No. 14B02

Taiho Kogyo Tribology Research Foundation

Main report

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Theme: Direct measurements of surface forces and friction between voltage-controlled graphene sheets

1. Progress and result of the research

The aim of the project was to carry out direct measurements of the forces between two macroscopic graphene sheets in face-to-face orientation. In order to do this we proposed a graphene Surface Force Balance (gSFB), which was previously set up in prototype manner in our lab[1]. The SFB allows confinement of fluids down to molecularly thin films between two smooth macroscopic surfaces in crossed-cylinder configuration, and measurement of their interaction forces in normal and lateral directions. The most common substrate for SFB experiments is mica, and with this project we developed the use of graphene in place of mica. Eventually, this would allow voltage-control of the surface forces. Figure 1a-b summarizes the geometry of gSFB experiments. During the course of this project we made substantial steps in developing the gSFB and succeeded to make the first force measurements involving molecular contact of the graphene sheets[2].

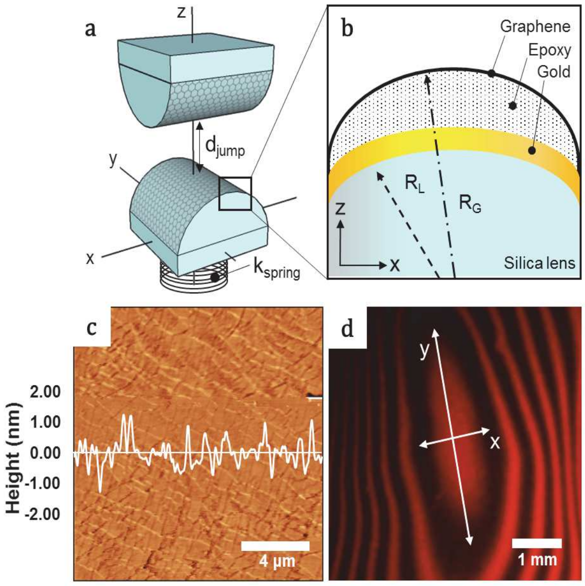

Figure 1: (a) Schematic illustration of the crossed-cylinder, single-contact geometry. **(b)** Schematic of multilayer geometry consisting of a smooth sheet of SLG or FLG glued onto epoxy, supported by a gold-covered silica lens of curvature R_L = 10 mm. Due to thickness inhomogeneity in the epoxy layer (exaggerated in the figure), the actual surface curvature (R_G) differs from R_L. **(c)** AFM height image. The inset shows the line profile over the line in the image. The RMS-roughness is 0.7 nm. **(d)** Optical image of Newton's rings for a prepared SFB lens viewed through a 560 nm filter. The y-axis corresponds to the direction along the lens (y-axis shown in a). The bright/dark fringes correspond to locations of constructive/destructive interference.

A large fraction of the time was taken up with improving our procedures for growing very large (~1cm^2) graphene sheets of single-layer thickness and 100% coverage, and transferring them from the copper growth substrate onto our optical lenses for force measurements. There is a very strict requirement that the graphene has no 'wrinkles' or tears when mounted on the lenses, and after much work we have achieved this: our graphene electrodes are now ca. 0.7nm rms roughness over 20µm x 20µm area (as measured with AFM, Fig.1c). Over the whole macroscopic surface of the cylindrical lens the height of the graphene varies by ~ 170nm over 1cm (Fig.1d). Figure 2 reveals our eventual transfer procedure.

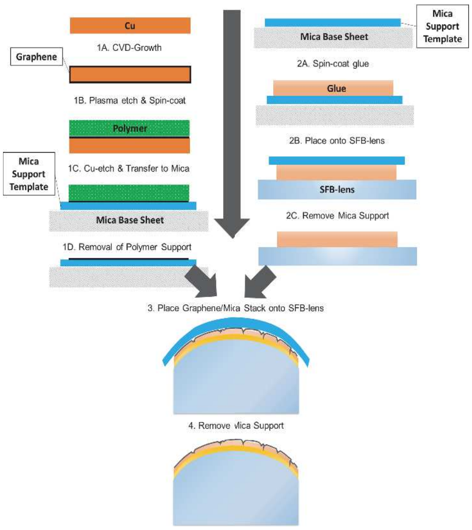

Figure 2: Cartoon detailing different steps involved in the fabrication process to eventually yield graphene covered SFB-lenses. The left side shows the growth of graphene and transfer onto mica as an atomically smooth template. The right side shows the preparation of smooth spin-coated polymer substrate. Below are the steps to combine these and achieve smooth graphene on a polymer spacer on top of the cylindrical optical lens.

The next important step in reaching high precision measurements was development of a robust and accurate method for interpreting the interference patterns arising from the multiple-beam interference spectra of the SFB. Graphene surfaces alter the interferometry, and the non-uniform and asymmetric polymer spacer layers (compared to mica) required additional analysis steps. In figure 3 we summarise the optical cavity.

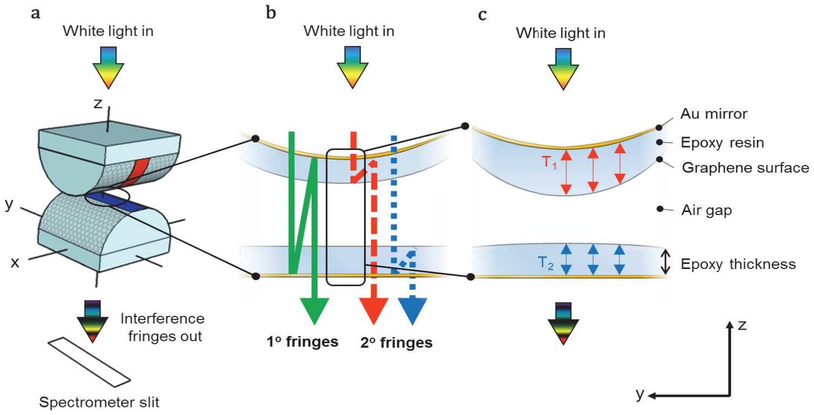

Figure 3: **(a)** Orientation of the surfaces relative to the spectrometer entrance slit. The ellipse indicates the contact position **(b)** Multiple reflections between the Au-mirrors give rise to primary fringes (green solid lines), whereas reflections inside the epoxy layers (i.e. between the Au mirror and the epoxy/graphene/air interface) produce secondary fringes (red dashed and blue dotted lines). **(c)** Exaggerated view of thickness inhomogeneities of the epoxy layers in the yz plane.

Having succeeded in all these steps, we then worked on a first test-experiment to measure the adhesion force between two face-to-face graphene sheets. These experiments were carried out in dry nitrogen, water, and other liquids. Interestingly, we found that despite consisting of a single atomically thin film coating the polymer substrate, graphene sheets lead to a huge enhancement of the adhesion force between surfaces compared to the adhesion between the substrates without graphene present. The results of many measurements are summarized in Figure 4.

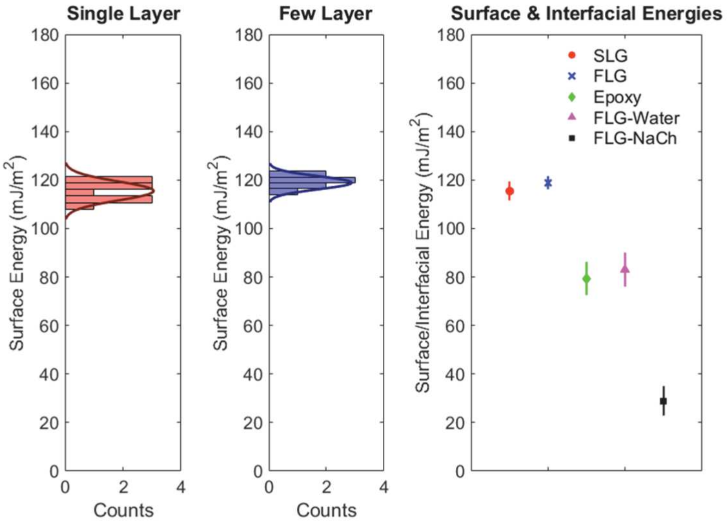

Figure 4: Overview of measured surface and interfacial energies. The histogram and probability distribution to determine the mean and standard deviation for SLG and FLG are shown on the left panels. The right panel shows all measured surface and interfacial energies. The surface energies of SLG, FLG and epoxy were measured in dry nitrogen.

These steps in setting up this very high resolution graphene-SFB and the measurements of adhesion were published earlier this year in Nano Letters, where support from the Taiho Kogyo Tribology Research Foundation is gratefully acknowledged[2].

Our next steps towards the aims of the project were to attach electrodes to the graphene sheets and measure surface forces with applied voltage. We have developed an electrochemical cell for this, as shown in Figure 5, and we are currently working on the force measurements with this setup. Early results are intruiging and we will need to continue with varying several paramters and working on theoretical interpretation before that final outcome is published.

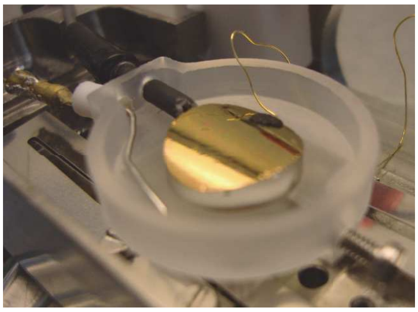

Figure 5: photograph of the graphene coated lens – appearing gold because the graphene (and polymer space) is semi-transparent and so we see the gold mirror underneath. Electrodes are connected using conductive glue and a counterelectrode of Pt is also connected into the cell.

[1] Britton, J.; Cousens, N. E. A.; Coles, S. W.; Van Engers C.D.; Babenko, V.; Murdock, A. T.; Koos A.; Perkin S.; Grobert, N. *A Graphene Surface Force Balance.* Langmuir 2014, 30, 11485-11492.

[2] van Engers, C., Cousens, N., Babenko, V., Britton, J., Zappone, B., Grobert, N., Perkin, S. *Direct Measurement of the Surface Energy of Graphene* Nano Letters 2017, 17, 3815-3821

2. Subjects remain to be solved in future/Subjects required further investigation

As discussed above, we continue the work with electrochemical control of the graphene surfaces and will work towards demonstrating control of friction using voltage-switching of the graphene surfaces.

3. Plan and past presentation or publication of your research results

See above in section 1: We have published the results of this project in Nano Letters in 2017, and work is ongoing with the electrochemical aspect to be published soon.