Reduction in high reset currents in unipolar resistance switching Pt/SrTiO$_x$/Pt capacitors using acceptor doping

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The high reset current, I_R, in unipolar resistance switching is an important issue which should be resolved for practical applications in nonvolatile memories. We showed that, during the forming and set processes, the compliance current, I_{comp}, can work as a crucial parameter to reduce I_R. Doping with Co or Mn can significantly reduce the leakage current in capacitors made using SrTiO$_x$ film, opening a larger operation window for I_{comp}. By decreasing I_{comp} with acceptor doping, we could reduce I_R in SrTiO$_x$ films by a factor of approximately 20. Our work suggests that the decrease in I_{comp} by carrier doping could be a viable alternative for reducing I_R in unipolar resistance switching. © *2010 American Institute of Physics*. [doi:10.1063/1.3486460]

Resistance switching (RS) is a physical phenomenon where reversible changes between two bistable resistance states can be achieved by the application of an external bias.[1–5] In unipolar RS, the switching conditions depend on the magnitude of the bias voltage irrespective of the polarity. Recently, unipolar RS has attracted renewed interest due to potential applications in nonvolatile memory devices, known as resistance random access memory (RRAM).[3–10] However, several scientific and technical issues remain to be resolved prior to the commercial realization of the technology.

One such issue is the reduction in the reset current, I_R.[6–8] During the reset process, i.e., a change from the low resistance state (LRS) to the high resistance state (HRS), there will be a large current in the RRAM device. By reducing I_R, however, the power consumption of the device will be reduced. In addition, to fabricate a high-density three-dimensional RRAM array structure, diodes and/or transistors are required as switch elements.[11] If I_R can be reduced, the requirements of the switches can become less demanding, enhancing the feasibility of practical three-dimensional RRAM devices. There have been a number of efforts to reduce I_R, for example using a nanowire as the switching material,[6] by reducing the dimensions of the electrode,[7] or reducing the parasitic capacitance in capacitor-type RRAM devices.[8] Here, we show that acceptor doping of SrTiO$_x$ (STO) can significantly reduce I_R in Pt/STO/Pt capacitors.

We used polycrystalline Pt/STO/Pt capacitors as the unipolar RS material. We prepared 60 nm thick undoped STO, Co-doped STO (Co:STO), and Mn-doped STO (Mn:STO) thin films, using pulsed laser deposition. The targets were stoichiometric STO, 0.5 wt % Co:STO, and 0.5 wt % Mn:STO, respectively. The fabrication conditions were as follows: a substrate temperature of 600 °C, an oxygen pressure of 100 mTorr, and a laser fluence of 2 J/cm^2. To characterize the switching properties, we placed Pt-top electrodes of 40 nm thickness and 50×50 μm^2 area by photolithography. The bottom electrode of the capacitor was connected to ground, and current-voltage (*I-V*) curves were measured. During the forming (set) process, the pristine state (the HRS) is switched into the LRS. The current that flows during this process can result in damage to the capacitors in the circuit. To prevent such damage, we limited the current to a value termed the compliance current, I_{comp}. For *I-V* measurements, we used a semiconductor parameter analyzer (Agilent 4155C; Agilent Technologies) and a transistor (2N2369) as the current-limiter. We kept the connection between the bottom electrode and the transistor as short as possible.[8] Using this method, we could set I_{comp} to be as small as 0.7 mA, and the maximum value of I_{comp} used was 20 mA.

We found that I_{comp} was a critical parameter for determining I_R. As shown in Fig. 1(a), I_R can be reduced in undoped STO capacitors by decreasing I_{comp}. Similar observations have been reported previously, but without physical explanations.[12–14] Unipolar RS is widely accepted to occur because of the formation and rupture of conducting filaments under an electric field.[2–5] To explain the relation between I_{comp} and I_R, we performed computer simulations using the random circuit breaker (RCB) network model.[3,4] As shown in Fig. 1(b), the RCB network model treats the switching medium as a network composed of circuit breakers with bistable resistance states, which are reversibly switchable using an applied voltage. Details of this model and simulations are described elsewhere.[3,4] This percolation model has explained numerous properties of unipolar RS, including the nonlinear *I-V* curves observed in the LRS,[4] wide distributions of reset voltages and currents,[3,15] and large $1/f$ noise.[16] Using the RCB network simulations, we could explain why I_R is closely related to I_{comp}. Figures 1(c)–1(e) show simulation results for network regions where the highly conducting percolating channels were developed during the forming (or set) process. With a smaller value of I_{comp}, the volume of the conducting filaments was reduced, and so I_R was also reduced.[17]

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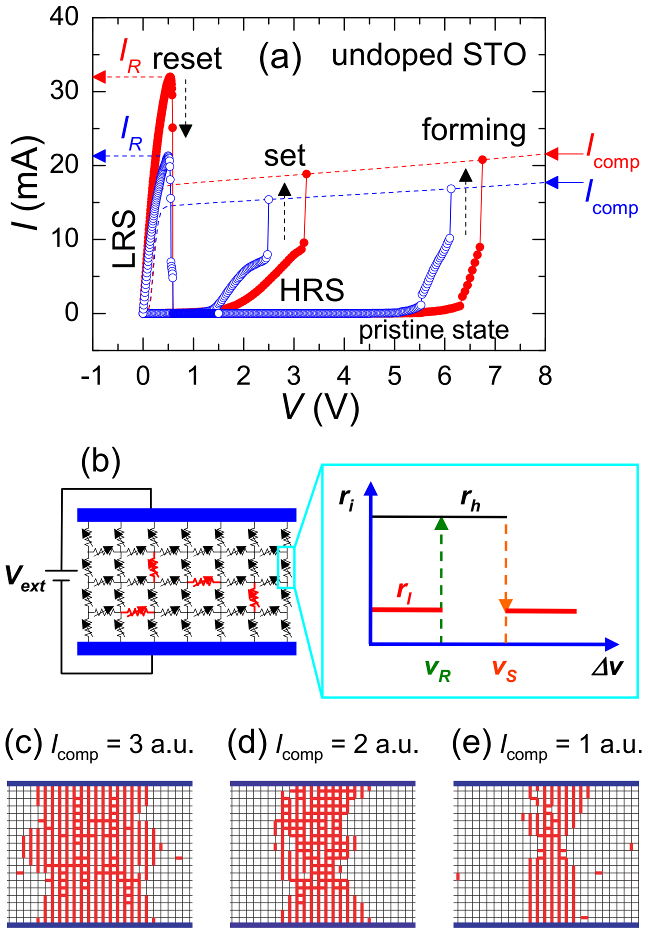

FIG. 1. (Color online) (a) *I-V* curves of undoped STO. The red closed and blue open circles show *I-V* curves for I_{comp} of 20 mA and 15 mA, respectively. (b) Schematic diagram of the RCB network model used in the simulations. The red thick and black thin bonds represent the circuit breakers in the on and off states, respectively. The right panel shows the switching conditions of the circuit breakers when driven at a bias of Δv. Simulated results for the RCB network model with different values of I_{comp}: (c) 3 a.u. (arbitrary units), (d) 2 a.u., and (e) 1 a.u. The red thick bonds show the volume of the conducting filaments, which is reduced when I_{comp} decreases.

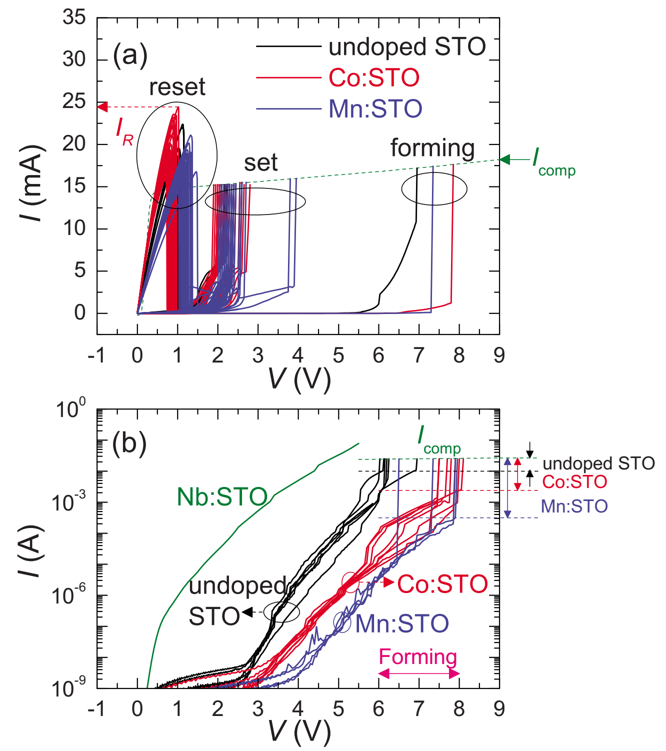

FIG. 2. (Color online) (a) Reset and set *I-V* curves, measured from each of the undoped STO (black), Co:STO (red), and Mn:STO (blue) capacitors. (b) *I-V* curves in the pristine state of undoped STO (black), Co:STO (red), Mn:STO (blue), and Nb:STO (green) capacitors. The arrows on the right-hand side indicate the working values of I_{comp} in our experimental setup.

There have been some reports of a reduction in the leakage current of STO thin-films by acceptor doping with Co or Mn for high-*k* dielectric applications.[18–20] The leakage current will set the minimum value of I_{comp}. Therefore, we proposed that the reduction in the leakage current using acceptor doping could help to decrease I_{comp}, which will result in a reduction in I_R.

All of the capacitors (i.e., undoped STO, Co:STO, and Mn:STO) showed reliable unipolar RS [Fig. 2(a)], and were highly insulating in the pristine state. The forming process occurs at approximately 6–8 V, with $I_{comp}=15$ mA, for all the capacitors. With I_{comp} fixed, the set processes occur at 2–4 V for most capacitors. This relatively large fluctuation in the set voltage is a well-known characteristic of unipolar RS.[3,15] It should be noted that, with $I_{comp}=15$ mA, I_R was quite similar in all the capacitors irrespective of doping. We also performed the switching operation by electrical pulse signal. The pulse switching speed for reset and set processes showed a distribution around 500 μs and 200 ns when we applied square pulses with pulse amplitudes of 2 and 3 V for the reset and set processes, respectively. But they were not explicitly dependent on the doping effects. We also measured temperature *T*-dependence of LRS in each acceptor-doped STO capacitor. It showed that $dR/dT>0$ in all T range of interest irrespective doping effects, so LRS should be in a metallic state. In addition, their temperature coefficients are nearly the same.

Figure 2(b) shows *I-V* curves of the capacitors in the pristine state. Note that the leakage current of the STO capacitors can be reduced by about one order of magnitude by Co doping, and doping with Mn results in a further reduction in the leakage current. For comparison, we also fabricated Nb-doped STO (Nb:STO) capacitors using 0.5 wt % Nb-:STO target and the same fabrication conditions. Nb is a donor in STO,[19] and the Nb:STO capacitors showed three orders of magnitude greater conduction than the undoped STO capacitors, as shown in Fig. 2(b). These results indicated that the leakage current in STO capacitors can be varied by controlling the doping, and smaller leakage currents result in larger operating windows in terms of I_{comp}, and most notably a lower minimum I_{comp}.

To achieve reliable forming, $I_{comp}>10$ mA was required with the undoped STO capacitors. However, we were able to form conducting filaments reliably in the Co:STO capacitors with $I_{comp}=2$ mA and in the Mn:STO capacitors with $I_{comp}=0.4$ mA. The range of I_{comp} required to achieve forming is shown in the right side of Fig. 2(b). Note that the minimum I_{comp} in the Mn:STO capacitors was lower than that of undoped STO capacitors by a factor of about 20. The forming voltages remained in the range 6–8 V, and were not significantly affected by the doping.

Figures 3(a)–3(c) show *I-V* curves in the LRS obtained with different values of I_{comp} for the undoped STO, Co:STO, and Mn:STO capacitors.[17] For all the capacitors, I_R was reduced by decreasing I_{comp}. Despite the difference in doping,

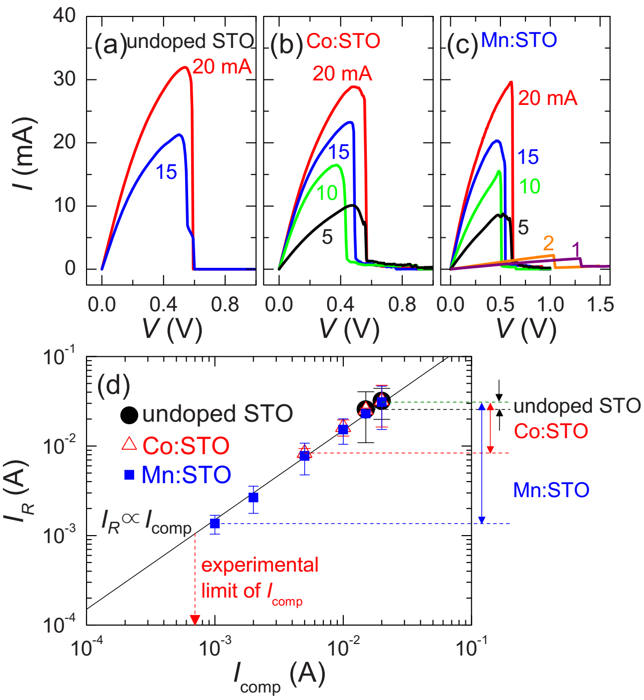

FIG. 3. (Color online) *I-V* for various different values of I_{comp} throughout the operating window, for (a) undoped STO, (b) Co:STO, and (c) Mn:STO capacitors. The numbers indicate the values of I_{comp} in milliampere. (d) Relationship between I_R and I_{comp}. The dashed lines show the lower limits of I_R, and the red arrow at the bottom indicates the lower limits of I_{comp}.

the *I-V* curves are quite similar for a given I_{comp}. Figure 3(d) shows the relationship between I_R and I_{comp}. We can make three important observations. (1) All of the I_R data can be mapped onto a single linear relationship, and I_R is proportional to I_{comp}. (2) Irrespective of doping, I_R remains almost constant for a fixed I_{comp}. (3) With acceptor doping in the *n*-type STO material system, we can reduce I_R by a factor of at least 20. This enhancement factor is limited by the precision of our measurement system, and so I_R in the Mn:STO capacitors may actually be smaller than the measured values. These characteristics were reproduced in more than 50 capacitors built on more than three different wafers for each doping process.

It is important to understand how the acceptor doping in STO can allow us to obtain a smaller I_R. One possibility is that the electron concentration in the conducting filament will decrease with acceptor doping.[20] If the dielectric constant of the material is assumed not to vary with doping, this will result in a decrease in the current in the percolating channel during the forming or set process, and consequently we will see a reduction in I_R. The other possibility is that, when acceptor dopants are introduced and I_{comp} is reduced, the volume of the percolating conduction channels can be decreased, such as in Figs. 1(c)–1(e). In our earlier work, we showed that reset voltage should decrease (increase) with reduction in I_R when the percolating channel was multiply (singly) connected.[15] As shown in Figs. 3(a)–3(c), the behavior that indicates single percolating channels only appears when $I_{comp} \leq 5$ mA, suggesting a decrease in the percolating channel volume. Both of these physical mechanisms can explain the same observed phenomena, and it is likely that both occur. Further systematic investigations are required to determine how doping can reduce I_R in STO, and whether this doping method will work for other unipolar RS materials.

In summary, we have shown that acceptor doping can significant reduce the reset current in $SrTiO_x$ capacitors. This study suggested that the decrease in compliance current by carrier doping is a viable means of reducing the reset currents in RRAM devices.

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