

## HIGH QUALITY GROWTH AND ADHESION ENERGY MEASUREMENT OF BILAYER GRAPHENE ON SAPPHIRE

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### Abstract

One bottleneck in integrating graphene in the next generation of microelectronics devices is the efficient and effective transfer of graphene from its growth substrate to the substrate that is targeted for device fabrication. Dry transfer offers the potential for a relatively fast manufacturing process with minimal contamination of and damage to graphene. The paper describes the development of a chemical vapor deposition process for growing graphene on sapphire rather metal. It also demonstrates that graphene can be dry transferred to another substrate via a polymer carrier by exploiting rate and mode-mix dependent interfacial fracture.

### 1. Introduction

In the present study, sapphire was used to carry out the metal-free growth of graphene at conventional metal-CVD temperatures, and the grown graphene is subsequently used in a dry transfer process for determination of interfacial properties. Two types of growths were carried out in this study. In the first type, after an initial cleaning using acetone and IPA, the sapphire substrates were directly loaded in the tube furnace and used for graphene growth. In the second type of growth, the samples were cleaned and annealed in air at 1100° C for 4 hours. Immediately following annealing, the substrates were loaded into the tube furnace for graphene CVD. Raman, SEM and AFM were used to characterize the as-grown samples.

Graphene was grown on sapphire strips measuring 55mm x 5mm for the dry transfer experiments. Laminated beam type specimens were prepared by sandwiching the as-grown graphene/sapphire strip with another sapphire strip through a thin layer of a low-viscosity epoxy (Masterbond EP 30). Post curing, a wedge was driven through the initial blunt crack or bimaterial corner between the epoxy terminus and the graphene, to create a sharp crack tip. For nominally mode I conditions, a dual actuator loading device applied equal end displacements the specimen, which is clamped at the other end. Measurements of the reactive loads and end displacements and rotations and initial crack length allow the J-integral and crack tip displacements to be determined and then used to extract the traction-separation relation of the interaction. Post transfer, the fracture surfaces were characterized using Raman spectroscopy, SEM and AFM.

### 2. Results

Raman, SEM and AFM were used to characterize the as-grown samples. The Raman signature of graphene, which is composed of the D peak (1300 cm<sup>-1</sup>), G peak (1600 cm<sup>-1</sup>) and 2D peak (2700 cm<sup>-1</sup>) can provide information on the quality and number of layers of the as-grown graphene. As confirmed by the I<sub>2D/G</sub> ratio in the Raman spectra of the as-grown graphene samples, bilayer graphene is obtained on sapphire following our current growth recipe. Additionally, the average I<sub>D/G</sub> ratio decreased by about 50% post annealing to a value of 0.14, which is one of the lowest reported values in literature for the direct, metal-free growth of graphene on sapphire. About 60 percent of the sample area had an I<sub>D/G</sub> ratio of 0.15-0.22, when the substrates were pre-annealed. Lorentzian deconvolution of the 2D Raman peaks indicated that bilayer graphene had grown on the sapphire. AFM images on sapphire show the formation of a well-defined surface consisting of atomic steps post high temperature annealing, without much variation in the surface roughness, when

compared to the as-received sapphire. It is believed that the formation of these steps during annealing is crucial to improving the crystallinity of the as-grown graphene as clearly evidenced by the reduction in the average  $I_{D/G}$ . It was observed that the  $I_{D/G}$  values increased slightly, however, if the samples were not used for growth immediately post annealing.

In our experiments, graphene was grown on sapphire strips measuring 55mm x 5mm tailored specifically for dry transfer. Laminated beam specimens were prepared by sandwiching the as-grown graphene/sapphire with another sapphire strip through a thin layer of a low-viscosity epoxy. The target substrate was chosen as sapphire to have a symmetric double cantilever beam specimen and allow for a nominally mode I testing configuration. After curing at 100°C for 2 hours, a wedge was driven through the initial blunt crack or bimaterial corner between the epoxy terminus and the graphene, to create a sharp crack tip. Loading tabs containing DIC (digital image correlation) targets were glued to the specimen for measuring transverse and lateral end displacements as well as the rotations. Both reactive loads were also measured. A dual actuator loading device applied equal but opposite end-displacements at a rate of 0.3 mm/s. Subsequent experiments will vary the ratio of applied displacements in order to introduce shear effects.

Post transfer, the fracture surfaces were characterized using Raman spectroscopy, which indicated that both layers of graphene had been transferred to the epoxy-coated surface of the target sapphire substrate. Low magnification SEM indicated that that 92% of the graphene had been transferred to the target sapphire substrate. Detected air bubbles in the epoxy suggested that they were responsible for leaving microscopic regions of graphene behind on the donor substrate. High magnification SEM and AFM identified some remaining wrinkles in the transferred graphene.

A beam on elastic foundation analysis was used to examine the stiffness of the load-displacement response. Based on the elastic properties and thickness of the bulk epoxy, the effective foundation stiffness of the epoxy was  $1.2 \times 10^{14}$  Pa/m. This is much higher than the extracted stiffness of  $9 \times 10^{12}$  Pa/m, so it was consequently attributed to the stiffness of the interaction between sapphire and graphene. The 3.5 MPa strength of the interaction was determined from the load level at which softening of the interaction began to occur. Subsequent increases in the crack length were determined from the change in the stiffness of the load-displacement response, thereby allowing a resistance curve to be developed. The steady state toughness of the interaction was  $2.0 \text{ J/m}^2$ , which was consistent with the area under its associated traction-separation relation, which had an interaction range of  $1.05 \text{ }\mu\text{m}$ .

### 3. Conclusions

It has been surprising to see that bilayer rather than one layer of graphene was transferred to the target substrate, given that toughness of the Van der Waals interaction between graphene layers is expected to be lower ( $\sim 0.5 \text{ J/m}^2$ ) than that of the determined interaction between graphene and sapphire. However, one explanation may lie in the fact that the strength of the interaction associated with the graphene/graphene interaction is much higher than the determined 3.5 MPa strength of the graphene/sapphire given that strength, rather than toughness, can govern competing delamination paths.

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