High performance vertical tunneling diodes using graphene/hexagonal boron nitride/graphene hetero-structure
Seung Hwan Lee, Min Sup Choi, Jia Lee, Chang Ho Ra, Xiaochi Liu, Euyheon Hwang, Jun Hee Choi, Jianqiang Zhong, Wei Chen, and Won Jong Yoo

View online: http://dx.doi.org/10.1063/1.4863840
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/104/5?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
Spintronics with graphene-hexagonal boron nitride van der Waals heterostructures

A cohesive law for interfaces in graphene/hexagonal boron nitride heterostructure

Interlayer coupling enhancement in graphene/hexagonal boron nitride heterostructures by intercalated defects or vacancies

Tunneling characteristics in chemical vapor deposited graphene–hexagonal boron nitride–graphene junctions

In-plane and tunneling pressure sensors based on graphene/hexagonal boron nitride heterostructures
High performance vertical tunneling diodes using graphene/hexagonal boron nitride/graphene hetero-structure

Seung Hwan Lee,1,2,a) Min Sup Choi,2,3,a) Jia Lee,1,2 Chang Ho Ra,1,2 Xiaochi Liu,1,2 Euyheon Hwang,1,2 Jun Hee Choi,4 Jianqiang Zhong,5,6 Wei Chen,5,6 and Won Jong Yoo1,2,3,b)

1Samsung-SSGU Graphene Center (SSGC), Sungkyunkwan University, 2066, Seobu-ro, Jangan-gu, Suwon, Gyeonggi-do 440-746, South Korea
2Department of Nano Science and Technology, SSKU Advanced Institute of Nano-Technology (SAINT), Sungkyunkwan University, 2066, Seobu-ro, Jangan-gu, Suwon, Gyeonggi-do 440-746, South Korea
3Center for Human Interface Nano Technology (HINT), Sungkyunkwan University, 2066, Seobu-ro, Jangan-gu, Suwon, Gyeonggi-do 440-746, South Korea
4Frontier Research Laboratory, Samsung Advanced Institute of Technology, Samsung Electronics Co., Ltd., Yongsin, Gyeonggi-do 446-711, South Korea
5Department of Physics, National University of Singapore, 2 Science Drive 3, Singapore 117542
6Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543

(Received 15 November 2013; accepted 18 January 2014; published online 3 February 2014)

A tunneling rectifier prepared from vertically stacked two-dimensional (2D) materials composed of chemically doped graphene electrodes and hexagonal boron nitride (h-BN) tunneling barrier was demonstrated. The asymmetric chemical doping to graphene with linear dispersion property induces rectifying behavior effectively, by facilitating Fowler-Nordheim tunneling at high forward biases. It results in excellent diode performances of a hetero-structured graphene/h-BN/graphene tunneling diode, with an asymmetric factor exceeding 1000, a nonlinearity of ~40, and a peak sensitivity of ~12 V−1, which are superior to contending metal-insulator-metal diodes, showing great potential for future flexible and transparent electronic devices. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4863840]

Since the initiation of studies of the electrical characteristics of metal-insulator-metal (MIM) structured TDs, the research community has recognized that these devices may potentially be used as rectifiers with asymmetric tunneling characteristics based on the difference between the work functions of the two electrodes.1 These characteristics have been utilized in a variety of applicable devices, including antenna-coupled infrared detectors,2–4 rectennas for energy harvesting,5,6 and high frequency mixers.7 The efficiency of the TD characteristics may be improved by modifying the layered structure, increasing the levels of asymmetry, nonlinearity, and sensitivity, and by reducing the diode resistance.8–10 These characteristics are determined mainly by the work function of the electrodes and the barrier height between the insulator and the electrode materials. Hence, an optimal TD can be fabricated by adjusting these parameters and choosing proper materials. However, it is difficult to design and fabricate optimal TDs, because the fabrication process can be complicated.

The design of a 2D rectifier has been actively pursued and is of great importance in such a device that provides a building block for future electronic devices. Compared with the MIM TDs, it does not show structural difference inducing similar rectifying one-direction current flow. However, the fabrication of a rectifier from 2D materials, such as graphene (as the electrode) or h-BN (as the insulator) gives rise to a variety of advantages: The work function of graphene has been reported to be adjustable through the application of an electrical field,10 chemical doping,11,12 metal deposition,13 or plasma treatment.14,15 In addition, as h-BN has a crystalline structure similar to that of graphene and is ultraflat with no dangling bonds, h-BN reduces the resistance of graphene. As the Fermi level (EF) of graphene is located quite near the center of the h-BN band gap as high as 6 eV, it may be used as an effective tunneling barrier.16–18 The large-scale preparation of high-quality graphene and h-BN with such advantages has become feasible through the emerging chemical vapor deposition (CVD) processes; therefore, this technique is expected to be applicable to a variety of flexible and transparent electronic devices and tunneling diodes in the future.19,20

The hetero-structured graphene/h-BN/graphene tunneling diode (GBG-TD) was fabricated by transferring CVD graphene and mechanically stacked thin h-BN layer on a Si substrate covered by 90 nm SiO2 as reported previously.16 Rectangular graphene patterns were formed (W/L = 5/40 μm) using photolithography techniques, followed by oxygen plasma etching. The work functions of graphene at either side were adjusted using chemical doping methods with benzyliviolgen (BV) and AuCl3.11,12 The circuit and schematic diagrams of the thus fabricated p-doped top graphene (p-GrT)/h-BN/n-doped bottom graphene (n-GrB) TD are shown in Fig. 1(a). Figs. 1(b) and 1(c) show the optical and atomic force microscopic (AFM) images of a fabricated GBG-TD. The white, yellow, and blue dotted lines indicate the GrT, GrB, and h-BN, respectively. The thickness of h-BN was measured by AFM (Inova Microscope in Veeco) and it has 6 nm thickness. Electrical measurements were performed using a semiconductor parameter analyzer (Agilent 4155 C).

a)S. H. Lee and M. S. Choi contributed equally to this work.
b)yoowj@skku.edu
down-shifted (4 and 3 cm$^{-1}$ transfers in the doped graphene. In AuCl$_3$ doped graphene, due to phonon renormalization induced by electron and hole doping states of the graphene. The G band may be shifted up due to enhanced electron–phonon coupling. This reaction results in p-Gr, and the G band shifts down due to a reduction in the electron–phonon coupling. These tendencies were apparent from the Raman spectra, which were consistent with the spectra of p- and n-Gr, as reported previously.$^{11,23}$

UPS measurement was conducted to identify the differences in the work functions of doped graphene using the chemical methods as described above. Fig. 2(b) shows the kinetic energy of the secondary electrons generated from graphene by the introduced energy from a He light source. Because the rapid increase in the secondary electrons corresponds to the Fermi-level energy ($E_F$) of graphene in the vacuum state, the different doping conditions of graphene could be derived by calculating the work function ($\Phi_g$) using the equation, $\Phi_g = h\omega - |E_{FE} - E_{sec}|$, where $h\omega = 21.2$ eV (He I source), $E_{sec}$ is the onset of the secondary emission, and $E_{FE}$ is the Fermi edge = 16.7 eV in this work (sample bias at $-10$ V). $E_{sec}$ for pristine graphene was determined to be 10 eV and corresponds to a work function of 4.5 eV, similar to the values obtained from previous reports.$^{10,11}$ The derived work functions from the 50 mM BV- and AuCl$_3$-doped graphene samples were 3.1 and 5.6 eV, respectively, and a total difference of 2.5 eV was obtained. As mentioned previously, the large difference in the work function of doped graphene improves the efficiency of operation and the performance of MIM diodes.

On the other hand, the neutralized BV$^{5+}$ ions provide electrons to graphene and are stabilized as BV$^{2+}$. This reaction results in n-Gr, and the G band shifts down due to a reduction in the electron–phonon coupling. These tendencies were apparent from the Raman spectra, which were consistent with the spectra of p- and n-Gr, as reported previously.$^{11,23}$

FIG. 1. (a) Circuit and schematic diagrams of a fabricated GBG-TD. The AuCl$_3$ solution was deposited on the GrT after device fabrication to compare the doping effect. (b) and (c) show the optical microscopy (scale bar, 15 $\mu$m) and AFM images (scale bar, 1 $\mu$m) of a fabricated GBG-TD, respectively.

FIG. 2. (a) Raman spectra of graphene before and after doping (BV for n-doping and AuCl$_3$ for p-doping). (b) UPS spectra around the secondary electron threshold for the pristine, n- and p-Gr. The extracted work-functions of graphene are 3.1, 4.5, and 5.6 eV for BV-doped, pristine, and AuCl$_3$-doped.
This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 18.140.1.248 On: Wed, 14 Jan 2015 23:21:27

FIG. 3. Electrical characteristics of the GBG-TD before and after p-doping of GrT: (a) \(I_{\text{F}}-V_{\text{F}}\) transfer characteristics. (b) Asymmetry factor \((I_{\text{forward}}/I_{\text{reverse}})\). (c) Nonlinearity \((dV/dI)^2\). (d) Sensitivity \((dV/dI)^{-1}\).

different values of the tunneling current under forward and reverse bias conditions indicate the good applicability as a diode that rectifies \(V_{\text{ac}}\) to \(V_{\text{dc}}\). The asymmetric rectifying characteristics are significantly enhanced after p-doping of GrT via spin-coating with the AuCl3 solution. Note that the tunneling current changed to ~5.2 pA at ~7 V and to 11.5 nA at ~7 V after p-doping of GrT, about a 1000-fold greater value at forward bias. For more precise analysis, the asymmetry factor, which is a figure of merit for TDs and expressed as the ratio of \(I_{\text{forward}}/I_{\text{reverse}}\), is calculated as shown in Fig. 3(b). After p-doping of the top graphene, the rectifying behavior is improved significantly due to the difference in the work functions of the doped graphene on either side. Thus, our observations agree well with the previous reports1,2 of the asymmetric tunneling characteristics measured using different types of electrode. This outstanding asymmetry factor is more than 100 times the values obtained from other types of electrodes (4-7)24 or metal-insulator-insulator-metal (MIIM) structure diodes (~10).9,26 Hence, the possibilies enabled by this hetero-structured diode showing effective rectifying characteristics are apparent.

After applying p-type doping to the GrT layer, the tunneling current changed insignificantly under a reverse bias, whereas the tunneling current changed significantly under a forward bias. In addition, the point of the voltage at which the F-N tunneling began decreased by as much as 2 V. A previous study of the h-BN tunneling characteristics has been reported that the dielectric strength of h-BN is about 7.94 MV/cm.18 Hence, it can be predicted that the tunneling current in a 6 nm thick h-BN layer rapidly increases at ~5 V, and this value is similar to the observed value in our experiment. In order to elucidate the effects of chemical dopants on the h-BN, the electrical characteristics before and after doping were confirmed by fabricating a tunneling device without a top graphene layer [Fig. S2]. The difference between before and after doping is insufficient to explain the great improvements of our GBG-TD. Thus, it is thought that the improvements in the TD arise from the asymmetric doping effects on only graphene layers.

Figs. 3(c) and 3(d) reveal the nonlinearity and sensitivity as the figures of merit for a TD which influence directly on the rectified current and voltage. The fabricated GBG-TD showed zero bias sensitivities of 2.75 V^{-1} and 0.32 V^{-1} before and after GrT doping, respectively, and peak sensitivities near 2.5 V of 12.5 V^{-1} and 11.8 V^{-1}, respectively. These figures are comparable with the zero bias sensitivities (0.00, 0.08, 0.45, and 0.74 V^{-1} measured for Al/AlOx/M (M = Al, Ti, Ni, and Pt))25 in conventional MIM-TD produced by means of different electrodes and the peak sensitivity of a MIIM structure diode (5.5 V^{-1} for Cr/Al2O3-HfO2/Cr).9 Moreover, the nonlinearity values are two or three times higher than those obtained from conventional MIIM structure diodes (~10) [Table S1].26

In order to understand the rectifying phenomenon, we described the energy band diagrams under zero, reverse, and forward bias conditions as shown in Fig. 4(a). A huge difference in the work functions of graphene on either side after doping causes the significant band-bending of h-BN at zero bias due to the \(E_F\) alignment of graphene layers. The effective barrier thickness of this bended band structure of h-BN can be tuned by applying forward and reverse biases. Under reverse bias, the band-bending in h-BN is alleviated by an increase in \(E_F\) of GrB and the tunneling current remains relatively low due to the thick effective barrier. By contrast, the forward bias accelerates band-bending in h-BN to produce a triangular band shape and induces a high tunneling current by reducing the effective barrier thickness.

Based on the F-N tunneling equation, \(\ln(I/I^2)\propto 1/V\), we plotted the \(\ln(I/I^2)\) versus \(1/V\) curve as shown in Figure 4(b) to demonstrate linear behavior and extract barrier height. At high bias regime, the linear characteristic is observed at ~0.24 V^{-1} which corresponds to ~4.2 V. Thus, we can
estimate that the F-N tunneling starts at 4.2 V which is lower than that without doping process of the previous report (F-N tunneling starts at ~6.6 V for similar thickness of the h-BN of 6 nm). This lowered value is probably attributed to the lowered tunneling barrier height. Using the slope of the graph, we could extract the barrier height: $\Phi_B = \left( \frac{-slope \times A}{8 \times 10^{-19}} \right)^{\frac{1}{2}}$. The extracted value (~2.4 eV) is lower than the previously reported value (~3 eV) and it seems that this lowered value is caused by chemical doping on graphene electrodes of both sides. This control of tunneling barrier height using chemical doping can be applied for optimization and development of TDs. Furthermore, we observed the insignificant temperature dependency of tunneling current as previously mentioned [Fig. S1]. The very little temperature dependence of tunneling current is understood to support Schottky emission and Poole-Frenkel (P-F) emission are strongly dependent on temperature.27

In summary, two typical 2D materials, graphene and h-BN, were stacked to form a hetero-structured TD. The graphene layers at either side of the h-BN were doped as p- or n-type using chemical doping methods to control the work-function and produce a rectifier which shows one-directional current flow. After chemical doping, the figures of merit for the TD, such as the asymmetry factor (~1000), nonlinearity (~40), and sensitivity (2.75 V$^{-1}$ zero bias sensitivity and 11.8 V$^{-1}$ peak sensitivity) were enhanced significantly compared with those obtained from conventional TD. These figures are superior to those of the conventional MIM-TD. Therefore, this study could contribute to the design of TD through controlling work-function of graphene and other 2D materials in the future.

This work is supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF): 2009-0083540, 2011-0010274, 2012H1A2A1004044, and 2013-015516, and by the Global Frontier R&D Program (2013-073298) on Center for Hybrid Interface Materials (HIM) funded by the MOSIP, Korea.

26. See supplementary material at http://dx.doi.org/10.1063/1.4863840 for electrical characteristics of GBG-TD depending on the low temperature, chemical doping effects of h-BN layer, and comparison of rectifying characteristics with conventional diodes.