. Subsequent work established the mixed-mode nature of delamination in blister tests [28,29]. However, all these blister tests were on transferred graphene. Direct measurement of adhesion energy of as-grown graphene using a blister test has not been reported.

A major challenge associated with the blister test of as-grown graphene on copper foil is the sample preparation. The thin graphene growth substrate needs to be supported by a rigid plate in order to avoid bulk deformation of the copper foil. Meanwhile, a pathway must be provided through the rigid plate and the copper foil for the pressurized medium to reach the top graphene layer and form a blister. Given that the thickness of copper foil is usually on the order of $100 \mu\text{m}$, the fabrication process must be carefully controlled to avoid deforming and damaging the top graphene layer.

In this study, we developed a novel approach to sample preparation and measuring the adhesion energy of as-grown graphene on its copper foil growth substrate using the blister test method. The samples were fabricated with a hybrid nano-milling and electropolishing technique. Prior to graphene growth, the copper foil was treated with acetic acid for different durations to achieve various levels of surface roughness. Therefore, the study not only yielded adhesion energy measurements, but also allowed us to investigate the surface roughness effect of copper growth substrate.

2. Experimental

The graphene samples used in the blister test were grown on $127 \mu\text{m}$ thick, oxygen-free copper foil (Alfa Aesar 13380) using a low-pressure chemical vapor deposition (LPCVD) procedure [1]. Copper growth substrates were treated with glacial acetic acid and triple rinsed with isopropyl alcohol, acetone and deionized (DI) water before CVD growth to remove surface oxidation. Acetic acid treatments of 4 h, 24 h and 48 h were used to alter the copper substrate surface roughness. Hydrogen and methane were flowed at a 1:1 vol ratio (5 sccm) during graphene growth with a peak growth temperature of $1030 \text{ }^\circ\text{C}$.

Fig. 1 shows an SEM image and Raman spectrum of CVD graphene on copper that was prepared in this study. Copper steps, a characteristic of CVD graphene, are seen in the SEM image of the sample surface in Fig. 1(a). A few patches of graphene ad-layers (darker regions) and copper grain boundaries are also observed. The Raman spectrum shown in Fig. 1(b) exhibits strong G (1580 cm^{-1}) and 2D (2690 cm^{-1}) peaks, and no discernible D peak (1350 cm^{-1}), confirming the presence of high-quality, monolayer graphene. Note that the peak at 0 cm^{-1} in the Raman spectrum is caused by laser excitation and the hump in the profile is the result of background fluorescent lighting.

As grown graphene samples were laminated with polyethylene terephthalate (PET)/ethyl vinyl acetate (EVA) film as shown in Fig. 2(a) to provide a backing layer for graphene during the blister test. PET/EVA film has been reported as the polymer support for roll-to-roll (R2R) graphene transfer [30,31], and it was used in this study due to its excellent top surface reflectivity and adequate adhesive strength to achieve complete graphene delamination. The PET/EVA film used in the experiments was Scotch Thermal Laminating Pouches (TP3854-100) with a $76 \mu\text{m}$ total thickness. A commercial hot laminator, GBC HeatSeal H425, was used with a temperature setting of $110 \text{ }^\circ\text{C}$. After the hot lamination, the PET/EVA film on one side of the specimen was removed manually to examine the quality of as-grown graphene as transferred onto the PET/EVA film, as shown in Fig. 2(b). The rest of the specimen was used to fabricate a blister test sample.

Fig. 3 shows an SEM image of the delaminated graphene on PET/EVA film obtained by manually peeling one side of the CVD graphene before the blister sample was made. The dark region brings out the graphene coverage on PET/EVA and the sporadic bright regions are due to cracks and holes in the graphene film that lead to charging of exposed polymer. The high coverage of graphene shows that the PET/EVA film is capable of peeling CVD graphene from its copper foil growth substrate.

Once the quality of graphene growth was verified, an acrylic plate ($51 \text{ mm} \times 102 \text{ mm} \times 2.8 \text{ mm}$) was bonded to the graphene-on-copper sample with cyanoacrylate, Loctite® (1365882), to prevent undesirable deformation in the copper foil during pressurization, as shown in Fig. 4(a). After curing at room temperature for 24 h, a copper lead wire was attached to the copper growth substrate to facilitate subsequent nano-milling and electropolishing in the sample preparation process (Fig. 4(b) and (c)). A blind hole, 4.7 mm in diameter and 1.6 mm in depth, was created in the acrylic plate using an end mill prior to bonding with the CVD graphene on copper. To create a through hole in the copper foil without damaging the graphene layer, the stacked sample was secured to a mini mill and an end mill of $500 \mu\text{m}$ diameter was used to mill into the copper substrate. Since the thickness of the copper foil was only $127 \mu\text{m}$, it was critical to control the feed rate of the milling process with submicron to nanometer resolution, such that the end mill would not damage the graphene layer. In the milling process, the electrical resistance between the mill bit and copper substrate was monitored as shown in Fig. 4(b). As soon as the resistance reduced to near zero, the mechanical milling process was stopped, and the hole making process was continued with an electropolishing process. The mini mill used in the experiments was Sherline Model 5401 and an end mill of 0.5 mm diameter was used (Bits & Bits - DP05MF). A Thorlabs Z825B motorized nanometer actuator with a displacement resolution of 29 nm was attached to the specimen holder for feed rate control.

Electropolishing was used to remove the remaining copper between the milled hole and the as-grown graphene layer without damaging the graphene, as shown in Fig. 4(c). A 3 kHz and 50% duty cycle square wave signal (BK Precision 4012 A) was used to control the polishing current from a constant 24 V DC power supply (BK Precision 1672). Sodium sulfate from Sigma-Aldrich (CAS No. 13462) was used to make the electrolytic solution of 0.5 M/L . The process was stopped when a through hole formed in the copper, which could be observed visually through the transparent PET/EVA layer. After the electropolishing process was completed, deionized water and compressed nitrogen were used to rinse and dry the sample, before it was attached to the pressure manifold with high-strength epoxy, Loctite® (1365736). The sample was then left to fully cure overnight before testing.

It should be noted that certain steps in the specimen preparation procedure such as drilling and electropolishing required

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