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Hydrogen induced redox mechanism in amorphous carbon resistive random access memory

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Abstract

We investigated the bipolar resistive switching characteristics of the resistive random access memory (RRAM) device with amorphous carbon layer. Applying a forming voltage, the amorphous carbon layer was carbonized to form a conjugation double bond conductive filament. We proposed a hydrogen redox model to clarify the resistive switch mechanism of high/low resistance states (HRS/LRS) in carbon RRAM. The electrical conduction mechanism of LRS is attributed to conductive sp^2 carbon filament with conjugation double bonds by dehydrogenation, while the electrical conduction of HRS resulted from the formation of insulating sp^3-type carbon filament through hydrogenation process.

Keywords: Carbon; Hydrogen redox; Conjugation double bond; RRAM

Background

Recently, portable electronic products which are combined memory circuits [1-3], display design [4,5] and IC circuits have popularized considerably in the last few years. To surmount the technical and physical limitation issues of conventional charge-storage-based memories [6-11], the resistance random access memory (RRAM) is constructed of an insulating layer sandwiched by two electrodes. This structure is a great potential candidate for next-generation nonvolatile memory due to its superior characteristics such as lesser cost, simple structure, high-speed operation, and nondestructive readout [12-21].

The carbon-based resistive memory (C-RRAM) has emerged as one of a few candidates with high density and low power. The resistive switching of C-RRAM relies on the formation and rupture of filaments due to redox chemical reaction mechanism, which is similar to most other reported RRAM devices [22-43].

In this paper, we investigated the resistive switching characteristics of amorphous carbon films prepared by RF magnetron sputter deposition technique for nonvolatile memory applications. Reliable and reproducible switching phenomena of the amorphous carbon RRAM with Pt/a-C:H/TiN structure were observed. In addition, the resistive switching mechanism of the amorphous carbon RRAM device is discussed and verified by electrical and material analysis.

Methods

The experimental specimens were prepared as follows. The carbon thin film (around 23 nm) was deposited on the $TiN/Ti/SiO_2/Si$ substrate by RF magnetron sputtering with a carbon target. After that, the Pt top electrode of 200-nm thickness was deposited on the specimen by DC magnetron sputtering. The photolithography and lift-off technique were used to shape the cells into square pattern with area of 0.36 to 16 μm^2. The electrical measurements of devices were performed using Agilent B1500 semiconductor parameter analyzer (Santa Clara, CA, USA). Besides, Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy were used

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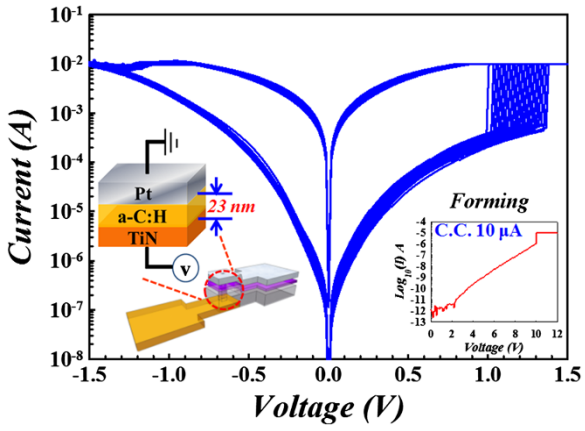

Figure 1 Current–voltage sweeps of Pt/a-C:H/TiN memory device.

to analyze the chemical composition and bonding of the amorphous carbon materials, respectively.

Results and discussion

Figure 1 shows the bipolar current–voltage (I-V) characteristics of the carbon memory cell in semi-logarithmic scale under DC voltage sweeping mode at room temperature. After the electroforming process (inset of Figure 1), the resistance switching behavior of the as-fabricated device can be obtained repeatedly, using DC voltage switching with a compliance current of 10 μA. By sweeping the bias from zero to negative value (about −1.5 V), the resistance state is transformed from low resistance states (LRS) to high resistance states (HRS), called as 'reset process'. Conversely, as the voltage sweeps from zero to a positive value (about 1.5 V), the resistance state is turned back to LRS, called as 'set process'. During set process, a compliance current of 10 mA is applied to prevent permanent breakdown.

To further evaluate the memory performance of amorphous carbon RRAM, the endurance and retention tests were shown in Figure 2. The resistance values of reliability and sizing effect measurement were obtained by a read voltage of 0.2 V. The device exhibits stable HRS and LRS even after more than 10^7 sweeping cycles (Figure 2a), which demonstrates its acceptable switching endurance capability. The retention characteristics of HRS and LRS at $T = 85°C$ are shown in Figure 2b. No significant degradation of resistance in HRS and LRS was observed. It indicates that the device has good reliability for nonvolatile memory applications. Figure 2c reveals the resistance of LRS and HRS states with various sizes of via hole, which is independent with the electrode area of the device. According to the proposed model by Sawa [44], the resistive switching behavior in carbon RRAM is attributed to filament-type RRAM.

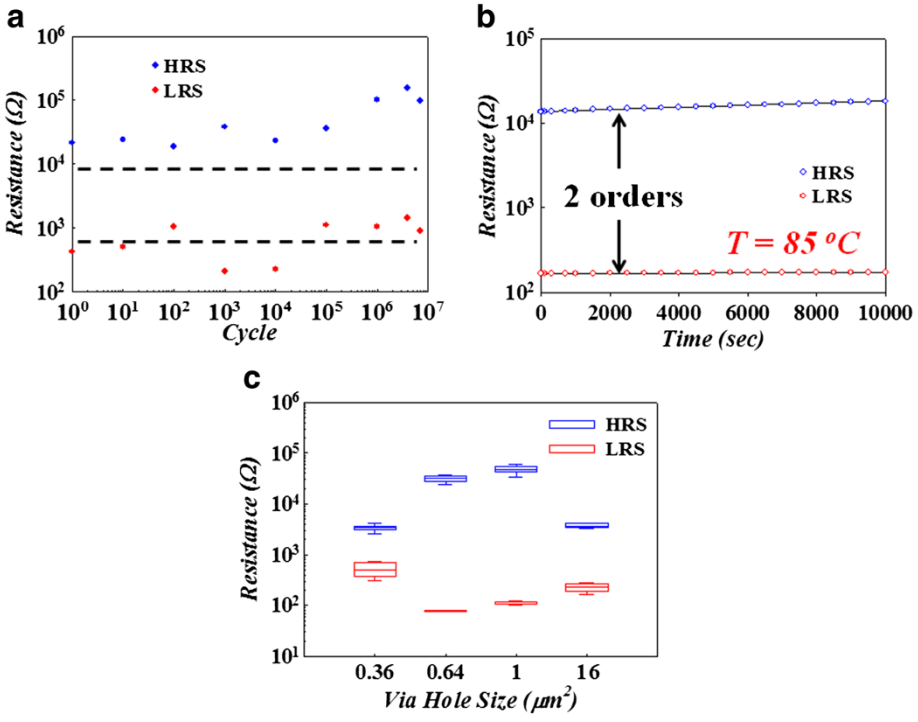

Figure 2 Endurance (a), retention properties (b), and sizing effect measurement (c) of Pt/a-C:H/TiN memory device.

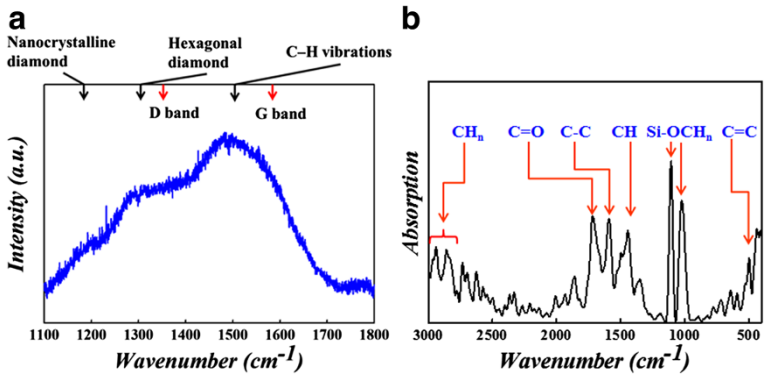

Figure 3 Raman spectra of C sp^2 and C sp^3 in amorphous carbon film (a); FTIR spectrum of amorphous carbon film (b).

To investigate the interesting phenomena, we utilized the material spectrum analyses to find out the reason of working current reduction and better stability. The sputtered carbon film was analyzed by Raman spectroscopy and the spectra revealed in Figure 3a. The broaden peak from 1,100 to 1,700 cm^{-1} demonstrates the existence of amorphous carbon structure [45].

In order to further testify the existence of the carbon layer and find its chemical bonding type, FTIR was used to analyze the sputtered carbon thin film. C-H stretch peak can be observed at the wave number of 2,800 to 3,000 cm^{-1}, as shown in the FTIR spectra of Figure 3b.

To clarify the current transportation mechanism, the current vs. voltage (I-V) is presented in Figure 4. The LRS shows symmetric I-V curve at positive and negative electrical field. The electron transport exhibits Poole-Frenkel and Hopping conduction at middle and high voltage. However, the I-V curve is asymmetric in HRS, but the current transportation mechanism is Schottky emission and Hopping at middle and high voltage. The resistive switching mechanism of LRS and HRS is given in detail as follows.

On the basis of the electrical and material analyses, we proposed a reaction model to explain the transfer of carrier conduction mechanism of the amorphous carbon RRAM as shown in Figure 5. The conductive filament will be formed after the forming process, which is attributed to the connection between sp^2 carbon fractions in the amorphous carbon layer [46]. Due to the current compliance, there is remaining amorphous carbon between

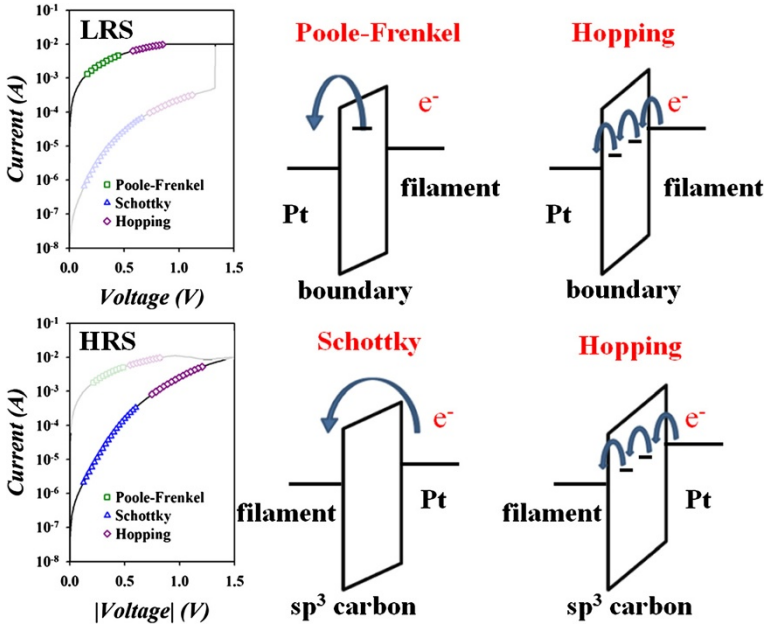

Figure 4 I-V curve fitting of Pt/a-C:H/TiN memory device with various carrier transport mechanisms.

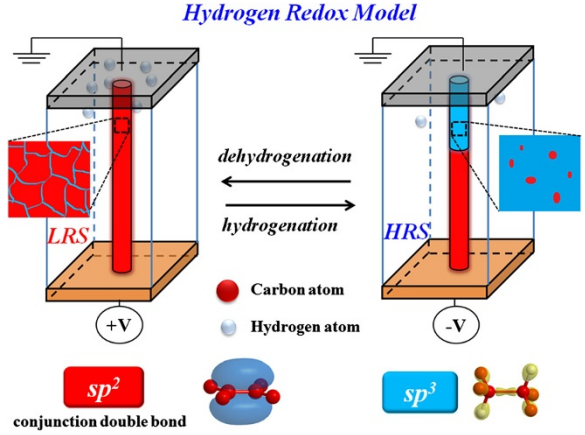

Figure 5 Hydrogen redox model of Pt/a-C:H/TiN memory device in LRS and HRS states.

conductive sp^2 regions, as shown in left insert of Figure 5. Because the current pass through the boundaries of sp^2 regions, the current fitting is dominated by Poole-Frenkel conduction in LRS. As higher voltage was applied, the significant barrier lowering caused the conduction dominated by hopping conduction through conjugation double bonds of sp^2 carbon filament. When the bottom TiN electrode is applied with a negative bias to perform a reset process, hydrogen atoms were pulled from the Pt electrode and absorbed by double bonds of sp^2 carbon, namely hydrogenation process. The hydrogenation reaction will transfer the conductive sp^2 carbon filament into insulated sp^3 carbon filament. As shown in the right insert of Figure 5, the region of filament near Pt electrode forms insulated sp^3 carbon dominated, which leads to the current conduction exhibit Schottky conduction in HRS. The Hopping conduction is attributed to significant barrier lowering as the higher voltage was applied. Contrariwise, the hydrogen atoms were repelled to Pt electrode to form sp^2 carbon filament during set process, called as dehydration process. Based on the hydrogen redox model, a repeatable switching behavior can be obtained in C-RRAM device.

Conclusion

In conclusion, the amorphous carbon RRAM has been fabricated to investigate the resistive switching characteristics. The device has good resistive switching properties due to hydrogenation and dehydrogenation of H atoms in carbon RRAM. The material and electrical analyses give convincing evidence of hydrogen redox induced resistance switching in amorphous carbon RRAM. The current conduction of LRS was contributed to formation of conjugation double bonds in the carbon layer after dehydrogenation. Moreover, the current conduction of HRS was dominated by insulating sp^3 carbon after hydrogenation at a reverse electrical filed.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

YJC designed and set up the experimental procedure. HLC conducted the electrical measurement of the devices. TCC and TFY planned the experiments and agreed with the paper's publication. TMT, KCC, KHC, and JCL revised manuscript critically and make some changes. RZ fabricated the devices with the assistance of TJC. JHC performed the Raman and FTIR spectra measurement. DHB and SMS assisted in the data analysis. All authors read and approved the final manuscript.

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