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Strain-controlled Graphene-Polymer Angular Actuator

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ABSTRACT

We demonstrate a suspended graphene-(poly(methyl methacrylate) (PMMA) polymer angular displacement actuator enabled by variable elastic modulus of the perforated stacked structure. Azimuthal flexures support a central disc-shaped membrane, and compression of the membrane can be used to control the rotation of the entire structure. Irradiating the PMMA on graphene stack with 5 kV electrons in a convention scanning electron microscope reduces the elastic modulus of the PMMA and allows graphene's built in strain to dominate and compress the flexures, thus rotating the actuator.

INTRODUCTION

The patterning and etching of suspended two-dimensional materials is a powerful method to control their mechanical properties and functionalities [1]–[3]. It has been demonstrated that the cutting of graphene resonators can be used to tune their maximum displacement, quality factor, and resonance frequency [1], [2]. Moreover, these schemes have been used to introduce mechanical motion; for example, the patterning of graphene-glass bimorphs has been shown to allow for autonomous self-folding, and graphene kirgami can be used to form dynamic 3D structures [2], [3]. As the ability to pattern two-dimensional materials approaches the single atom scale [4], [5], these methods are templates for machines that can interact with their environment at both the nano- and micro- scales. However, in order to study these mechanical systems, specialized equipment like mechanical probes and laser interferometers are required to drive and detect their motion [2].

In this work, we report a novel angular displacement graphene-based mechanical device that uses only a conventional scanning electron microscope (SEM) or electron beam lithography system, common to many standard fabrication facilities, to both drive and detect its motion. The device consists of a patterned PMMA (poly(methyl methacrylate)) on graphene laminate, and rotational actuation is enabled by relaxation of the built in strain of the graphene. Azimuthal flexures support a central membrane, and compression of the membrane, via electron irradiation[6], produces rotation. The method demonstrates that irradiation from a conventional scanning electron microscope or electron beam lithography tool can be used to control the motion and rotation of suspended membranes, suggesting that this technique can be exploited for numerous applications. The actuation relies only on the ability to tune the elastic modulus of the PMMA, and therefore this device may lend itself to being driven by other means [7]–[9].

EXPERIMENT AND RESULTS

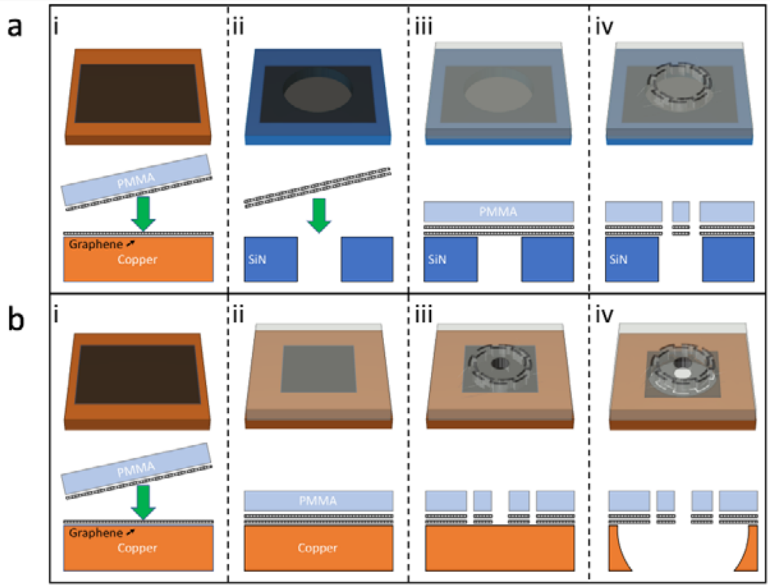

Figure 1: The process used to fabricate the PMMA on graphene angular displacement structures on a.) Silicon Nitride membranes and b.) copper foils. a.), i.) First several layers of graphene are transferred sequentially onto a graphene monolayer on copper foil, leaving a four to eight layer stack of graphene on the foil , ii.) the copper foil is dissolved and the graphene multilayers are transferred to holey silicon nitride, iii.) the graphene is coated with PMMA, and iv.) the PMMA is patterned using electron beam lithography and the graphene is etched by plasma. b.) i.) Several layers of graphene are transferred sequentially onto a commercially available graphene monolayer on copper foil, ii.) the multilayer graphene is left on the copper foil and coated with PMMA, iii.) the PMMA is patterned using electron beam lithography and the graphene is etched by plasma, iv.) the copper is etched below the patterned graphene with a sodium persulfate wet etch.

Figure 1 illustrates the process for the fabrication of suspended PMMA on graphene angular displacement actuators on commercially available holey silicon nitride (Norcada) or copper foil. First, four to eight layer stacks of commercially available single-layer graphene (Grolltex) are prepared on copper foil by repeatedly using a conventional PMMA assisted wet transfer [10], [11]. This sequential transfer ensures spatial homogeneity of the mechanical properties of our multilayer graphene film.

Next, for the devices on silicon nitride (Figure 1(a)), the multilayer graphene is transferred. In order to reduce the built-in tension for the graphene membrane, we use a polymer free wet transfer to suspend the four layer graphene. In this process, the copper substrate is dissolved from below the four-layer graphene in sodium persulfate solution and the free-floating graphene is rinsed in three deionized water baths. The graphene is then scooped onto a 200 nm thick holey silicon nitride membrane. The suspended graphene is spin-coated with 250 nm of PMMA (molecular weight = 950k) dissolved at 4% weight in anisole (A4) and hard baked at 185 ºC.

The PMMA is then patterned with the actuator shape using electron beam lithography and developed in a 3:1 mixture of isopropanol and methyl isobutyl ketone. We use a newly developed pattern (Figure 1(a iv)) that is comprised of a central membrane supported by eight flexures such that when the flexures compress rotation is induced The graphene is then etched to the same shape as the PMMA by exposure to oxygen plasma with two steps of 60 seconds of 50 W at 50 s.c.c.m. O_2 plus 20 seconds of 40 W at 20 s.c.c.m. O_2.

For the devices prepared on copper foil (Figure 1(b)), the multilayer graphene is left on the growth substrate. First, the multilayer graphene is coated with PMMA using the same recipe detailed above. Next, electron beam lithography is performed to generate arrays of the actuator pattern and the graphene is patterned using a similar oxygen plasma etch. Finally, the copper is selectively etched below the graphene actuator by floating the sample with its top side facing down on sodium persulfate (1mg/ml) for approximately 30 minutes.

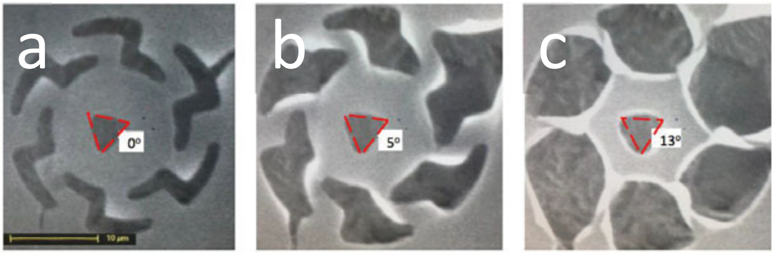

Figure 2: A PMMA on graphene angular displacement actuator as it rotates under SEM irradiation. This device is suspended over a hole in copper. a) The actuator in its initial state, b) the actuator after it has been exposed to ~1 x 10^{15} e^-/cm^2 causing it to twist 5º, and c) the actuator when it has reached its final rotation of 13º after being exposed to ~3 x 10^{15} e^-/cm^2. All images are at same scale.

After the fabrication of the suspended PMMA on graphene device, its rotation can be controlled using electron beam irradiation. The actuators are loaded into an SEM operating at 5 kV with a beam current of 1.0 nA over a roughly 1000 μm^2 area. The motion can be simultaneously driven and imaged using the electron beam.

Figure 2 shows a suspended PMMA on multilayer graphene device (with a copper trench) as it undergoes angular displacement due to electron exposure. A triangle is patterned in the middle of the central membrane in order to track the angle of the actuator. Figure 2a shows the initial configuration of the device before it is driven. In Figure 2b, the flexures supporting the central membrane begin to compress after the device is irradiated by ~1 x 10^{15} e^-/cm^2, and the triangle at the center of the membrane is seen to be rotated by 5º. In Figure 2c, the flexures are fully compressed and have folded over allowing the actuator to reach its full displacement after the device is irradiated by 3 x 10^{15} e^-/cm^2.

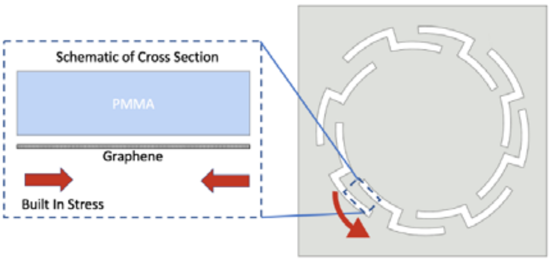

Figure 3: An illustration of the angular displacement mechanism. (Right) Eight PMMA on graphene flexures support a central membrane. (Left) The much thicker PMMA dominates the structural properties of the stack while the underlying graphene has a built in compressional strain as shown by the two red arrows on the left. When the PMMA is made less rigid by electron beam exposure, compression of the flexures result in angular displacement as shown by the red arrow on the right.

Figure 3 sketches the mechanism for angular displacement of the graphene actuator. Suspended graphene has been shown to have its mechanical properties dominated by a large built in tension [12]–[14]. This stress pulls inward on the PMMA on graphene flexures. As the PMMA is irradiated by the electron beam, the coordination of its polymer chains is reduced causing a decrease in its molecular weight and elastic modulus. This reduction in elastic modulus allows the built in stress of the graphene membrane to compress and fold the PMMA. The stress relaxation rotates the graphene transducer as shown schematically in Figure 3 and experimentally in Figure 2.

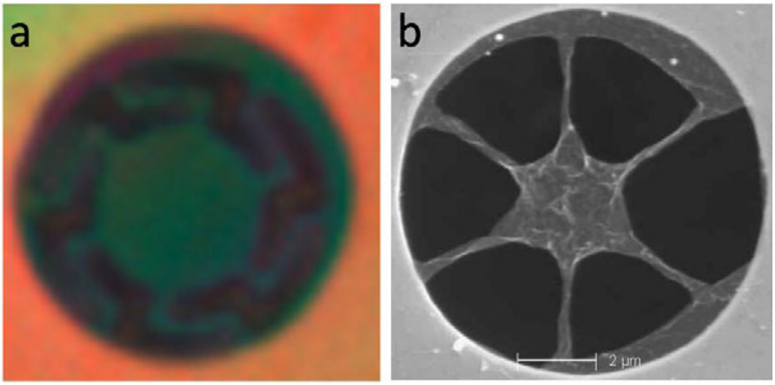

Figure 4: The effect of removing the PMMA from the PMMA on graphene stack. a.) An optical image of a patterned PMMA on graphene stack. b.) An SEM image of the relaxed graphene after the PMMA is removed. The hole is 10 μm in diameter in each image.

In order to confirm that the built in stress of the graphene produces the observed membrane angular displacement, we fabricate a batch of actuators over 10 μm holes and remove the PMMA by annealing at 350 ºC in a ~1 Torr H_2 environment [15]. This simulates the condition of reducing the elastic modulus of the PMMA to zero. Figure 4 shows the device before (optical image) and after (SEM) the removal of the PMMA. Before the PMMA is removed, the suspended PMMA on graphene holds its patterned structure. When the PMMA is removed, the graphene relaxes under its built in tension. This results in a ~15º rotation as the arc of the flexures fully compress. There is also compression and folding in both central membrane and the flexures. This confirms that the rotation of the graphene actuator is driven by the built in stress in the graphene membrane

This mechanism highlights the potential versatility of our method. First, we have found that electron irradiation can be used to selectively and controllably relax the stress in suspended PMMA on graphene stacks. While we have used this effect to drive pre-patterned angular displacement actuators, this same principle could be used to write stress-strain field into pristine PMMA on graphene stacks, thereby controlling the mechanical [16] and electrical [17]–[19] properties of the membrane or its 3D morphology [20]. Given the maturity of electron beam writing technologies, near arbitrary patterns can be generated over large scales.

Also, we have found using our specific angular displacement actuator pattern that a simple reduction in the rigidity of our PMMA layer can result in mechanical motion. This suggests that any phenomena that tunes the elastic modulus of a polymer on graphene could produce similar motion. Effects like temperature [9], solution environment [19] - [20], and light irradiation [8] could all be detected by this device or used to drive its motion.

CONCLUSION

We have demonstrated a novel PMMA on graphene angular displacement actuator that can be driven using a convention SEM. By reducing the rigidity of the PMMA, the built in stress of the graphene causes a compression of the flexures in our pattern yielding a controlled twist. This method is broadly applicable to other structures which can benefit from precise stress relaxation or can be driven by other processes which soften polymers.

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