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Solution-Processed Black Phosphorus Nanoflakes for Integrating High Performance of Nonvolatile Resistive Random Access Memory

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Abstract

In this study, we demonstrated an easy way to prepare RRAM with black phosphorus (BP) which is one of the emerging two-dimensional (2D) materials. We first used solution-based BP nanoflakes embedded with polystyrene (PS) as an active layer in a sandwich-structured resistive random access memory (RRAM). Raman spectrum and transmission electron microscopy (TEM) were conducted to verify the quality of BP nanoflakes. As a result, Al/BP nanoflakes embedded in PS/Al memory device shows excellent performances such as forming-free, nonvolatile, low operation voltage (1.75 V), high ON/OFF ratio (2.5 × 10^3) and long retention time over 10^3 s. Moreover, the mechanism of switching behavior was conducted. The proposed route could pave a way to next-generation of memory devices.

1. Introduction

Nonvolatile resistive random access memory (RRAM) with the advantages of nonvolatile, low power consumption, and having a CMOS-compatible process is attracted in emerging memory. By controlling difference resistance between the high resistance state (HRS) and the low resistance state (LRS), which were used to define the resistance switching (RS) behaviors of "0" and "1", respectively. Recent works by employing the vertically-sandwiched metal-insulation-metal (MIM) structure reveals improved RS behaviors through the additives of the adding metal nanoparticles or two-dimensional (2D) materials with polymers [1,2]. Currently, atomic layered black phosphorus (BP), the so-called phosphorene, demonstrating attractive electronic structures, performing the high mobility and tunable band, which was regarded as the potential candidate for frontier nano-electronics [3]. It was reported that active layer in flash memory comprising BP quantum dots (BPQDs) with polyvinylpyrrolidone (PVP) exhibits high ON/OFF current ratio and good stability [4]. The BPQDs sandwiched between two polymer layers as an active layer demonstrated higher ON/OFF ratio of 3.0 × 10^7 [5]. However, few-layers BP nanoflakes has not yet been discussed in memory devices. In this work, for the first time, we used BP nanoflakes mixed with polystyrene (PS) as the active layer sandwiched by aluminum electrodes, demonstrating a nonvolatile RRAM with low operation voltage (1.75 V), high ON/OFF ratio (2.5 × 10^3) and long retention time (10^3 s). Moreover, the solution-processed method shows advantages of low cost, high production rate and massive scalability, which was promising for the practical applications.

2. Experimental methods

Preparation of dispersed BP nanoflakes suspension with PS

Bulk BP crystals were grounded into powders and immersed in N-Methyl-2-pyrrolidone (NMP) in the centrifuge tube with a concentration of 1 mg/ml. Then, the prepared sample was sonicated under high power ultrasonicator for 4 hours (total input energy = 1.2 MJ). All of the process was conducted in a glove box. Afterward, as prepared BP dispersions were gradually centrifuged to extract few layers BP nanoflakes (Fig. 1(a)). The PS was mixed into the as-prepared BP nanoflakes solution with the concentration of 6.5 mg/ml (PS/NMP).

Fabrication of memory device by integrating BP nanoflakes

First, the thickness of 100 nm Al as bottom electrode (width=0.5 mm, length=10 mm) was deposited by e-gun evaporator on a 300 nm SiO_2/Si substrate. The prepared PS mixed NMP solution was subsequently coated on the surface by spin-coating method. Then, it was transferred into the glovebox and annealed at 120°C for 5 hours. The thickness of the active with 50 nm was obtained after dried. Finally, 100 nm in thickness of Al top electrode were deposited on top of the active layer. As the result, 10 × 10 array of sandwich-structured (Al/BP:PS/Al) devices were integrated.

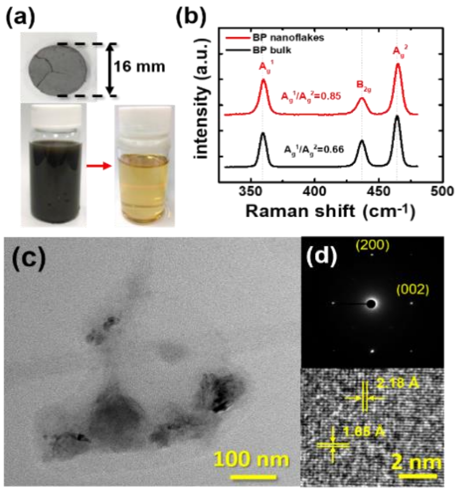

Fig. 1 (a) Photograph of BP bulk and the as-prepared few-layered BP suspension in NMP. (b) The Raman spectra on and bulk BP and layered BP. (c) TEM image of a few-layered BP nanoflakes and its corresponding (d) SAED pattern and high-resolution TEM.

Characterization of BP nanoflakes and RRAM device

The morphology and nanostructure analysis were carried out by SEM, TEM, and Raman spectroscopy. The electrical performance was characterized by using Keithley 4200-SCS under ambient conditions (compliance current = 0.01 A). The bottom electrode was grounded when applying the bias voltage to the top electrode.

3. Results and discussion

Material characterizations

In order to verify the quality of BP dispersions, Raman spectroscopy were conducted. Three peaks located at the A_g^1 (360.0 cm^{-1}), B_{2g} (436.8 cm^{-1}) and A_g^2 (464.8 cm^{-1}) corresponding to three feature peaks of a typical BP (Fig. 1(b)). The observed blue shift compared with bulk BP further indicates the formation of few atomic layered BP flakes. HRTEM was used to evaluate the nanostructure of the as-exfoliated BP nanoflakes. TEM image accompanied with the selected area electron diffraction (SAED) patterns in Fig. 1(c-d) indicated the highly crystallinity of BP nanoflakes.

Electronic measurement of RRAM

The electronic properties and switching effect were presented in Fig. 2(a), the transfer cvurve of the integrated device shows an identical two states, which corresponds to the HRS and LRS of RRAM, respectively. When the applied positive voltage swept from 0 to 3.5 V, the device was initially in the HRS with the current order of 10^{-9} A. The abrupt jump occurred at 1.75 V (turn on voltage) with the current order reached 10^{-5} A, indicating the switching behavior from HRS to LRS. It consisted with the writing/SET process in a digital memory cell. The LRS was retained not only when decreasing the positive voltage but even when removing the voltage. After that, *I-V* sweeping from 0 to -3.5 V and then from -3.5 to 0 V, the current suddenly decreased at -1.25 V (turn off voltage), consisted with the erasing/RESET process from LRS to HRS in a digital memory cell. This device displayed bipolar switching characteristics. Moreover, the device showed forming-free, nonvolatile, low power operation which are excellent advantages in development of emerged memories. On the other hand, the retention test was taken at HRS and LRS as shown in fig. 2(b) with retention time over 10^3 s and the ON/OFF ratio reached 2.5×10^3 at bias voltage of 0.5 V.

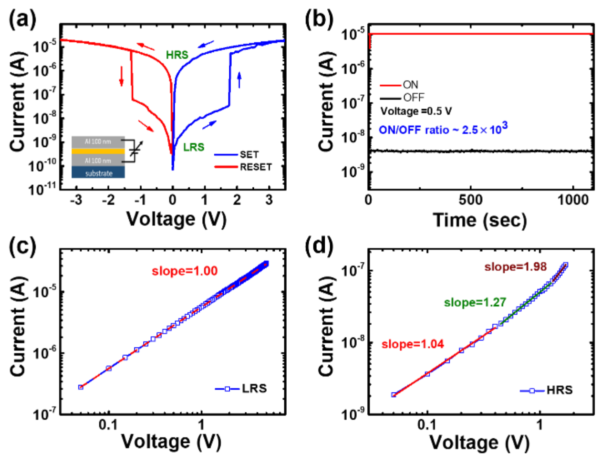

Fig. 2 (a) Typical *I-V* curve of BP-based memory devices. (b) Retention time test at bias voltage at 0.5 V. Analysis *I-V* curve with fitting line at (c) LRS and (d) HRS.

Mechanism of switching behaviors

To understand the carrier transport mechanisms of switching behaviors, *I-V* characteristics with different fitting lines were analyzed in LRS and HRS, respectively. Fig. 2(c) shows the double logarithm scale *I-V* curve which was fitted with a linear line (slope = 1) at LRS, indicating the ohmic-conduction is dominated on carrier transport. While at HRS (Fig. 2(d)), the fitted slope in *I-V* curve gradually increase from 1.04 to 1.98, indicating the characteristic of space-charge-limited current (SCLC). It is assumed that the charge carriers are trapped by the BP nanoflakes embedded in the active layer under low electric field condition; however, when applying large electric field, the traps are filled inside BP nanoflakes and other carries will no longer be affected. Finally, the current abruptly increased to high conductivity condition (Fig. 3).

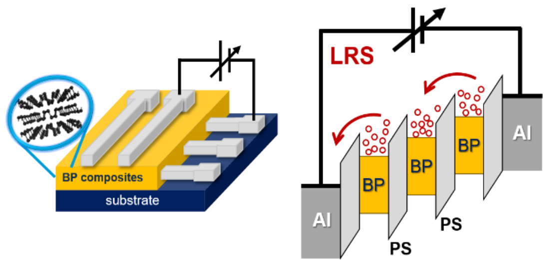

Fig. 3 Schematic diagram of (a) BP nanoflakes embedded MIM memory device and (b) the band diagram of sandwiched structure at LRS.

4. Conclusions

In this study, we investigated the embedded MIM sandwich structure memory device using solution-based BP nanoflakes mixed with PS composites. According to the charge carriers trapped in the active layer, RS and nonvolatile behaviors was observed. Furthermore, characteristics of forming-free, low operation voltage (1.75 V), high ON/OFF ratio (2.5×10^3) and long retention time (10^3 s) were achieved, suggesting the promising candidate of potential memory for next generation.

Acknowledgements

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