Transient Current Study on Pt/TiO$_{2-x}$/Pt Capacitor

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1. Introduction

In recent years, various switch phenomena have been reported in TiO$_2$-based devices, such as resistance switch and rectification polarity switch of a capacitor-like structure composed of the TiO$_2$ film sandwiched between two electrodes (metal/TiO$_2$/metal) [1-5], and field-programmable rectification in rutile TiO$_2$ crystal [6] etc. Most authors suggested that the driving mechanisms of the switch phenomena closely relate to drift of oxygen vacancy (V_O) under an applied electric field. Until now, few experimental evidences of V_O motion have been reported, such as motion of color center due to applying voltage in rutile crystal [7, 8]. As an effect method, transient analysis has been often used to estimate the mobility of V_O [9-11], which is very important to switch characteristic. A peak was always reported in the current density versus time curve. The peak position depends on the applied voltage and temperature, which has been explained by several models such as the space-charge-limited current (SCLC) theory [12], and change of electron and hole conduction due to V_O redistribution under dc field [13].

In this work, we investigate current density as a function of time at various applied voltage and temperature in TiO$_{2-x}$ capacitors with platinum electrodes. From the transient analysis, origin of the peak in current-time curve is studied, and the thermal activation energy of it has been estimated. It should be noted that in the same device a rectifying polarity switch behavior has been also observed [4, 5].

2. Experiments

Current measurements were performed on the devices of Pt/TiO$_{2-x}$/Pt structure. The TiO$_{2-x}$ layer was fabricated by radio frequency (rf) sputtering. The preparation details have been reported elsewhere [5]. The dc current response as a function of time at various voltages and temperature was acquired with a Keithley 4200 semiconductor parameter analyzer. The voltage pulse and the corresponding time were monitored by Agilent 6000 oscilloscope (OSC), which was connected in series with the Pt/TiO$_{2-x}$/Pt capacitor. Current measurements were carried out by applying negative voltage to the top electrode. A fresh capacitor Pt/TiO$_{2-x}$/Pt was used for each pulse voltage and temperature measurement.

3. Results and discussion

Figure 1 shows the typical current-time characteristics of the Pt/TiO$_{2-x}$/Pt devices measured at 150 $^{\circ}$C at varying applied voltage. Firstly, the current density increases with time and reaches its maximum value at time τ. And then,
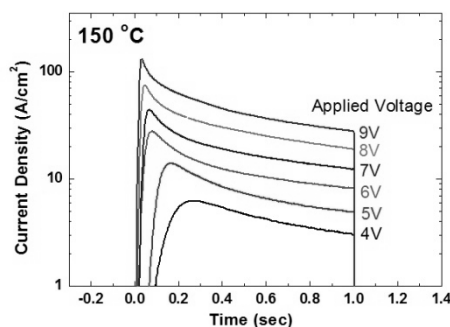

Fig. 1 Dependence of current density on time at 150 $^{\circ}$C for varying applied voltage of Pt/TiO$_{2-x}$/Pt.

current density decreases with time. It should be noted that at temperature which is lower than 100 $^{\circ}$C, the current peak is very broad, and τ could not be accurately decided. Therefore, considering the limit temperature of our equipment, we chose temperatures from 100 $^{\circ}$C to 175 $^{\circ}$C for measurement. And the holding time for applied voltage is 1 second.

Similar current-time characteristic has been reported in titanate perovskites, such as (Ba$_x$Sr$_{1-x}$)TiO$_3$ (BST) and SrTiO$_3$ (ST). So far, peak in the current versus time curve has been always explained by SCLC theory [12], where the movement of the charged oxygen vacancies contributed to the current directly, or electron/hole conductivity change due to the oxygen vacancy redistribution under dc field [13, 14].

According to typical SCLC theory, the peak position (τ) relates to the drift mobility (μ) of the injected charge such as V_O, which is shown in the following equation [15]:

$$\tau = \frac{0.78d^2}{\mu V} \qquad (1)$$

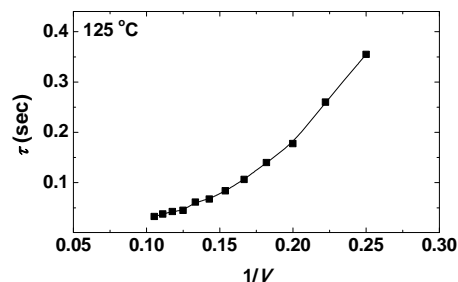where d is the thickness of the TiO$_{2-x}$ film and V is the applied voltage.

Fig.2 Dependence of τ on 1/V at 125 $^{\circ}$C.

Regarding the reports on BST [9, 11], it is expected that a linear relation could be found between τ and $1/V$, which is differ from our result, as shown in Fig. 2. Alternatively, Wang *et al.* [10] reported a relationship of $\tau \propto d^{n_2}/(\mu V^{n_1})$, therefore, it could be changed into $\ln \tau \propto n_1 \ln(1/V) + n_2 \ln d + \ln(1/\mu)$. Figure 3 shows the dependence of $\ln \tau$ on $1/V$. The values of n_1 are estimated to be 3.18, 2.78, and 2.54 respectively for 100, 125, and 175 $^{\circ}$C, which is reasonable compared to the reported results by Waser and Wang *et al.* [10, 13]. They have attributed the transient current peak to the effect of oxygen redistribution on the electron and hole conduction due to dc field.
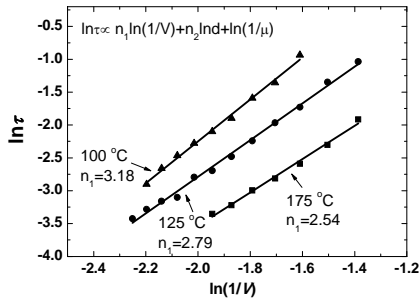

Fig.3 The dependence of $\ln \tau$ on $\ln(1/V)$ at 100, 125 and 175 $^{\circ}$C

Moreover, τ decreases with an increase of temperature, indicating that origin mechanism of the current peak is a thermal activated process. Therefore, activation energy was determined using Arrhenius equation as following [16]:

$$\tau/T = A \exp(E_o/kT) \qquad (3)$$

where A is a preexponential constant, E_0 is activation energy, k is Boltzmann's constant, and T is measurement temperature.
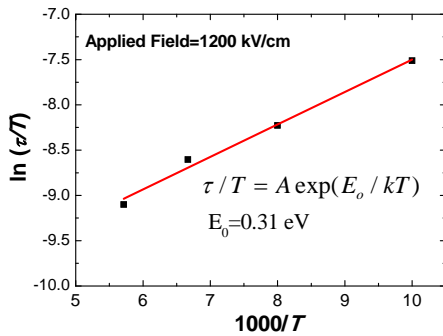

Fig.4 Dependence of $\ln(\tau/T)$ on $1000/T$ at applied field of 1200 kV/cm

Figure 4 shows the dependence of $\ln(\tau/T)$ on $1000/T$ at an applied field of 1200 kV/cm. The activation energy is estimated from the slope given by the linear fit of the experimental data. Using the same method, values of E_0 at various electric fields were estimated, which ranges from 0.18 eV (@1200 kV/cm) to 0.34 eV (@1000 kV/cm). It is much lower than the value of $E_0 \sim 1.0$ eV, which relates to V_O migration in SCLC theory [9-11].

Moreover, Boschloo *et al.*[17] has reported a thermally activated process with activation energies in the range of

0.10-0.15 eV in TiO_2 solar cells, which is contributed to electron transport, such as migration of the electron localized at donor level with E_0=0.1-0.3 eV [18, 19]. DAS *et al.* estimated activation energy (0.07-0.24 eV) of conduction in sintered TiO_2 [20].

Due to the low value of E_0 and disagreement between experimental result and Equ. (1), it suggests that the current peak in the Pt/TiO$_{2-x}$/Pt capacitor could not be explained by typical SCLC theory. Moreover, considering the value of τ (0.01- 1 sec), the observed transient current behavior is proposed to relate to the charge transport process controlled by low mobility carriers such as oxygen ions and trapped electrons, and further study is required.

4. Conclusions

The current-time characteristic has been studied in the Pt/TiO$_{2-x}$/Pt capacitor. A peak has been observed in current versus time curve. The peak position (τ) exhibits a dependence on measurement temperature and applied voltage. The activation energy is estimated to 0.18-0.34 eV. After critical analysis, the origin of this characteristic is attributed to the charge transport process controlled by low mobility carriers.

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