Leakage current conduction in IrO$_2$/PZT/Pt structures

E Bouyssou$^{1,2}$, P Leduc$^{2}$, G Guégan$^{2}$ and R Jérisian$^{1}$

$^1$Université de Tours, Laboratoire de Microélectronique de Puissance (LMP), 16 rue Pierre et Marie Curie, 37071 Tours, France
$^2$STMicroelectronics, 16 rue Pierre et Marie Curie, 37071 Tours, France

E-mail : emilien.bouyssou@st.com

Abstract: Over the last few years, thin films of PbZr$_x$Ti$_{1-x}$O$_3$ (PZT) have been the focus of extensive researches for high-k capacitor applications. However, we believe that the reliability properties and the degradation mechanisms of PZT capacitors need to be better understood. A good way to learn about failure mechanisms is to investigate the characteristics of leakage current conduction. In this paper we propose a model for current density evolution of IrO$_2$/PZT/Pt structures as a function of time, voltage and temperature. The voltage and temperature evolution of leakage current is interpreted as an interface controlled thermoionic injection of carriers over a potential barrier at the cathode/PZT contact. The time evolution of the leakage current is mainly characterized by the resistance degradation phenomenon which results in a large increase in current density. A quantitative analytical model based on the redistribution of oxygen vacancies near the cathode interface has already been developed to account for this effect [1]. We propose a more complete model that also includes the role of oxygen vacancies on dielectric relaxation and trapping phenomena. The contributions of Pt and IrO$_2$ electrodes on leakage current evolution are also discussed.

1. Introduction
Over the last few years, ferroelectric materials such as PbZr$_x$Ti$_{1-x}$O$_3$ (PZT) have been the focus of extensive researches for both memory devices (DRAM) and decoupling capacitors applications. These devices require extremely low failure rates at operating electrical fields and long operating life. A characterization of the leakage and degradation mechanisms is therefore very important. We believe that a good approach to gain insights into the failure mechanisms of these structures is to investigate deeply their leakage current conduction properties. Hence, the first purpose of this paper is to provide a qualitative and quantitative behavioral model for the current density evolution of our IrO$_2$/PZT/Pt structures as a function of time, voltage and temperature. The impact of oxygen vacancies migration and the effect of Pt and IrO$_2$ electrodes on leakage current are discussed.

2. Experimental
PZT thin films with Zr/Ti ratio of 52/48 were prepared by spin-on sol gel processing on Pt/Ti coated SiO$_2$/Si substrates. After each spin, films were fired at 350°C for 5 minutes in air and then processed by rapid thermal annealing (RTA) at 700°C for 1 minute in air. The final multi-layered PZT film thickness is around 250 nm. IrO$_2$ top electrodes were sputter deposited. The top electrode contacts have an area of 2.5×10$^4$ µm$^2$. 
The DC electrical current was measured using a Keithley 236 Source Measure Unit. The polarity of the applied voltage is referenced to the top IrO2 electrode, the bottom Pt electrode being grounded. A new capacitor was used for each measurement.

3. Results and model for conduction mechanisms in IrO2/PZT/Pt structures
Figure 1 shows a typical current vs. time behavior of PZT capacitors under a constant electric field. The data reported here correspond to a 5 V dc stress applied during 2000 seconds at 125°C. Three main regions can be distinguished on such a curve: dielectric relaxation (A), resistance degradation (B) and current decrease (C). Figure 2 shows the time evolution of leakage current for temperatures ranging from 25 to 240°C.

![Figure 1](image1.png)

**Figure 1.** Electrical current density as a function of time under a constant voltage of 5V at 125°C, together with the simulated curves for true leakage current and dielectric relaxation.

![Figure 2](image2.png)

**Figure 2.** Electrical current density as a function of time under a constant voltage of 5V for temperatures ranging from 25 to 240°C. The positive bias is applied to the top IrO2 electrode.

3.1. Dielectric relaxation
The initial time period is characterized by a decrease in current due to the dielectric relaxation. The dielectric relaxation follows a Curie Von-Schweidler law:

\[ J = J_{true} + J_0 \times t^{-n} \]  

(1)

The relaxation mechanism is clearly visible on figure 2 for temperatures below 125°C. The relaxation slope \( n \) appears to be temperature independent (\( n = 0.55 \)) whereas the \( J_0 \) term is thermally activated. The Arrhenius plot of figure 3 reveals an activation energy for \( J_0 \) close to 0.3 eV.

Many possible explanations of dielectric relaxation process are available in the literature. Chen *et al.* states that the relaxation may be attributed either to electrical charge hopping or to a Maxwell-Wagner polarization with a wide distribution of relaxation times [2]. In reference [3], the relaxation is attributed to charge entrapment. Oxygen vacancies as well as Ti^{4+} ions are considered as possible trapping sites. Also considering the energy levels of defects in the band gap of PZT established by Miller and Glower [4], we considered that the electrons associated with oxygen vacancies are effectively the best candidates to account for the relaxation current. Indeed, these defect levels are reported to be located at 0.22 to 0.28 eV beneath the conduction band, which is quite close to the activation energy of 0.3 eV extracted from figure 3.

![Figure 3](image3.png)

**Figure 3.** Arrhenius plot of the initial relaxation current value \( J_0 \). The slope of the curve gives an activation energy for the relaxation process of 0.3 eV.
3.2. True leakage current

As can be seen on figure 1, the time evolution of leakage current can be described as a superposition of the relaxation component $J_0 \times t^{-n}$ and the “true” leakage current $J_{true}$ [5,6], which becomes predominant after a certain duration. Reaching the true leakage current values is of major importance to correctly analyze the conduction mechanisms.

PZT materials can exhibit different types of conduction behavior depending on physical parameters such as film microstructure, thickness, doping level and electrode materials, so that different processes of elaboration can lead to very different electrical properties. Furthermore, the time dependency of the current density makes it difficult to obtain I-V curves representative of the true leakage current. As a consequence, numerous physical models have been proposed to describe the leakage current behavior in PZT films: interface-controlled mechanisms (Schottky emission [2,5,7], tunnel emission [7]) as well as bulk controlled mechanisms (Space Charge Limited Conduction [8], Pool-Frenkel emission [9]) are reported.

Among such a variety of results, the model that seems to be the most adapted to describe the conduction mechanisms for our samples is a thermoionic injection of negative carriers (electrons) through the cathode/PZT contact, as described by equation (2):

$$J_{min} = AT^2 \exp(\frac{-\Phi}{kT})$$  \hspace{1cm} (2)

$A$ and $k$ are the Richardson and Boltzmann constants, $T$ is the temperature, $\Phi$ is the effective barrier for electron injection: $\Phi = \Phi_h + A\Phi_h$ where $\Phi_h$ is the energy barrier between the conduction band of PZT and the Fermi level of the cathode and $A\Phi_h = -\frac{e^2(E-E_b)}{4\pi\varepsilon_0\varepsilon_h}1/2$ is the barrier lowering due to the Schottky effect [5]. $E$ is the applied electrical field, $E_b$ is the built-in electrical field resulting from the presence of space charge in the film, $\varepsilon_h$ is the relative dielectric constant at optical frequencies and $\varepsilon_0$ the dielectric permittivity of vacuum.

3.3. Resistance degradation

As can be observed on figures 1 and 2, the true leakage current increases until a maximum value $J_{max}$ is reached. Such a process is referred as “resistance degradation”. Based on a comprehensive study of strontium titanate by Waser et al. [10], it is often suggested that oxygen vacancies play an important role in the resistance degradation of thin polycrystalline PZT films. Oxygen vacancies are present in significant concentrations in alkaline-earth titanates. They are positively charged with respect to the regular lattice and, thus, in a dc electrical field they migrate toward the cathode. The redistribution of the oxygen vacancies near the interfaces alters the shape of the barrier for carrier injection, making it easier to overcome [9]. In other words, the increase in current density with time can be attributed to a decrease in the effective barrier height $\Phi$ at the cathode. A quantitative analytical model for resistance degradat ion has already been reported in reference [1]. In such a model, the barrier lowering is assumed to have a stretched exponential dependence on time, as described by equation 3.

$$\delta \Phi_1(t) = \delta \Phi_{max1} \{1-\exp\left[-\left(\frac{t}{r_1}\right)^{\beta_1}\right]\}$$  \hspace{1cm} (3)

$\delta \Phi_{max1}$ is the maximum decrease in $\Phi$, $\beta_1$ is a constant that determines the shape of the stretched exponential, and $r_1$ is the characteristic time of the phenomenon. The extraction of parameters from the i(t) curves of figure 2 leads to an activation energy for $r_1$ close to 0.95 eV. This result is in good agreement with the values reported elsewhere for oxygen vacancies diffusion in perovskyte materials [1,10].

3.4. Current decrease

At the end of the resistance degradation process, the current density reaches a maximum value and begins to diminish. We interpret this current decrease as a neutralization of a certain proportion of oxygen vacancies accumulated near the cathode. The consequence of this neutralization is a
decrease in the space charge density at the cathode interface and hence an increase in the barrier height for electron injection. The resulting barrier evolution can be described by equation (4):

$$
\delta \Phi_2(t) = \delta \Phi_{\text{max}2} \{1 - \exp\left[-\left(\frac{t}{\tau_2}\right)^2\right]\}
$$

(4)

$\delta \Phi_{\text{max}2}$ is the maximum increase in $\Phi$ after the end of the resistance degradation process, $\beta_2$ is a constant, and $\tau_2$ is the characteristic time of the phenomenon.

### 3.5. Polarity dependence

Implementing the barrier height evolution $\delta \Phi_1(t)$ and $\delta \Phi_2(t)$, as well as the relaxation term $J_0 \times t^n$ in equation (1), the temperature and time dependency of leakage current becomes:

$$
J(t) = J_0 \times t^n + AT^2 \exp\left(-\frac{\Phi_{\text{ini}} - \delta \Phi_1(t) + \delta \Phi_2(t)}{kT}\right)
$$

(5)

$\Phi_{\text{ini}}$ is the effective barrier for electron injection at $t = 0$ seconds; $\delta \Phi_1(t)$ and $\delta \Phi_2(t)$ are given by equation (4) and (5) respectively.

The maximum barrier lowering $\delta \Phi_{\text{max}1}$ is a key parameter of the resistance degradation process. This parameter enables to quantify the effect of oxygen vacancies accumulation near the cathode interface. When a positive voltage is applied with respect to the top electrode, the carriers are injected through the Pt/PZT contact, whereas for a negative bias applied to the top electrode, carriers are injected through the IrO$_2$/PZT contact. In agreement to reference [1], the analyses of $i(t)$ curves obtained from 25 to 240°C in the two polarities leads to a value for $\delta \Phi_{\text{max}1}$ that is quasi-independent of temperature. Besides, $\delta \Phi_{\text{max}1}$ turns out to be much larger when the positive bias is applied to the Pt electrode ($\delta \Phi_{\text{max}1+} = 0.3$ eV) than to the IrO$_2$ ($\delta \Phi_{\text{max}1-} = 0.1$ eV). Hence the impact of oxygen vacancies migration is much less significant when the IrO$_2$/PZT interface is the injecting contact. This result could be related to the observed improvements of ferroelectric fatigue for PZT structures associated to conductive oxide electrodes in replacement of platinum electrodes [5].

### 4. Conclusion

The leakage current conduction in our IrO$_2$/PZT/Pt structures is found to be controlled by the energetic barrier height at the cathode interface. During the application of a prolonged DC stress, the redistribution of oxygen vacancies induces an alteration of energetic contacts at the interfaces. However, the modification of the IrO$_2$/PZT contact induced by the oxygen vacancies accumulation appears to be quite small compared to the Pt/PZT interface behavior. Conductive oxide electrodes have already been introduced for memory device structures because of their improvements on fatigue properties. Further studies are necessary to figure out if these materials could be also of any interest to enhance the time dependent dielectric breakdown characteristics of PZT capacitors.

### 5. References

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