**Introduction**

Since last five decades, the scaling performance of microelectronics successfully meets the prediction of Moore's law of doubling of transistors after two years. However, now, it has been realized that due to the physical limits in the scaling of the silicon-based devices, it will be difficult to follow the Moore’s law. In this regard, various crystalline and amorphous materials have received significant interest due to the presence of resistive switching (RS) properties that offer several advantages, such as higher scaling, very simple cross-bar structure, lower power consumption, fast operation, and capability, over the Si-based memory devices to meet the criteria beyond the Moore's law.\(^1\)\(^-\)\(^2\)\(^3\) Multilevel resistive states or analogous resistive states of the RS memory devices can also be referred as memristors.\(^3\)\(^-\)\(^4\) The RS phenomena are controlled by a defect-driven process and various physical and chemical properties such as photo-catalytic properties, superconductivity, thermal stability, and higher dielectric constant.\(^5\)\(^-\)\(^7\) The pure STO is an electrical insulator with a large band gap of \(\sim 3.2\) eV. However, the electrical conductivity of the STO can be altered by tailoring its compositional design. Due to this, the RS phenomena in the STO have been widely studied for the future generation non-volatile RAM applications. Filamentary types of the RS phenomena have been reported when active electrodes, such as Ag and Cu, were used.\(^8\) In the case of the inert metal electrodes such as Au and Pt, oxygen vacancies were introduced to attain resistive switching.\(^9\)\(^-\)\(^10\) Several studies on the RS phenomena in SrTiO\(_3\) have been reported. An STO is a popular perovskite oxide due to its multifunctional properties such as photo-catalytic properties, superconductivity, thermal stability, and higher dielectric constant.\(^16\)\(^-\)\(^19\) The pure STO is an electrical insulator with a large band gap of \(\sim 3.2\) eV. However, the electrical conductivity of the STO can be altered by tailoring its compositional design. Due to this, the RS phenomena in the STO have been widely studied for the future generation non-volatile RAM applications. Filamentary types of the RS phenomena have been reported when active electrodes, such as Ag and Cu, were used.\(^10\) In the case of the inert metal electrodes such as Au and Pt, oxygen vacancies were introduced to attain resistive switching. These oxygen vacancies were generated by different methods such as incorporating doping elements such as Fe\(^{25}\) and Cr,\(^{26}\) ultraviolet irradiation while measuring the switching effect.\(^{27}\)

A robust unipolar resistive switching (URS) was successfully observed in sol–gel derived perovskite type Fe-doped strontium titanate (FeSTO) thin films, deposited on an ITO-coated glass substrate by a spin-coating technique. The surface topography of the films was characterized by atomic force microscopy that suggested a smooth surface with an average surface roughness nearly 1–2 nm. The crystal structure, URS phenomena, current–voltage characteristics, and dielectric and impedance behavior were analyzed for both high resistance state (HRS) and low resistance state (LRS). The X-ray photoelectron spectroscopy (XPS) was also employed to investigate the valence states of the host and dopants elements. The Au/FeSTO/ITO device offers a large resistance ratio of HRS and LRS (\(R_{\text{on}}/R_{\text{off}}\)) around \(10^5\), long stable retention characteristics for \(10^4\) s, and a distinguished and large non-overlapping voltage window of \(\sim 4\) to 6 V for SET and RESET operations.

**Unipolar resistive switching behavior in sol–gel synthesized FeSrTiO\(_3\) thin films**

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and thermal treatment. Both filamentary and non-
filamentary RS phenomena have been reported for the STO
system. Filamentary and non-filamentary types of the RS
phenomenon were observed mainly because of the accumula-
tion of the oxygen vacancies inside the STO thin film and near
the interface of the electrode–dielectric.
Muenstermann et al. reported the coexistence of filamentary and homoge-
nenous BRS behaviour in the 1% Fe-doped STO thin films
fabricated on a Nb:STO substrate by pulsed laser deposition
(PLD) technique. Similarly, Lenser et al. demonstrated a
filmy resistive switching in the less than 5% Fe-doped STO
thin films grown by PLD with a small $R_{ff}/R_{on}$ ratio.
Among these studies on the RS phenomena in strontium
titanate, most were limited to a single crystal, epitaxial thin
films, and pure SrTiO$_3$ fabricated by the expensive and complex
deposition techniques. On the other hand, solution-
based methods provide a very inexpensive and easy way to
synthesize and fabricate oxide thin films. In this study, we
present a very stable and robust unipolar resistive switching
(URS) behavior in a sol–gel synthesized perovskite Fe-doped
SrTiO$_3$ thin film deposited by a spin coating technique on an
ITO electrode.

**Experimental details**

The Fe-STO thin films were prepared by the spin-coating tech-
nique. The solutions were prepared by a sol–gel method. The
sol–gel method is a chemical synthesis method having several
advantages such as relatively simple, ease of control over the
compositional stoichiometry, lesser impurities, and economical.

To prepare the FeSTO solution, strontium acetate (SrC$_4$-
H$_8$O$_4$·1/2H$_2$O) and titanium IV isopropoxide (Ti(OCH(CH$_3$)$_2$)$_3$)
were used as precursors. Acetic acid and 2-methoxy ethanol
were used as solvents. Initially, a solution (called solution A) of
acetic acid and 2-methoxy ethanol having a ratio of 1 : 1 was
prepared. Then, a calculated amount of strontium acetate was
dissolved in solution A and stirred for half an hour with heating
at 50 °C till it formed a transparent solution. Later, a calculated
amount of titanium isopropoxide and iron pentanoate
(C$_5$H$_7$FeO$_5$) was added separately in a 19 : 1 ratio for Fe doping
of 5 mol% concentration. Titanium isopropoxide was added
drop by drop by a micropipette while stirring the solution, fol-
lowed by stirring for 5 h in a closed flask.

The indium tin oxide (ITO)-coated glass slides were used as
substrates. Initially, the 10 mm × 10 mm substrates were
cleaned with acetone for two minutes and later by isopropyl
alcohol for 10 minutes. The spin coater NXGM1 model was used
for the thin film preparation at 5000 rpm for 30 s. The obtained
thin films were annealed at 700 °C for one hour. For the elec-
trical measurements, the top Au electrode was deposited
through a shadow mask, having a diameter of 200 μm and
a thickness of 20 nm, by a DC sputtering technique. The
electrical measurements were performed using a microprobe
system and an optical microscope. All the current–voltage and
impedance spectroscopy measurements were performed using
Agilent B2901a and Hioki 3532-50 LCR Hi Tester, respectively.
The impedance spectroscopy measurements were performed
with an oscillation voltage of 0.5 V and frequency ranges from
100 Hz to 1 MHz. The surface topography and the crystal
structure were investigated by atomic force microscopy and X-
ray diffraction techniques. An ultra-high vacuum surface analy-
ysis system equipped with a monochromatic Al K$\alpha$/non-
monochromatic Mg K$\alpha$ X-ray source and an EA125 electron
energy analyser was utilized to carry out the X-ray photoelectron
spectroscopy (XPS) study. The C 1s (284.8 eV) core level was used
for binding energy (BE) and charge correction.

**Results and discussion**

The XRD patterns of the FeSTO thin films coated on the ITO
glass substrate annealed at 700 °C are shown in Fig. 1(a). The
peaks at 32.3° and 47.4° corresponding to STO (110) and STO
(200) of the FeSTO thin film are indexed properly using the
pseudo-cubic crystal structure. The surface topography image of
the FeSTO thin film is shown in Fig. 1(b). The topographical
study of the films was performed using a Gwyddion software
tool. The average film thickness is near ~70 nm, as probed by
the profilometer. The average grain sizes are in the range of
~30 nm with an average surface roughness in the range from
~1 to 2 nm.

The energy band diagram for the Au/FeSTO/ITO resistive
switching device is shown in Fig. 2(a). The energy band situa-
tion is for the FeSTO thin film with Au (work function is 5.1 eV)
as the top electrode and ITO (work function is 4.4 eV) as the
bottom electrode. The electron affinity of the FeSTO thin film is
speculated to be ~4.1 eV, as reported for STO. When the
metal electrode and dielectric thin film is brought into contact,
free charge carriers will flow until an equilibrium condition
is achieved. In this electrode–dielectric interaction, due to a large
work function of Au and FeSTO's n-type nature, a space charge
deposition region and large barrier height are developed at the
Au/FeSTO interface that forms a Schottky-type potential barrier.

Similarly, due to a low work function of ITO, at the ITO/
FeSTO interface, the barrier height is almost negligible (0.3 eV),
and an ohmic contact may be possible. The barrier height
varies with a change in the magnitude and direction of the
applied electric field. When a positive voltage is applied to the
top Au electrode, the electrode-FeSTO junction is forward
biased that lowers down the Schottky barrier height. Initially,
the memory device is in HRS, and after the positive potential is

![Fig. 1](image)
applied on the top Au electrode, the oxygen vacancies present in
the FeSTO film are pushed downwards towards the bottom
ITO electrode; this eventually results in the formation of a series
of conducting paths into the oxide film. This conducting
path formation results in the LRS of the memory
device. Later, the voltage sweep with an increased compliance
current (100 mA) is applied; the temperature of the previously
formed filament increases with the increase in the passing
current due to the Joule heating effect, which results in the
rupturing of the filament and RESET of the device. The rupturing
and filament formation process are not homogeneous for each cycle of SET and RESET process and a set of devices that intrinsically develops a memory voltage window for SET and RESET process.

The XPS measurements have also been performed to analyze
the valence states of the host and doped elements, which are
shown in Fig. 2(b) and (c). In Fig. 2(b), two peaks at 458.2 eV and
463.9 eV belong to the Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$, respectively. These
peaks correspond to the Ti$^{4+}$ oxidation state. In Fig. 2(c), we have shown the Fe 2p core level of the 5% Fe-doped SrTiO$_3$ thin
film. The Fe 2p core level has been fitted with two nearly
Gaussian components. The peaks located at 708.9 and 710.4 eV
can be assigned to Fe$^{2+}$ and Fe$^{3+}$, respectively. The calculated
area% for Fe$^{2+}$ and Fe$^{3+}$ is roughly 60% and 40%, respectively,
which suggests the presence of significant mixed valence states
of Fe. It may indicate the presence of oxygen vacancies in the
FeSTO thin film. This scenario has also been suggested by Wan
et al. in the Cr-doped STO thin films.

In the RS behaviour testing process, the top Au electrode was
kept positively biased, whereas the bottom ITO electrode was
kept negatively biased. Initially, the pristine FeSTO devices are
in HRS and have the resistance in $\Omega$. For switching the
device into LRS, an initial electroforming voltage ($\sim$8.5 V) has
been obtained. At first, we have increased the applied potential
through the device, which abruptly increases at $\sim$8.5 V, which in
turn develops current filaments (Fig. 3(a) and (b)). This
switching process from HRS to LRS is called the SET process. To
the SET the device, a voltage sweep from 0 V to 10 V with a fixed
compliance current of 1 mA was applied. Most of the devices
show a lower SET voltage as compared to the electroforming
voltage. To RESET the device, again a voltage sweep from 0 V to
4 V with a compliance current of 100 mA was applied. When the
applied potential approaches $\sim$2.5 V, the current through the
device drops abruptly, and hence, the resistive state of the
device changes from LRS to HRS (RESET process). Herein, the
maximum drawing current in the LRS state is near $\sim$30 mA in
each SET operation, which is acceptable for the NVRAM
applications.

For the application point of view, charge retention and
endurance characteristics of the FeSTO thin film devices are
shown in Fig. 3(c) and (d), respectively. For the retention

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**Fig. 2** (a) The energy band diagram of the Au/FeSTO/ITO capacitive structure, (b) Ti 2p XPS core level, and (c) Fe 2p XPS core level (dots) along with fitting component (patterned).

**Fig. 3** (a) The $I$–$V$ plot for the URS behavior of the Au/FeSTO/ITO memory device, (b) SCLC mechanism linear fitting for the URS behavior, (c) The retention characteristics and (d) the endurance characteristics of the FeSTO memory device.
characteristic measurement, a very low constant potential of 0.5 V with a compliance current of 1 mA was applied across the device for both HRS and LRS, and the respective currents were obtained. The obtained current values are almost constant in both the HRS and LRS states over 10^4 s. It concludes that the device exhibits an excellent retention characteristic. To carry out the endurance characteristic test for the devices, consecutive multiple SET and RESET operations were performed for up to 50 cycles. Herein, the FeSTO devices have shown very stable and repetitive endurance characteristics.

The conduction mechanism is analyzed for the FeSTO thin films. For both LRS and HRS, the I-V data were re-plotted as log J vs. log E and linearly fitted to investigate the space charge limited conduction (SCLC) mechanism for the resistive switching, as shown in Fig. 3(b). In the HRS state, for the lower applied field region (up to around 4V cm^{-1}, in log scale), the slope value is nearly around ~0.4, indicating a very high resistance state. Further increment in the applied electric field causes a gradual increment in the slope to 2.7; this indicates the presence of the formation of an ohmic conductive filament within the capacitive device, which dominates over the Schottky interface barrier between FeSTO and the top Au electrode. Thus, it signifies the filamentary resistive switching process. Similarly, for the LRS state, the measured slope of the logarithmic J-V characteristics is close to one, indicating an ohmic behavior. In the RESET process, the rupturing of the conductive filament can be explained by the Joule heating effect. The high passing current (around ~30 mA) causes the increase in the temperature of the filament (~800 K) and thus ruptures it at the reset voltage (V_{reset}).

The relationship between the current density and the applied electric field is denoted by

\[ J_{SCLC} = \frac{9}{8} \mu e \theta E^2 d \]

where \( \mu \) is the mobility of free charge carriers, \( e \) is the static dielectric constant, \( \theta \) is the ratio of injected free charge carriers to total free charge carriers, \( E \) is the applied electric field, and \( d \) is the thickness of the film. Apart from the SCLC, the conduction mechanism is further analyzed with Schottky emission and Pool–Frankel conduction mechanisms (the results are not shown in this report). The observed respective slopes from the linear fitting of \( \ln J \) vs. \( E^{1/2} \) and \( \ln J/E \) vs. \( E^{1/2} \) provide an unrealistic optical dielectric constant of the FeSTO.

The conduction mechanism is further explored by the impedance spectroscopy technique. In this measurement, after each SET and RESET operation, impedance, capacitance, phase angle, and tangent loss were determined in the frequency range from 100 Hz to 1 MHz at a constant AC voltage (0.5 V). The frequency response of capacitance and tangent loss are shown in Fig. 4(a) and (b), respectively. Fig. 4(a) shows that in the HRS region, the capacitance is almost linear and gradually decreases over the whole frequency range; this indicates a very high resistive device; on the other hand, for the LRS, the capacitance exponentially decreases in the lower frequency region and then gradually decreases in the higher frequency region. It indicates the presence of the formation of an ohmic conductive filament (CF) (free charge carriers), where \( C_p \) is decreasing with an increase in the frequency. The capacitance of the devices is almost the same for both HRS and LRS above 1 kHz probe frequencies; however, at the same time, these devices show many folds increase in tangent loss. These results suggest the formation of the conducting filament in LRS that creates several

![Figure 4](image_url)

**Fig. 4** The frequency dependent plot of the capacitance (a) and tangent loss (b) in HRS and LRS for the FeSTO memory device.

![Figure 5](image_url)

**Fig. 5** The impedance vs. frequency plot in HRS (a) and LRS (c). The Nyquist plot for the FeSTO thin films in HRS (b) and LRS (d) with an equivalent circuit fitting (solid orange line).
capacitors connected in parallel and hence a negligible change in capacitance with a large tangent loss (>1 kHz).

Fig. 5(a) and (c) show the frequency response of real and imaginary impedance for HRS an LRS, respectively. The impedance properties for HRS and LRS (see Fig. 5(a) and (b)) indicate a drastic decrease (~2 × 10^3) in the impedance and a huge shift in the relaxation frequency (peak f_{max}) towards the higher frequency side. In Fig. 5(b) and (d), the Nyquist plots for HRS and LRS are shown, respectively. The obtained experimental data were fitted with an equivalent electrical circuit comprising a parallel combination of R_{bulk} (bulk resistance) and C_{bulk} (bulk capacitance) with the R_{a} (contact resistance) connected in series.

The equivalent circuit fitting for the Nyquist plots show that there is a drastic change in the bulk resistance (R_{bulk} for HRS is ~135 MΩ and for LRS is ~9 kΩ) after the occurrence of the SET process, whereas there is a subtle change in the capacitance (C_{bulk} changes ~20 pF in the resistive state transition process). The contact resistance is almost the same for both HRS and LRS (R_{a} ~ 89 Ω). Thus, it indicates that the switching mechanism is driven by the formation of multiple ionic conducting filaments in the thin film.

Conclusions

In summary, the resistive memory devices based on the sol–gel synthesized FeSTO thin films deposited on an ITO substrate were successfully prepared by a spin coating technique at room temperature. These devices exhibit a repetitive and stable URS behavior. The URS is mainly attributed to the migration of oxygen vacancies induced due to the replacement of some Ti^{4+} ions by Fe^{3+} and Fe^{2+} ions and the creation of oxygen vacancies at high sintering temperatures. The conduction mechanism study comprising I–V and impedance spectroscopy for the FeSTO thin films shows the electroformation of the conductive filament and rupturing due to the Joule heating effect. As per the device perspective, our results exhibit an excellent retention characteristic of 10^5 s and an endurance property. This study demonstrates that the Au/FeSTO/ITO memory cell has promising potential applications as NVRAM elements.

Conflicts of interest

There are no conflicts of interest to declare.

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