Persistent hysteresis in graphene-mica van der Waals heterostructures

Jens Mohrmann\textsuperscript{1}, Kenji Watanabe\textsuperscript{2}, Takashi Taniguchi\textsuperscript{2} and Romain Danneau\textsuperscript{1}

\textsuperscript{1} Institute of Nanotechnology, Karlsruhe Institute of Technology, Hermann-von-Helmholtz Platz 1, D-76021 Karlsruhe, Germany
\textsuperscript{2} Advanced Materials Laboratory, National Institute for Materials Science, Tsukuba, Japan

E-mail: romain.danneau@kit.edu

Received 7 July 2014, revised 11 October 2014
Accepted for publication 31 October 2014
Published 8 December 2014

Abstract

We report the study of electronic transport in graphene-mica van der Waals heterostructures. We have designed various graphene field-effect devices in which mica is utilized as a substrate and/or gate dielectric. When mica is used as a gate dielectric we observe a very strong positive gate voltage hysteresis of the resistance, which persists in samples that were prepared in a controlled atmosphere down to even millikelvin temperatures. In a double-gated mica-graphene-hBN van der Waals heterostructure, we found that while a strong hysteresis occurred when mica was used as a substrate/gate dielectric, the same graphene sheet on mica substrate no longer showed hysteresis when the charge carrier density was tuned through a second gate with the hBN dielectric. While this hysteretic behavior could be useful for memory devices, our findings confirm that the environment during sample preparation has to be controlled strictly.

Keywords: graphene, mica, boron nitride, heterostructure, hysteresis

(Some figures may appear in colour only in the online journal)

1. Introduction

As a membrane of only one atomic layer of sp\textsuperscript{2}-hybridized carbon, graphene is extremely sensitive to its environment. Therefore, it is important to understand the interaction of graphene with the supporting substrate or gate dielectric materials. This is particularly relevant when graphene is integrated into a stack of other two-dimensional (2D) materials, forming a new material with properties that will be defined by interfacial effects and by the interaction of its components. The building blocks of these so-called ‘van der Waals heterostructures’ \cite{1} are materials with layered crystal structures in which single or few layers can be isolated and manipulated using the same techniques that are being used to isolate and manipulate graphene sheets.

Out of the variety of dielectric materials, so far, hexagonal boron nitride has been the center of attention \cite{2}, allowing the discovery of the effect of a Moiré superlattice on the electronic transport in graphene \cite{3–5}.

Other promising candidates that have not yet been investigated as comprehensively are the members of the mica group of naturally occurring sheet silicates. The most commonly used one is muscovite mica, with the formula KAl\textsubscript{2}[Si\textsubscript{3}, Al\textsubscript{10}O\textsubscript{20}(OH)\textsubscript{2}] \cite{6}. The structure is a stack of triple layers, each consisting of two identical tetrahedral layers of (Si, Al)\textsubscript{2}O\textsubscript{3} sandwiching a layer of octahedrally coordinated aluminum atoms. The triple layers are negatively charged due to the substitution of about one fourth of the fourvalent Si by trivalent Al. They are separated and only weakly bound by interlayer potassium cations, compensating for the negative charge. The layered structure allows cleaving the crystals along the (001) planes using either a scalpel or Scotch tape, leading to macroscopic, atomically flat surfaces. In this process, the potassium ions get distributed between the cleaved surfaces, causing a varying, high electrostatic surface potential \cite{7} and making the surface strongly hydrophilic.
Depending on the humidity, this leads to the formation of water adlayers, which have been studied using various techniques [8–12].

Mica is a common material for electronic components such as capacitors. Due to its high dielectric strength and permittivity of \( \varepsilon_r = 6.4–9.3 \) [13, 14] it is used for insulation. In particular, in high frequency applications its high resistivity and low loss tangent are valuable. Furthermore, mica is flat, transparent, flexible and cheap. These properties also make mica an appealing substrate and dielectric for graphene devices [15, 16]. So far, thin mica layers have been utilized as a dielectric for organic electronics [17–19] and carbon nanotube field-effect transistors [20].

It was shown that graphene on mica conforms to the atomically flat mica substrate and becomes atomically flat itself [21]. On the other hand, Xu et al showed that water adsorbed on the surface due to the strong hydrophilicity can be encapsulated between graphene and the mica surface [22, 23]. As for the electronic properties, Shim et al [24] used Raman spectroscopy to probe substrate-induced charge doping. Ponomarenko et al [25] and Kretinin et al [26] measured the conductivity of graphene on various substrates, including mica, to investigate the role of charged impurities on charge carrier mobility in graphene. However, no detailed study of electronic transport in graphene-mica systems has been reported yet. Here, we show electronic transport experiments in graphene-mica heterostructures in which mica is used as a gate dielectric and/or substrate. We find a very strong positive hysteretic behavior of the resistance with respect to tuning the gate voltage. It persists down to millikelvin temperatures and can be strongly tuned by varying the sweeping speed, the sweeping range and the charging time at a fixed gate voltage. In addition, we show that when mica is only used as a substrate, no hysteresis is observed. Finally, we discuss the possible mechanisms responsible for the behavior.

2. Experiments, results and discussions

In our study, we have designed different graphene-mica heterostructures to investigate the role of mica as a dielectric and as a substrate. In total, twelve different samples were fabricated and characterized. Electronic transport experiments have been performed in a two-terminal configuration using standard low-frequency lock-in detection and/or using a LR700 resistance bridge. We have used a cryo-free dilution refrigerator BlueFors LD250 for the low temperature measurements.

Our first sample design is depicted in figure 1(a). Thin mica crystals (muscovite mica V1 grade, supplied by Plano GmbH) are directly deposited onto a heavily doped Si wafer with 320 nm SiO\(_2\) using mechanical exfoliation [27]. Using an optical microscope, mica crystals below 10 nm thickness can easily be located, as the apparent color of the SiO\(_2\)/mica stack heavily depends on the crystal's thickness [20]. Then, a graphene sheet is transferred on top using a PMMA-based dry transfer at ambient conditions [2]. Figure 1(b) shows the resistance versus the gate voltage for a device that consists of a stack of 320 nm SiO\(_2\) and 31 nm mica. The gate sweep (figure 1(b)) was performed with a ramping speed of 0.25 V s\(^{-1}\) and a charging time of two minutes at ±75 V measured on a graphene monolayer on a 320 nm SiO\(_2\)/31 nm mica dielectric bilayer. The second x-axis shows the displacement field, defined as \( D = \frac{\varepsilon_0 \varepsilon_r}{d} \cdot V_G \). The charge neutrality point for the up and down sweeps shift by 104.5 V.

**Figure 1.** (a) Sketch of a graphene on mica field-effect device. (b) Gate sweep at 0.25 V s\(^{-1}\) with a charging time of two minutes at ±75 V measured on a graphene monolayer on a 320 nm SiO\(_2\)/31 nm mica dielectric bilayer. The second x-axis shows the displacement field, defined as \( D = \frac{\varepsilon_0 \varepsilon_r}{d} \cdot V_G \).
However, like in the experiments using ferroelectric coatings by Zheng et al. [35, 36], the sole polarization of \( \text{H}_2\text{O} \) molecules should induce a negative hysteresis [31, 37]. Thus, if there are effects caused by the polarization of water molecules, they are obscured by the much stronger positive hysteresis.

In order to elucidate the effect of trapped water at the graphene-mica interface, we have prepared samples inside of a glove bag in a nitrogen atmosphere with relative humidity <5%. Additionally, the sample stage and mica substrate were heated to 140 °C during the transfer to further reduce the amount of water adsorbed on the surface that could get trapped at the mica/graphene interface. The amount of water that is adsorbed by the mica surface depends on the humidity, and it was reported that it completely disappears below 2% relative humidity (RH) [22]. Graphene sheets on suspended PMMA membranes were prepared in advance outside of the glove bag. Then, all of the following procedures were done in advance of the stack of 320 nm SiO\(_2\) and 12 nm mica, together with the effect of varying the charging time at maximal gate voltage.

Figure 2 shows the resulting gate sweeps of graphene on a stack of 320 nm SiO\(_2\) and 12 nm mica, together with the effect of varying the charging time at the minimal and maximal gate voltage before reversing the sweeping direction. To decrease distortions, the sweep speed was increased to 0.83 V\(\text{s}^{-1}\), and the sweeping range was decreased to ±50 V. Still, a very large hysteresis remains, which can be strongly tuned by varying the charging time (here, from 0 to 6 min). Figure 2(b) shows the difference between the position of the charge neutrality points for the up and down sweeps with respect to the charging time. Starting at 12 V for the direct reversion of the sweeping direction, the hysteresis increases up to 56 V for a charging time of 10 min without showing a sign of saturation. Raman spectroscopy measurements have shown that a direct contact between the graphene and the mica surface can cause strong p-doping, which gets suppressed by interfacial water layers [26]. As we don’t observe this doping effect, it seems likely that despite the preparation in a dry atmosphere, water might get trapped at the interface between mica and graphene after exposure to ambient air, suppressing the charge transfer. As shown in figure 3, we observe interfacial water even when graphene was directly exfoliated onto mica inside an argon glovebox with <5 ppm water. The image was recorded at 30% relative humidity and shows islands of water with a height of 0.4 nm at the edge of the graphene sheet. In the inner part, the water formed a closed film. The mobility of the interfacial water seems to depend on details of the sample fabrication [38]. While Xu et al. [22] see a clear dependence of the amount of trapped water with respect to the humidity during graphene deposition and report that graphene permanently traps and immobilizes water adlayers for weeks, Severin et al. [39] observe reversible dewetting of the mica/graphene interface when changing the humidity.

Although a lot of charges seem to accumulate in the vicinity of the graphene sheet during the gate sweeps, which effectively screen the gate, the curves only get shifted, while their shape does not show a dependence on the charge neutrality point’s position. Thus, either the trapped charges are too far away from the graphene to act as scatterers, or the density of fixed charge impurities is much higher than the density of additional trapped charges.

In order to investigate the difference between using mica as a substrate and as a gate dielectric, as well as the role of
impurities and adsorbates on top of the graphene sheet, we designed a mica-graphene-hBN van der Waals heterostructure. Instead of the dual layer SiO2/mica dielectric, the mica crystals were directly exfoliated onto pre-patterned metal back gates. After the transfer, connection and etching of a graphene sheet, a thin crystal of hexagonal boron nitride was added on top; finally, a metal top gate was created in another electron beam lithography step. The sample thus features a single graphene sheet sandwiched between a back gate with a 20 nm thin mica dielectric and a local top gate with a 13 nm thin hBN dielectric (figure 4(a)). The resulting gate sweeps are shown in figures 4(b) and (c). The second x-axis shows the displacement field \( D = \epsilon_{r}\epsilon_{0}V_{G} \) for \( \epsilon_{r,mica} \approx 8.1 \), \( \epsilon_{r,hBN} \approx 3.9 \). First, the back gate was swept from −7 V to +7 V and back at a sweeping speed of 0.12 V s\(^{-1}\) with a charging time of one minute between the sweeps. Then, the top gate was swept from −4 V to +4 V and back, with the back gate at 0 V. While the gate sweep using the mica back gate again showed a very strong hysteresis of 6 V, which corresponds to a difference in the displacement field strength of \( 1.4 \times 10^{13} \) e \( \text{cm}^{-2} \), the hysteresis in the resistance curve for the sweep using the top gate with hBN dielectric almost vanishes. As both measurements were performed not only on the same sample but on the same area of graphene, this excludes adsorbates, PMMA residues or water on top of the graphene sheet as dominant sources for the gate hysteresis, as their effect should still be visible in the top-gated measurement. We can conclude that the hysteresis must therefore be caused by charge trapping either in the bulk mica crystal or at the graphene/mica interface.

Finally, the temperature dependence of the gate hysteresis was investigated in another sample featuring a 50 nm thin mica dielectric on top of a metal back gate. Graphene on SiO2 devices typically shows some hysteresis due to charge traps in the oxide. Lowering the temperature is known to freeze out charge traps and therefore suppresses the gate hysteresis [40], (different behavior was observed in [41] on one device). In our sample, the back gate voltage was swept from −10 V to +10 V and back with a sweeping rate of 0.06 V s\(^{-1}\) and a charging time of one minute between each sweep. Figure 5 shows the temperature dependence of the gate voltage hysteresis, i.e. the shift of the gate voltage of the charge neutrality point between the up and down gate sweep. Starting at a shift of 6 V at room temperature, which corresponds to a displacement field of \( 5.5 \times 10^{12} \) e \( \text{cm}^{-2} \), the hysteresis is reduced by cooling the sample until it reaches about 3.1 V or \( 2.8 \times 10^{12} \) e \( \text{cm}^{-2} \) at 150 K. Astonishingly, further cooling only slightly lowers the hysteresis to about 2.7 V or \( 2.5 \times 10^{12} \) e \( \text{cm}^{-2} \), which even remains down to 7 mK and unexpectedly does not vanish.

How can we explain this hysteretic behavior? Electrochemical effects, such as those proposed by Veligura et al [30], are most likely suppressed at these very low temperatures. Instead, we believe the hysteresis is caused by electrons tunneling into charge traps at the graphene/mica interface or in the bulk mica.

Interlayer water might play a crucial role [42], especially since potassium ions, such as those that exist on the mica surface, are known to cause dissociation of water molecules on metal surfaces. The valence electron of potassium adsorbed on an ice adlayer on a metal substrate can tunnel into the metal substrate, leaving behind an ion, which causes the dissociation through electrostatic perturbation and creates trap...
sites [43, 44]. This effect is further enhanced by the application of an external electric field. A similar mechanism could be responsible for charge traps in ice adsorbed on the mica surface. Here, the potassium ions already exist at the surface, randomly distributed after cleaving the crystal. The dissociation of water molecules causes trapping sites in the ice adlayers at the mica surface. Charge carriers in graphene might then tunnel into these traps when a gate voltage is applied. This layer of trapped charges underneath the graphene will then screen the gate. It remains to be investigated where the trapped water originates from and eventually how it can be avoided. This could be achieved by further reducing the humidity during sample preparation and ideally measuring the sample without ever exposing it to moisture.

3. Conclusions

To conclude, we have investigated the use of mica as a substrate and/or gate dielectric for graphene field-effect devices. When using mica as a gate dielectric, we find a pronounced hysteresis of the sample resistance with respect to the gate voltage. The hysteresis persists even at millikelvin temperatures, but it vanishes in a double gated device when the mica is used only as a substrate and the charge carrier density is modulated through a top gate with hBN dielectric. This behavior can be explained by charge trapping at the graphene-mica interface in which the interplay between potassium ions at the surface of mica crystals and water enclosed in the interface may enhance the charge trap density. Avoiding the formation of interfacial trapped water layers turned out to be difficult; solely reducing the relative humidity and heating the substrate during sample preparation did not lead to the desired effect. While the hysteretic behavior could be exploited in memory applications, the use of mica in graphene devices requires strict control over the manufacturing conditions to adjust the amount of trapped water. Furthermore, it could be necessary to encapsulate graphenemica devices to prevent the intrusion of water into the interface even after sample preparation.

Acknowledgments

We thank C Benz, J Bordaz, R Du and F Wu for their technical assistance and fruitful discussions. R.D.’s Shared Research Group SRG 1-33 received financial support from the Karlsruhe Institute of Technology within the framework of the German Excellence Initiative. This work was supported by the EU project MMM@HPC FP7-261594.

References

[1] Geim A K and Grigorieva I V 2013 van der Waals heterostructures Nature 499 419
[2] Dean C R et al 2010 Boron nitride substrate for high-quality graphene electronics Nat. Nanotechnol. 5 722
[3] Ponomarenko L A et al 2013 Cloning of Dirac fermions in graphene superlattices Nature 497 594
[4] Dean C R et al 2013 Hofstadter’s butterfly and the fractal quantum hall effect in moiré superlattices Nature 497 598
[5] Hunt B et al 2013 Massive Dirac fermions and Hofstadter butterfly in a van der Waals heterostructure Science 340 1427
[6] Fleet M 2003 Rock-Forming Minerals Vol 3A: Micas (Geological Society Pub House)
[7] Müller K and Chang C 1969 Electric dipoles on clean mica surfaces Surf. Sci. 14 39
[8] Hu J, Ogletree X X D F and Salmeron M 1995 Wetting and capillary phenomena of water on mica Surf. Sci. 344 221
[9] Odellius M, Bernasconi M and Pannierllo M 1997 Two dimensional ice adsorbed on mica surface Phys. Rev. Lett. 78 2855
[10] Miranda P, Xu L, Shen Y and Salmeron M 1998 Icclike water monolayer adsorbed on mica at room temperature Phys. Rev. Lett. 81 5876
[11] Bluem H, Inoue T and Salmeron M 2000 Formation of dipole-oriented water films on mica substrates at ambient conditions Surf. Sci. 462 L599
[12] Teschke O, Filho J F V and de Souza E F 2010 Imaging two-dimensional ice-like structures at room temperature Chem. Phys. Lett. 485 133
[13] Weeks J 1922 The dielectric constant of mica Phys. Rev. 19 319
[14] Dye D and Hartshorn L 1924 Dielectric properties of mica Proc. Phys. Soc. London 37 42
[15] Castellanos-Gomez A, Wojtaszek M, Tombros N, Agraït N, van Wees B J and Rubio-Bollinger G 2011 atomically thin mica flakes and their application as ultrathin insulating substrates for graphene Small 7 2491
[16] Castellanos-Gomez A, Poot M, Amor-Amorós A, Steele G A, van der Zant H S J, Agraït N and Rubio-Bollinger G 2012 Mechanical properties of freely suspended atomically thin dielectric layers of mica Nano Res. 5 550
[17] Matsumoto A, Onuki R, Ueno K, Ikeda S and Saiki K 2006 Fabrication of an organic field-effect transistor on a mica dielectric Chem. Lett. 35 354
[18] Lu X F, Majewski L A and Song A M 2008 Electrical characterization of mica as an insulator for organic field effect transistors Org. Electron. 9 473
[19] He Y, Dong H, Meng Q, Jiang L, Shao W, He L and Hu W 2011 Mica, a potential two-dimensional-crystal gate insulator for organic field-effect transistors Adv. Mater. 23 5502
[20] Low C G and Zhang Q 2012 Ultra-thin and flat mica as gate dielectric layers Small 8 2178
[21] Lui C H, Liu M, Mak K F, Flynn G W and Heinz T F 2009 Ultraflat graphene Nature 462 339
[22] Xu K, Cao P and Heath J R 2010 Graphene visualizes the first water adlayers on mica at ambient conditions Science 329 1138
[23] He K T, Wood J D, Doidge G P, Pop E and Lyding J W 2012 Scanning tunneling microscopy study and nanomanipulation of graphene-coated water on mica Nano Lett. 12 2665
[24] Shim J, Lui C H, Ko T Y, Yu Y J, Kim P, Heinz T F and Ryu S 2012 Water-gated charge doping of graphene induced by mica substrates Nano Lett. 12 648
[25] Ponomarenko L A, Yang R, Mohiuddin T M, Katsnelson M I, Novoselov K S, Morozov S V, Zhukov A A, Schedin F, Hill E W and Geim A K 2009 Effect of a high-κ environment on charge carrier mobility in graphene Phys. Rev. Lett. 102 206603
[26] Kretinin A V et al 2014 Electronic properties of graphene encapsulated with different two-dimensional atomic crystals Nano Lett. 14 3270
[27] Novoselov K S, Jiang D, Schedin F, Booth T J, Khotkevich V V, Morozov S V and Geim A K 2005 Two-dimensional atomic crystals *PNAS* **102** 10451

[28] Robert-Peillard A and Rotkin S 2005 Modeling hysteresis phenomena in nanotube field-effect transistors *IEEE Trans. Nanotechnol.* **4** 284

[29] Lee Y G, Kang C G, Jung U J, Kim J J, Hwang H J, Chung H-J, Seo S, Choi R and Lee B H 2011 Fast transient charging at the graphene/SiO2 interface causing hysteretic device characteristics *Appl. Phys. Lett.* **98** 183508

[30] Veligura A, Zomer P J, Vera-Marun I J, Jozsa C, Gordiuchuk P I and van Wees B J 2011 Relating hysteresis and electrochemistry in graphene field effect transistors *J. Appl. Phys.* **110** 113708

[31] Wang H, Wu Y, Cong C, Shang J and Yu T 2010 Hysteresis of electronic transport in graphene transistors *ACS Nano* **4** 7221

[32] Imam S A, Deshpande T, Guermoune A, Siaj M and Szkopek T 2011 Charge transfer hysteresis in graphene dual-dielectric memory cell structures *Appl. Phys. Lett.* **99** 082109

[33] Kim W, Javey A, Vermesh O, Wang Q, Li Y and Dai H 2003 Hysteresis caused by water molecules in carbon nanotube field-effect transistors *Nano Lett.* **3** 193

[34] Borisov V S, Karnakov V A, Ezhova Y V, Ruhstova O B and Shcherbachenko L A 2008 Specific features of the polarization of thin water films in the field of the active surface of a mica crystal *Phys. Solid State* **50** 1022

[35] Zheng Y, Ni G-X, Toh C-T, Tan C-Y, Yao K and Özyilmaz B 2009 Gate-controlled nonvolatile graphene-ferroelectric memory *Appl. Phys. Lett.* **94** 163505

[36] Zheng Y, Ni G-X, Toh C-T, Tan C-Y, Yao K and Özyilmaz B 2010 Graphene field-effect transistors with ferroelectric gating *Phys. Rev. Lett.* **105** 166602

[37] Sabri S S, Lévesque P L, Aguirre C M, Guillemette J, Martel R and Szkopek T 2009 *Appl. Phys. Lett.* **95** 242104

[38] Hattendorf S, Georgi A, Liebmann M and Morgenstern M 2013 Networks of ABA and ABC stacked graphene on mica observed by scanning tunneling microscopy *Surf. Sci.* **610** 53

[39] Severin N, Lange P, Sokolov I M and Rabe J P 2012 *Nano Lett.* **12** 774

[40] Liao Z-M, Han B-H, Zhou Y-B and Yu D-P 2010 Hysteresis reversion in graphene field-effect transistors *J. Chem. Phys.* **133** 044703

[41] Barthold P, Lüdtke T, Schmidt H and Haug R J 2011 Low-temperature hysteresis in the field effect of bilayer graphene *New J. Phys.* **13** 043020

[42] Lafkioti M, Krauss B, Lohmann T, Zschieschang U, Klauk H, von Klitzing K and Smet J H 2010 Graphene on a hydrophobic substrate: doping reduction and hysteresis suppression under ambient conditions *Nano Lett.* **10** 1149

[43] Henderson M A 2002 The interaction of water with solid surfaces: fundamental aspects revisited *Surf. Sci. Rep.* **46** 1

[44] Meyer M 2012 Ultrafast electron dynamics at Alkali, Ice structures adsorbed on a metal surface *PhD Thesis* Freie Universität Berlin (www.diss.fu-berlin.de/diss/servlets/MCRFileNodeServlet/FUDISS_derivate_000000010681/PhD_thesis_MMeyer.pdf)