

# Strong, Controllable, Robust and Scalable Graphene n-Doping for Optoelectronic and Micro/Nano-Electronics Applications

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## ABSTRACT

Graphene holds promise for many applications such as microelectronics and optoelectronics due to its combination of outstanding properties such as optical transparency and electronic mobility. The realization of these applications, however, requires tailoring graphene's electronic properties via controlled doping (addition or removal of electrons). Previous approaches to n-dope graphene (adding electrons), like chemical doping, have yielded low electron density and the doping typically degrades over time. We recently developed a new approach that yields strong, robust, and spontaneous graphene n-doping on low-cost (\$5/m<sup>2</sup>) soda-lime-glass (SLG) via surface-transfer doping from sodium (Na), without any external chemical, high-temperature, or vacuum processes. For applications to micro/nano-electronics, applying this approach to a wider range of substrates and semiconductors has the potential to enable high-performance, low-cost devices. We examine the challenges to realizing this vision, and next steps required.

**Keywords:** graphene, doping, MOSFET, GFET, photovoltaics, sensors

## 1 INTRODUCTION

Graphene, a one-atom thick sheet of carbon, has great potential for technological applications due to its combination of remarkable properties such as its mechanical strength, electrical conductivity, and optical transparency. Scalable and low-cost doping (n or p) of pristine graphene could improve a wide range of technologies such as batteries, sensors, fuel cells, microelectronic-circuits and could also serve as transparent, highly-conductive, and electrically-tunable junctions for optoelectronic applications. Unlike the ubiquitous p-doping in graphene [1-6], attempts to n-dope graphene using methods other than electrostatic-gating, such as chemical doping, have yielded relatively low electron densities (< 9.5x10<sup>12</sup> cm<sup>-2</sup>), and have been shown to be strongly susceptible to degradation over time [7-13].

In a step toward overcoming these challenges, we recently published a rigorous and comprehensive experimental investigation of a facile and

readily scalable method to strongly (electron density > 2x10<sup>13</sup> e/cm<sup>2</sup>) and persistently n-dope chemical-vapor-deposited (CVD) graphene using low-cost soda-lime glass (SLG) substrates [14]. Using this effect, we demonstrated a graphene(n-type)/semiconductor(p-type) Schottky junction diode with strong photo-response using a standard thin-film photovoltaic p-type semiconductor (CIGS), and demonstrated control over the doping strength with an oxide spacer layer placed between the graphene and semiconductor [14].

The ability to achieve strong and persistent graphene n-doping on low-cost, industry-standard materials paves the way toward an entirely new class of graphene-based microelectronic and optoelectronics devices, such as photodetectors, photovoltaics and sensors, and electrochemical devices such as batteries and supercapacitors. In order to realize this potential, however, many questions must be answered and many challenges must be overcome. After summarizing our recent results in this area in greater detail, we discuss remaining open questions and challenges to realizing this vision, and lay out what we view as the experimental next steps required to answer these questions and overcome these challenges. Finally we describe our initial progress toward addressing these challenges.

## 2 RESULTS

As briefly summarized in the introduction, we recently demonstrated that strong and persistent graphene n-doping can be accomplished by transferring CVD-grown graphene onto low-cost (\$5/m<sup>2</sup>) soda-lime glass (SLG) [14]. Previous research had shown that adsorption of alkali metals can produce n-doping on graphene, but lack of scalability and the reactivity of most alkali metals proved problematic, resulting in degradation of the doping strength over time [11]. In contrast, our method uses industrial-grade SLG with ~8% Na<sub>2</sub>O as a substrate for CVD graphene, and achieves strong (> 2x10<sup>13</sup> e/cm<sup>2</sup>) and persistent (no change in doping observed upon exposing the device to air for several weeks) n-doping via Na surface-transfer doping [14]. We believe that the stability of doping over time is due to the inert, and effectively inexhaustible (from the perspective of the graphene) supply of Na in the substrate.

This overcomes one of the primary shortcomings of competing methods whereby degradation occurs due to evaporation or reactivity of a fixed supply of introduced dopants [6-8].

The doping effect was initially observed by depositing CVD graphene onto a thin-film photovoltaic material (copper-indium-gallium-diselenide - CIGS), which itself is deposited onto a thin layer of molybdenum (Mo), all of which sits on a 3mm SLG substrate. Forming graphene field-effect transistors (FETs) with the graphene on these substrates showed that the graphene is strongly n-doped upon transfer to the CIGS due to Na that diffuses through the Mo and throughout the CIGS from the SLG. The CIGS/Mo/SLG structure is widely used within the photovoltaics community, and the CIGS semiconductor in this case is known to be p-doped. Typically an n-type CdS layer forms a p-n junction with the CIGS, and ZnO and Al:ZnO form the transparent top layers. In our case, we replaced the CdS, ZnO, and Al:ZnO with n-doped graphene, forming a photoactive Schottky diode between the p-type CIGS and n-type graphene with ~1% power conversion efficiency, an ideality factor of 1.21, and photocurrent of 13.5mA/cm<sup>2</sup> under 1000 W/m<sup>2</sup> illumination [14].

Subsequent measurements also revealed that graphene n-doping can also be achieved by direct transfer onto SLG, as already described above. Again, transconductance was measured on a graphene FET, revealing the n-doping of the graphene to be  $1.33 \times 10^{13}$  e/cm<sup>2</sup> and a shift in Fermi energy ( $\Delta E_F$ ) of +426meV. Calculations performed via density functional theory (DFT) closely agreed with the experimental values. A similar device was fabricated as a control experiment whereby a FET was constructed by depositing CVD graphene on common borosilicate glass (BSG) which was sodium-free. No graphene doping was observed when using the Na-free BSG substrate, confirming the observation that Na is responsible for the n-doping observed on SLG [14].

### 3 OPEN QUESTIONS AND CHALLENGES

Successfully applying and commercializing these discoveries will require additional research to address many open questions and challenges, some of which are outlined below.

1. What are the details of the doping mechanism? In order to better control the doping strength and resulting electronic properties of graphene, we must gain a more complete understanding of the n-doping mechanism by probing the coordination of Na at the surface of SLG and CIGS. Although Na in SLG is known to be in the form of Na<sub>2</sub>O, the transfer of graphene involves several steps which can alter this chemical state. While Na is likely in the form Na<sub>2</sub>O in the SLG, the diffusion process of sodium through the CIGS p-type semiconductor can change the chemical form to Na<sub>2</sub>CO<sub>3</sub>, NaSeO<sub>3</sub> or NaOH [17].

2. How can we control the graphene properties and the graphene-semiconductor junction properties? In order to control the graphene-semiconductor junction properties, we must have fine control over the doping strength and interfacial recombination rate. Initial experiments suggest that the thickness of a few-nm thick spacer layer between the graphene and semiconductor can drastically reduce recombination and be used to tune the graphene Fermi-level shift [14]. We have observed that the graphene n-doping strength in the presence of a 4nm thick TiO<sub>2</sub> spacer layer between the graphene and Na-containing semiconductor is 13% lower than the case without the spacer layer, and that the open circuit voltage of a CIGS/graphene junction increases from 0.23V without the TiO<sub>2</sub> layer to 0.49V with the TiO<sub>2</sub> layer due to a reduction in interfacial recombination. Additional transconductance measurements on samples with a range of spacer layer materials and thickness are required to optimize this process.

The electronic structure of graphene can be controlled not only through doping, but also by control over the number of graphene layers [18], and therefore precise engineering of the junction properties requires control over the number of graphene layers. Most devices we have studied to-date consist of five-layer graphene, but the ability to adjust the number of layers, down to a single layer, is desired.

3. How can we extend this technique to a wider array of substrates and semiconductors? In order to ensure the maximum impact on a wide range of technologies, including micro/nano-electronics, it is important to extend these results to other substrates that are compatible with these applications. For example, FET devices where the doping originates from the top layers such as the gate dielectric itself, rather than the substrate, would enable graphene(n)-semiconductor(p) junctions with any desired semiconductor.

4. How can we achieve higher mobility in substrate-transferred graphene? The mobility for devices using CVD graphene transferred onto substrates (substrate-transferred graphene) is generally much lower than that of suspended graphene. The deposition of metal oxides, used for gate dielectrics in graphene FETs, do not directly deposit onto pristine graphene [15]. Instead, the oxides use defect regions within the graphene or boundaries of the graphene layer itself as nucleation sites, creating an uneven or damaged oxide layer that causes unacceptable leakage currents. This is primarily due to the lack of dangling bonds in the graphene plane [15]. In addition, oxide deposition via ALD actually damages the graphene [16], leading to reduced carrier mobility. Commercialization of our doping method, which relies on surface-transfer doping from substrates, depends on greatly improving the mobility of substrate-transferred graphene.

## 4 INITIAL PROGRESS ADDRESSING FUTURE CHALLENGES

We have made some initial progress in addressing the second question regarding the control over the graphene properties. Further experiments were carried out in order to understand the tunability of n-doping where a metal oxide layer is placed between the graphene and SLG. In the initial study [14], a 4nm of TiO<sub>2</sub> was deposited between the graphene and SLG, demonstrating that interfacial recombination and Schottky barrier height can be reduced using this method. Experiments are currently underway to examine quantify the variation of doping strength with oxide thickness, and also to more systematically measure the change of this doping strength over time due to degradation.

Preliminary studies [14] have shown that the doping strength had not diminished over several weeks during exposure to air (the graphene remains n-doped since it does not directly contact the air due to the Al<sub>2</sub>O<sub>3</sub> gate dielectric). To more systematically examine longer-term degradation, several matched pairs of graphene FET samples with varying oxide thicknesses are being prepared and measured. Half the samples will be left in open atmosphere, while the other half will be held under vacuum. Transconductance measurements on these devices will be performed every week or so over the next several months to quantify the degradation.

## 5 CONCLUSIONS

Strong, persistent, and controllable n-doping of graphene is important for future applications, but has proven to be challenging. Here we describe our recent work that demonstrated a new method of achieving strong, controllable, and persistent graphene n-doping using commercially available, low-cost soda-lime-glass substrates, and also described our use of this method to form photoactive Schottky junctions. These results could help pave the way toward an entirely new class of graphene-based microelectronic and optoelectronics devices, but only if certain challenges are addressed, such as obtaining fine control over the graphene doping strength and increasing the mobility. We have identified the most important open questions and challenges to commercializing this discovery, and also described our initial progress in addressing these challenges.

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