Mapping Conductance and Switching Behavior of Graphene Devices In Situ

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Graphene is proposed for use in various nanodevice designs, many of which harness emergent quantum properties for device functionality. However, visualization, measurement, and manipulation become nontrivial at nanometer and atomic scales, representing a significant challenge for device fabrication, characterization, and optimization at length scales where quantum effects emerge. Here, proof of principle results at the crossroads between 2D nanoelectronic devices, e-beam-induced modulation, and imaging with secondary electron e-beam induced currents (SEEBIC) is presented. A device platform compatible with scanning transmission electron microscopy investigations is introduced. Then how the SEEBIC imaging technique can be used to visualize conductance and connectivity in single layer graphene nanodevices, even while supported on a thicker substrate (conditions under which conventional imaging fails) is shown. Finally, it is shown that the SEEBIC imaging technique can detect subtle differences in charge transport through time in non-ohmic graphene nanoconstrictions indicating the potential to reveal dynamic electronic processes.

1. Introduction

Scanning transmission electron microscopy (STEM), through the advent of effective aberration correction, is now able to probe the position, bonding, and elemental composition of single atoms in materials.\(^1\) These capabilities have been complemented by the introduction of standard tools and techniques for in situ experimentation, which have both advanced in capability and ease over the past decade.\(^2\) The combination of these capabilities has made the STEM a powerful tool to understand nanoscale electronics and materials broadly, among other applications. Additionally, there has been an increasing push to develop the STEM as an atomic-scale fabrication tool, shifting the instrument from solely a characterization tool to a fabrication tool, analogous to the differences between a scanning electron microscope (SEM) and an electron beam lithography (EBL) system.\(^3,4\) The aim of these fabrication efforts is to structure matter first at the nanoscale and then the atomic scale, with the goal of developing new electronic, quantum, and nanoelectronic devices.\(^5–12\)

However, in nanoscale electronics and molecular electronics, the flow of charge carriers is of primary interest for the function of the devices. While in situ biasing techniques have allowed this aspect to be probed in tandem to characterization via more common techniques, it does not permit spatial understanding of the conductivity and only permits a rudimentary understanding of connectivity (e.g., whether the device is connected to both leads or not). One mechanism to perform such direct spatial characterization and mapping of connections is electron beam included current (EBIC) imaging. We will focus, in particular, on a subclass of EBIC known as secondary electron EBIC (SEEBIC) imaging, which is sensitive enough to detect single layers of graphene.\(^13\) This work builds on both the work in advancing STEM secondary electron (SE) imaging\(^15\) and STEM SEEBIC. We will begin with a description of the operando platform, describe the basic physics behind SEEBIC image formation and then examine several examples illustrating the usefulness of the method for characterization of graphene-based nanodevices.

2. Experimental Description

Figure 1a shows renderings of an overview of the device design. The inset on the left shows the full chip. The main background image shows the central region that has an electron transparent, 20 nm thick, SiN\(_x\) membrane support over which the devices are fabricated. The inset image on the right shows a magnified view of a graphene nanoribbon device suspended over an aperture in the SiN\(_x\) membrane. Contact pads facilitate electrical connection to a Protochips electrical holder.
to facilitate operando experimentation in the STEM. The base platform can be adapted to a variety of different experimental designs. A detailed description of the general fabrication procedure can be found in the Supporting Information as well as a description of the specific device design used here. Transfer of graphene grown on Cu foil via chemical vapor deposition was accomplished on the wafer scale by Graphenea (San Sebastián, Spain).

While suspended regions of the graphene are amenable to high resolution imaging, graphene in supported regions of the device and in devices without apertures is almost completely invisible to conventional medium/high angle annular dark field (M/HAADF) imaging by virtue of the fact that the graphene signal is mixed with the signal from the 20 nm silicon nitride window. This situation can be resolved through the use of SEEBIC imaging as will be described. Next we will introduce the SEEBIC imaging technique and distinguish it from other similar variants like the more common EBIC technique.

EBIC imaging is a technique that has been used widely in semiconductor fabrication (particularly for failure analysis) and has been employed as a characterization method for over 50 years. Broadly speaking, EBIC techniques attempt to spatially measure currents occurring within a sample driven by a focused primary e-beam in a scanning electron microscope (SEM). The most well-know EBIC technique, shown in Figure 1b, uses an electron beam to measure electron-hole (e–h) pair recombination lengths and maps the depletion region in a semiconductor p–n junction. Because each incident electron can generate multiple e–h pairs the resultant signal current, IEBIC, can exceed the primary beam current, IBeam. A variation of this technique, shown in Figure 1c, measures absorbed electron current from the beam and can be used in probing disconnects in a nondestructive manner, when accelerating voltage is kept low. This configuration we term electron beam absorbed current (EBAC) imaging. In this configuration the signal current generated, IEBAC, is less than (or at most equal to) the primary beam current. While both signals are electron beam induced (in the most general sense), the mechanism generating image contrast is different for the two configurations.

For thin samples and with higher primary beam energies, as is the case in a STEM, the beam removes electrons from the sample resulting in a hole current into the amplifier. This is due to e-beam-induced emission of secondary electrons (SE) so we refer to this imaging mode as secondary electron EBIC (SEEBC), summarized in Figure 1c.
This follows the naming conventions proposed by Hubbard et al.\cite{13} In this imaging mode, the signal intensity, ISEEBIC, is governed by the secondary electron yield of the specimen, the sample interaction volume, and primary beam energy, among other parameters. Because the interaction volume is small for thin samples, and the secondary electron yield is low for beam energies typically used in STEM, ISEEBIC can generally be assumed to be much less than the primary beam current.\cite{17} It should be noted that each of these configurations is dependent upon beam/specimen interactions, electrical connections within the sample and electrical connections to the sample. For example, EBAC is only possible when the beam (or some measurable fraction of the electrons) can be stopped in the conductive portion of the specimen and as such is typically not possible at all in high accelerating voltage STEM imaging where almost all electrons, as the name suggests, transmit through the sample. Likewise, SEEBIC depends on electrons being emitted from the surface, which depends on the escape depth for secondary electrons for that material. The probability for emission decays exponentially with depth and is therefore primarily confined to emission from the top (or bottom) several nanometers of the specimen.\cite{17} Because of the limited interaction volume, SEEBIC is often higher resolution, but typically at the expense of less signal current.

Detecting the SEEBIC signal depends on a conductive pathway to the amplifier. In the configuration shown in Figure 1d, the entire conductor would appear of similar intensity. Figure 1e shows a conceptual diagram of the SEEBIC signal intensity that would be observed when imaging two conductors with a resistive element connecting them. The conductor connected to the amplifier appears bright (higher signal), while the conductor connected to ground appears dark (lower signal). Technically speaking, both conductors are grounded but we are measuring the current flow on the amplifier side and not the other side, which we will refer to as the grounded side. SEs are generated by the primary beam in both regions equally, however the grounded electrode can dissipate charge accumulation through the path to ground which is not detected by the amplifier. In the resistor/insulator region charge flow is hampered by the material. In this instance the relative resistivity in the pathway to ground determines the SEEBIC intensity. Reversing the connections produces a complementary inverse image. This variant of SEEBIC imaging is akin to resistive contrast imaging but with the current flowing in the opposite direction.\cite{18,19,13}

To acquire SEEBIC images of our devices we connected the electrodes to a Femto DLPCA-200 transimpedance amplifier (TIA) with a gain set to 10 V A$^{-1}$\cite{11} and 3 dB bandwidth of 1.1 kHz. The signal from the TIA was mapped according to e-beam position to generate a new image channel that can be acquired in parallel with conventional HAADF imaging. Figure 2 shows a summary of a typical dataset. Figure 2a shows a labeled HAADF image of the device. Note that the supported regions of the graphene (i.e., the graphene directly on the SiNx) are not distinguishable. The IV trace, inset, shows an ohmic response and indicates the device is functioning. Figure 2b shows a labeled SEEBIC image which was acquired concurrently with the HAADF image. In this image we can now clearly observe the electrically connected and conductive regions of the device. Two example profiles were extracted from the SEEBIC data and are displayed in Figure 2c. A significant amount of spurious interference was present in all the SEEBIC images collected. This interference was found to be synced to the electrical mains and was removed as described in the supplemental materials.

Figure 2. Example HAADF/SEEBIC image dataset. a) HAADF image of a graphene device with various features labeled. Inset on the upper right is the IV trace acquired during examination. b) SEEBIC image acquired simultaneously with the HAADF image. The supported graphene is now clearly visible (outlined in green). c) SEEBIC intensity profiles from the locations marked in (b).
Several features are worthy of comment. In the suspended region, at the center of the profiles, we have a reference intensity for vacuum and can clearly distinguish this from the intensity of the suspended graphene. While we refer to this as “graphene” it should be noted that this signal is likely significantly enhanced by surface contaminants that are nearly always present on graphene.\(^{[14]}\) The signal from bare SiN\(_x\) is not substantially different from vacuum. As SiN\(_x\) is an insulator, a positive charge will build up quickly and act to recapture SEs thus exhibiting no net signal into the TIA. The graphene on SiN\(_x\) region shows a pronounced increase in signal above the suspended graphene region. This is because SEs emitted from both the graphene and SiN\(_x\) can be replenished through the electrically conductive path to the TIA. The signal is again increased at the electrical contacts, however, perhaps less than one might expect especially when compared to the increase in intensity observed in the HAADF image. The contrast in HAADF is generated by total scattering of the primary beam. But the contrast in SEEBIC is generated by emission of secondary electrons, mostly near the surface. Thus, the sample thickness, elemental mass, and work function of the material in this region plays a less significant role in contrast generation in SEEBIC compared to HAADF.

3. Resistive Contrast Imaging

SEEBIC is only possible with a conductive path from the region being imaged to the TIA. This gives the technique substantial utility in probing electrical conductance and connectivity and can be useful in diagnosing aspects of the device that could not otherwise be observed through more common STEM imaging mechanisms (e.g., HAADF/MAADF imaging or EELS). Here, we discuss how SEEBIC can aid understanding of device structure during in situ experimentation by providing insight into graphene cracks. In situ electrical characterization of the devices shown in Figure 3 permitted understanding of a general failure of the device (open circuit) as shown by the IV traces in Figure 3d,h. Without the ability to spatially resolve or correlate electrical data to the resolution of the STEM, we are given little insight into the location or nature of the failure. The HAADF image in Figure 3a gives us no additional insight into the failure. However, in this instance the discontinuity in the circuit and the electrical contacts on each side of the device, permit independent SEEBIC imaging of each half, Figure 3b,c, while keeping the other half grounded in a resistive contrast imaging mode. Such imaging produces a strong SEEBIC signal up to the discontinuity, with a sharp drop in intensity as the beam crosses to the grounded other half of the device. Superimposing the two images gives an intuitive high-resolution map of the device failure, Figure 3d. Here, we see that the discontinuity exists at the edge of the bottom contact, an extremely difficult location to detect with other means since the contact itself is also discontinuous at the same location. A second example of this type of characterization is shown in Figure 3e,h where a fully supported graphene nanoribbon is examined and found to have a discontinuity on the SiN\(_x\) substrate.

Figure 3. Example of SEEBIC open circuit device diagnostics. a) HAADF-STEM image of a suspended graphene device with labeled features. b,c) Artificially colored SEEBIC images acquired with the transimpedance amplifier connected to alternate electrodes as indicated. d) Composite SEEBIC image where color denotes the parent image, (b) and (c). e,f) Second example on a fully supported graphene nanoribbon.
4. Dynamic Conductance Switching

These examples illustrate the usefulness of the SEEBIC technique in revealing conductivity and electrical connectivity in static nanodevices. In this case the device properties are constant through time and do not depend on the beam position. However, within the field of nanodevices more generally we are very interested in properties that can be influenced by local changes like electrical or structural variations. One such device configuration is the molecular tunnel junction formed within a graphene nanogap.[20–24] In this configuration a nanosized gap between two graphene contacts allows an interface with a molecule facilitating a tunneling current through the molecule.[20,22] A fairly reliable method has been established to create such nanogaps through the use of feedback-controlled electroburning.[21,22] Current is passed through a graphene nanoconstriction, like that shown in Figure 3e–h, until joule heating in the narrowest region starts to sublimate and a resistance increase is observed. The voltage is then rapidly ramped down to prevent run-away device failure. This process is repeated until a nanogap is formed.

In some experiments molecules are introduced into the nanogap to create the tunnel junction.[20,22] However, within these graphene nanogaps a reversible conductance switching behavior has been observed in the absence of the introduction of additional molecular species to the junction.[20,23] It was suggested that the formation and destruction of carbon filaments bridging the gap act to facilitate the transport.[20,24] In addition, electroburning has also been observed to spontaneously form graphene quantum dots within the gap acting as single electron transistors.[23,26] A recent study also employed the use of the e-beam to charge an MoS2 device substrate creating a gating field, dependent on beam position.[27] In these examples the device can dynamically change in response to charge accumulation and dissipation.

Since the SEEBIC imaging technique is well positioned to examine conductance, connectivity and charge flow, we performed in situ electrical breakdown to create a nonohmic nanostructure within a graphene nanoconstriction to investigate the SEEBIC response to a dynamically varying system. Figure 4a shows a concurrently acquired HAADF/SEEBIC image pair with an accompanying IV trace acquired prior to

**Figure 4.** Observation of conductance switching in a graphene nanogap using SEEBIC. a) Initial sample state. A concurrently acquired HAADF/SEEBIC dataset shows the electrode and graphene nanoribbon location. The electrical connections to the TIA for the SEEBIC acquisition are shown schematically around the SEEBIC image. The IV trace shows the initial ohmic response of the device. b) Plot of the device resistance recorded during the electric breakdown process to form a nonohmic nanostructure. c) Sample state after the electric breakdown process. The IV trace now illustrates the nonohmic device response. d) Magnified views of the region where the nonohmic nanostructure has formed. e) SEEBIC images acquired by connecting each electrode individually to the TIA and the opposite electrode to ground. f) Plot of the SEEBIC intensity observed as a function of time illustrating a reversible change in conductance. The intensities were clustered using a Gaussian mixture model and the kernel density estimates of each cluster are shown plotted on the right.
the electrical breakdown procedure. The plot in Figure 4b shows the resistance measured during the electrical breakdown procedure where the dramatic increase in resistance over the last few cycles indicates the formation of a non-ohmic nanostructure in the graphene ribbon (this could be a nanogap, quantum dot, series of quantum dots, or various combinations). Figure 4c shows a HAADF/SEEBIC image pair acquired after the electrical breakdown procedure with an accompanying IV trace showing the nonohmic response. A higher magnification HAADF/SEEBIC image pair of the electrical breakdown region are shown in Figure 4d. We can clearly observe mass loss from the SiN substrate in the HAADF image. The SEEBIC images in Figure 4a,c,d were acquired with both electrodes connected to the TIA. In Figure 4e we connected each side independently to the TIA in resistive contrast imaging mode. In this configuration we no longer observe static differences in conductance as observed previously (Figure 3). Instead we observe strong dynamic signals due to a combination of electron beam gating, substrate charging (also induced by the beam), and voltage induced switching (from varying the potential on the leads and posibly field-induced restructuring of bridging molecules within the gap).[20,23]

In Figure 4f, we examine a portion of the image in Figure 4e more closely. The SEEBIC intensity is plotted as a function of time, instead of beam position, and we can clearly observe the existence of telegraph noise. A Gaussian mixture model clustering routine was used to cluster the intensities and a kernel density estimate of the clusters is shown on the right side of the plot illustrating the degree of separation in intensity between the two states. This indicates a reversible and sustained conductance switching is occurring during the imaging process. The companion image shown in the lower portion of Figure 4e displays a similar switching behavior over various portions as well as variations on a longer timescale and many more switching states (i.e., SEEBIC intensities). Intensities in this image are more closely examined in the supplemental information.

The specifics of the beam induced switching require and deserve additional study. What we stress here is that these dynamics can be detected using SEEBIC. However, we can postulate several mechanisms that could produce such behavior. First, as is clear from SEEBIC imaging, the beam interacting with the sample generates an excess of charge that is replenished when the device is connected to ground. Given the high resistivity of graphene devices, this will result in a voltage relative to ground, which, if excessive, will result in modification of the device. Second, electron beam gating was recently demonstrated by Das and Drndić.[23] In this work they show how e-beam induced substrate charging can act as a gate that can be switched off and on through e-beam irradiation. These results begin to show how the electron beam could readily modulate the transport by merely being in the vicinity of a charge sensitive (i.e., field effect sensitive) device. Taken together, we see that by inducing a voltage and then modulating the conductance, dramatic changes in transport can be observed and spatially correlated to the beam position to map the conductance of the specimen.

5. Conclusion

These collective results point toward future directions for STEM SEEBIC to analyze conductance with spatial resolution in situ. The results also have important implications for routine STEM characterization of nanoelectronic devices, since the transport measured here suggests that device modification beyond beam damage and other known effects[26] may occur during imaging solely due to the buildup and movement of charge. However, as the nature of these results hint, further understanding of the mechanisms and improved protocols will be necessary to probe the richness of device transport. These results hopefully help to steer that research on a productive path.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

graphene, resistive contrast imaging, scanning transmission electron microscopy, secondary electron e-beam induced current, secondary electron yield

[1] R. Erni, Transmission Electron Microscopy: An Introduction, 2nd ed., World Scientific Publishing Company, Singapore 2015.
[2] M. L. Taheri, E. A. Stach, I. Arslan, P. A. Crozier, B. C. Kabius, T. LaGrange, A. M. Minor, S. Takeda, M. Tanase, J. B. Wagner, R. Sharma, Ultramicroscopy 2016, 170, 86.
[3] S. V. Kalinin, A. Borisevich, S. Jesse, *Nature* **2016**, *539*, 485.
[4] O. Dyck, S. Jesse, S. V. Kalinin, *MRS Bull.* **2019**, *44*, 669.
[5] S. Jesse, B. M. Hudak, E. Zarkadoula, J. Song, A. Maksov, M. Fuentes-Cabrera, P. Ganesh, I. Kravchenko, P. C. Snijders, A. R. Lupini, A. Y. Borisevich, S. V. Kalinin, *Nanotechnology* **2018**, *29*, 255303.
[6] O. Dyck, C. Zhang, P. D. Rack, J. D. Fowlkes, B. Sumpter, A. R. Lupini, S. V. Kalinin, S. Jesse, *Carbon* **2020**, *161*, 750.
[7] O. Dyck, L. Zhang, M. Yoon, J. L. Swett, D. Hensley, C. Zhang, P. D. Rack, J. D. Fowlkes, A. R. Lupini, S. Jesse, *Carbon* **2021**, *173*, 205.
[8] O. Dyck, M. Yoon, L. Zhang, A. R. Lupini, J. L. Swett, S. Jesse, *ACS Appl. Nano Mater.* **2020**, *3*, 10855.
[9] H. Park, Y. Wen, S. X. Li, W. Choi, G.-D. Lee, M. Strano, J. H. Warner, *Small* **2020**, *17*, 2100693.
[10] T. Susi, J. C. Meyer, J. Kotakoski, *Ultramicroscopy* **2017**, *180*, 163.
[11] T. Susi, D. Kepaptsoglou, Y.-C. Lin, Q. M. Ramasse, J. C. Meyer, K. Suenaga, J. Kotakoski, *2D Mater.* **2017**, *4*, 042004.
[12] T. Susi, J. Kotakoski, D. Kepaptsoglou, C. Mangler, T. C. Lovejoy, O. L. Krivanek, R. Zan, U. Bangert, P. Ayala, J. C. Meyer, Q. Ramasse, *Phys. Rev. Lett.* **2014**, *113*, 115501.
[13] W. A. Hubbard, Z. Lingley, J. Theiss, M. Brodie, B. Foran, in 2020 *IEEE International Reliability Physics Symposium (IRPS)*, IEEE, Piscataway, NJ 2020, pp. 1–5.
[14] O. Dyck, J. Swett, A. Lupini, S. Jesse, *Microsc. Microanal.* **2020**, *26*, 1704.
[15] X. F. A. Zhang, *Microsc. Today* **2011**, *19*, 26.
[16] T. E. Everhart, O. C. Wells, R. K. Matta, *J. Electrochem. Soc.* **1964**, *111*, 929.