Metrological Suitability of Functionalized Epitaxial Graphene

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***Abstract* — This work presents one solution for long-term storage of epitaxial graphene (EG) in air, namely through the functionalization of millimeter-scale devices with chromium tricarbonyl - Cr(CO)₃. The carrier density may be tuned reproducibly by annealing below 400 K due to the presence of Cr(CO)₃. All tuning is easily reversible with exposure to air, with the idle, in-air, carrier density always being close to the Dirac point. Precision measurements in the quantum Hall regime indicate no detrimental effects from the treatment, validating the pursuit of developing air-stable EG-based QHR devices.**

***Index Terms* — quantized Hall resistance, epitaxial graphene, functionalization, carrier density.**

I. INTRODUCTION

Monolayer epitaxial graphene (EG) has been demonstrated to exhibit highly favorable properties for the continued advancement of quantized Hall resistance (QHR) standards [1-3]. Because QHR devices based on EG experience an unpredictable, time-dependent drift in the charge carrier density (n_e) due to adsorption of atmospheric molecular dopants, it is crucial to understand how one may stabilize n_e in ambient conditions. Such an improvement renders these devices user-friendly and extends their shelf life for commercial purposes.

In resistance metrology, a narrow range of n_e between 1×10^{11} cm^{-2} and 3×10^{11} cm^{-2} is needed to produce a resistance plateau of $R_H = h/2e^2$ at easily accessible magnetic flux densities (*B*-fields). Though early efforts to control n_e in EG devices have had a range of successes [4-6], finding a method that was fully reversible while still maintaining EG's metrological usefulness proved difficult. This work presents one solution whereby EG devices retained a constant, low value of n_e even with long-term storage in air. This stability is achieved through the functionalization of EG with chromium tricarbonyl - Cr(CO)₃. From these low, stable values of n_e, a reproducible tuning process (via annealing) for n_e is described [7], making the devices easier for an end-user to adjust.

II. PREPARATION OF GRAPHENE DEVICES AND SETUP

EG is formed during thermal decomposition of the SiC, causing the substrate surface to become rich with carbon atoms. For EG growth, SiC(0001) samples were prepared with a weak solution of AZ5214E polymer and placed on a polished disk of glassy carbon with the Si-face in direct contact with the disk for face-to-graphite growth [3]. The annealing process at 1900 °C was performed in argon at atmospheric pressure with a graphite-lined resistive-element furnace. After growth, EG was inspected with various microscopies to rapidly identify successful growths over large areas [8]. After devices were lithographically etched and electrically contacted, they underwent a functionalization method that greatly reduced the electron doping in EG, stabilizing the long-term behavior of n_e [3].

III. DATA AND RESULTS

A. Tuning the Carrier Density

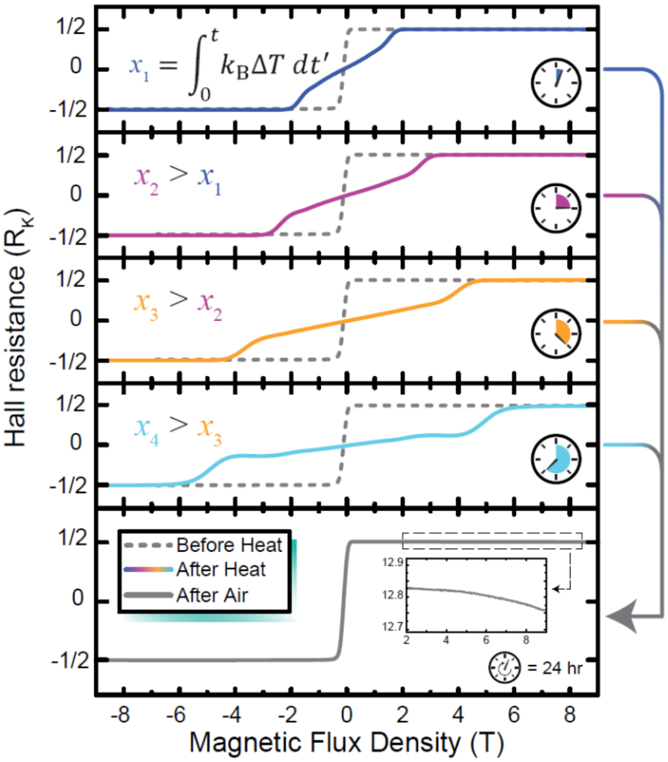

Fig. 1. The Hall resistances for an example device at 1.6 K, with all dotted gray curves representing data (temporally spaced on the order

of months) before the device has been adjusted via annealing. Each of the top four panels depicts a different measurement where, after device functionalization (dotted gray), annealing in vacuum was performed for successively longer times. The bottom panel shows an example set of data prior to annealing, which exhibits plateau onsets at around 2 T or less due to electron and hole puddles (but requires annealing to be metrologically useful). In all cases, device exposure in air for at least 24 h yielded the bottom panel.

After numerous trials of annealing devices at different temperatures for different amounts of time (called the integrated heat exposure, or IHE), and by using the relation below, a roughly linear correlation was found between the IHE and n_e (shown in Figure 1) [3]:

$$IHE = \int_0^t k_B\left(T_{\text{applied}} - T_{\text{RT}}\right)dt'$$

The found empirical relationship, which is an estimate for $n_e \leq 5 \times 10^{11}$ cm^{-2}, enabled us to correctly predict the approximate n_e which could be obtained with a given annealing temperature and time. For instance, an anneal of 350 K for 20 min yields a carrier density of close to 3×10^{11} cm^{-2}. Once devices obtain this value, they can retain it in vacuum or an inert gas with very little shifting (5 % shift over one day at room temperature and virtually negligible at temperatures under 200 K), but air immediately begins resetting the device to its near-Dirac point value [7].

B. Metrological Performance

Hall resistance measurements were collected using a nanovoltmeter (longitudinal resistivity ρ_{xx}) and a cryogenic current comparator (CCC) bridge for high resistance measurements.

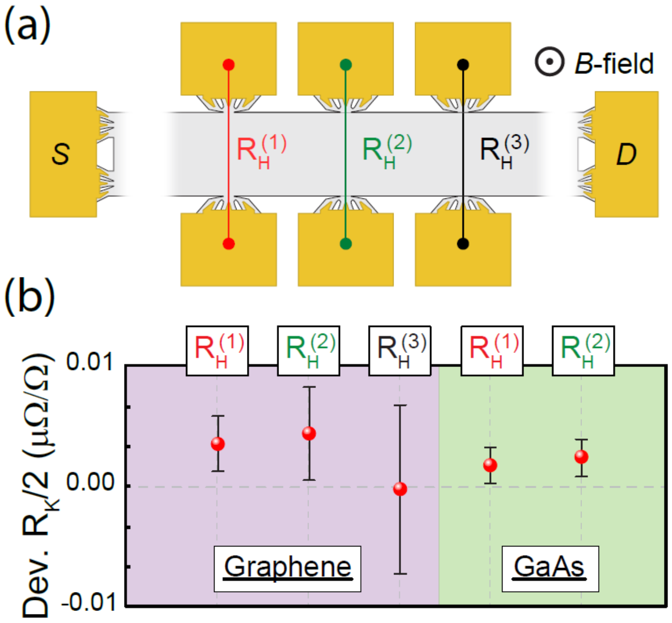

Fig. 2. (a) Schematic of device measurement configuration. (b) For high B-fields (7 T), resistance quantization for three orthogonal contact pairs in the EG QHR device are shown (and two for a reference GaAs QHR device). The data represent weighted CCC means. Error bars represent Type A uncertainties at 1σ. All data were collected at 77.5 μA (1 V) and 1.5 K.

The voltage source was operated at ±1.0 V, allowing for a maximum current of 77.5 μA. Three orthogonal Hall pairs in EG were measured and compared with two measurements from a standard GaAs-based QHR. A 1 kΩ standard resistor was used as the basis for comparison, with its value being predicted by historical calibration data. Measurements yielded $\rho_{xx} = 250$ μΩ (about 10^{-8} R_K).

IV. CONCLUSION

Functionalized EG has been shown to maintain a low and stable carrier density, allowing it to be a suitable treatment for EG QHR standards to increase shelf life. We have shown that these treated QHR standards can be operated at 1.2 K and 7 T. Overall, these results support the notion that EG devices can be given long lifetimes and predictable characteristics accompanied by a simple recipe for annealing.

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