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Author(s)	Kajen, R. S.; Chandrasekhar, Natarajan; Pey, K. L.; Vijila, C.; Jaiswal, M.; Saravanan, S.; Ng, A. M. H.; Wong, C. P.; Loh, K. P.
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Trap Levels in Graphene Oxide: A Thermally Stimulated Current Study

R. S. Kajen,[a,b] N. Chandrasekhar,[c] K. L. Pey,[b,d,*,z] C. Vijila,[a,z] M. Jaiswal,[e,f] S. Saravanan,[g] Andrew M. H. Ng,[a] C. P. Wong,[h] and K. P. Loh[f]

[a]*Institute of Material Science and Engineering, Singapore 117602*
[b]*Division of Microelectronics, School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore 639798*
[c]*19th Cross, Malleswaram, Bangalore 560 055, India*
[d]*Singapore University of Technology and Design, Singapore 138682*
[e]*Department of Physics, Indian Institute of Technology, Madras, Chennai 600036, India*
[f]*Graphene Research Center and Department of Chemistry, National University of Singapore, Singapore 117543*
[g]*Tera-Barrier Films Pte Ltd, Singapore 117602*
[h]*School of Physical & Mathematical Sciences, Division of Physics & Applied Physics Nanyang Technological University, Singapore 637371*

We report thermally stimulated current (TSC) experiments on graphene oxide (GO) to study the effects of various defect levels near the GO Fermi level. The TSC peaks are ascribed to detrapping from defect levels to the GO hopping transport energy level, and are found to be in agreement with the GO density of states reported in the literature. This work will be useful in evaluating the use of GO in memory/dielectric/barrier applications.
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Graphene oxide has evolved from being a precursor for solution processable graphene[1] to a material with potential applications as a gate dielectric[2] or a memory device.[3] Although several groups have reported GO bandgaps ranging from 1.7 eV to 5.4 eV,[4,5] these measurements have been optical in nature and do not represent the electronic bandgap, which is necessary to understand charge transport. Differences in these two bandgaps arise due to trap states, and differences in the physical behavior of excitons and single particles. Recent ballistic electron emission microscopy[6] experiments by our group[7,8] showed that graphene oxide has several defect levels in the gap, in agreement with the experimental/theoretical density of states.[5,9] We extend our previous work by using the thermally stimulated current technique (TSC) to characterize the trap levels near the GO Fermi level, which was not possible to measure by the BEEM technique due to the silicon collector blocking effect.[7]

The transport gap in graphene oxide (with minimal reduction) has been found by Eda et al. to be of the order of only a few tenths of meV,[10] which is in agreement with transport gap measurements on GO by scanning tunneling microscopy.[11] While this is in stark contrast with the optical experiments, it is the transport gap which matters in electrical measurements. Transport through a disordered semi-amorphous material[9] such as GO should be differentiated from delocalized band transport models.[12] Hence, the transport in graphene oxide is expected to be through a hopping/ tunneling mechanism. Charge injection from the electrode itself is by hopping injection[13] near the Fermi level rather than thermionic emission into the conduction/valence band, as commonly seen in conventional thick insulators. The hopping transport problem could then be mapped to a multiple trap and release model[14] with the transport energy level playing the role of the mobility edge (above which delocalized band transport occurs in the case of electrons). We utilize this concept to investigate charge detrapping from defect states to the transport energy level in TSC experiments.

In a typical TSC experiment,[15] the material under investigation is illuminated by light (with bandgap equivalent to the optical bandgap of the material) to fill up defect levels at low temperatures. Thereafter the sample is heated up at a constant bias voltage and heating rate. At certain characteristic peak temperatures/energy levels, charge detrapping is enhanced causing the TSC current to rise and finally reach a plateau when all trapped charges in this particular energy level have been detrapped and the current level drops to the intrinsic conduction level of the material. This simplified model could be extended to include charge retrapping and recombination effects. While traditionally traps are filled using a laser with wavelength equivalent to the optical bandgap of the material, such a technique could cause reduction of GO[16,17] depending on the incident power of the laser and the exposure time. Hence in our experiment, we avoid the use of trap filling with optical irradiation. However, we note that the trap states below the GO Fermi level are likely to be already filled as shown in the experimental DOS of Ref. 5, and exploit this advantage in our experiment. This then allows us to bypass the optical trap filling step. As the temperature is ramped up, we expect transitions from filled trap levels below (in the case of electrons) the GO Fermi level to the transport energy level (approximated to be at the Fermi level itself since the transport gap is of the order of a few tenths of meV). From our BEEM experiments,[7,8] we have shown that the metal Fermi level coincides with the GO Fermi level, allowing the GO Fermi level to act as the reference level for the TSC experiment. Under a negligible retrapping assumption,[15] we could then describe the characteristic energy level at the TSC peak temperature as defined in Eq. 1:

$$E_i = k_B T_m ln \frac{16\pi m_n^* k_B^3 (g_{i0}/g_{i1}) \sigma_{ni} e^{\alpha_i/k_B} T_m^4}{h^3 a E_i} \quad [1]$$

where, the terms m_n^* refers to effective mass of electrons in the material, k_B is the Boltzmann constant, h is Planck's constant, g_{i0}/g_{i1} the bound-state degeneracy factor, σ_{ni} the coefficient for a thermally activated capture cross section, α_i the reduced Fermi energy, T_m is the absolute peak temperature, a is the heating rate and finally E_i the characteristic trap energy level to be measured.

Eq. 1 can be rewritten as:

$$\frac{E_i}{k_B T_m} = ln \frac{T_m^4}{a} + ln \frac{16\pi m_n^* k_B^3 \sigma_{ni} (g_{i0}/g_{i1}) e^{\alpha_i/k_B}}{h^3 E_i} \quad [2]$$

By substituting $(g_{i0}/g_{i1}) = 1$, $m_n^* = m_0$ (free electron rest mass), $\alpha_i \approx 0$, $\sigma_{ni} = 10^{-14}$ cm^2 and a = 1/60 K/s, it can be shown that the contribution from the 2nd term on the right hand side of Eq. 2 is negligible (except at very low temperatures).[15] We hence arrive at Eq. 3 which approximates the peak Temperature (T_m) to the characteristic trap energy level (E_i).

$$E_i \cong k_B T_m ln \frac{T_m^4}{a} \quad [3]$$

The experimental details are discussed below.

*Electrochemical Society Active Member.
[z]E-mail: peykinleong@sutd.edu.sg; c-vijila@imre.a-star.edu.sg

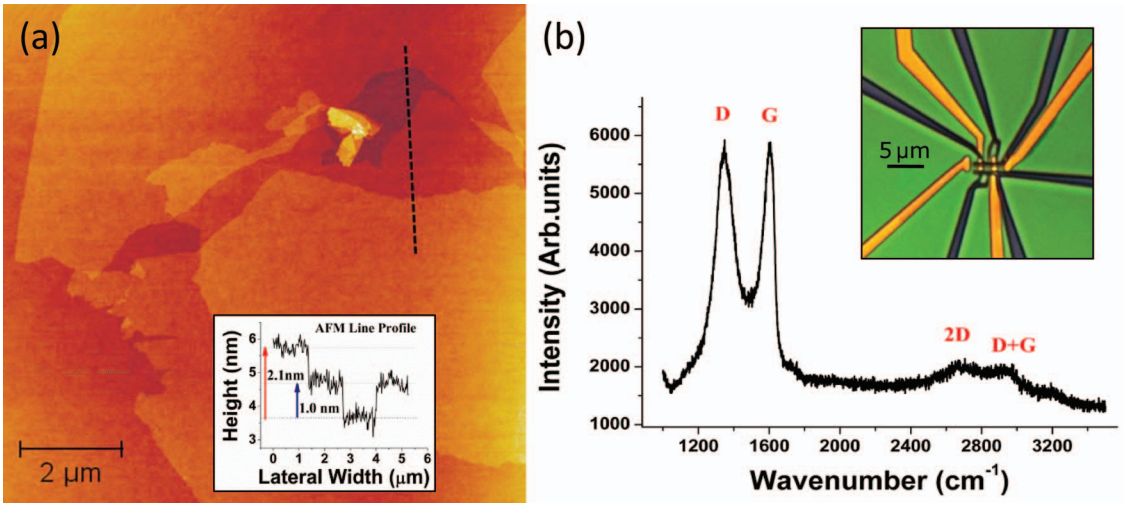

Figure 1. (a) A 10 μm × 10 μm atomic force microscope (AFM) image of GO flakes on a 300 nm SiO_2 on Si substrate. The inset of Fig. 1a shows the line profile (dotted line) across a typical single/double layer flake.[19] (b) Presence of GO confirmed by strong D and G peaks from Raman spectroscopy.[20] The minor 2D peak arises due to the presence of intact sp^2 regions. The inset of Fig. 1b depicts a typical GO device with the electrodes (yellow) isolated from one another by the GO-free etched areas (purple) outside the active device area.

Experimental

A modified Hummer's method[18] was used to synthesize GO flakes in solution. The GO sheets were spin-coated on to Si/SiO_2 substrate (300 nm SiO_2 on Si) and characterized using atomic force microscopy (AFM) and Raman spectroscopy. Fig. 1a confirms the presence of single/double layer flakes (extending beyond the scan limits). The inset of Fig. 1a presents a line profile (dotted line) across a typical region which confirms the presence of single/double layer flakes from their respective heights of 1 nm and 2.1 nm.[19] Electrodes were then patterned onto the GO flakes using electron-beam (E-beam) lithography followed by the thermal evaporation of 5/35 nm of Cr/Au in vacuum (10^{-5} Pa). To isolate the active GO device areas, a second step of E-beam lithography/etching was performed to form the GO device as shown in the inset of Fig. 1b.

Raman spectroscopy was performed in the active device region, using a 532 nm laser of spot size 1 μm to confirm the presence of GO. The spot size of 1 μm minimizes the fraction of the GO sample under irradiation. In addition, the laser power was kept well below 1 mW and the Raman spectra was acquired using an integration time of 10 s to avoid laser induced heating of GO.[16,17] Devices with GO gave strong D (1350 cm^{-1}) and G peaks (1600 cm^{-1}) as shown in Fig. 1b.[20] The weak 2D peak ~2700 cm^{-1} signal corresponds to the presence of intact sp^2 regions. In order to carry out the TSC experiments, the electrodes were wire bonded to a chip carrier/socket and placed in a cryostat (Janis-model CCS-450K) with the temperature being monitored by a Lakeshore 331 controller.

The TSC experiments were performed at a bias voltage of 60 V applied through a Keithley femto-ammeter (model-6430) with a remote pre-amplifier. The GO/reduced-GO (RGO) samples were heated to 325 K for 30 minutes to evaporate any existing water vapor and subsequently brought down to 12 K and kept for 8-9 hours before making any measurements. The TSC measurements were then conducted under a constant heating rate of 1 K/min. All measurements were repeated several times on several devices to ensure repeatability/consistency.

Results and Discussion

The TSC spectrum of GO (see inset of Fig. 2) showed several peaks suggesting the presence of several defect levels near the GO Fermi level. To eliminate random noise contribution, we use a 50 point Savitzky-Golay algorithm to smoothen our data and obtain a distinctive TSC spectrum (as shown in Fig. 2) with major peaks at 94 K, 121 K, 192 K, 259 K and 303 K corresponding to trap states at 0.181 eV, 0.243 eV, 0.416 eV, 0.588 eV and 0.704 eV (using Eq. 3) from the GO Fermi level. The extracted defect levels correlate well with the GO DOS (approximately 0.2 eV, 0.4 eV, −0.6 eV and 0.7 eV from Ref. 5 and 0.2 eV, −0.4 eV, 0.6 eV and −0.7 eV from Ref. 9 respectively). While there is a good correlation of the magnitude of the trap energy levels, it is difficult to comment on the whether the trap energy level exists above/below the GO Fermi level.

We also postulate that the poor signal to noise ratio is likely to originate from Johnson noise[21] across the highly resistive GO (which has a characteristic resistance of a few teraohms). To reduce the Johnson noise contribution and to evaluate the effect of mild reduction on the defect levels, we also performed additional TSC experiments on reduced GO (RGO). To form reduced GO (RGO), the GO devices were reduced in vacuum with a combination of laser irradiation (1 mW 630–670 nm solid state laser with a spot size of 1 mm for 100 s) and mild thermal annealing at 423 K for 2 hours. After this procedure

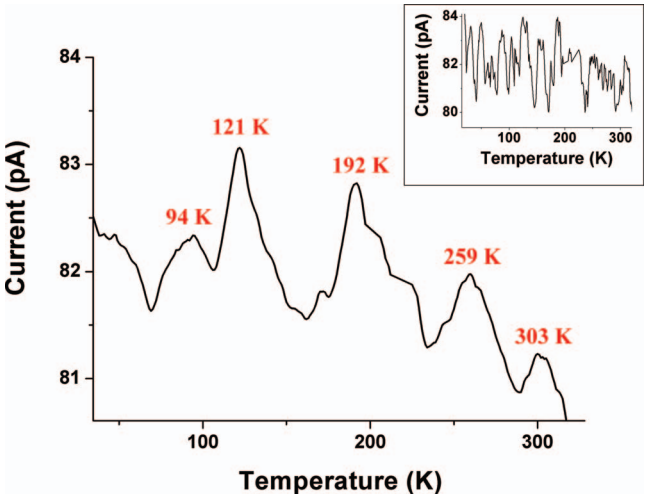

Figure 2. TSC curve for GO smoothed via a 50 point Savitzky-Golay algorithm to remove high frequency and random noise from the measurement. The TSC peak temperatures correspond to trap energy levels through the relationship given in Eq. 3. The raw TSC data obtained at a bias voltage of 60 V and a heating rate of 1 K/min is depicted in the inset.

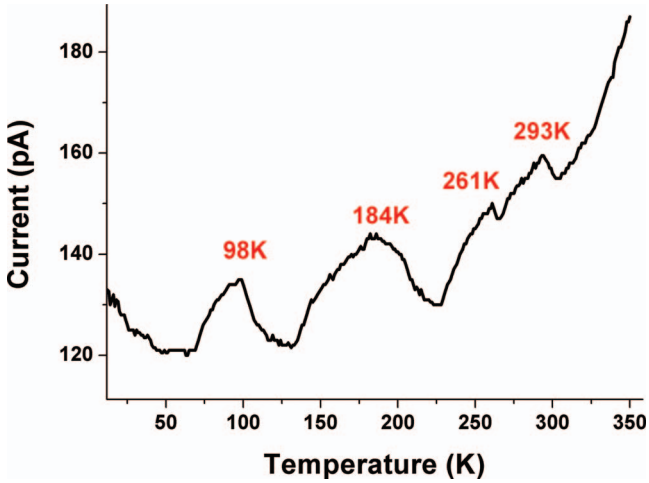

Figure 3. TSC spectrum for RGO showing 4 distinct peaks. The TSC spectrum was obtained at a constant bias of 20 V and a heating rate of 1 K/min. A conservative bias of 20 V was used to minimize the effect of field induced detrapping, yet obtain a measurable signal with our apparatus. The TSC peak temperatures correspond to trap energy levels through the relationship given in Eq. 3.

the GO resistance had dropped from a few tera-ohms to approximately 200 giga-ohms. We find that most of the TSC peaks seen in Fig. 2 are reproduced (within a 10 K tolerance) in the RGO TSC spectrum (taken at a bias of 20 V and heating rate of 1 K/min) as shown in Fig. 3 without any need for data-smoothing, which was required for the GO TSC spectrum described earlier. A conservative bias of 20 V was used to minimize the effect of field induced detrapping, yet obtain a measurable signal with our apparatus. Although the disappearance of the 121 K peak suggests the possibility of defect healing which is in agreement with Kaniankandy et al.,[22] further investigations need to be carried out to verify this finding.

Conclusions

In summary, we carry out TSC measurements on GO and observe several peaks in the TSC spectra. The TSC data is consistent with a multiple-trap and release model, with the transport energy level playing the role of the mobility edge. We extract defect levels after a Savitzky-Golay smoothing procedure to obtain trap energy levels at 0.181 eV, 0.243 eV, 0.416 eV, 0.588 eV and 0.704 eV from the GO transport energy level (approximated to be at the GO Fermi level). The extracted defect levels are in agreement with the GO density of states found in the literature.[5,9] We also report on the possibility of defect healing using photothermal reduction of GO. While this opens up the possibility of optimizing reduction techniques for defect engineering, the presence of several defect states near the GO Fermi level poses an immediate problem for the direct use of GO as a gate dielectric or as a charge transport barrier material. However, this work indicates one potential use of GO as a material for memory applications due to its ability to trap and retain charges.

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