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Observation of resistive switching in a graphite/hexagonal boron nitride/graphite heterostructure memristor

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Abstract: With the atomically sharp interface and stable switching channel, van der Waals (vdW) heterostructure memristors have attracted extensive interests for the application of high-density memory and neuromorphic computing. Here, we demonstrate a new type of vdW heterostructure memristor device by sandwiching a single-crystalline h-BN layer between two thin graphites. In such a device, a stable bipolar resistive switching (RS) behavior has been observed for the first time. We also characterize their switching performance, and observe an on/off ratio of >10^3 and a minimum RESET voltage variation coefficient of 3.81%. Our work underscores the potential of 2D materials and vdW heterostructures for emerging memory and neuromorphic applications.

Key words: hexagonal boron nitride; van der Waals heterostructure; memristor

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1. Introduction

The hexagonal boron nitride (h-BN) with a large band gap and excellent thermal conductivity[1–3] has been widely used as a protective layer to enhance the reliability and insulation of electronic devices[4–7]. Memristors using h-BN as the resistive switching (RS) layer (active layer) have shown outstanding performance, including the coexistence of bipolar and threshold RS[8], ultra-low power consumption[9, 10], resistance multi-states[11], and large switching ratio[12]. However, metal electrodes used in these memristors can be harmful to the device performance[13–15], resulting in high contact resistance and unreliable RS[16], due to the non-atomically flat contact interface and defect doping introduced during the electrode deposition processes[17, 18]. Utilizing layered electrode materials in vdW heterostructures rather than normal metals are expected to solve these challenges[19–26].

In this work, we use a polymer touch-free transfer method and fabricate a high-quality single-crystalline graphite/h-BN/graphite (Gra/h-BN/Gra) heterostructure. In such a heterostructure, we observe reliable bipolar RS, with an on/off ratio larger than 10^3 and low variation coefficients (6.21% and 3.81% for SET and RESET voltages, respectively). Our work proposes a new type of single-crystalline vdW heterostructure for future memristor applications.

2. Results and discussion

The mechanical exfoliation method is adopted to obtain the thin graphite and h-BN films. The typical thickness is around 4.5 nm for h-BN film (Fig. 1(a)) and around 55 nm for graphite film (Fig. 1(b)). We use a standard e-beam lithography process followed by plasma etching to obtain the graphite strips. Firstly, graphite flakes are mechanically exfoliated on the SiO_2(300 nm)/Si substrate. Secondly, the PMMA (620 nm thickness) is spin-coated on the surface of graphite flakes and dried at 170 °C for 5 min. Thirdly, the standard e-beam lithography is applied to acquire electrode patterns on the PMMA layer, followed by the oxygen plasma treatment using an inductively coupled plasma (ICP) system. The plasma etching power and duration are strictly controlled according to the graphite thickness to avoid excessive etching. Finally, the PMMA is removed by the acetone solution, and the prepared graphite electrodes are annealed at 350 °C in the argon atmosphere for 2 h to get a clean electrode surface.

The Raman spectra of the h-BN and graphite layer are shown in Figs. 1(c) and 1(d), in which the E_{2g} mode of h-BN at 1365 cm^{-1} exhibited a full width at half maximum (FWHM) of 8 cm^{-1} and no defective D-peak was observed for the graphite. Besides, the thickness and morphology of the materials were characterized by the atomic force microscopy (AFM) (Fig. 1(a) and 1(b)). The flat surfaces of graphite and h-BN offered the possibility for an atomically sharp interface.

Figs. 2(a) and 2(b) show the schematic structure and optical microscope image of the Gra/h-BN/Gra memristive device. The red dashed box indicates the protective layer (thick h-BN) on the top of the device. The white dashed box represents the outline of the h-BN RS layer. The blue arrows indicate the graphite top electrode (TE) and bottom electrode (BE). The heterostructure fabrication is conducted based on a polymer touch-free transfer method. The protective h-BN layer is first picked up by the PC film, followed by the exfoliated graphite strips (as the TE) and the h-BN RS layer. The whole

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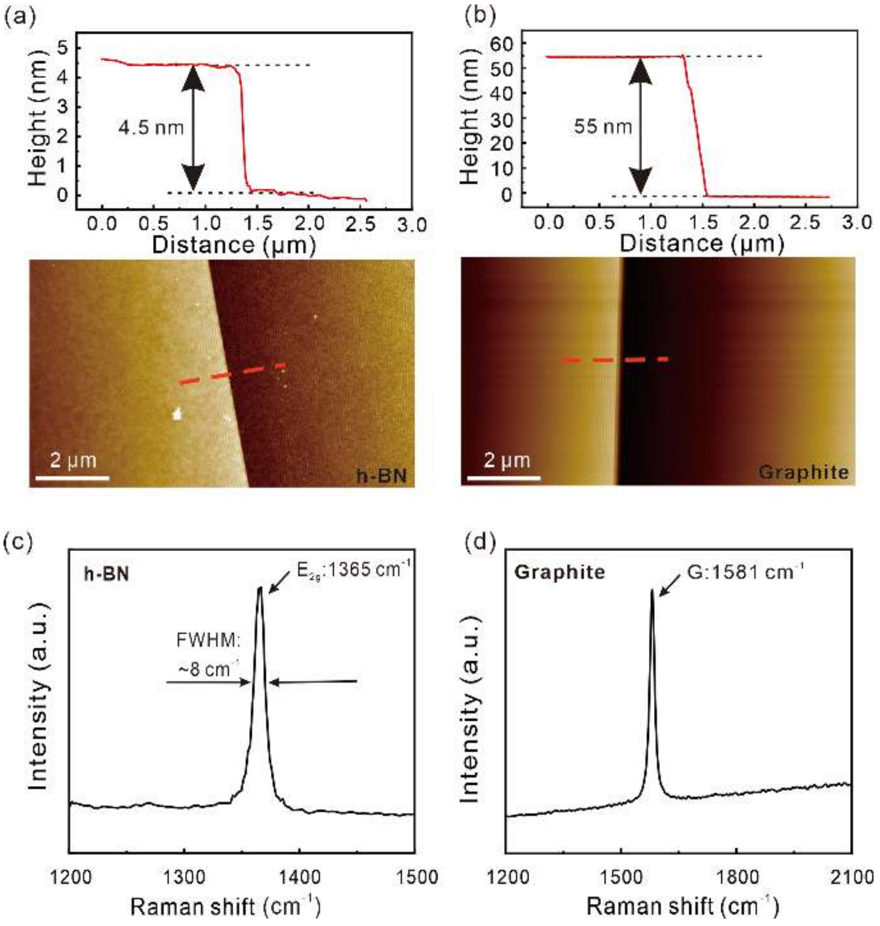

Fig. 1. (Color online) The characterization of Gra/h-BN/Gra heterostructure. (a, b) The AFM characterization of the h-BN and graphite layer with the thickness and appearance displayed. (c, d) The Raman spectra of h-BN and the graphite layer.

PC film is then released on top of the BE graphite and removed by soaking in the $CHCl_3$ solution for 20 min. Since the stacking process of different layers is polymer-free, this method guarantees the interfaces of the heterostructure are very clean. Finally, metal electrodes (5 nm Ti/45 nm Au) are deposited for connecting the graphite electrodes.

In order to explore the electrical behavior of the memristor devices，Cascade Summit Series Probe Systems and an Agilent B1500A semiconductor device analyzer are employed for electrical measurements. All the measurements were carried out in the nitrogen atmosphere at room temperature. The bias voltage was applied on the top graphite electrode and the bottom graphite electrode was always grounded. The RS behavior observed is shown in Fig. 2(b). With the applied bias voltage increasing from 0 V toward the positive, a sudden current change was observed at ~ 7 V, showing the first transition from the high-resistance state (HRS) to the low-resistance state (LRS). This phenomenon is attributed to the first dielectric breakdown (also called electroforming) of h-BN and the threshold voltage of this process is called forming voltage[27]. After the forming event, stable bipolar RS cycles were realized in the range below the forming voltage, and the black arrows indicated the switching directions of a stable bipolar I–V curve. When the DC voltage sweep was applied from 0 to 4 V and then back to 0 V, the device exhibits an HRS in the "1" stage and a LRS in the "2" stage. The transition from "1" to "2" is called the SET process and the voltage at the upward jumping point is called the SET voltage (V_{set}). When the DC voltage sweep was applied from 0 to –4 V and then back to 0 V, the LRS of "2" stage continues to be maintained in the "3" stage and reverted to the HRS in the "4" stage. The transition from "3" to "4" is called the RESET process and the voltage at the downward jumping point is called the RESET voltage (V_{reset}). A complete cycle has been performed during the process from "1" to "4". The current compliance (I_{cc}) of 800 μA was applied to the SET process and the voltage compliance of –4 V was used for the RESET process. The distribution of I–V curves for all cycles is relatively concentrated.

We further analyzed the cycle-to-cycle variability of the device with results shown in Fig. 3. In order to explore the resistance variation of different cycles, we counted the resistance value (read at 0.8 V) of the HRS and the LRS over 40 cycles (Fig. 3(a)). Fig. 3(b) shows that the cumulative probability of high/low resistance is limited in a minimum region, which indicates the low cycle-to-cycle dispersion resistance. A large on/off ratio around 10^3 is also clearly observed from the results, which suggests the HRS may correspond to an electron tunneling process[14].

The $V_{\text{set}}/V_{\text{reset}}$ distribution is another important figure of merit for analyzing the electrical performance of memristor devices (Fig. 4). The V_{set} and V_{reset} variabilities were obtained from the coefficient of variation (C_{v}), which is the ratio of standard deviation (σ) and mean value (μ) of cycle-to-cycle $V_{\text{set}}/V_{\text{reset}}$. Here, for V_{set}, the σ and μ are equal to 0.183 and 2.955 V, respectively; whilst for V_{reset}, the σ and μ are equal to 0.142

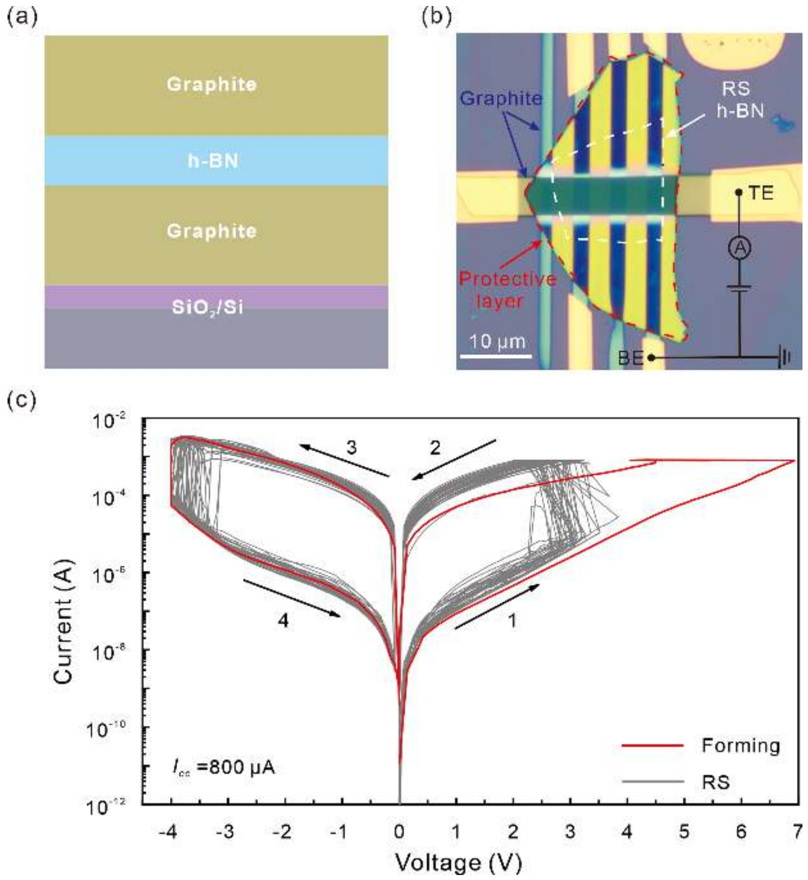

Fig. 2. (Color online) The image and switching curves of the Gra/h-BN/Gra device. (a, b) The schematic diagram and optical microscope image of the memristive device. The scale bar is 10 μm. (c) Typical *I*–*V* curves of the Gra/h-BN/Gra device during the DC voltage sweep. The process of the DC voltage sweep is 0 → 4 → 0 → –4 → 0 V.

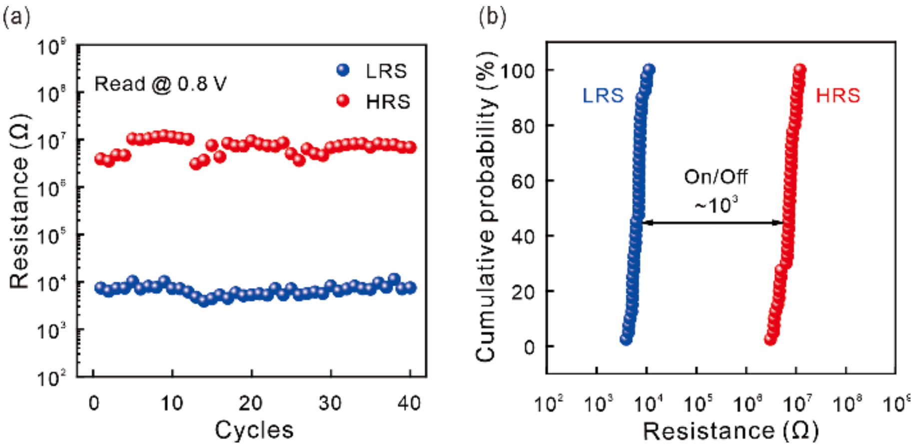

Fig. 3. (Color online) The switching performances of a Gra/h-BN/Gra device. (a) The stable RS behavior. (b) The cumulative distribution plot of the high and low resistance measured over 40 cycles.

and −3.732 V, respectively. As a result, the C_v value of V_{set} and V_{reset} are obtained to be 6.21% and 3.81%, respectively. The small values of C_v indicate the low cycle-to-cycle variability of the device. As discussed above, the prominent performances of the fabricated memristors are derived from full 2D material vdW heterostructures endowed with an atomically sharp interface between the electrode and the active layer, which could be beneficial to the forming of a well-confined conduction channel[23, 24].

Finally, we propose a potential model based on the formation of carbon conductive filaments which could explain the switching behaviors we observed[27–30]. According to previous reports, the first breakdown process could create a defect path in the h-BN film. Such a path is more likely to be composed of boron vacancies[31–33], and attributed to the lower diffusion activation energy of boron vacancies/ions[34]. In the positive bias voltage and defect charge induction, the carbon atoms turn into carbon ions with positive charge, and migrate along the defect path to form the localized C–N bonding served as the carbon conductive filaments which connect the TE and BE[34], and trigger the SET process. With a reverse voltage applied, the carbon ions migrate back to the

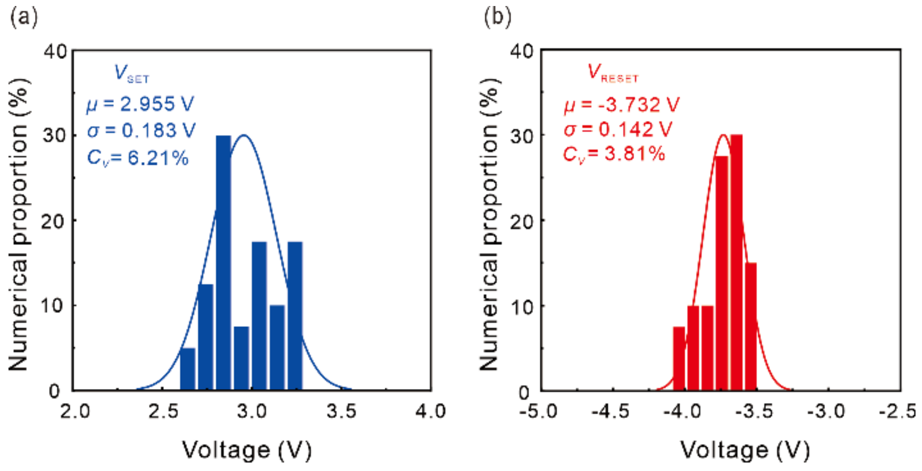

Fig. 4. (Color online) The distributions of cycle-to-cycle (a) $V_{\rm set}$ and (b) $V_{\rm reset}$.

graphite electrode, resulting in the rupture of the carbon conductive filaments and therefore the RESET process.

3. Conclusions

In conclusion, we have fabricated a single-crystalline Gra/h-BN/Gra vdW heterostructure memristor with atomically sharp interface. The device exhibits a stable bipolar RS behavior, with an on/off ratio of around 10^3, and a low coefficient of variation for both $V_{\rm set}$ ($C_{\rm v}$ = 6.21%) and $V_{\rm reset}$ ($C_{\rm v}$ = 3.81%). We also propose a possible model which could explain the observed switching behavior. Our work demonstrates a new type of vdW heterostructure memristor for future memory and neuromorphic applications.

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