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All-Carbon Graphene Bioelectronics*

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***Abstract*— We report nano field-effect transistor (nanoFET) biosensors built from the monolithic integration of graphene and graphite. The monolithic integration enables nanoscopic field-effect detection of chemical and biological signals with mechanically flexible and robust interface with biological systems in several respects. Our nanoFET biosensors exhibit superior detection sensitivity, mechanical flexibility and nanoscopic detection resolution. First, we demonstrate that electrical detection can be achieved from nanoscale electric field modulation of the graphene channel while the signal integrity is not perturbed by mechanical deflection of graphene nanoFET sensors. Such capability is introduced by the advanced design of monolithic graphene-graphite without any need for metal-graphene heterointerfaces. Second, we explore the chemical detection capability of graphene nanoFET sensors, and show that our sensors are responsive to localized chemical environmental changes/perturbations. Our nanoFET sensors not only show clear response to nanoscopic charge perturbation but also demonstrate potential 3-D sensing capability due to the advanced monolithic graphene-graphite mechanical design. These unique capabilities of our monolithic graphene-graphite bioelectronics could be exploited in chemical and biological detection and conformal interface with biological systems in the future.**

I. Introduction

The soft, 3-dimensional (3D) nature of cells and tissues of biological systems require that integrated bio-electronics conform to the mechanical characteristics and multi-dimensionality of the cells/tissues. However, conventional electronics are typically constructed from hard, planar surfaces, which present substantial challenges for intimate, 3D interfacing with biological systems. These contrasts in mechanical properties and dimensionality could result in the separation of the electronic device from biological systems and severe inflammation of tissue in long-term implantation. For example, brain bio-electronics present the most significant challenges, in that the brain is very soft (elastic modulus <500 Pa) in contrast to rigid conventional electronics (>100 GPa) [1].

To address such challenges, past research efforts have focused on advancing the design of device/substrate structures to ensure conformal coverage over the tissue [1] or utilizing ultra-small nano-devices for non-invasive 3D, bio-interfacing [2]. Unlike these previous works which have focused on advanced designs or reducing the size of devices to overcome inherent limitations, this paper presents the introduction of new materials optimized for biological applications.

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Superb electromechanical properties of graphene, where more than 20% of elastic deformation is achievable without perturbation of the electrical properties [3-5], have been explored as flexible electronic materials. For example, practical applications, such as graphene-based conducting electrode [6], have been implemented, demonstrating potential for flexible touch screen applications. Such unique electromechanical properties can be applied to biological systems, in particular the electrical bio-interface, where mechanical flexibility and electrical functions of graphene membrane can be fully utilized.

Here we report an unconventional approach for interfacing monolithically-integrated graphene-graphite electronic device networks with biological systems. We show that these fully-formed all-carbon structures can be used to demonstrate real-time, multiplexed chemical sensing, and furthermore, flexible and conformal interface for bio-electronics.

II. Monolithic Graphene Electronics

A. Synthetic Control of Graphene Layers and Electronic Properties

We demonstrate thickness control of graphene layers by utilizing differences of carbon solubility in heterogeneous catalyst metals during chemical vapor deposition (CVD) synthesis [5]. Such capability, together with patterning of catalyst metals, yields localized graphene areas with differing numbers of layers. Multilayer graphene is formed by segregation and precipitation of the dissolved carbon on the metal surface, such as Ni or Co [5-7]. In contrast, Cu catalyst has negligible carbon solubility (< 0.0001 at.% at 1000 ^{o}C) compared to Ni or Co catalysts, and single layer graphene can be synthesized by carbon adsorption on the Cu surface [7, 8]. As demonstrated in Figure 1, we are able to control the number of graphene layers by patterning heterogeneous metal structures. Furthermore, our one-step synthesis allows continuous and seamless interface between different thicknesses of graphene.

Figure 1. Synthetic control of graphene layers. Optical microscope image of graphene with differing number of layers. Letters ‘o’ are composed of ~6-10 layers and letters ‘m’ and ‘n’ 850 layers. Background is composed of bilayer graphene on 285 nm thick SiO_2 on Si substrate. Scale bar, 200 µm.

Such capability in synthesizing differing thicknesses of graphene layers is further translated to controllability of electronic properties of multilayer graphene. We show that conductivity or sheet resistance of multilayer graphene multilayers can be controlled more than two orders of

magnitude by synthesizing graphene multilayers with different metal catalysts. We demonstrated that as the thickness increases from a bilayer to ~850 layer-graphene, the sheet resistance reduced by a factor of about ~25 (from ~2.5 kOhm/sq to ~100 Ohm/sq) [5]. Low sheet resistance and metallic nature of graphite are advantageous for applications in conductive electrodes whereas superior transconductance level of thinner few-layer graphene is appropriate for active channels of field-effect sensors.

B. Monolithic Graphene-Graphite Electronics

The capability to modulate the sheet resistance and transconductance with number of graphene layers enabled us to form monolithically integrated transistors with graphene channels and graphite electrodes. We achieve the synthesis of these monolithically integrated field-effect transistors (FETs) in a single step by using differing catalyst metals. Inset of Figure 2 shows the fabricated graphene transistors with graphite source (S)/drain (D) transferred on a SiO_2 substrate. Electrical S/D current versus backgate bias (V_{bg}) characterization of these monolithic FETs (Figure 2) showed ambipolar behaviors consistent with the expected character of graphene [9, 10] with a positive charge neutrality point of ~3.5 V.

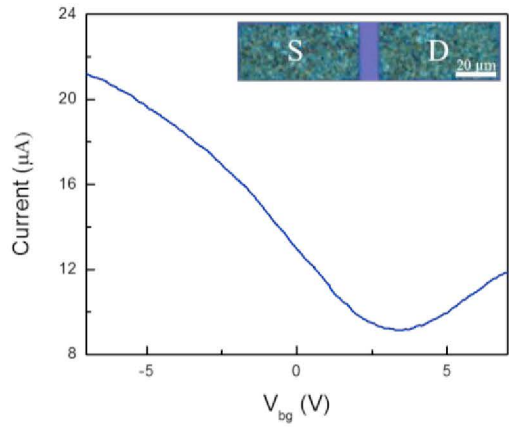

Figure 2. Monolithic graphene-graphite electronics. Backgate transfer characteristics of monolithic graphene-graphite FET device. Inset shows optical microscope image of monolithic field-effect transistor.

III. Monolithic Graphene Bioelectronics

A. Chemical and Biosensing Capability

Device integration by a single step synthesis allowed us to create large number of monolithic graphene-graphite biosensor arrays. An array form of the monolithic FETs was synthesized and transferred on a flexible transparent substrate (Figure 3a). Due to optical transparency of all-carbon device array on transparent substrate, the logo on the background can be clearly seen through the device array. Optical microscope image of the array is shown in Figure 3b. Here the graphite interconnect is connected to graphene channels in a large scale array (c.a. 100 devices were integrated in this structure). Furthermore, we have integrated microfluidic channels (horizontal lines shown in Figure 3b) for controlled delivery of small molecules and simultaneous electrical detection of binding events.

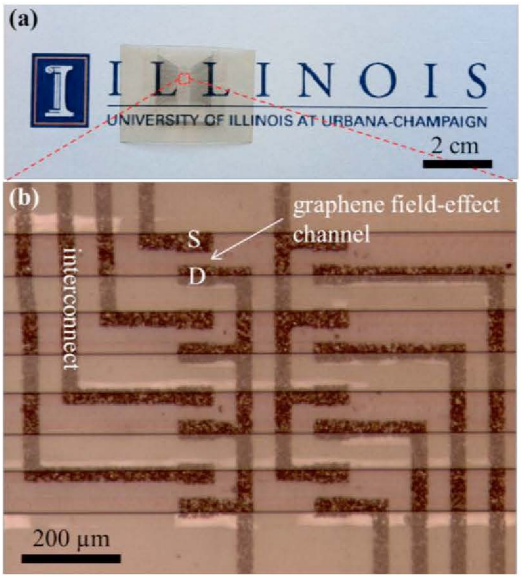

Figure 3. A picture and optical microscope image of monolithic graphene-graphite sensor arrays. (a) Transparent, all-carbon graphene-graphite sensor arrays integrated on a flexible, transparent substrate. (b) Optical microscope image of device array. Dark brown pattern shows graphite interconnects. Graphene field-effect sensor channel is between S/D graphite electrodes, which is not shown in the image due to low contrast of a single layer graphene.

To test realtime chemical detection using all-carbon monolithic graphene-graphite field-effect sensors, we measured current versus watergate potential (Ag/AgCl electrode) characteristics as different polymer solutions (poly-lysine and polyacrylic acid, both at 100 μM) were introduced to the microfluidic channel. As clearly shown in Figure 4, we were able to observe that when positively charged polymer molecules (poly-lysine) were introduced to the device, charge neutral point of graphene sensor shifted to the lefthand side (blue curve in Figure 4), whereas righthand side shift was observed when negatively charged polymers were introduced. Such events can be explained by the non-specific binding/interactions of hydrophobic molecules with graphene surfaces and consequent molecular gating effect [12]. When we fix our watergate potential at -0.2 V (as the dotted line), we are able to observe that the current level of our graphene sensor will decrease (increase) when positively (negatively) charged molecules are introduced and bound to the surface. Furthermore, due to the ambipolar nature of the graphene sensors, the signal polarity is inversed in the positive watergate voltage (e.g., when V_{wg} is at +0.3 V). We believe our multiplexed monolithic graphene biosensor arrays can be exploited as chemical and biological sensors, where high sensitivity and simultaneous, multiplexed monitoring are critical.

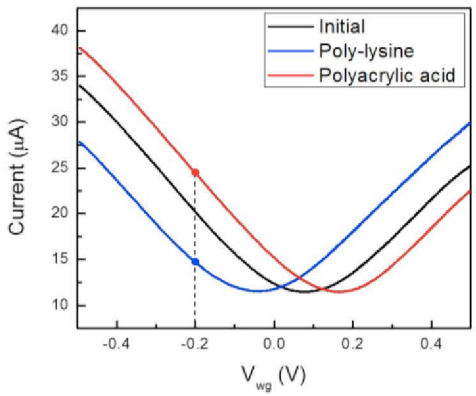

Figure 4. Chemical sensing capability of monolithic graphene-graphite field-effect sensor. Current versus watergate potential of monolithic graphene-graphite sensor during exposure to polymer molecules with different charges (DI-water, positively-charged poly-lysine and negatively-charged polyacrylic acid).

B. *Flexible and Conformal Graphene Bioelectronics*

Flexible and conformal bioelectronics represent an important application area that can take advantage of monolithically integrated graphene-graphite devices. We performed electrical characterization of the field-effect devices when the substrate was flat and when it was bent, and observed no significant change in the electrical response. Such trends remain almost constant when applying a maximum strain of ~4%, demonstrating the unique mechanical flexibility of our monolithic graphene-graphite integrated electronics [5].

More significantly, our ultra-thin monolithic graphene-graphite structures allowed the transfer of the whole device onto various non-planar substrates. As an example, Figure 5 displays the transfer of our monolithic device on a human eye model, demonstrating the unique potential for application to an artificial retina where softness of our electronic material lends itself for conformal interface with the corresponding mechanical properties of biological systems.

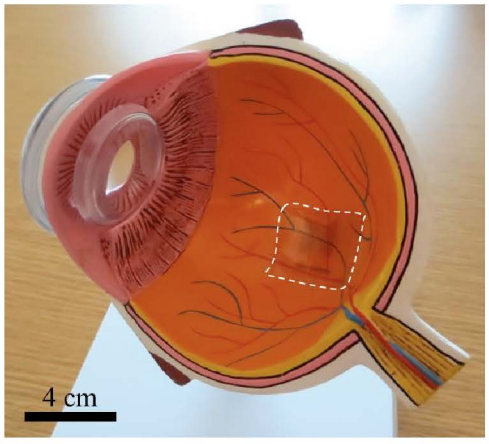

Figure 5. Flexible and conformal monolithic graphene-graphite bioelectronics. Here monolithic graphene-graphite sensor array film is transferred onto a model of a human eye where the device is capable of electrical stimulation and detection of biological signals.

IV. Discussion

We believe our single-step synthesis of all-carbon monolithic graphene-graphite integrated electronics exhibits unique features and potential superior to conventional bioelectronics. First, the one-step synthesis of the entire graphene integrated electronics simplifies the complicated fabrication steps in Silicon based electronics (e.g. lithography, ion-implantation, annealing, deposition, etching, etc.), and further enables the integration onto various substrates such as flexible plastics. Second, ultrahigh sensitivity of chemical binding events and potential multiplexing capability is demonstrated for large-scale device arrays, and demonstrates substantial improvement in scalability over other nanoscale biosensors [12]. Third, our monolithic graphene-graphite integrated electronics possess intrinsic advantages in mechanical flexibility versus conventional integrated electronics which have mechanically fragile heterogeneous metal-semiconductor interfaces, and such mechanical flexibility could be further explored up to the extent of the intrinsic mechanical properties of graphene [13].

V. Conclusion

In conclusion, we have demonstrated a unique one-step synthesis of all-carbon flexible sensor arrays which can be transferred to various substrates and surfaces. The monolithic integration enables nanoscopic field-effect detection of chemical and biological signals with mechanically flexible and robust interface with biological systems. We believe the capability to synthesize monolithic graphene-graphite integrated electronics provides a promising strategy towards flexible, wearable electronics and implantable biosensor devices, and also suggests substantial promise towards chemical and biological detection and conformal interface with biological systems in the future.

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