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Memristive Behavior Based on Ba-Doped $SrTiO_3$ Films *

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The $Sr_{0.95}Ba_{0.05}TiO_3$ (SBT) nanometer film is prepared on the commercially available Pt/TiO_2/SiO_2/Si substrate by radio-frequency magnetron sputtering. The x-ray diffraction pattern and the scanning electron microscope image of the cross-sectional profile of the SBT nanometer film are depicted. The memristive mechanism is inferred. The mathematical model $M(q) = 12.3656 - 267.4038|q(t)|$ is calculated, where $M(q)$ denotes the memristance depending on the quantity of electric charge, and $q(t)$ denotes the quantity of electric charge depending on the time. The theoretical I–V characteristics of the SBT nanometer film are obtained by the mathematical model. The results show that the theoretical I–V characteristics are consistent with the measured I–V characteristics. Moreover, the mathematical model could guide the research on applications of the memristor.

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In 1971, Chua postulated a memristor as the fourth fundamental circuit component, along with the well-known basic circuit elements: the resistor R, capacitor C and inductor L.[1] It can be used to reveal the relationship between magnetic flux ϕ and charge q. Usually, the memristance $M(q)$ is described using the equation $M(q) = d\phi(q)/dq$. Afterwards, this element was studied only theoretically, until 2008, when the first physical memristor became a reality, which rekindled the attention to the memristive system.[2] A memristor, with the characteristics of nonvolatile, synapse function and nanoscale structure, has great potential for a variety of applications including nonvolatile memory and artificial neural network.[3−9] Therefore, it has become a research hotspot in recent years.[10−21]

With the discovery of the Hewlett–Packard (HP) memristor, many new material systems have been reported towards the physical memristor with different mechanisms, such as memristive systems based on the boundary drift model (HP TiO_2-TiO_{2-x} memristor[2] or Pd/WO_3/W memristor[22]), memristive systems based on the phase-transition mechanism (VO_2 memristor[23]), memristive systems based on the wire conductive mechanism (Ag/Si memristor[4] or Ag_2S memristor,[24] memristive systems based on spin transport model.[13] However, the research on the mechanism of the physical memristor is insufficient. Some new memristive mechanisms need to be explored.

Strontium titanate ($SrTiO_3$) has already been extensively studied because of its practical applications in the electronic ceramic field. The basic properties of $SrTiO_3$ depend on many factors, such as ceramic processing conditions, various dopant ions and the oxygen vacancies. It is well known that a large number of elements can be substituted into the cation sites of the perovskite structure. Many researchers have investigated the defect chemistry of perovskite structure $SrTiO_3$ or $BaTiO_3$ ceramics to modify some characteristic properties.[25−27]

Recently, we found that the Ba-doped $SrTiO_3$ ($Sr_{0.95}Ba_{0.05}TiO_3$, SBT) ceramics are rich in oxygen vacancy. Under the condition of bias voltage, the SBT ceramic samples show nonlinear resistive changes associated with the applied voltage time, and keep record of the transiting quantity of charge. The characteristics are similar to some basic characteristics of a memristor. According to the theoretical formula about the memristance,[2] memristance becomes more important for understanding the underlying electric characteristics, as the critical dimensions shrink to the nanometer scale. Consequently, we study the I–V characteristics of the SBT nanometer film. Our experimental result illustrates that the resistance shows a non-ohmic behavior and that the I–V curves are hysteretic. They both indicate that the SBT is a memristive system. The variation of the resistance of SBT is related to the amount of generated mobile carriers. The mathematical model of the SBT memristive system is also calculated and discussed.

The SBT was prepared by the sol-gel method using reagent-grade $Ba(CH_3COO)_2$ (99.0%), $Ti(OC_4H_9)_4$ (98.0%) and $Sr(CH_3COO)_2$ (99.0%), according to the desired stoichiometry. After drying at 80℃, the powders were pressed into one disk-type pellet (5.0 cm in

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diameter and 0.5 mm in thickness), and then heated to 1200℃ for 3 h in air. After the SBT target was cooled slowly to room temperature, the SBT nanometer film was prepared on the commercially available $Pt/TiO_2/SiO_2/Si$ substrate at the fixed temperature of 200℃ by radio frequency (RF) magnetron sputtering, heated in air at 750℃ for 2 h, and then cooled slowly inside the furnace. The metal/SBT/metal capacitor structures were fulfilled after the deposition of Au top electrodes with the diameter of 0.2 mm, through a shadow mask at room temperature by the direct current (DC) magnetron sputtering.

Crystalline phases of the SBT film were identified by x-ray diffraction (XRD: PANalytical B.V., X'Pert PRO) using Cu Kα radiation and lattice parameters were obtained by least squares refinement. The microstructures were characterized by using a scanning electron microscope (SEM: Philip, XL30TM). For electrical measurements, the Agilent B2900 source-measure unit was used to test the current–voltage (I–V) characteristics. The memristive mechanism was inferred, the memristive model was built, and the memristive properties were systematically investigated.

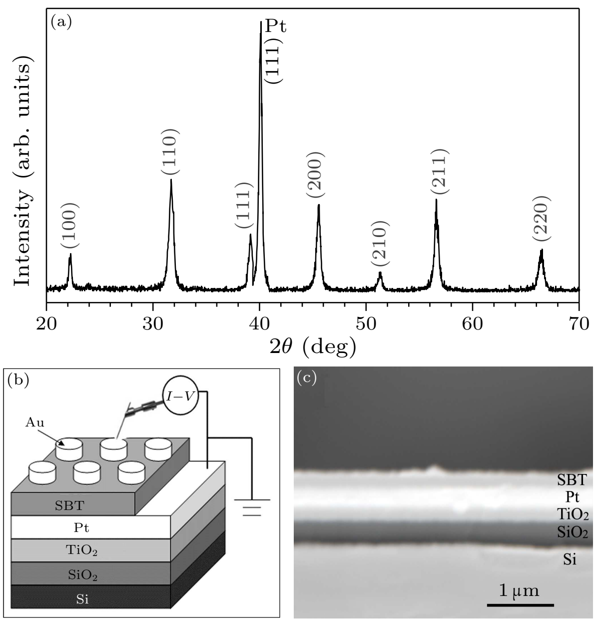

Fig. 1. (a) The XRD patterns of the SBT nanometer film on the $Pt/TiO_2/SiO_2/Si$ substrate, (b) the schematic drawing of the $Au/SBT/Pt/TiO_2/SiO_2/Si$ measurement configuration, and (c) the SEM image of the cross-sectional profile of the SBT nanometer film.

Figure 1(a) depicts the XRD pattern of the SBT nanometer film on the $Pt/TiO_2/SiO_2/Si$ substrate. The SBT nanometer film is polycrystalline, and the Miller indexes are shown in Fig. 1(a). The schematic drawing of the $Au/SBT/Pt/TiO_2/SiO_2/Si$ measurement configuration and the SEM image of the cross-sectional profile of the SBT nanometer film are shown in Figs. 1(b) and 1(c). Figure 1(c) shows that the SBT nanometer film is about 200 nm.

Figure 2(a) shows the measured current–voltage (I–V) characteristics of the SBT nanometer film on the $Pt/TiO_2/SiO_2/Si$ substrate. In the first and third quadrants, the I–V trace is hysteretic, which ramps up and then ramps back down, making a loop rather than retracing its path with increasing and decreasing voltages. The curve is nonlinear, illustrating a non-ohmic behavior. It is anchored at the origin ($I = 0$, $V = 0$), indicating that this SBT film does not store capacitive or inductive energy. Thus the I–V characteristics fully comply with a fundamental requirement for a memristive system.

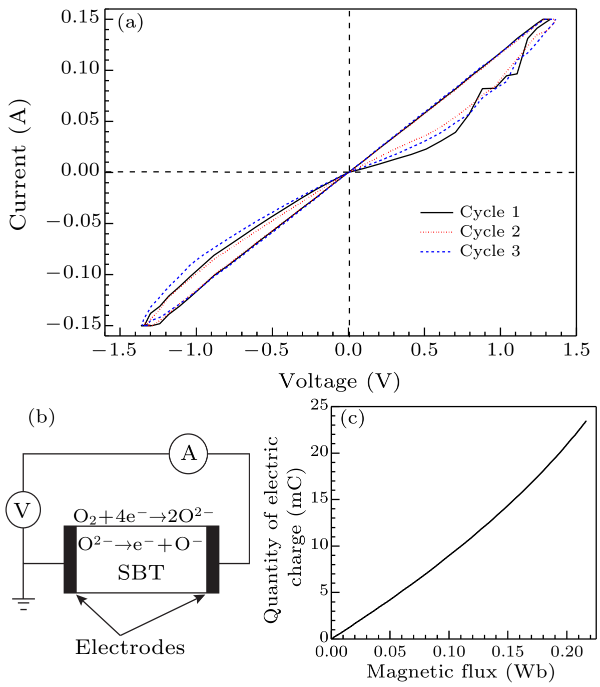

Fig. 2. (a) In three circles, the measured current–voltage (I–V) characteristics of the SBT nanometer film on the $Pt/TiO_2/SiO_2/Si$ substrate, (b) the memristive mechanism schematic drawing of the monolayer SBT nano-film, and (c) the fitting q–ϕ characteristic of the SBT nanometer film.

According to the memristive theory, if the conducting state of some materials can be changed with external voltage or current, the materials could be considered as the potential memristive system.[2] Different from the HP TiO_2 memristor with the double membrane structure, the resistances of the SBT nanometer film depend on the change of charge carriers. The SBT memristor can be designed to the monolayer SBT nano-film structure, sandwiched between two electrodes, as shown in Fig. 2(b).

Based on the results of some similar research,[26,27] we infer the memristive mechanism and calculate the mathematical model of the SBT memristor.

When an external voltage or current is added to the monolayer SBT nano-film, a small voltage will produce a great electric field. The electrons provided by SBT react with the oxygen in air ($O_2+4e^- \rightarrow 2O^{2-}$), resulting in generating the hole for the loss of electrons in the nano-film. The bivalent oxygen ions can generate ionized oxygen ions (O^-) by releasing electrons ($O^{2-} \rightarrow e^- + O^-$). For the effect of electric field, holes and ionized oxygen ions (O^-) move directionally as charge carriers. With the increase of the holes and ionized oxygen ions (O^-), the resistance between the two electrodes will decrease. When the external voltage or the current direction changes, the ionized oxygen ions (O^-) in the film react with electron (e^-) as follows: $e^- + O^- \rightarrow O^{2-}$ and $2O^{2-} \rightarrow O_2 + 4e^-$. The reactions cause the charge carriers decreasing and the resistances increasing, until the resistances return to the original state. Corresponding to the whole reaction process, the resistances of the SBT nano-film will present nonlinear variation with the maximum value ($R_{\rm max}$) and the minimum value ($R_{\rm min}$). During the whole process, if the voltage is interrupted, the resistance remains the same value as that at the interrupted moment, for the amount of holes and ionized oxygen ions (O^-) are unchanged. This may be related to the facts as follows: when the voltage is interrupted, the driving electric field disappears; and the movement of the ions, electrons and holes are not active in the nano-film at the room temperature. That is, the resistances of the SBT nano-film have the characteristic of being non-volatile.

As the amount of generated holes and ionized oxygen ions (O^-) depends on the current intensity and duration (charge accumulation) $\frac{dO(t)}{dt} = v\frac{R_{\rm min}}{D}i(t)$, $O(t) = v\frac{R_{\rm min}}{D}|q(t)|$, the resistances of the SBT nano-film ($M(q)$) are the function of quantity of electric charge $q(t)$ and duration t,

$$\begin{aligned} M(q) &= R_{\rm min}\frac{O(t)}{D} + R_{\rm max}\Big[1 - \frac{O(t)}{D}\Big] \\ &= R_{\rm max} - (R_{\rm max} - R_{\rm min})\frac{O(t)}{D} \\ &= R_{\rm max} - (R_{\rm max} - R_{\rm min})v\frac{R_{\rm min}}{D^2}|q(t)|, \quad (1) \end{aligned}$$

where $O(t)$ denotes the amount of generated charge carriers in the SBT nano-film at one point, D denotes the maximum amount of generated charge carriers, and v denotes the velocity of generated charge carriers. The resistances of the SBT nano-film show a nonlinear variation associated with the duration of applied voltage, and the resistances of the SBT nano-film can record the charge carriers at one point. That is, the resistances of the SBT nano-film have the characteristics of memory. Here $M(q)$ denotes the memristance depending on the quantity of electric charge.

The characteristics of the SBT memristor can be described by the mathematical model of the SBT memristor. However, $O(t)$, D and v are just theoretical parameters, and they cannot be accurately measured by the existing test methods. To our pleasure, we can calculate the other parameters from the I–V characteristics of the SBT nanometer film. Supposing that $A = (R_{\rm max} - R_{\rm min})vR_{\rm min}/D^2$, the memristance $M(q)$ can be simplified to

$$M(q) = R_{\rm max} - A|q(t)|. \quad (2)$$

As we all know, the relationship between the magnetic flux ϕ and the voltage V is $V = d\phi/dt$, and the relationship between the quantity of electric charge q and current I is $I = dq/dt$. Using the MATLAB software, the fitting q–ϕ characteristics of the SBT nanometer film are derived by the integral of the I–V characteristics, as shown in Fig. 2(c). Using the data in Fig. 2(c) and the equation $M(q) = d\phi(q)/dq$, $R_{\rm max}$ and A are calculated by the MATLAB software, i.e., $R_{\rm max} = 12.3656\,\Omega$ and $A = 267.4038\,\Omega$/C. Then we obtain the mathematical model

$$M(q) = 12.3656 - 267.4038|q(t)|. \quad (3)$$

Figure 3 shows the theoretical (solid) and measured (dashed) I–V characteristics of the SBT nanometer film at the sinusoidal voltage. Three circles were measured at the corresponding amplitudes of 1.3 V (Fig. 3(a)) and 1.0 V (Fig. 3(b)), respectively. The theoretical I–V characteristics of the SBT nanometer film were obtained by the mathematical model. The results show that the theoretical I–V characteristics are consistent with the measured I–V characteristics (Fig. 3). Therefore, we should make a further study so that we can use the mathematical model to guide the research on the practical application of the SBT memristor.

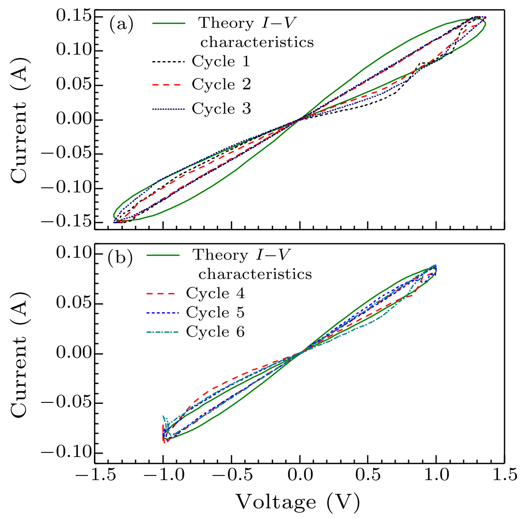

Fig. 3. The theoretical (solid) I–V characteristics and the measured (dashed) I–V characteristics of the SBT nanometer at different sinusoidal voltages: (a) the amplitude of 1.3 V, and (b) the amplitude of 1.0 V.

In summary, the SBT nanometer film has been prepared on the commercially available Pt/TiO_2/SiO_2/Si substrate by the RF magnetron sputtering. The XRD pattern and the SEM image of the cross-sectional profile of the SBT nanometer film are depicted. The memristive property of the SBT nanometer film is studied, and the results are as follows: (1)

The current–voltage (I–V) characteristics of the SBT nanometer film are measured (Fig. 2(a)). The I–V trace is hysteretic and nonlinear. Thus the I–V characteristics fully comply with a fundamental requirement for a memristive system. (2) The memristive mechanism is inferred. SBT belongs to the solid electrolyte, with holes and ionized oxygen ion (O^-) as the charge carriers. The resistance of the SBT film is determined by the amount of generated holes and ionized oxygen ions (O^-), depending on the current intensity and duration (charge accumulation). (3) The mathematical model is calculated by the MATLAB software $M(q) = 12.3656 - 267.4038|q(t)|$. (4) The theoretical I–V characteristics of the SBT nanometer film are obtained by the mathematical model. The results show that the theoretical I–V characteristics are consistent with the measured I–V characteristics (Fig. 3). Moreover, we should make a further study, and we can use the mathematical model to guide the research on memristor, which has great potential in applications. Further studies will be reported elsewhere.

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