Chapter 5

Tunability of voltage pulse mediated memristive functionality by varying doping concentration in SrTiO₃

Abstract

The potential applications of memristive devices extend far beyond what can be realised using digital computing with utilisation prospects in data encryption and in mobile communication. This necessitates widening the scope of memristive attributes to include the intrinsic variability of the resistive states between cycles for security applications. We demonstrate the ability to controllably influence resistive switching in Nb-doped SrTiO₃-based interface memristors of different doping concentrations. We find that the reset switch from low to high analogue resistance states is faster than for the reverse process and the switching speed increases with doping. Memristive functionalities such as resistance window, stochasticity and nonlinearity are similarly influenced with doping. We demonstrate that a train of pulses applied in different sequences can encode information, exhibited as distinguishable resistance states, and read by applying a small voltage signal. We attribute these findings to the increased interfacial electric field at higher doping concentrations. The doping concentration is a useful handle to tune the memristive functionality for a wide range of different utilisations, beyond those prevalent today.

This chapter is based on work published in:
5.1 Introduction

Their ability to exhibit different resistance states may stem from a wide variety of origins including changes in the orientation or magnitude of electric or magnetic polarisation, phase transitions, and ionic motion. This wealth in mechanisms found in material classes that have been studied is manifested as different responses in, for example, switching times, endurance and retention characteristics\cite{2}. Implementation of memristive devices, which typically have a metal-insulator-metal structure, as memory elements in complementary metal-oxide semiconductor (CMOS) devices or in-memory computing for non-von Neumann applications are envisioned. The potential applications of memristive devices extend far beyond what can be realised using digital computing and they are also being investigated for data encryption\cite{3, 4} and in mobile communication\cite{5, 6}, discussed in Chapter 1, where ultra-high density is not a requirement. However, this necessitates the scope of memristive attributes to widen, such as using the intrinsic variability of the resistance ratio over time or between cycles for security applications and true random number generators\cite{7}.

Resistive switching in such devices can be studied using gradual voltage sweeps, which provides the most transparent insight at every point of a switching cycle. For practical applications, however, resistance changes brought about by applying voltage pulses are of significant importance for emulating low-power synaptic behaviour. Spiking neural networks (SNNs) are thought to more closely resemble biological neural networks\cite{8}. Neurons do not constantly transmit information but rather transmit information in the form of spikes. This sparse activity greatly contributes to the high energy efficiency of the brain\cite{9, 10}. This further amplifies the need for harnessing new attributes in memristive devices for example in resistance change brought about by voltage pulses that can be used to emulate synaptic weight changes induced by the spiking behaviour of neurons.

In this chapter, we investigate the influence of the doping concentration of the semiconductor in interface memristive devices consisting of Co electrodes on Nb-doped SrTiO$_3$ (Nb:STO) substrates. We study resistive switching in dopant concentrations varying from 0.01 wt% to 0.5 wt% by either a continuous voltage sweep or by a train of voltage pulses. Varying the dopant concentration gives us the extra handle to design the potential profile across the interface, modifying the electric field across the Schottky interface and giving rise to differences in their transport as manifested in distinct changes to the high and low resistance states of the devices. We also model the interface to study the correlation between the electric field and the doping concentration.

Further, we extend the characteristic determinant of memristive properties by studying the effects of resistive switching by applying single or multiple pulses. By
changing the pulse times, we find that the reset switch, from low to high resistance, occurs faster than the reverse switch. We also find that the switching speed, in particular the switch from high to low resistance, increases as the doping concentration increases. For higher doping concentrations, we observe that we can reliably and repeatedly switch between clearly distinguishable resistance states with minimal cycle-to-cycle variation. Applying a positive pulse gives rise to a low resistance state (LRS) while a negative pulse gives rise to a high resistance state (HRS), which can subsequently be read with a low amplitude voltage pulse of either positive or negative polarity. When a sequence of two pulses is applied, and the small voltage signal current is read after, we see that while the last pulse has the most significant influence on the current, both pulses influence the resistance state. This allows information to be encoded in a train of pulses in a meaningful way, which is required for SNNs. It also establishes the potential of such memristive devices beyond those used in storage and computing to new possibilities such as in data encryption.

To fabricate the studied memristive devices, we used the two-step electron beam
5.2 Voltage Sweeps

Figure 5.2: 0.1 wt%: (a) 1000 consecutive current-voltage sweeps from +2 V to -3 V to +2 V for Nb:STO (0.1 wt%). Starting from a set voltage of +2 V, the device is in an LRS, reaching the RESET voltage of -3 V and sweeping back, the devices are switched to an HRS. The first and last sweep are marked red and blue, respectively. The current read at -1 V while sweeping the voltage (b) and when voltage pulses are used (c). The LRS and HRS are indicated by black circles and red triangles respectively.

lithography protocol, described in Chapter 4, to create Co contacts on Nb:STO substrates of different doping concentrations in which the devices are electrically isolated from each other using Al$_2$O$_3$. The measurements shown in this chapter were measured on circular devices with radii of 1 µm and doping concentrations of 0.01 wt%, 0.1 wt% and 0.5 wt%, corresponding to carrier concentrations of $10^{19}$ cm$^{-3}$, $10^{20}$ cm$^{-3}$ and $5 \times 10^{20}$ cm$^{-3}$ [11]. Measurements were conducted using either a source measurement unit (SMU) or Waveform Generator/Fast Measurement Unit (WGFMU) of a Keysight B1500A Semiconductor Device Analyzer.

5.2 Voltage Sweeps

Figure 5.1(a), Fig. 5.2(a) and Fig. 5.3(a) show the device response upon sweeping the voltage repeatedly between a set voltage of +2 V and a reset voltage of -3 V for doping concentrations of 0.5 wt%, 0.1 wt% and 0.01 wt%, respectively.

For the highest doping concentration (0.5 wt%), stable switching between two clearly distinguishable states is observed with minimal cycle-to-cycle variation over
5. Tunability of voltage pulse mediated memristive functionality by varying doping concentration in SrTiO$_3$

Figure 5.3: 0.01 wt%: (a) 1000 consecutive current-voltage sweeps from +2 V to -3 V to +2 V for Nb:STO (0.01 wt%). Starting from a set voltage of +2 V, the device is in an LRS, reaching the RESET voltage of -3 V and sweeping back, the devices are switched to an HRS. The first and last sweep are marked red and blue, respectively. The current read at -1 V while sweeping the voltage (b) and when voltage pulses are used (c). The LRS and HRS are indicated by black circles and red triangles respectively.

the 1000 cycles shown. This is also represented by the blue and black symbols in Fig. 5.1(b) and (c), showing the current extracted at reading voltages of -0.5 V and +0.3 V, respectively. The realised ratios are $\sim 10^6$ at -0.5 V and $\sim 2 \times 10^4$ at 0.3 V. These ratios decrease to $\sim 7 \times 10^4$ at -0.5 V and $\sim 4 \times 10^3$ at 0.3 V when the doping concentration is lowered to 0.1 wt%, as shown in Fig. 5.2.

From Fig. 5.3 it is apparent that for 0.01 wt% doped Nb:STO, the switching is significantly different with the same (re)set voltages. The cycle-to-cycle variation is substantially more pronounced in the first few cycles and then levels off. There is almost no difference in resistance between the high and low resistance in the forward bias direction making it unfeasible to read in this regime. However, in reverse bias we can observe an opening in the current-voltage loop, but due to the low current in reverse bias there is a large region in which the current is below the measurement limit of the apparatus. These factors limit the reading voltages to higher reverse bias voltages in the current experiment. Figure 5.3(b) shows that even at -1 V the HRS is still not clearly readable. It is, however, observed from the first few cycles that the resistance ratio between the two states is $\sim 10$. The spread in data for both the LRS and
5.2. Voltage Sweeps

Figure 5.4: Resistance ratio with cycling under various conditions: (a) 0.01 wt% with voltage sweeps (black) and voltage pulses (red) read at -1 V. (b) 0.1 wt% with voltage sweeps (blue) and pulses (orange) read at -0.5 V, voltage sweeps (green) and pulses (purple) read at +0.3 V and voltage sweeps (black) read at -1 V. (c) 0.5 wt% with voltage sweeps (blue) and pulses (orange) read at -0.5 V, voltage sweeps (green) and pulses (purple) read at +0.3 V and voltage sweeps (black) read at -1 V. The set and reset voltages are +2 V and -3 V, respectively, in all cases. (d) Graphically summarises the average resistance ratios as a function of the doping concentration; the error bars represent the standard error.

HRS is significantly larger than that observed in Fig. 5.1 and 5.2(b) and (c). While for the HRS this can partially be explained by considering the measurement resolution of the experimental apparatus, this is not the case for the LRS and indicates this is an attribute of the device itself. This inherent stochasticity is a key requirement for memristive data encryption, where random current fluctuations within a small range are needed.\[7\]
5.3 Voltage Pulses

Next, we study the resistive switching behaviour brought about by voltage pulses of $\sim 100$ ms. Each cycle consists of administering a +2 V set pulse followed by a reading pulse and a -3 V reset pulse followed by another reading pulse. The results of the 0.5 wt% doping concentration are shown in Fig. 5.1(b) (green) for reading pulses of -0.5 V and (c) (red) read at +0.3 V. Again the cycle-to-cycle variation is minimal, albeit small decreases in the resistance ratios are observed, but the states remain clearly distinguishable. The results for 0.1 wt%, shown in Fig. 5.2 reveal a similar scenario where the cycle-to-cycle variation is small and the resistance ratio is diminished compared to the voltage sweeps. The resistance ratios achieved upon the different measurement schemes as a function of doping concentration are shown in Fig. 5.4. Similar measurements, with a reading voltage of -1 V, were conducted for the 0.01 wt% Nb:STO sample as shown in Fig. 5.3(c) and in this case, no stable switching is observed, which may be related to the use of a relatively high reading voltage. It is however clear that the spread in data points is significantly larger than for the higher doping concentration, highlighting again a greater degree of random fluctuations.

5.4 Switching Speed

Figure 5.5: Switching speed results for 0.1 wt% Nb-doped SrTiO$_3$. The first 10 measurement points are during the first reading event and the latter 10 are during the second reading pulse after the (a) reset (b) set pulse. (a) A change in current is observed for all pulse durations. (b) No clear change in current is observed for pulse durations of 10 $\mu$s and lower, hence the minimum switching time is determined to be in the order of 10 $\mu$s.
5.4. Switching Speed

Figure 5.6: Switching speed results for 0.5 wt% Nb-doped SrTiO$_3$. The first 10 measurement points are during the first reading event and the latter 10 are during the second reading pulse after the (a) reset (b) set pulse. (a) A change in current is observed for all pulse durations. (b) No clear change in current is observed for pulse durations of 1 µs, hence the minimum switching time is determined to be in the order of 1 µs.

<table>
<thead>
<tr>
<th>Doping concentration (wt %)</th>
<th>Reset (µs)</th>
<th>Set (µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>&lt;1</td>
<td>~ 10</td>
</tr>
<tr>
<td>0.5</td>
<td>&lt;1</td>
<td>~ 1</td>
</tr>
</tbody>
</table>

Table 5.1: Waveform used for determining (a) reset time and (b) set time. Switching speeds for different doping concentrations.

The waveforms used to establish the reset and set times are shown in Table 5.1(a) and (b) respectively. To determine the set (reset) speed, a voltage of -3 V (+2 V) was applied to realise a high (low) resistance state. The small signal current was then measured using a low voltage pulse (read 1). This was followed by applying a +2 V (-3 V) pulse of varying time (1 µs-1 s). Finally, a second low voltage reading pulse
Figure 5.7: Magnitude of the current read at (a) +0.3 V and (b) -0.5 V after applying different combinations of two pulses. In each case, the reading was carried out for ~2 s. Each measurement consists of two writing pulses and a reading step (shown in (c)-(e) for reading at +0.3 V).

(read 2) was used and the current during reads 1 and 2 were compared. The measurement results are shown in Fig. 5.5 and 5.6 and the results for doping concentrations of 0.1 wt% and 0.5 wt% are summarised in Table 5.1 due to the small ratios and unreliable switching behaviour we could not accurately determine switching times for the lowest doping concentration.

For both doping concentrations, we observe asymmetric switching times, with the reset switching being faster than the set operation. The minimal reset switching time in both cases was longer than the minimum pulse times we could apply and hence we cannot comment on whether the reset time depends on the doping concentration. For the set time, on the other hand, we found that the more highly doped sample showed faster switching. Figure 5.5 and 5.6 show that the change in resistance depends on the pulse width, with longer pulses giving rise to a greater change. This also explains why the resistance ratio is lower when using shorter voltage pulses rather than voltage sweeps, as seen in Fig. 5.1 and 5.2.

5.5 Two-Pulse Scheme

As proof of principle of the possibility of encoding information in a train of pulses that can be interpreted by the memristive devices in a meaningful way, we applied
two-pulse sequences and observed the output response at a low reading voltage after. The results for 0.5 wt% are shown in Fig. 5.7 for four different combinations of pulses followed by reading voltages of (a) 0.3 V and (b) -0.5 V. The pulse durations are ∼100 ms with amplitudes of +2 V and -3 V and combinations thereof, as shown in Fig. 5.7(c)-(e). The starting current magnitude is lowest when two negative pulses were applied. This is followed by the case where a positive pulse precedes a negative pulse, the starting current magnitude further increases when a negative pulse is followed by a positive pulse. Finally, the highest current value is observed when two positive pulses were applied. Noteworthy is that the appearance of four distinct states clearly shows that each pulse in the sequence contributes to the reading current. Another observation is that there are two distinct trends: one showing a small increase in current, seen for the two cases where the last pulse was negative and one that shows a slight decrease in current, seen when the last pulse was positive. Hence, we can conclude that the rate of change is determined by the last pulse in the sequence while the resistance state is influenced by both the first and last pulse. The rate of change of the current is greatest when the reading pulse has the opposite polarity to the subsequent writing pulse; this likely arises due to a small writing effect induced by the continuous application of the reading voltage. Given that the resistance level is influenced by the pulse time, as can be seen in Figs 5.5 and 5.6, these differences can be controlled by tuning the pulse timing. By increasing the pulse times, the influence of the last pulse on the resistance will be amplified; this can be used in potential applications where earlier parts of a sequence are not important, such as last digit recollection. Alternatively, more weight can be attached to earlier terms in the sequence by decreasing the pulse times; this will be useful for encoding information in a spike train.

5.6 Modelling the Schottky Barrier Profile

The above findings demonstrate the expansion of memristive functionalities beyond those applied thus far and obtained by tailoring the potential landscape at the interface. To understand the differences observed for the different doping concentrations, we have to consider how the electric field is influenced by doping.

\[
\frac{d^2 \psi(x)}{dx^2} = -\frac{qN_D}{\epsilon_0 \epsilon_r(E)} \quad (5.1)
\]

\[
V(x) = \frac{\sqrt{ab\epsilon_0}}{N_D} \left( \cosh \frac{qN_D}{be_0} (W - x) - 1 \right) + q(V_a - V_F) \quad (5.2)
\]

The dependence of the electric field on temperature, \( T \), and distance from the
5. Tunability of voltage pulse mediated memristive functionality by varying doping concentration in SrTiO$_3$

Table 5.2: Temperature (top) and doping (bottom) dependent parameters used in modelling the barrier profiles.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>295 K</td>
</tr>
<tr>
<td>a</td>
<td>$2.47 \times 10^{15}$ V$^2$/m$^2$</td>
</tr>
<tr>
<td>b</td>
<td>$1.40 \times 10^{10}$ V/m</td>
</tr>
<tr>
<td>$\epsilon_r$</td>
<td>281.80</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Doping concentration (wt%)</th>
<th>Carrier concentration (cm$^{-3}$)</th>
<th>W (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>$10^{19}$</td>
<td>56.4</td>
</tr>
<tr>
<td>0.1</td>
<td>$10^{20}$</td>
<td>15.8</td>
</tr>
<tr>
<td>0.5</td>
<td>$5 \times 10^{19}$</td>
<td>5.39</td>
</tr>
</tbody>
</table>

Figure 5.8: Computed profiles of (a) the electric field, (b) the dielectric permittivity, and (c) the Schottky barrier profile of the Co/Nb:STO interface as a function of distance from the interface for doping concentration of 0.01 wt% (black), 0.1 wt% (blue) and 0.5 wt% (red).

The conduction band, $x$ can be described by\cite{12}:

$$E(x, T) = -\sqrt{a(T)} \sinh \left( \frac{qN_D}{b(T)\epsilon_0} (W(T) - x) \right)$$  \hspace{1cm} (5.3)

Where $a$ and $b$ are temperature dependent parameters with values of $2.47 \times 10^{15}$ V$^2$/m$^2$ and $1.40 \times 10^{10}$ V/m at room temperature, respectively. The carrier concentrations, $N_D$ (estimated from \cite{11}), and the depletion widths, $W$, depend on the doping concentration and are summarised in Table 5.2 (bottom). The field dependence of the dielectric permittivity of SrTiO$_3$ is given by\cite{12, 14}:

$$\epsilon_r(E) = \frac{b}{\sqrt{a + E^2}}$$  \hspace{1cm} (5.4)

The temperature-dependent constants used in the relevant equations are determined from Equations 5.5, 5.7, \cite{12, 13} and are summarised in Table 5.2 (top).

$$\epsilon_r(T) = \frac{1635}{\coth \left( \frac{44.1}{T} \right) - 0.937}$$  \hspace{1cm} (5.5)
\[
    b(T) = 1.37 \times 10^9 + 4.29 \times 10^7
\]

\[
    a(T) = \left( \frac{b(T)}{\epsilon_r(T)} \right)^2
\]

Here we assume the interfaces are ideal and there are no fixed charges, trap states or gap states and use the Schottky-Mott model to calculate the barrier height. The work function of the Co is 5 eV while the electron affinity of Nb:STO is 3.9 eV.

Figure 5.8(a) shows how the electric field varies as a function of distance from the interface. The field is strongest at the interface and becomes zero at the edge of the depletion region. With increasing doping densities, the interfacial field strength increases and the depletion region decreases.

### 5.7 Discussion

#### 5.7.1 Impact of Doping

![Graphs showing current density vs. voltage for different doping concentrations.](image)

Figure 5.9: Virgin state measurements conducted on four different devices of (a) 0.01 wt% (b) 0.1 wt% and (c) 0.5 wt%. (d) The average of the four devices is plotted in the same graph.

Due to the field dependence of the dielectric constant, the different electric field profiles will result in decreases in \( \epsilon_r \) in the depletion regions depending on the dop-
5. Tunability of voltage pulse mediated memristive functionality by varying doping concentration in SrTiO$_3$

The strongest reductions of the $\varepsilon_r$ are present at the interface where the value is reduced by 22% (0.01 wt%), 75% (0.1 wt%), and 94% (0.5 wt%). Finally, this influences the Schottky barrier profile, causing an increasingly steep profile with higher doping as shown in Fig. 5.8b). With increasing doping concentration we observe (i) a significant increase in the current flow in reverse bias, (ii) a large increase in the hysteresis in reverse bias, (iii) the appearance of an observable hysteresis in forward bias, and (iv) a more symmetric current-voltage curve. By fitting the thermionic emission equation for the virgin device state, we can determine the ideality factor, describing how well the electron flow can be described by thermionic emission. We opted to compare the virgin device states, before any switching events have taken place, to ensure any conclusions drawn are not influenced by previously conducted measurements. It is determined that the ideality factor increases with increasing doping concentration from $1.36\pm0.06$ (0.01 wt%) to $2.59\pm0.17$ (0.5 wt%) (Fig. 5.9). This indicates that at higher carrier concentrations there is an increasing contribution from other transport mechanisms, which is enabled by the decreasing Schottky barrier width, facilitating electronic tunnelling through the barrier. This suggests that in the low resistance state, an increased contribution of tunnelling gives rise to a change in the current in both forward and reverse bias. In lower doped devices, the Schottky barrier is wider and tunnelling is less pronounced giving rise to almost no hysteresis in forward bias and a less pronounced reverse bias hysteresis. Figure 5.8c shows that with 0.01 wt% of doping Nb:STO is non-degenerate, but above 0.1 wt% the Fermi level lies within the conduction band. Hence, this observation is consistent with the expectation that tunnelling in forward bias is not possible in non-degenerate semiconductors and highlights the importance of field emission for resistive switching[15–17]. It is well accepted that there exist defect states at the interface[18–20], when tunnelling is an important transport mechanism, electrons will interact more strongly with these trap states. In reverse bias, electrons may become trapped in these states giving rise to an HRS; this is amplified when the doping concentration is higher. In addition, it has been shown that mobile defect migration can play an important role in mediating the switching. The increased electric field can facilitate the movement of defects, such as oxygen vacancies when the doping is increased. The increasing electric field with doping concentration is also responsible for the faster switching reported in Table 5.1 as the resistive switching process is field-driven.

Hence by tuning the doping concentration we can change the Schottky barrier profile and consequently influence the transport mechanisms. With a low doping concentration, the Schottky barrier is wider and thermionic emission is the dominant mechanism which gives rise to a relatively low current and a significant rectification of forward compared to reverse bias. Increasing the doping concentration leads to an increasingly narrowing barrier which is accompanied by an increase in tunnelling
and gives rise to an overall higher current flow, less rectification and an increase in the resistance window in both bias directions. The increasing field with doping concentration furthermore gives rise to faster switching.

5.7.2 Implications for Applications

Memristors have already been used in integrated circuits for memory applications and have the potential for a wide range of other applications in many technologies. The specific requirements that a device should fulfil strongly depend on the application [7, 21]. In some architectures, it may be beneficial to have a relatively high resistance in both states to limit the impact of a voltage drop in other parts of the circuit [7]. This can easily be achieved using a substrate with a lower doping concentration. If, on the other hand, a particular application calls for a large memory window in which a multitude of states can be defined, a higher doping concentration is more suitable.

An important issue in memristive networks, such as crossbar arrays, is sneak path currents flowing through non-selected devices during reading and writing. To avoid this, selector devices may be required to isolate a specific memristive element. Such devices, which typically may be transistors, diodes or resistors, limit the scalability and significant efforts are made to avoid having such elements [22, 23]. The integration of a three-terminal transistor reduces the integration density of the full circuit and while the diode and the resistor are two-terminal devices that can be integrated on top of a memristor without consuming additional area on a chip, their integration can still complicate fabrication and increase variability. Different schemes have been implemented aiming to either increase the nonlinearity or asymmetry of the current-voltage characteristics of memristive devices [24]. This presents a significant challenge in many types of memristors, especially in the low resistance state which often has a strong metallic character. Due to the strong diodic nature of the devices investigated here, they possess both a high degree of nonlinearity, as well as asymmetry between forward and reverse bias. This characteristic is most pronounced in the lower doping concentration, making these devices highly suitable for acting as self-selectors.

5.8 Conclusions

In this chapter, we have demonstrated the ability to controllably influence resistive switching in Nb-doped SrTiO$_3$-based interface memristors using voltage pulses. The resistance can either be reliably switched between different and clearly distinguishable states by applying single pulses, or a train of pulses can be used to encode
information that can be interpreted by the memristive device by analysing the small signal current after the pulses. We find that the switch from LRS to HRS, which occurs in reverse bias, is faster than the switch from HRS to LRS. The switching speed is also found to increase with doping concentration, most clearly evident from the HRS to LRS transition under forward bias. We attribute these findings to the increased interfacial electric field found for higher doping concentrations. Our results highlight the suitability of Nb:STO memristors for a wide variety of applications, whereby the doping concentration can be used to optimise specific task-dependent device parameters.
Bibliography


5. Tunability of voltage pulse mediated memristive functionality by varying doping concentration in SrTiO$_3$


