Effects of Gamma Ray Irradiation on the Conduction Mechanisms of RF-Sputtered Stacked Ta$_2$O$_5$/TiO$_2$ Films

Jian-Feng Li (李建鋒)$^a$, Guan-Ting Chen (陳冠廷)$^a$, Shih-Fang Chen (陳士芳)$^b$, Ching-Wu Wang (王欽戊)$^a$, and Wen-Kuan Lin (林文寬)$^a$

$^a$: Electronic Engineering Department, I-Shou University
$^b$: Electrical Engineering Department, I-Shou University

ABSTRACT

The microstructural and electrical conduction properties of pre-irradiated and $\gamma$-ray-irradiated sputtered Ta$_2$O$_5$/TiO$_2$ films were systematically investigated. Analytical results revealed that the crystallinity and the leakage current of the pre-irradiated sample were effectively improved by raising the irradiation dose at low doses of irradiation [1M~4M rad(Ta$_2$O$_5$/TiO$_2$)]; however, $\gamma$-ray irradiation of 12M rad(Ta$_2$O$_5$/TiO$_2$) undesirably deteriorated the film crystallinity, yielding a larger leakage current. Such a result leads to the Frenkel-Poole conduction (pre-irradiated sample) transformed to Schottky emission conduction process [1M~8M rad(Ta$_2$O$_5$/TiO$_2$) of $\gamma$-ray-irradiated samples] and then, gradually transformed to the Frenkel-Poole conduction [12M rad(Ta$_2$O$_5$/TiO$_2$) of $\gamma$-ray-irradiated samples] again. We suggested that the electrode-limited Schottky emission conduction effect occurring in the 1M~8M rad(Ta$_2$O$_5$/TiO$_2$) of $\gamma$-ray-irradiated samples due to the repair of oxygen deficiency and the superior was crystallinity of the Ta$_2$O$_5$/TiO$_2$ films caused by the low doses of $\gamma$-ray irradiation.
INTRODUCTION

High quality dielectric thin films that have high dielectric constant, high breakdown field strength, and low leakage current density are used for many semiconductor devices. As DRAM density increased to 1Gbit and beyond, the use of Ta$_2$O$_5$ is expected to be limited to only one generation of DRAM, because its scaling limit is about 2.5 nm. However, it is not adequate because its low permittivity. Besides, the TiO$_2$ has a high permittivity, but the leakage current is high due to its columnar structure. For this reason, in order to take advantage of low leakage current of Ta$_2$O$_5$ and high permittivity of TiO$_2$, the dielectric thin films stacked with TiO$_2$ and Ta$_2$O$_5$ are being investigated. Some researchers have tried to use Ta$_2$O$_5$ and TiO$_2$ as the base constituents in composite or multilayer thin film to meet to the purpose of the low deposition temperature, higher permittivity and leakage current reduction [1]-[2]. By growth of ultra-thin layer to prevent the formation of interfacial layer and to further obtain a low leakage current as well as a high dielectric robustness has also been reported [3]-[4].

On the other hand, the stacked Ta$_2$O$_5$/TiO$_2$ thin films may play an important part in memory devices such as metal-oxide-semiconductor (MOS). Therefore, it is important to study the various conduction mechanism of leakage current in Ta$_2$O$_5$/TiO$_2$ films in order to improve the electrical and dielectric properties. Additionally, since memory devices can be employed in hostile environment such as nuclear or space environment, the effect of radiation on the conduction behavior of Ta$_2$O$_5$/TiO$_2$ thin film as an insulator is important to study. When memory devices are exposed to radiation, the radiation effects may influence the modulation and/or degradation in device characteristics and its operating life. Nonetheless, no clear mention has been made about the electrical property of $\gamma$-ray irradiation Ta$_2$O$_5$/TiO$_2$ thin films.

In this study, we will investigate the effects of $\gamma$-ray irradiation on the conduction mechanism of rf-sputtered stacked Ta$_2$O$_5$/TiO$_2$ thin films. Moreover, the electrical
properties of Ta2O5/TiO2 thin film in relation to the dose of γ-ray irradiation by analyzed compositional and microstructure characterization are discussed.

EXPERIMENTAL

In the beginning, Ta2O5/TiO2 thin films were deposited at room temperature by a radio-frequency (RF) sputtering method using Ta2O5 and TiO2 targets with 99.999% purity. The substrate used was a boron-doped 0.01 Ω·cm P-type (111)-oriented silicon wafer. A thin TiO2 film (60 nm) was first deposited at 700°C and then, a Ta2O5 thin film (140 nm) was deposited on top of TiO2 film at 600°C. The total gas pressure of Ar-O2 mixture during TiO2 and Ta2O5 deposition was held at 5×10⁻³ torr. After deposition, the samples were annealed by rapid thermal annealing (RTA) at 700°C in O2 ambiance for 10 min. Subsequently, some annealed Ta2O5/TiO2 thin films were exposed to Co-60 γ-ray irradiation with various doses [1M~12M rad(Ta2O5/TiO2)] at a dose rate of 100 rad(Ta2O5/TiO2)/sec at around 50°C. It is noted that no any biased voltage was applied on the device during irradiation.

After irradiation, the crystallinity of Ta2O5 and TiO2 films was examined using x-ray diffraction (XRD) with a Cu-Kα radiation source. Compositional analyses of different doses of γ-ray-irradiated samples and their comparisons with pre-irradiated ones were carried out employing secondary ion mass spectrometry (SIMS). Next, electrical properties of the films were measured using Al/Ta2O5/TiO2/P⁺-type Si/Al capacitor structures. An Al film of 500 nm thick was deposited on the Ta2O5/TiO2 by evaporation and patterned by standard photolithography processes to form a top electrode. The bottom electrode was formed by depositing Al on the backside of the silicon substrate. The Ta2O5/TiO2 capacitors were electrically characterized using a computer-controlled HP4156A precision semiconductor parameter analyzer for current-voltage (I-V) measurement and an HP4194A impedance-gain phase analyzer for capacitance-voltage (C-V) measurement at 100 kHz with a 10-mV ac sweeping signal. The relative dielectric constants of Ta2O5 and TiO2 were calculated to be around 20.5~24.6 and 28.4~36.7, respectively. Moreover, the relative dielectric constant (εr) of stacked Ta2O5/TiO2 was measured to be 25.3~28.1 for all pre-irradiated and γ-ray-irradiated samples using the relationship C_{OX}=εrε0S/T_{OX}, where ε0,
S, and $C_{OX}$ were the permittivity of vacuum, the area of the Al electrode, and the capacitance of oxides in the MOS capacitor. It is noted that the $C_{OX}$ values were given as the maximum capacitance for all C-V characteristics.

**Result and Discussion**

Typical I-V characteristics in MOS capacitors with Ta$_2$O$_5$/TiO$_2$ thin films pre-irradiated and $\gamma$-ray irradiated at various doses are shown in Fig. 1, indicating that the leakage current density was strongly influenced by $\gamma$-ray irradiation. As illustrated in Fig. 1, for low doses of $\gamma$-ray irradiation [1M-4M rad (Ta$_2$O$_5$/TiO$_2$)], the leakage current density was observed to decrease with the increasing doses and reached a minimum level for samples treated by 4M rad (Ta$_2$O$_5$/TiO$_2$) of $\gamma$-ray irradiation. Conversely, for higher doses of irradiation [>4M rad(Ta$_2$O$_5$)], the leakage current density increased with increasing irradiation dose.

The two main conduction mechanisms, Schottky emission (SE) and Frenkel-Poole (FP) effect, were invoked to explain the current transport in Ta$_2$O$_5$/TiO$_2$ thin films. The former is a process occurring across the interface between a metal and an insulating film as a result of barrier lowering due to the applied field and the image force. The latter is associated with the field enhanced thermal excitation of charge carriers from traps. The current ($I_{SE}$) governed by the SE mechanism is described as follows [5]:

$$I_{SE} = AT^2\exp[-q(\phi_b - \sqrt{qV/4\pi\varepsilon_1d})/KT]$$  \hspace{1cm} (1)

where $A$ denotes a constant, $\phi_b$ the Schottky barrier height, $\varepsilon_i(=\varepsilon_r\varepsilon_0$) the dielectric constant of the insulator, $V$ the external applied voltage, and $d$ is the insulator thickness. The barrier height, $\phi_b$, depends on many parameters, e.g., the work function of the metal, barrier lowering by image force, and surface states. The SE mechanism can be modified to the FP mechanism if the conduction is governed by carriers that are thermally emitted from trapped centers under a strong electric field, which is known to occur in large band gap insulators such as Si$_3$N$_4$ thin films. The current ($I_{FP}$) dominated by the FP effect can be expressed as [6]:

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\[ I_{FP} = BV \exp[-q(\phi - \sqrt{qV/\pi \varepsilon \varepsilon_0 d})/KT] \]  \hspace{1cm} (2)

where B represents a constant and \( \phi \) the trapped level. Although these two transport mechanisms are very similar, they can be distinguished from the measured slope obtained from the straight line region of the I-V curve in the form of \( \ln(J) \) vs. \( E^{1/2} \) plot (Schottky emission) and \( \ln(J/E) \) vs. \( E^{1/2} \) plot (Frenkel-Poole effect). The slope can also be calculated using the static dielectric constant measured from an independent C-V measurement at 100 kHz. By comparing the slopes determined from Eqs. (1) and (2) with static dielectric constant and with the slope measured from I-V characteristics, the mechanism can be determined in principle [7].

In order to determine the dominant leakage current mechanism in Ta\(_2\)O\(_5\) and TiO\(_2\) layers of pre-irradiated and irradiated Ta\(_2\)O\(_5\)/TiO\(_2\) thin films, respectively, Figs. 2(a) and 2(b) illustrate the electrical measurement results in terms of \( \ln(J/E) \) vs. \( E^{1/2} \) (Frenkel-Poole plot). Here, the electric field is calculated by Ta\(_2\)O\(_5\) equivalent field (\( \varepsilon_r = 20.5-24.6 \)) and by TiO\(_2\) equivalent field (\( \varepsilon_r = 28.4-36.7 \)) for Frenkel-Poole plot as shown in Figs. 2(a) and 2(b), respectively. The evidence showed that these Ta\(_2\)O\(_5\)/TiO\(_2\) films with different irradiation treatment behaved in significantly different conduction processes. As shown in Figs. 2(a) and 2(b), both Ta\(_2\)O\(_5\) and TiO\(_2\) equivalent field clearly followed a linear relationship in the \( \ln(J/E) \) vs. \( E^{1/2} \) (FP mechanism) plot in pre-irradiated and 12M rad(Ta\(_2\)O\(_5\)/TiO\(_2\))-irradiated films. The relative dielectric constants calculated from the extraction of slopes by Ta\(_2\)O\(_5\) and TiO\(_2\) equivalent field for these two samples were closely approaching to the values (20.5-24.6) and (28.4-36.7), respectively, which were obtained directly from the C-V measurement. However, the observed random distribution model of relative dielectric constants calculated from the slopes by linear regression for 1M, 4M, and 8M rad(Ta\(_2\)O\(_5\)/TiO\(_2\))-irradiated Ta\(_2\)O\(_5\)/TiO\(_2\) films strongly indicated that for samples treated by 1M-8M rad(Ta\(_2\)O\(_5\)/TiO\(_2\)) irradiation, the FP conduction mechanism would not play the predominant role in determining the conduction mechanism. On the contrary, as shown in Figs. 3(a) and 3(b), the linear relationship in \( \ln(J) \) vs. \( E^{1/2} \) plot and the reasonable relative dielectric constants of Ta\(_2\)O\(_5\) and TiO\(_2\) in 1M, 4M, and 8M rad(Ta\(_2\)O\(_5\)/TiO\(_2\))-irradiated Ta\(_2\)O\(_5\)/TiO\(_2\) films, revealed that when samples treated with low doses of \( \gamma \)-ray evident Schottky emission conduction in both Ta\(_2\)O\(_5\) and TiO\(_2\) films were conducted.
In order to investigate the causes of the FP and SE leakage current conduction mechanisms which occurred in our samples, XRD measurements were first employed to examine the microstructure of Ta$_2$O$_5$/TiO$_2$ films. Fig. 4 reveals the variation of XRD spectra of Ta$_2$O$_5$/TiO$_2$ pre-irradiated and γ-ray-irradiated. It was observed that for low doses of γ-ray irradiation [1M–4M rad(Ta$_2$O$_5$/TiO$_2$)], the poly-crystallinity of pre-irradiated Ta$_2$O$_5$/TiO$_2$ films could be effectively improved by raising the irradiation dose up to 4M rad(Ta$_2$O$_5$/TiO$_2$). However, the crystallized structure was evidently altered when samples treated by higher doses of γ-ray irradiation. According to the XRD measurements, it is suggested that for low dose of γ-ray [1M–4M rad(Ta$_2$O$_5$/TiO$_2$)] irradiated Ta$_2$O$_5$/TiO$_2$ films, a superior crystallinity and fewer defects could exist in the material. Such a result implies that a more perfect metal-insulator interface could be formed, resulting in a major Schottky emission conduction process although the minor role of Frenkel-Poole conduction process is also simultaneously existent. On the contrary, the bulk-limited Frenkel-Poole conduction process was suggested to predominantly occur in the insulator possessing considerable amount of traps due to inferior crystallinity, which happened in the pre-irradiated and 12M rad(Ta$_2$O$_5$/TiO$_2$)-irradiated samples.

It has been suggested that a chain of defects due to broken bonds in the oxides could form a filamentary conductive path between the cathode and the anode, causing an excessive leakage current [8]. In order to determine the origins of the different leakage current conduction mechanisms, we took a further investigation on defect status for all tested films. Fig. 5 shows the oxygen SIMS depth profiles for samples treated by different doses of γ-ray irradiation. Obviously, at low doses of γ-ray irradiation [1M–4M rad(Ta$_2$O$_5$/TiO$_2$)], the more doses of γ-ray, the more energy-transfer benefits the Ta$_2$O$_5$/TiO$_2$ film to proceed partial recrystallization. Thus, the crystallinity of Ta$_2$O$_5$/TiO$_2$ becomes better (as shown in Fig. 4) and fewer defects could exist owing to the repair of the oxygen deficiency. In this situation, a superior Ta$_2$O$_5$/TiO$_2$ film creating a more perfect metal/oxides contact can be expected and result in SE conduction [1M, 4M, and 8M rad(Ta$_2$O$_5$/TiO$_2$)-irradiated samples as shown in Figs 3(a) and (b)]. However, under 12M rad(Ta$_2$O$_5$/TiO$_2$) γ-ray irradiation, besides some parts of energy-transfer from irradiation promoting the film recrystallization, undesirably excessive irradiation energy takes on the destructive role deteriorating the crystallinity of Ta$_2$O$_5$/TiO$_2$ film and yielding a
considerable oxygen vacancy, thus creating the donor defect states, that result in a FP conduction process. The donor trap states created by oxygen vacancy resulting in a FP conduction behavior and undesirable leakage current have also been reported [9]-[10]. In this work, we strongly suggested that different doses of γ-ray irradiation on Ta₂O₅/TiO₂ thin films could affect the concentration variation of oxygen, which not only change the film crystallinity, but also determine the dominant conduction mechanism in Ta₂O₅/TiO₂ films.

CONCLUSIONS

The γ-ray irradiation effects on the conduction mechanism and crystallinity characteristics of sputtered Ta₂O₅/TiO₂ films were systematically studied. Evidence showed that the electrode-limited SE conduction effect dominantly occurring in the 1M, 4M, and 8M rad(Ta₂O₅/TiO₂)-irradiated samples was deduced to be due to the repair of oxygen deficiency and the superior crystallinity of the Ta₂O₅/TiO₂ films. Contrarily, the major mechanism of bulk-limited FP conduction happened in the pre-irradiated and 12M rad(Ta₂O₅/TiO₂)-irradiated samples was suggested to be due to the deteriorated crystallinity and considerable oxygen vacancy in the Ta₂O₅/TiO₂ films.

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Fig. 1. Leakage current density for Ta$_2$O$_5$/TiO$_2$ films pre-irradiated and exposed to various doses of $\gamma$-ray irradiation, as a function of the effective oxide electric field ($E_{\text{eff}}$) at room temperature. The $E_{\text{eff}}$ is defined by $E_{\text{eff}} = V_g/T_{\text{eff}}$, where $T_{\text{eff}}$ is the equivalent Ta$_2$O$_5$/TiO$_2$ thickness and the $V_g$ is the voltage applied on the gate of Ta$_2$O$_5$/TiO$_2$ capacitor.
Fig. 2. The Frenkel-Poole plots ($\ln(J/E)$ vs $E^{1/2}$): (a) by Ta$_2$O$_5$ equivalent field and, (b) by TiO$_2$ equivalent field for pre-irradiated Ta$_2$O$_5$/TiO$_2$ thin film and samples treated by different doses of $\gamma$-ray irradiation.
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Fig. 3. The Schottky emission plots ((ln(J) vs $E^{1/2}$): (a) by Ta₂O₅ equivalent field, and (b) by TiO₂ equivalent field for pre-irradiated Ta₂O₅/TiO₂ thin film and samples treated by different doses of $\gamma$-ray irradiation.
Fig. 4. Typical x-ray diffraction patterns of pre-irradiated Ta$_2$O$_5$/TiO$_2$ thin film and samples treated by different doses of γ-ray irradiation.
Fig. 5. O SIMS depth profiles of pre-irradiated Ta$_2$O$_5$/TiO$_2$ thin film and samples treated by different doses of γ-ray irradiation.