Fabrication of the Resistive Device with a Structure of Ag/$RbCuZnS_2$/Au and Its Resistive Switching Properties

Xin Tan

School of Physics and Optoelectronic Engineering, Guangdong University of Technology,
Guangzhou, Guangdong, 510006, China

Abstract

In this study, the solvothermal method was adopted to fabricate $RbCuZnS_2$ powder samples, which were compressed into compacted cylinders via the tablet press technique at room temperature. Subsequently, the resistive device with a structure of Ag/$RbCuZnS_2$/Au was assembled by using $RbCuZnS_2$ wafers as the materials in the resistive layer and Ag and Au as electrodes. The morphology of the resistive layer was characterized by a scanning electron microscope, and the I-V characteristics and stability of this device were analyzed by an electrical test. The results showed that a large voltage was required for activating the resistive transition ability of this resistive device. Besides, the on-off ratio (HRS/LRS) of this device remained above 20 after 103 s of continuous operation and 102 times of fast reading, and the high resistance state (HRS) and the low resistance state (LRS) were stably distributed in the corresponding range, which fully demonstrated the excellent resistive switching properties of this device. The unipolar resistive switching phenomenon in the resistive device with a structure of Ag/$RbCuZnS_2$/Au can be explained by the thermochemical mechanism (TCM). These findings revealed the great application potential and broad commercial application prospects of $RbCuZnS_2$ in the field of nonvolatile memory, thus providing a novel direction for the development of resistive random access memory.

Keywords

Resistive device; thermochemical mechanism; on-off ratio; stability.

1. Introduction

With the rapid expansion of the semiconductor industry and the increasingly higher requirements of the miniaturization and intelligentification of portable storage devices for the properties of memories, it is an urgent demand for developing the next generation of nonvolatile storage techniques. Benefiting from their fast access speed, high storage density and low power consumption, such novel nonvolatile memories (NVMs) as ferroelectric random access memory (FRAM), phase change random access memory (PCRAM) and resistive random access memory (RRAM) have ushered in a broad development space[1-3]. Among various nonvolatile memories, the RRAM characterized by simple structure, low fabrication cost and compatibility with CMOS process has attracted wide attention from researchers. It is expected for RRAM to break through the technical bottleneck encountered by conventional memories and receive in-depth explorations, and it will be the leading trend for the development of the next generation of memory products.

The structure of RRAM is similar to the three-layer structure of a "sandwich". Specifically, the middle layer is a resistive layer with multiple resistance states, and the upper and lower layers are metal electrode layers. According to some scientific reports, the materials with resistive switching properties can be generally classified into three types, including solid electrolyte materials, oxide materials and organic materials[4-6]. Among them, solid electrolyte materials are generally transition metal chalcogenides (TMCs), which are also called fast ionic conductors[7-10]. The electrodes at both ends of the TCM-based resistive devices with solid electrolyte materials as the dielectric in the resistive layer are usually composed of inert metal electrodes (Au, Pt) and electrochemical active electrodes (Ag, Cu). Different resistance states can be stably switched back and forth in RRAM via applying a certain electric field. In RRAM device, the resistance change in the resistive layer is utilized to realize the information storage and read-write operation. On account of its high efficiency and low error rate in data processing, RRAM has received increasing attention as a device that may bring breakthrough progress to the existing nonvolatile memory techniques.

In this work, an in-depth investigation was conducted in an attempt to explore the phase structure of $RbCuZnS_2$ synthesized by the solvothermal method and the stability and retention of the resistive device with a structure of Ag/$RbCuZnS_2$/Au fabricated based on this solid electrolyte material. Moreover, the mechanism of resistive switching behavior in the $RbCuZnS_2$ resistive layer was explored by combining the structure unit composition of this device, which would lay a foundation for applying a similar transition metal sulfide system to RRAM devices.

2. Experimental Process

The high-quality $RbCuZnS_2$ crystals were fabricated by the solvothermal method. According to the required stoichiometric ratio, rubidium carbonate (99%), copper powder (99.9%), sulfur powder (99.5%) and zinc acetate (99.5%) were mixed together and added into the polytetrafluoroethylene-lined reactor. Subsequently, ethylenediamine was used as the solvent to perform the reaction at 200 ℃ for 14 days. After the fully reacted products were subjected to filtration, solvent drainage and other operations, the light gray powder samples were obtained. Finally, $RbCuZnS_2$ wafers with compact texture and uniform thickness were fabricated with the assistance of a tablet press.

This RRAM device was fabricated by depositing metal Au electrodes with a small ion sputtering instrument and dropping conductive silver paste on the surface of $RbCuZnS_2$ wafers. The crystal structure, microstructure and element distribution of $RbCuZnS_2$ were characterized by Bruker D8 Advance X-ray diffractometer and Hitach SU8220 scanning electron microscope. The electrical performance test was performed by the semiconductor characterization system (Keithley 2400 SCS) and its supporting probe bench. Prior to the resistive switching property indicator test, the I-V curve test would be conducted, with the aim of ensuring that the proper contact was formed between the electrodes, $RbCuZnS_2$ resistive layer and measuring probe, which avoided the inaccuracy in reading the resistance value of the device.

3. Results and Discussion

The PXRD spectrum of $RbCuZnS_2$ powder samples is shown in Figure 1. It can be seen that the characteristic diffraction peaks are very sharp and the intensity is high, which indicates that the sample has higher crystallinity. When such solid electrolyte materials are fabricated into the resistive layer of RRAM devices, it contributes to presenting distinct resistive switching properties. Compared with the results reported in the previous literature[11], it can be found that the synthesized $RbCuZnS_2$ is a pure tetragonal $ThCr_2Si_2$ crystal structure, the space group is I4/mmm, and the unit cell parameters are a = b = 3.96093(11) Ǻ and c = 13.5870(4) Ǻ, respectively[12]. The illustration in Figure 1 shows the structure of the $RbCuZnS_2$ crystal with a layered structure. As can be seen from this figure, it is composed of the alternate stacking of $[CuZnS_2]^{-1}$ tetrahedral layer and potassium ion layer along the c axis, and potassium ions in the potassium ion layer are located at the face center or four vertices of the tetrahedral layer. The above findings suggest that the crystal structure of $RbCuZnS_2$ is similar to that of $RbCuFeS_2$[13].

Figure 2 shows the surface morphology and element distribution of $RbCuZnS_2$ samples. As shown in Figure 2(a), the crystal particles of the sample have a smooth surface and excellent crystallinity, which is consistent with the results of the phase analysis. The relatively regular shape of crystal particles and the smaller particle size conduce to obtaining compact wafer samples by the pressing technique, which can be used to fabricate the resistive layer in RRAM devices. The EDS distribution of elements in $RbCuZnS_2$ is shown in Figure 2(b), which indicates that the distribution of Rb, Cu, Zn and S in the sample is uniform and dense, further demonstrating that these samples meet the requirements for fabricating resistive devices.

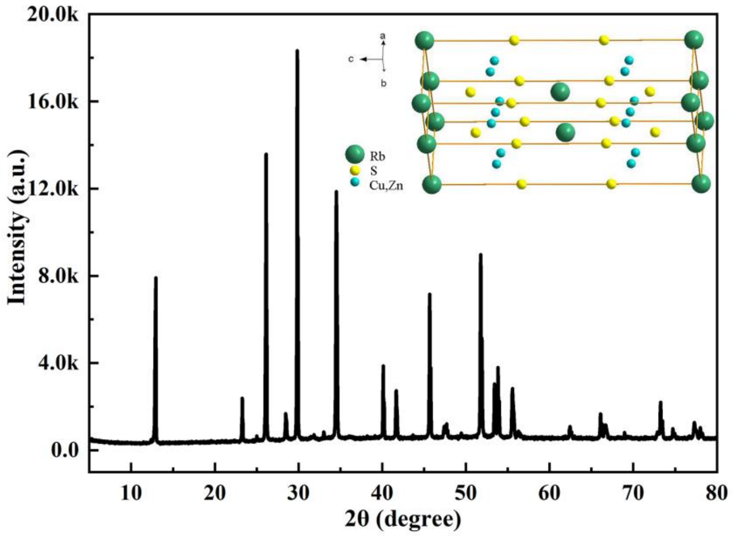

Figure 1: The PXRD diagram of $RbCuZnS_2$ powder samples, and the insert map is a schematic diagram of the crystal structure of $RbCuZnS_2$.

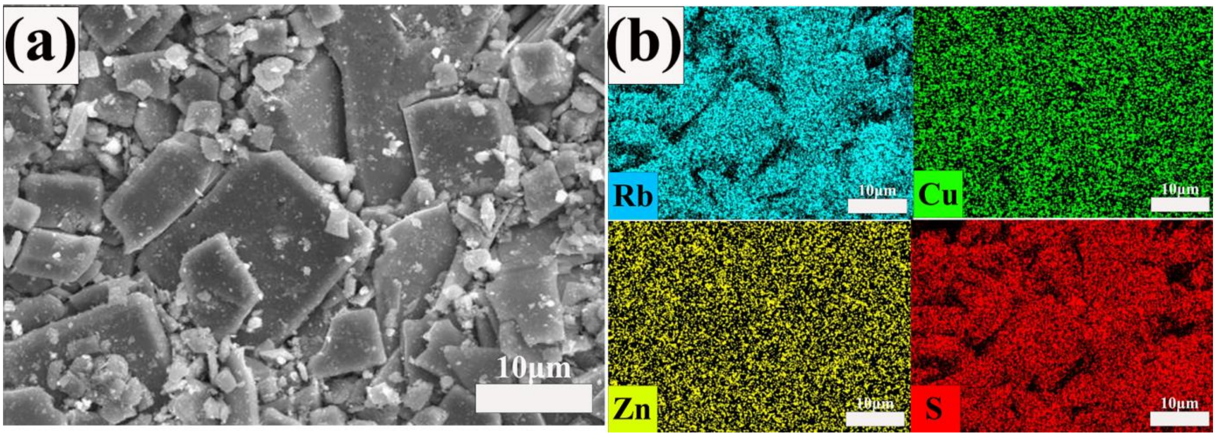

Figure 2: (a) The SEM diagram of the surface morphology and (b) the EDS distribution diagram of elements of $RbCuZnS_2$ samples. The scale is 10μm.

Figure 3 shows the cyclic volt-ampere characteristic curve of the resistive device with a structure of Ag/$RbCuZnS_2$/Au under the condition of applying a cyclic voltage of -2~2 V. The illustration shows the structural schematic diagram of the electrical test of the device with the $RbCuZnS_2$ wafer as the middle layer. The results of the I-V test indicate that the resistance of this device is not a constant value, and the I-V curve presents a nonlinear relationship, which demonstrates that a favorable contact has been formed between the electrodes at Au and Ag and the $RbCuZnS_2$ resistive layer. As can be seen from the first-turn I-V curve of this device, the current passing through the device under the same voltage at the beginning is smaller, which indicates that the resistance of the device is higher at the moment. This phenomenon is caused by the fact that the material of resistive layer is high resistance state when it has been not excited by voltage. Before the newly fabricated resistive device undergoes the electrical test for the first time, it shall be activated by a large voltage, which enables the resistive device to normally generate stable resistance transition behavior. Therefore, it is necessary to set the maximum protection current of 100 mA during all electrical tests, which could prevent the emergency that the whole resistive layer is broken down due to the excessive current passing through the RRAM device. As can be seen from the multi-turn I-V test curves, there is a unipolar resistive switching effect in this resistive device. That is to say, the resistance value of the device changes regularly with the increase of voltage, and this change is only related to the voltage value, regardless of the polarity of the voltage[14]. As shown by the arrow in Figure 3, the cyclic scanning process of the I-V loop is divided into two processes, namely the order of voltage change in the process indicated by arrow "1" (0 V→ +2 V→ 0 V) and that indicated by arrow "2" (0 V→ -2 V→ 0 V). During these two voltage changes, the resistance changes of the device are similar. With the increase of voltage value, the device is set from HRS to LRS, and then reset from LRS to HRS with the decrease of the voltage value. These two processes constitute a complete cycle, which is constantly repeated in the RRAM device. Therefore, the resistance of this resistive device switches in cycles between HRS and LRS under the continuous excitation by cyclic voltage from -2 V to +2 V. In other words, the resistance state of this device can be controlled to switch stably by changing the excitation voltage (the result presented in the storage process is the HRS/LRS state of the circuit or the data reading/writing). During the test, it can be found that the resistance value of the device will remain in the previous resistance state without changes after stopping applying voltage to the device, which is regardless of its original resistance state. This phenomenon suggests that the resistive device with a structure of Ag/$RbCuZnS_2$/Au has the related properties of nonvolatile memories. There is no abrupt change in the I-V curve during 100 cycles, and the scanning loops under different cycles are basically the same, which demonstrates that this device possesses favorable repeatability.

In an attempt to identify the reason for the resistive switching behavior in the RRAM device with a structure of Ag/$RbCuZnS_2$/Au, the I-V curve is analyzed, with the results showing that there is a stable unipolar resistive switching phenomenon with obvious discrimination in this device. The structure of the electrodes at both ends of this device implies that the resistive switching behavior can be explained by thermochemical mechanism, and the resistive switching effect is caused by the aggregation and dispersion of some defects in solid electrolyte materials under the action of strong electric fields[15]. The resistance changing process of the device may be elucidated as follows. These solid electrolyte materials are initially in HRS, and partial solid electrolyte materials decompose and hence sulfur vacancies are generated under the action of electric fields. These sulfur vacancies will gradually penetrate the resistive layer and form some local conductive channels and connect the upper and lower electrodes, which significantly enhances the conductivity of the resistive layer. At this moment, the device changes from HRS to LRS. Under the continuous action of the voltage with the same polarity, the current in the resistive layer is mainly transmitted through the small-sized local conductive channel, which results in a larger current passing through the conductive channel. A large amount of joule heat is accumulated on the conductive filament, which will make the temperature of solid electrolyte materials near the conductive channel rise sharply after reaching a certain critical point, and finally induce the fracture of the conductive filament, which will make the device return to HRS. This transition from LRS to HRS is called the reset process. When a small voltage with the same polarity is continuously applied for scanning, the fractured filaments will be reconnected under the action of electric fields, and the device will be switched from HRS to LRS again. This transition is called the set process. The above-mentioned process occurs cyclically in the resistive device with a structure of Ag/$RbCuZnS_2$/Au under the action of cyclic working voltage, which induces the formation and rupture of conductive filaments composed of sulfur vacancies in the resistive layer, thus realizing the reversible switching between HRS and LRS[16].

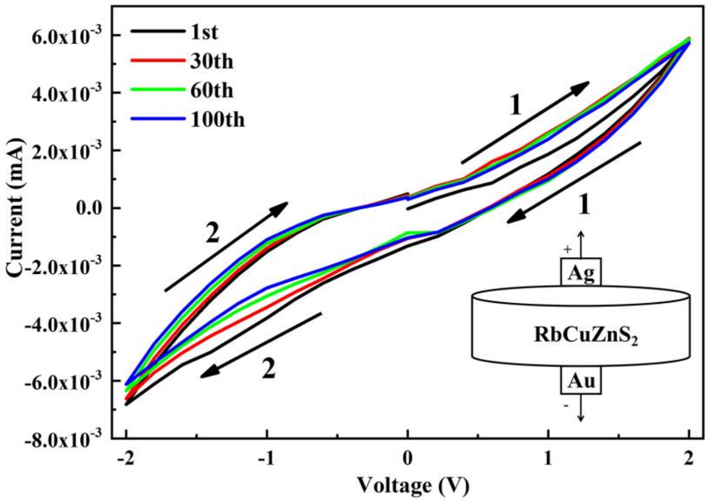

Figure 3: The cyclic I-V curve of the resistive device with a structure of Ag/$RbCuZnS_2$/Au, the illustration is the structural schematic diagram of the electrical test.

Moreover, other important indicators of the resistive switching properties of the RRAM device with a structure of Ag/$RbCuZnS_2$/Au are explored, in an attempt to further verify the capability of this device as a nonvolatile memory. During data storage and transmission, it is the most basic requirement to ensure that data will not be lost and misjudged. Hence, the resistance stability and retention property of memory devices are decisive in this process. The fatigue resistance and resistance stability of this device are shown in Figure 4(a). During the 100-cycles fast reading of the resistance, there is obvious discrimination in the resistance values between different resistance states. They are concentrated and distributed in their respective interval ranges. The binary data storage or open circuit and close circuit can be identified by selecting the proper intermediate value. In the switching process between HRS and LRS with the number of cycles, no switching failure or the trend of significant decreases in the HRS/LRS ratio can be observed. The on-off ratio of the device is always kept above 20, which indicates a significant resistive switching effect. This finding is consistent with the results of the cyclic I-V test curve, which suggests that this device possesses excellent repeatability and stability. At the initial stage of resistance switching, the resistance value of the device in HRS will be relatively high, and then gradually tend to be a stable value; while, the resistance value of the device in LRS has remained relatively stable. It may be caused by the fact that there is larger randomness for the fracture of conductive filament at the very beginning of the fusing process, and the number of conductive filaments fractured at a time is not stable. With the increase of cycle times, the number and size of conductive filaments involved in the formation and fracture of the resistive layer approach to the same, and finally reach a dynamic equilibrium state. Furthermore, as shown in Figure 4(b), the resistance values of the device in HRS and LRS are recorded under a read voltage of 0.1 V with a fixed time interval (10 s). It can be found from the changes of HRS and LRS with time that there is no significant change in the resistance value of this device in each resistance state within 10^3 s, and the HRS/LRS ratio remains above 20, which demonstrates that this device has favorable retention property. The above test results show that the resistive device with a structure of Ag/$RbCuZnS_2$/Au has favorable resistance stability and a high HRS/LRS ratio, thus validating that $RbCuZnS_2$ is a potential nonvolatile memory material.

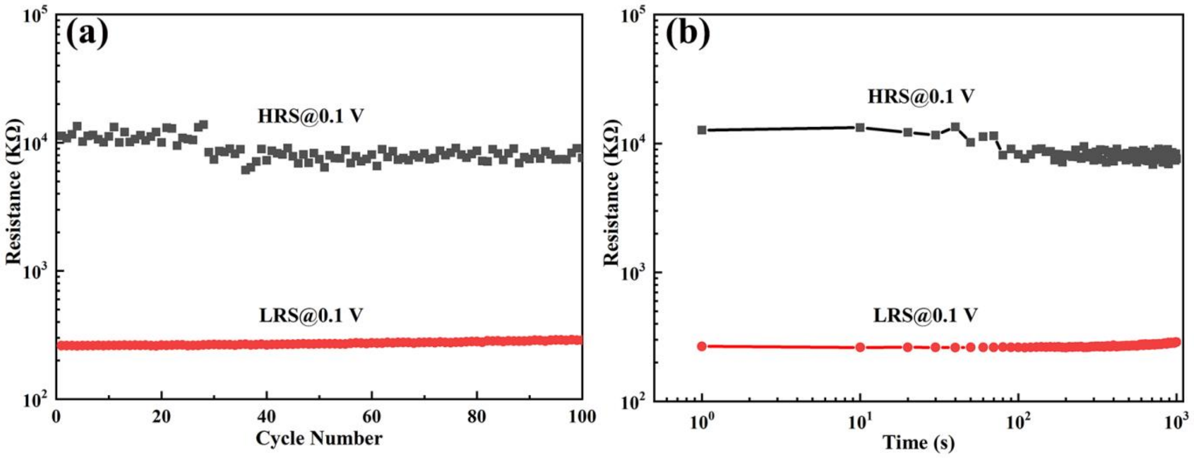

Figure 4: (a) The fatigue resistance and resistance stability and (b) retention properties of the resistive device with a structure of Ag/$RbCuZnS_2$/Au.

4. Conclusion

The solvothermal method was adopted to successfully synthesize a solid electrolyte material $RbCuZnS_2$. Besides, the $RbCuZnS_2$ wafers are used as the material in the resistive layer for the first time to fabricate the resistive device with a structure of Ag/$RbCuZnS_2$/Au. The various resistive switching properties of this device are tested. The cyclic I-V curve shows that there are both typical unipolar resistive switching properties and excellent repeatability in this device. Under the action of electric fields, the formation and fracture of conductive channels formed by sulfur vacancies induce the back-and-forth transition between HRS and LRS of the RRAM device. The distribution of the resistance values of the device in low resistance state and high resistance state is concentrated in a small range, with excellent reliability. During 100 cycles or 10^3 s of I-V test scanning, the HRS/LRS ratio of the device is always kept above 20 at the voltage of 0.1 V, which indicates that the device has favorable data retention and fatigue resistance. The findings of this study contribute to providing in-depth insights into the nonvolatile resistive switching properties of $RbCuZnS_2$-based RRAM device with broad application prospects. Furthermore, these efforts provide a new possibility for developing the next generation of RRAM devices.

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