Minimizing Carbon Buildup on Graphene Facilitates Electron Transmission

Vikas Kumar, Dhiraj Prasai, Jonathan Jarvis, and Charles Brau

KEYWORDS. Graphene, carbon buildup, electron transmission, thermionic electron apparatus, LEEPS

BRIEFS. Carbon buildup on graphene hinders transmission of electrons.

ABSTRACT. Current biomolecular imaging techniques use either x-rays or high energy electrons and are thus hindered by radiation damage. However, recent investigations of DNA with low-energy electron point source (LEEPS) microscopy suggest that biomolecules are not damaged by electrons with an energy between 30 and 200 electron volts (eV). The current substrate used for LEEPS microscopy is an irregular carbon film, with bumps and holes that cause an uneven electric field near the sample. This uneven field causes distortion of the image. Graphene, a flat, single-atom thick allotrope of carbon, would be an ideal substitute for the currently used substrates. Our results indicated that graphene did not allow passage of low energy electrons due to carbon buildup. Heating the graphene to high temperatures, however, allowed passage of electrons but only at somewhat higher voltages (>500 eV). We predict that optimizing the conditions for annealing graphene will allow enhanced electron transmission at lower voltages and make LEEPS microscopy a reality.

INTRODUCTION.

The development of modern medicine has coincided with great improvements in imaging technology. To fully understand the fine structure of microscopic biological samples, new high-resolution microscopy techniques are in demand, because optical microscopes cannot capture the detail required. In order to resolve very fine features, a high-energy source of electrons, on the order of many kilo-electron volts (keV), is necessary. Unfortunately, high-energy electrons can destroy sensitive samples [1], which makes the process impractical for most biological specimens. In 1997, Fink and others developed a technique to use low energy electrons to create high-resolution images. This technique, known as low-energy electron point-source (LEEPS) microscopy, images small samples by passing an electron beam through the sample and observing patterns based on the diffraction of electrons. The pattern of the diffraction can be used to reconstruct a hologram or image of the sample. [1, 2].

This process has been relatively inefficient due to the irregular carbon film or mesh supporting the sample, which creates an uneven electric field [1], and distorts the image [1, 2]. One alternative substrate is a single layer of carbon called "graphene". We hypothesize that graphene may be a more effective substrate in LEEPS microscopy because it provides a uniform electric field due to its uniform, hexagonal structure [3]. To be able to utilize this technology it is essential to understand the relationship between low-energy electrons and graphene [2]. Theoretical computations indicate that electron transmission through graphene should be excellent [4], and recent experiments show that over the range from 100 to 200 eV the transmission is approximately 75% [5]. Here, we wished to test the efficiency of electron transmission over a range of 10 to 2,000 eV. To this end, we built a thermionic electron beam apparatus and characterized the electron beam produced by it. We then used the thermionic electron beam apparatus to determine the efficiency of electron transmission through graphene.

MATERIALS AND METHODS.

Construction of thermionic electron beam apparatus.

The thermionic electron beam apparatus (Figure 1) used in this study consisted of an yttrium-coated cathode and a phosphor screen separated by a 100 micrometer (μm) aperture containing anode and either a 20 μm aperture anode or a 5 μm aperture pinhole containing silicon nitride (SiN) membrane carrying the graphene. A camera was used to record the visible light produced when the electrons from the cathode hit the phosphor screen. The potential and current on each of the apertures and the phosphor screen were measured using an ammeter. The voltages at each of the aperture bearing anodes could be independently regulated. Two metal cylinders placed around the cathode, served to prevent black body radiation, emanating from the hot cathode (at 2,200 Kelvin (K), from interfering with the image produced by the electrons on the phosphor screen.

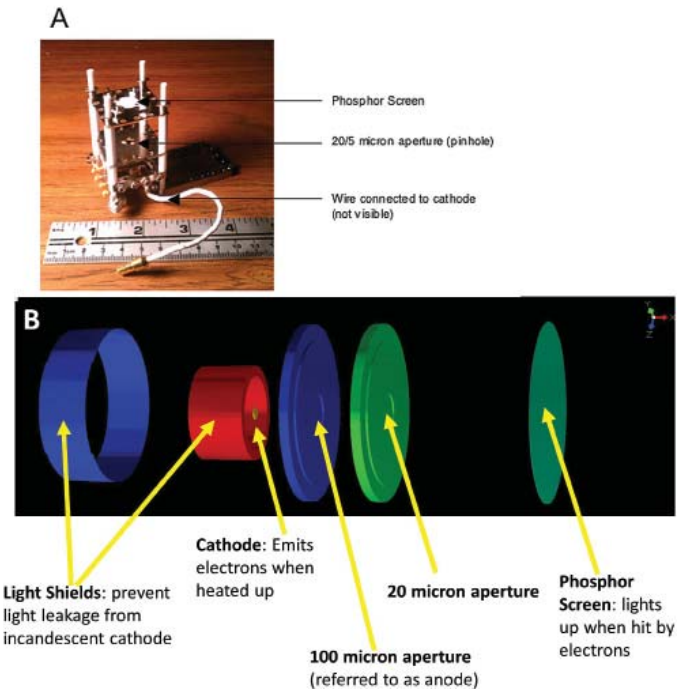

Figure 1. Thermionic Electron Beam Apparatus: A) A photograph of the apparatus. The wire at the bottom is attached to a cathode. The white disc on top is the phosphor screen. In between are plates housing the 100 μm (not visible) and 20 μM or 5 μm apertures. B) A schematic representation of the apparatus showing cathode (golden sphere) within the red shield, which, in turn, is housed within another light shield (blue). The phosphor screen is the disc on the right. Separating the cathode and the phosphor screen are discs showing 100 μm and 20 μm or 5 μm apertures. Each part of the same color is electrically isolated from the other colors and is hooked up to a separate power supply. Electrons are emitted from the cathode, and pass through the 100 μm and 5 μm apertures before hitting the phosphor screen, which produces visible light. The camera (not shown) is situated to the right of the phosphor screen and records the visible light produced.

Aperture alignment.

The 100 μm and the 5 μm pinhole apertures were aligned using a microscope with a 20x objective as follows. First the SiN membrane housing the 5 μm aperture and the phosphor screen were removed. The apparatus was then locked on to the microscope stage and the position of the anode aperture was visualized and noted on the computer monitor screen. The SiN membrane containing the 5 μm aperture was then placed and aligned into position using a 3-axis piezoelectric nanopositioner specially designed for this purpose. The SiN membrane was then fixed in place using a vacuum-compatible suspension of colloidal silver.

Voltage and Current Settings.

The electron beam apparatus was run using the voltage and current settings as described below. The current heating the cathode was set at 1.75 amperes. The anode voltage was varied between 100 and 500 volts (V). The voltage at the 5 μm pinhole was also modulated between 100 and 500 V. The voltage at the phosphor screen was 2,000 V.

Fabrication of graphene.

Graphene was grown on a 25 μm copper foil. To remove contaminants and oxides from the Cu surface, before graphene growth, the copper foil was heated at 1,000°C in the presence of hydrogen at a flow rate of two standard cubic centimeter per minute (sccm) while maintaining a pressure of 25 milliTorr (mTorr). Hydrogen was then replaced with methane (CH_4) at 35 sccm, and the pressure was increased to 250 mTorr to release elemental carbon and hydrogen. The carbon was deposited onto the copper (Cu) film and bonded to form graphene. Afterwards, the temperature was slowly cooled to room temperature. Polymethyl methacrylate (PMMA) was then spin-coated on to the graphene. The entire sample was etched in Cu etchant (type CE 100) for about 1 hour, which dissolved away the Cu. The graphene was then soaked in deionized water for 20 minutes. It was then laid onto a SiN membrane and dried on a hotplate at room temperature for one hour. The PMMA was removed by heating the sample at 400°C for 2 hours [6] either under hydrogen or under vacuum (10^{-7} torr). After this heating process, what remained was a graphene film on a SiN membrane.

Scanning electron microscopy.

The graphene was visualized using a Hitachi scanning electron microscope with setting of 20 KeV and a magnification of 20,000 x.

Simulation of electron transmission through apparatus.

This was done using software package SIMION (Version 8) that allows calculation of electric fields and the trajectories of charged particles after providing the voltages at the electrodes and other parameters. It also allows data recording and visualization.

Analysis of data.

Laboratory Virtual Instrumentation Engineering Workbench (LabView by National Instruments) was used to analyze the images on the phosphor captured by the camera.

RESULTS.

Thermal Equilibration.

When heated, the yttrium cathode in the electron beam apparatus emits electrons that proceed towards and are captured by the anode. As a first step towards using the thermionic electron beam apparatus, we wished to determine how long it would take, after turning on the instrument, at any given voltage, for the electron beam to reach a steady state. The results of this experiment are shown in Supplemental Figure 1, which shows that the current measured at the anode gradually increased and finally reached a steady state after 75 minutes. Therefore, all subsequent experiments were conducted after an initial warm-up period of this duration.

Transmission of electrons through 20 μm aperture.

Initially, transmission experiments were carried out using only the anode and the 20 μm aperture. The current at the anode as well as the electron flashes at the phosphor screen were recorded as a function of anode voltage. A gradual increase in anode current was observed with increasing voltage with an initial rapid increase followed by a slower gradual increase. A similar response of the phosphor screen to the anode voltage was also observed indicating that the electrons traversed through the aperture to reach the screen (Supplemental Figures 2A and 2B). The proportion of the current that reached the phosphor screen from the 20 μm aperture was 0.5%. The beam spot radius was 15 μm.

Simulation of electron transmission through 100 μm and 20 μm apertures in the absence of graphene.

This was done using the SIMION software package (*Materials and Methods*). The results of the simulation (not shown), where the random thermal distribution of electron velocity were described by a Gaussian velocity distribution, indicated that more electrons passed through the larger aperture (100 μm) than the smaller aperture (20 μm). The simulations also showed an expansion and radial deflection of the electron beam as it exited each aperture. The proportion of the current that reached the phosphor screen from the 20 μm aperture by simulation was 2%. The simulated beam spot radius was 30 μm.

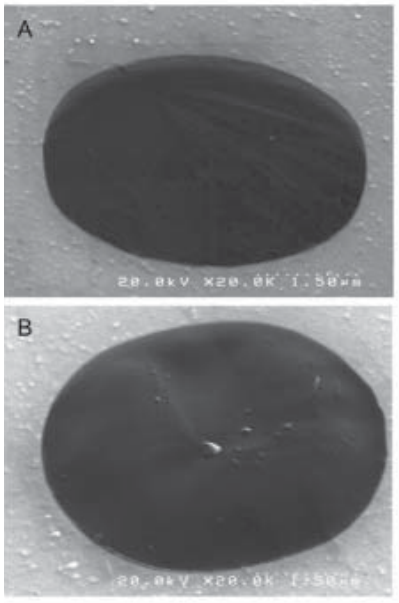

Figure 2. Scanning electron microscopy of graphene before (A) and after (B) electron transmission experiment. Carbon build up is noticeable in 'B'.

Electron transmission through graphene annealed under hydrogen.

Having established the baseline electron transmission in the apparatus, we proceeded to test transmission through graphene. For this, the 20 μm copper pinhole was replaced by a 5 μm SiN aperture covered by a graphene layer that was annealed in the presence of hydrogen. Surprisingly, no current could be detected at the phosphor screen from pinhole voltage 10-1,000 V (Electron energy 10eV-1,000eV).

Scanning electron microscopy of graphene reveals carbon buildup.

To determine possible reasons for lack of electron transmission, we analyzed the graphene by scanning electron microscopy before and after the electron transmission experiment. The results showed a buildup of carbon on the graphene after electron transmission (Figure 2A and 2B), which likely hampered transmission.

Electron transmission through graphene annealed under vacuum.

Based on the previous observations of Mutus, *et al.* [5] that graphene samples heated in an oxygen-rich atmosphere poorly transmit electrons, we hypothesized that lack of electron transmission through graphene in the previous experiment was a consequence of annealing under less than optimal conditions. To this end, we annealed graphene by heating under high vacuum (10^{-7} torr) instead of hydrogen. The annealed graphene was then tested for transmission of electrons at different anode voltages. The results of this experiment are shown in Figure 3. With this modification to the annealing process, graphene exhibited increased electron transmission with increasing anode voltage up to 1,000 V. The threshold electron energy at which point electrons began penetrating through the film was 400 eV (E_{TH} in Figure 3). The critical voltage at the phosphor screen, at which point the trend followed a linear increase (the dotted red line in Figure 1), was 560 V (E_C in Figure 3).

Simulation of electron transmission through graphene.

Software simulation electron transmission was done as described in *Materials and Methods*. The results of this simulation are shown in Figure 3 (dotted-line in blue).

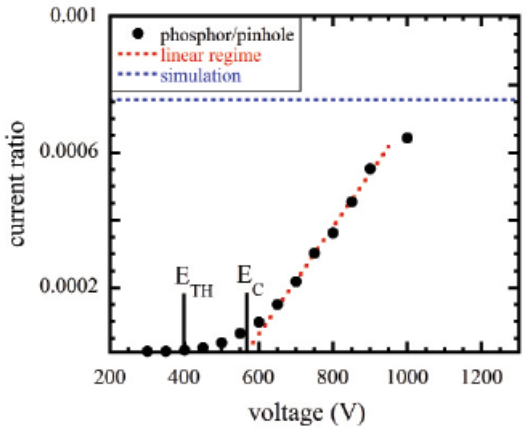

Figure 3. Experimental and simulated electron transmission after annealing under vacuum. Electron transmission is depicted as ratio of the current at the phosphor screen to that at the 5 μm pin hole (y-axis) vs phosphor voltage (x-axis). The threshold energy voltage (E_{TH}), and the critical energy voltage (E_C) at which transmission occurred are shown. The linear portion of the curve (linear regime) is shown as a dotted red line. Software simulation of electron transmission at various voltages is depicted as a dotted blue line.

DISCUSSION.

In this study, we constructed a thermionic electron transmission apparatus to study the effect of low energy electron transmission through graphene. The design ensured that the electrons initially passed through a 100 μm aperture-containing anode, followed by a SiN membrane with a 5 μm aperture. The passage of electrons through the graphene was visualized when the electrons impinged on a phosphor screen.

We first determined the minimum time it took to obtain steady state levels of electron emission from the cathode (around 75 minutes). The reason for this is that the thermionic emission is an exponentially sensitive function of the cathode temperature, as described by the Richardson equation. Initial electron transmission experiments were conducted in the absence of graphene to determine the maximal electron transmission possible with the apparatus. The results indicated that electrons traversed successfully through the 100 μm and 20 μm apertures to reach the phosphor screen. The transmission of electrons through the apparatus was also simulated using the SIMION software package. The simulation results and the experimental data showed overall good correspondence. However the experimental transmission of electrons (0.2%) was lower than what the simulation predicted (2%). This result can be explained as follows: The number of particles that pass through the 20 μm aperture in simulation is relatively small (typically 5 particles pass through the 20 μm aperture per 30,000 particles that are launched from the cathode), and thus there is a relatively high statistical error. The difference between the simulated electron beam and the geometric calculations can be explained by the divergence of the electron beam as it traveled from the anode to the pinhole. This difference could be accounted by space charge and different energy distributions. In future simulations, we hope to decrease the error and improve accuracy by increasing the simulated number of electrons emitted from the cathode.

Having established that the apparatus was capable of detecting electrons passing through both the 100 μm and 20 μm apertures, we proceeded to place graphene on a 5 μm SiN aperture to determine how this would affect transmission of electrons. Surprisingly, we found that the graphene did not allow the passage of low energy electrons. This result could be attributed to carbon build up on the graphene as revealed by scanning electron microscopy. We hypothesized that the carbon buildup occurred during the synthesis and annealing of the graphene to the SiN membrane. Similar observations have been made by Mutus and coworkers. We hypothesized that this build up could be reduced by annealing of the graphene under vacuum. When we carried out annealing in vacuum (10^{-7} torr) transmission of electrons was observed above 500 V.

From the E_{TH} and E_C values in Figure 3, we were also able to estimate the carbon build up using the method described by Kantor and Sternglass [7]. These calculations indicated a carbon build up of 33 nm. The source of this carbon build up is likely due to residual atmospheric gas inside of the vacuum chamber. This gas forms a monolayer on the graphene that gets chemically activated by the electron beam and attaches strongly to the graphene. The contamination layer builds up under continued electron bombardment. We hypothesize that annealing of graphene under ultra-high vacuum (10^{-10} torr) will further reduce the rate of carbon build up by 3 orders of magnitude, potentially leading to further improvements in electron transmission. These changes to the apparatus are the subject of ongoing investigations.

CONCLUSION.

We have successfully designed and tested a thermionic electron beam apparatus for graphene transmission experiments. More importantly, we have also quantified, for the first time, the amount of carbon build up that occurred on the vacuum-annealed grapheme sample. This allows us to optimize graphene production by determining which production method causes the least carbon build up. We predict that ultra-high vacuum annealing will allow for increased transmission, making graphene a viable substrate for LEEPS microscopy in the future.

ACKNOWLEDGMENTS. We thank the faculty and students of the Departments of Physics, Chemistry, and the School for Science and Math at Vanderbilt University for their encouragement and support throughout this research project. We also thank Drs. Michail Zaboikin and Srinivas Kumar for helpful comments during the revision of the manuscript. The project described was supported by Award Number R25RR024261 from the National Center For Research Resources. The content is solely the responsibility of the authors and does not necessarily represent the official views of the National Center For Research Resources or the National Institutes of Health.

SUPPORTING INFORMATION.

Figure S1.

Figure S2A and S2B.

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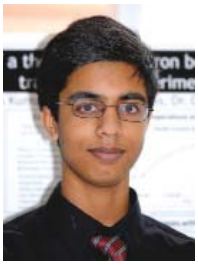

Vikas Kumar is a student at Hume-Fogg Academic Magnet High School and enrolled in the School for Science and Math at Vanderbilt.