Performance analysis of resistive switching devices based on BaTiO$_3$ thin films

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Abstract. Resistive switching devices, memristors, have recently attracted much attention due to promising performances and potential applications in the field of logic and memory devices. Here, we present thin film BaTiO$_3$ based memristor fabricated using ink-jet printing technique. Active material is a single layer barium titanate film with thickness of ~100 nm, sandwiched between metal electrodes. Printing parameters were optimized aiming to achieve stable drop flow and uniform printed layer. Current-voltage characteristics show typical memristive behavior with pinched hysteresis loop crossed at the origin, with marked differences between High Resistive State (HRS) and Low Resistive State (LRS). Obtained resistive states are stable during numerous switching processes. The device also shows unipolar switching effect for negative voltage impulses. Variable voltage impulse amplitudes leads to the shifting of the energy levels of electrode contacts resulting in changing of the overall current through the device. Structural characterization have been performed using XRD analysis and SEM micrography. High-temperature current-voltage measurements combined with transport parameter analysis using Hall effect measurement system (HMS 3000) and Impedance Analyzer AC measurements allows deeper insight into conduction mechanism of ferroelectric memristors.

1. Introduction

Expanding interest for the devices with memristive behaviour is caused by favourable future applications such as in: new generation of memory device, artificial synapses, unconventional computing systems and overcoming of the Moore’s law. Various materials and mechanism have gained memristive effect, however one of the most promising types are ferroelectric junctions, due robustness during read-out process, long retention time, possibilities for scaling down to few unit cells, chemical stability and high $R_{OFF}/R_{ON}$ ratio [1].

Widely used ferroelectric memristive structures are based on BaTiO$_3$ thin films [2], while underlying switching mechanisms is explained as field induced charge redistribution at the interface metal/ferroelectric, which lowers the ferroelectric barrier height and enables conduction. Accumulation of the charge carriers at the interface contributes to the stability of the memorized
states, wherein interface property, i.e. selection of the electrode material is critical issue for the current control [1].

In this paper, we present detailed performance analysis of Au/BaTiO$_3$/Ag memristive device. Inkjet printing fabrication technique was chosen for deposition of active BaTiO$_3$ layer with advantages of additive, controlled and low-cost deposition. Memristive effect was identified through current-voltage measurement, while further electrical and structural analysis bring contribution in still open issues of underlying resistive switching effects mechanism.

2. Materials and Methods
Active material is BaTiO$_3$ thin film deposited using Dimatix DMP 3000 ink-jet printer on Si wafer (SG 108, CrysTec) substrate on which was previously evaporated Au layer. Details about BaTiO$_3$ ink synthesis and properties have been reported elsewhere [3].

Stable drop flow during from 10 pl nozzles was obtained with trapezoidal actuation voltage waveform with amplitude of 26V and 1 kHz printing frequency. Deposition was performed in the clean room environment; class ISO 7 at room temperature. Drop spacing was set to 35 $\mu$m, matching the half diameter of the printed drop on Si wafer substrate. Square-shaped patterns of BaTiO$_3$ one-layer film were well defined and reproducible. Post-processing step involves sintering at temperature of 700$^\circ$C for 1 hour. Top electrode of the device is Ag two-component conductive paste (CircuitWorks® Conductive Epoxy), cured for 24 hours at room temperature.

3. Results and discussion
3.1. Structural and morphology analysis
Structural XRD analysis (Rigaku XRD Miniflex 600), resolved characteristics peaks for BaTiO$_3$ crystalline phase (Figure 1a), with the presence of Si peaks from the substrate. SEM micrograph (JEOL JSM 6460 LV), Figure 1b, showed uniform layer of BaTiO$_3$ thin film with thickness $\sim$100 nm.

![XRD pattern](a)

![SEM micrograph](b)

Figure 1. Structural analysis of Au/BaTiO$_3$/Ag resistive switching device a) XRD patterns b) SEM micrograph

3.2. Electrical analysis
The current-voltage characteristics were measured using Keithley 2410 High Voltage Source Meter in voltage source mode with 0.1V per second step voltage sweep. Bottom electrode Au was grounded during measurement, while voltages pulses are applied to the top (Ag) electrode with amplitude of +/-5V. Pinched hysteresis loop crossed at origin, the fingerprint of memristive effect, with bipolar switching behavior shown in Figure 2. Dissymmetry of the characteristics originates from Joule heating on the contact regions, as well as differences between barrier heights and metal work functions.
at Au/BaTiO$_3$ and Ag/BaTiO$_3$ interfaces. Exponential behavior of current-voltage relation is most likely caused by dominant Fowler-Nordheim tunneling mechanism above critical electric field [4], while low voltage switching is controlled by barrier height modulation due to charge accumulation and dissipation at the interface. Namely, in the ON state barrier height is reduced, which lowers the resistance values, in contrary in the OFF state resistance increases as a consequence of charge dissipation.

Unipolar negative voltage pulses were applied from -1V to -5V, however only above 3V amplitude hysteretic I-V curve is visible, Figure 2 (inset). The relation between $R_{\text{OFF}}$ and $R_{\text{ON}}$ state, decreases as the voltage amplitude decrease, which is the resulted of less attracted carriers included in the current flow. Considering that BaTiO$_3$ acts as n-type of semiconductor, at room temperature [5] it is expected that main accumulated charge carriers included in the transport are electrons.

Figure 2. The current-voltage characteristics of Au/BaTiO$_3$/Ag printed memristor

Specific conductivity of the Au/BaTiO$_3$/Ag sample was measured in temperature range from 300K-400K, results are shown in Figure 3. Results are in accordance with typical semiconductor behavior described with Arrhenius relation $\sigma_{\text{DC}}(T) = \sigma_0 \exp (-\Delta E/kT)$, where $\Delta E$ is activation energy, $k$-Boltzmann’s constant, $T$-absolute temperature and $\sigma_0$ pre-exponential factor [Ω cm]$^{-1}$. According to measured results and fitted curve, activation energy is estimated $\Delta E = 0.25$ eV, corresponding to previously obtained value for BaTiO$_3$ thin films [6] . Activation energy indicates that film has shallow traps near conduction band edge, which could origin from the vacancies introduced during high temperature treatment or impurities [6].

Further electrical analysis was performed by means of impedance spectroscopy (Impedance Analyzer HP4194A), resulting in Cole-Cole diagram shown in Figure 4a, for frequency range from 100 Hz- 40 MHz.

Figure 3. Temperature dependence of DC conductivity for BaTiO$_3$ memristive device

Figure 4. Cole-Cole diagram (a) and Zimag=f(frequency) (b)
As it is known from the literature [7], the semicircular in the Cole-Cole diagram formed from resistance and capacitance of the grain boundaries are much larger to then the resistance and capacitance of the bulk grains. Accordingly, dominant middle-frequency semicircular, Figure 4a, corresponds to grain boundaries contribution to the total conductivity of the BaTiO$_3$ sample.

Grain resistivity can be estimated according to graphical impedance spectroscopy analysis approach proposed in [8], as $R_\infty \approx 35 \ \Omega$, which is equal to the dislocation of the semicircle from the origin, while parallel resistance and capacitance of the grain boundary arc is estimated to $R_{GB} \approx 110 \ \Omega$ and $C_{GB} \approx 1 \text{nF}$, respectively. Maximum frequency of the complete semicircular is evident in Figure 4b, is $\omega \approx 1.53 \text{ MHz}$. Accordingly grain boundary relaxation time amounts $\tau \approx \frac{1}{\omega} = R_{GB}C_{GB} = 1.0 \times 10^{-7} \text{s}$.

Additionally, we performed Hall effect measurement (HMS 3000) of one layer BaTiO$_3$ film deposited on Si wafer substrate connected in four points with the sample holder. Measurement results showed negative Hall coefficient $R_H = -5.91 \times 10^3 \ [\text{cm}^3/\text{C}]$, which confirms n-type conductivity of the sample, bulk concentration $N_b = 1.05 \times 10^{15} \ [1/\text{cm}^3]$ and mobility $\mu_n = 0.1 \times 10^{-2} \ [\text{cm}^2/\text{Vs}]$ in good agreement with results from literature [6].

4. Conclusion

In this paper we originally presented Au/BaTiO$_3$/Ag thin film memristor fabricated using ink-jet printing deposition technique. Current-voltage characteristics is in the form of pinched hysteresis, for both bipolar and unipolar impulse. Ratio of $R_{OFF}/R_{ON}$ state could be improved by increasing the contribution of ferroelectric phase in the BaTiO$_3$. High temperature DC conductivity measurement, revealed typical semiconductor behavior, with 0.25 eV shallow trap near the conductive band gap, probably due to introduced vacancies upon high-temperature treatment. Transport parameter measurement, proved that the sample is n-type semiconductor, thus electrons present the main charge carriers. Impedance spectroscopy graphical analysis revealed separate influence of the grain and grain boundaries in the overall conduction.

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