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Graphene Kirigami and its Use in Biocompatible Strain Sensor

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Abstract

Graphene's large fracture strain (>30%), chemical inertness, and piezoresistive nature make it well suited for use as a biocompatible strain sensor. A rectangular multilayer structure with graphene as its operative component was designed. It consists of a bottom layer of SU-8, a center layer of graphene, and a top layer of SU-8 and gold, with gold acting as the electrical contact. Kirigami-style patterning is applied via photolithography and oxygen plasma etching, allowing for a greater fracture strain. Additionally, the kirigami affects the stress concentration in the graphene, affecting its piezoresistive gauge factor. The complete (patterned) structure exhibited a fracture strain of 40%, a 900% increase over unpatterned SU-8 of similar thickness.

Graphene Kirigami

Since its discovery in the early 2000s, graphene, sometimes called a "wonder material", has been studied for use in a wide variety of applications. Graphene is the world's first studied two-dimensional material, consisting of a single layer of carbon atoms, arrayed in a hexagonal crystal lattice. It is mechanically strong, and has many desirable properties, including high electron mobility, thermal conductivity, and near-transparency. Because many of its properties are directly related to its regular lattice structure, any alteration to that structure in turn affects the properties of the graphene. Graphene can be stretched up to 20-30% beyond its natural length without breaking or permanent deforming, which makes it a prime candidate for kirigami.

Kirigami is the Japanese art of paper cutting for the creation of particular designs (in contrast to origami, which consists of paper folding). Kirigami has been shown to increase the maximum strain obtainable before fracture by up to 400% [1]. Kirigami patterns in graphene will provide a more flexible and stretchable version of graphene. Graphene is well suited to kirigami-style patterns because its Föppl–von Kármán number, "an indication of the ratio between in-plane stiffness and out-of-plane bending stiffness," is similar to that of paper [2]. The goal of this project is to determine a robust methodology for the fabrication of polymer encapsulated kirigami graphene as well as to characterize its piezoresistivity (resistance change with strain) following the enhanced mechanical flexibility/stretchability. Kirigami graphene makes a functional piezoresistive material partially due to graphene's natural piezoresistivity, and additionally because stretched kirigami structures have high local strain concentration, increasing piezoresistivity further. As part of determining a fabrication process, suitable kirigami patterns have been chosen, prioritizing increased strain and mechanical robustness.

Motivation / Rationale

Patterned graphene and devices that incorporate it have been studied for many applications, but only at the micro- and nano- scale [2–6]. While micro-scale devices are fascinating, they are difficult to use handle manually, and can be fragile, limiting their practical applications. In addition, no work has been done to create a graphene device where the graphene is protected and structurally stable enough such that it is versatile and can be used in many contexts. Graphene is a very thin and strong material. It is also nearly transparent and has useful electrical properties. For example, graphene on nitride has been shown to have a large (on the order of 10^4) piezoresistive (PR) gauge, though this was measured with harmonic stretching at 153.8 kHz [7]. However, other researchers have found the PR gauge factor to be much lower, with values between 2 and 7 [5,8]. This project combines the piezoresistance of graphene with additional stretchability from kirigami to create a flexible, mostly transparent strain sensor. The piezoresistivity of kirigami graphene is largely untested, though the value of the gauge factor is likely to vary with different patterns due to different stress distribution. Applications of a graphene strain sensor include biosensors that monitor muscle contractions, including seizure

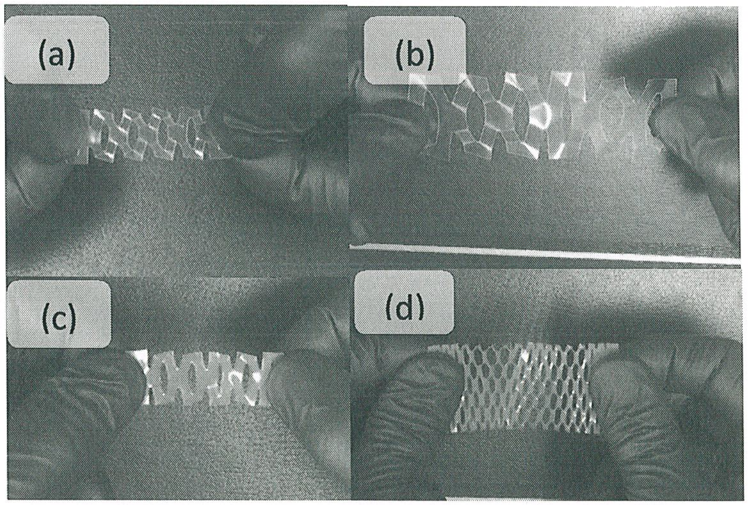

Figure 1. Kirigami structures in PET under manual strain. (a) and (b) are single-layer PET, (c) and (d) are PET with a layer of vinyl. Note that identical patterns did not always show identical stress when strained, as seen in (a), (b), and (c).

detectors or novel pacemakers.

Graphene kirigami has been studied before [2,3,6], but work has been either computational and theoretical in nature or focused on the mechanical properties of kirigami. The effect of kirigami on the electronic properties of graphene, however, has not been studied. Independent of graphene, kirigami has been studied experimentally for strain engineering of nanocomposites, and as a general rule kirigami patterning greatly increases the mechanical flexibility and elasticity of materials [1].

Research Process and Design

The first major segment of this project is to develop a robust methodology for creating kirigami graphene. The planned method is to first design patterns in AutoCAD, then to simulate stretching and observe the behavior to gain intuition about strain patterns in graphene. We desire a pattern that can stretch at least 50% more than a rectangular shape. Before attempting to fabricate anything with graphene, proof of concept on the stretchability of kirigami was needed. Building off the work of previous researchers [1,3], we decided that a simple kirigami pattern was best. We fabricated a variety of patterns in PET (polyethylene terephthalate) using a Silhouette Cameo cutting tool. The machine uses a sharp blade to cut patterns into plastic sheeting. The Cameo was chosen both for speed and simplicity, as the patterns can be fabricated in minutes with reasonable precision. Figure 1 shows some of the patterns created under manual strain. This preliminary test confirmed that kirigami can indeed be used to increase strain and flexibility in a thin film. However, this stretchability comes at the cost of highly localized strain that can cause tears (at least in PET, and the strain pattern is unlikely to be vastly different in other materials). In addition, we observed that an array of "cuts" was stronger and less prone to tearing than a single row. For further designs, a wider array was used.

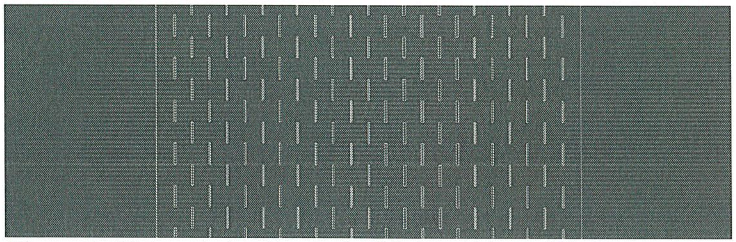

Figure 2. Kirigami structure to be fabricated in multilayer structure. Gold is to be deposited for electronic contacts on the non-kirigami ends

The next step in the process was to actually fabricate the design in graphene. The end goal of fabrication is a passivated layer of kirigami graphene with electrical contacts on both ends of the pattern (passivated meaning that graphene is covered top and bottom to prevent further contamination). While the Cameo could be used for the final fabrication, the available resolution (~100 microns) is not as small as is favorable for micro-scale sensors, and in our testing, it struggled to cut through two layers, which would be required for graphene patterning to prevent contamination.

In order to be used as a wearable sensor, the final product needs to be completely biocompatible and ideally mostly transparent, so as to be usable for wearable forms. It must also be fairly thin, flexible, chemically inert, (e.g. resistant to sweat) , and patternable. One material that fits these requirements is SU-8, a negative photoresist manufactured by MicroChem. Thicknesses ranging from 2 to 100 microns are readily attainable, and SU-8 can be patterned directly using photolithography, with a resolution of 15-20 microns available without optimization.

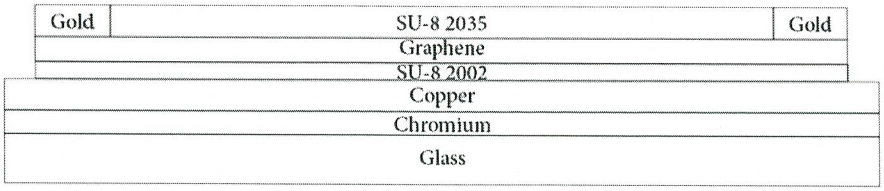

Figure 3: Complete layer diagram prior to copper etch (not to scale). Layers are deposited bottom to top.

In order to be able to release the structure after fabrication, all photolithography was done on glass slides coated with 5 nm of chromium followed by 30 nm of copper, deposited by thermal evaporation. After the structure is completed atop the slide, the copper can be etched away using a sodium persulfate bath, releasing the structure, which floats on the surface. It will then be cleaned via multiple deionized (DI) water baths.

The photomask was designed in AutoCAD and fabricated as a chromium mask on glass. The first layer fabricated was the pattern in SU-8 2002, with a thickness of about 3 microns. After the layer's integrity was confirmed visually (via a microscope), the next step is to transfer a layer of graphene on top of it.

The graphene used in our lab was grown on thin copper foil by LP-CVD (low pressure chemical vapor deposition). After growth, the graphene on the back side of the foil is removed via oxygen plasma etch and a layer of poly(methyl methacrylate) (PMMA), more commonly known by its trade name, Plexiglas®, is spin-coated on top of the graphene so it can be seen easier, and to protect it during the transfer process. It is then manually cut with scissors to a size slightly larger than the underlying pattern it is to be laid on top of. This smaller piece is floated on a sodium persulfate bath to etch the copper, leaving the PMMA/graphene floating on the surface. This can then be lifted out onto a glass slide and passed through multiple de-ionized (DI) water baths to clean it. Once clean, it is lifted out of the DI water onto the SU-8 2002 pattern that is on the copper-coated glass slide. This is left to dry overnight, then the PMMA is removed via an acetone etch, which does not affect the SU-8.

Immediately following the acetone etch, a layer of SPR-220, a positive photoresist also manufactured by MicroChem will be deposited and patterned on top of the structure. It is designed to be identical to the SU-8 layer below only on the kirigami portion of the design, not the contacts at the end so that the unwanted graphene (the graphene that covers the holes in the kirigami pattern) can be removed via oxygen plasma etching. After the plasma etch is complete, the sacrificial SPR layer will be removed with acetone. A layer of SU-8 2035, around 30 microns thick can then be added on top of the existing structure. It is almost identical to the SU-8 pattern beneath, except it leaves the outer ends free of SU-8 for gold electrical contacts to be deposited directly on the graphene, as SU-8 is not electrically conductive. The gold contacts will be deposited via thermal evaporation.

Now that the structure is complete, it is placed in a sodium persulfate bath to remove the underlying layer of copper, releasing the structure, which floats on the surface. This is cleaned by passing through multiple DI water baths. In order to stretch the structure evenly, a rectangular hole whose width is about equal to the length of the kirigami pattern is cut into a PET sheet. The structure is placed over this hole so that the contacts are above the PET, but the kirigami hangs free. The PET can be cut so that by pulling the two pieces apart, the kirigami structure will be stretched. This entire setup will be clamped and placed on a micrometer to allow for accurate determination of strains. In this setup, electrical current (I)- voltage (V) measurements will be taken at various strains to determine the relation between resistivity and strain (piezoresistivity).

Results

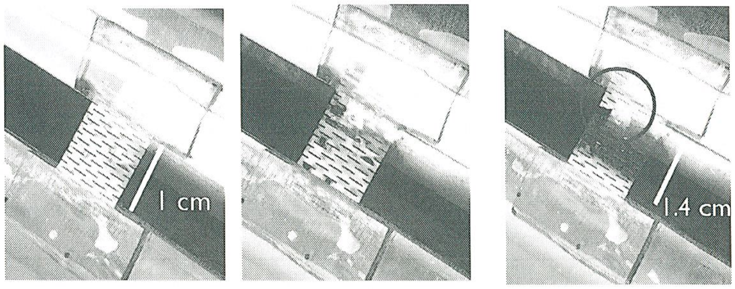

Fig. 4 Bilayer Su-8 2035 with thickness ~50 microns atop a micrometer, stretched until fracture. Note the out of plane bending visible in the middle image, shortly before breakage.

A strain of 40% was attained before the structure fractured. On inspection of the fracture regions under a microscope, it was determined that the fracture was almost certainly not due to any local imperfections in the structure, or that such imperfections were invisible. This 40% fracture strain is consistent with Singamaneni, et al[9],though they used a pattern dissimilar to ours. Feng and Farris show that unpatterned SU-8 has a fracture strain of 3-7%, depending on thickness and bake times[10]. The kirigami pattern used in this project is 9 times more stretchable than unpatterned SU-8, and is functional as a scaffold for a graphene-based strain sensor.

Discussion

For the final product, a balance of flexibility and rigidity is required – the structure must be strong enough to handle, but also flexible enough to stretch and mold to whatever shape surface it is placed on. SU-8 2002 is quite thin (~3 microns), and it bends out of plane easily. This can be a problem, as multiple steps in the fabrication process require a wet etch process, with the SU-8 structure left floating on top that must be removed. It cannot be picked up directly, except onto a flat surface such as a glass slide, as the surface tension of water will fold the structure in half, which can cause it to break. Additionally, on one occasion when graphene was layered with a 3 micron layer of SU-8 and the structure released from the copper substrate, the graphene/SU-8 structure curled in on itself, much like a film roll. While it did not break, it also made itself unusable. While ideally, there should be no stress in the graphene-SU-8 binding, this is not guaranteed, and thicker SU-8 is strong enough to contain the stress with little to no bending.

This brings up the second major challenge – thicker SU-8 layers. SU-8 has many different versions available, with thicknesses ranging from 2 to over 200 microns. For the purposes of this project, the “thick” layers were to be in the 25-40 micron range. Before processing, all SU-8 is stored in bottles as a liquid. However, Su-8 2035 is a very viscous gel, and regardless of how it was applied onto the Cu/glass slide, bubbles formed during the spin coat process and remained through the rest of the processing. This issue was solved by heating the SU-8/Cu/glass slide to 70 °C and allowing it to cool before spinning the sample. In addition, the thicker SU-8 is prone to cracking at sharp (90°) corners, likely due to thermal cracking from rapid cooling following the post-exposure bake (PEB). This was reduced significantly (though not entirely removed) by powering off the hot plate after the PEB was complete, and allowing the sample to cool very slowly to ~30 °C before proceeding with development.

When preparing samples for mechanical testing, the height of the sample was measured by a profilometer. It is interesting to note that when creating bilayer SU-8/SU-8 structures, the height of the bilayer structure was measured to be between 135-50% the thickness of the monolayer, with minimal evenness across the entire structure. This is likely due to the way the liquid/viscous SU-8 behaves on an uneven surface, leaving a minimal amount atop the preexisting SU-8. In order to counteract this effect, it is recommended for the bottom layer of SU-8 to be considerably thinner than the top layer. It will still provide passivation and protection, but allow for more control over the thickness and evenness of the entire structure.

There was some difficulty in removing the SPR-220 from the graphene/SU-8 structure after the oxygen plasma etch to remove the unwanted graphene. Most of the SPR dissolved in acetone, but a small amount of it remained adhesed to the graphene, though in a liquid, not solid form. The cause of this is unknown, though longer development times may assist the process. Heating the sample significantly, even in solution, is not recommended, as the graphene will contract and pull the SU-8 with it, in essence ruining the sample.

Finally, a word about the effect of the type of kirigami pattern itself. In the preliminary testing, the prototype patterns in PET showed significantly more stretching in the single-wide patterns (fig. 1a-c) than the patterns with multiple holes across the width. As the wider arrays were more stable and less prone to cracking, it was decided to use them for further patterning. However, much of the stretchability of the structure comes from out-of-plane bending. From observations during the mechanical tests of our samples, a wide pattern in bilayer SU-8 exhibited minimal to no out-of-plane bending, and then only just before fracture. From testing, we infer that a key component of a highly stretchable structure is one with a high ratio of cut length to the width of the entire pattern. That is, one longer cut is preferable to multiple shorter cuts. However, this would also cause higher stress concentrations on the corners of the holes, meaning that failure is more likely.

Conclusion

This project has succeeded in designing and optimizing a fabrication process for a polymer/graphene/polymer kirigami structure. It is expected that kirigami graphene will exhibit a fairly high gauge factor, suggesting that our structure can be used as a biocompatible, thin, mostly transparent strain sensor.

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