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A New Mechanism of Symmetry of Current-Voltage Characteristics for High-k Dielectric Capacitor Structures

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Historically, there has been a controversy regarding whether the leakage current versus voltage (I-V) relationship is governed by the Schottky mechanism or by the Poole-Frenkel (P-F) mechanism for several decades. For the P-F mechanism, the I-V characteristics is expected to be symmetrical. In this paper, the author points out that there is an extra mechanism for symmetrical I-V characteristics.

Introduction

There is a controversy regarding whether the leakage current versus voltage (I-V) relationship for a thin film capacitor structure is governed by the Schottky mechanism or by the Poole-Frenkel (P-F) mechanism for several decades. The P-F effect arises from the defect states in the bulk of the insulating film and the I-V characteristics due to the P-F effect is expected to be symmetrical. However, the I-V characteristics of practical capacitor structures involving high-k dielectric materials is quite frequently asymmetrical and the Schottky mechanism is required to explain the polarity dependence of the I-V characteristics. For some applications, the symmetry of the I-V characteristics is important as pointed out by Hirai et al (1).

The author believes that quite frequently the P-F and the Schottky mechanisms happen simultaneously and so a unified Schottky-Poole-Frenkel model, as shown in Fig. 1, is quite frequently needed to explain experimental results (2). In Fig. 1, the nonlinear resistance RNL represents the P-F mechanism and the I-V characteristics of RNL is independent of bias voltage polarity. The I-V characteristics of the Schottky diodes D1 and D2 in the proposed model shown in Fig. 1 is not symmetrical but instead it has a highly conductive “forward” I-V characteristics and a much less conductive “reverse” characteristics. Part of the reverse I-V characteristics for relatively large bias voltage can be represented by the Schottky mechanism.

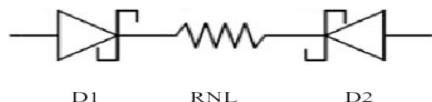

Fig. 1 A capacitor structure involving a high-k dielectric can be thought as two back-to-back Schottky diodes D1 and D2 with a non-linear resistor RNL in between.

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Mechanism A Symmetry

Let us represent an MIM (metal-insulator-metal) involving two different metals by an M_1IM_2 capacitor structure. For an M_1IM_2 capacitor, the I-V characteristics is expected to be symmetrical when the P-F effect dominates over the Schottky effect; that is when RNL is more insulating than D1 and D2 in Fig. 1. This happens when the insulating film is thick or when the insulating film is very much free of defect states. In fact symmetrical I-V characteristics has been observed by Saitoh et al. for M_1IM_2 capacitor with n^+ silicon as M2 when Ti doping of tantalum oxide was done (3). This can be seen in Fig. 2.

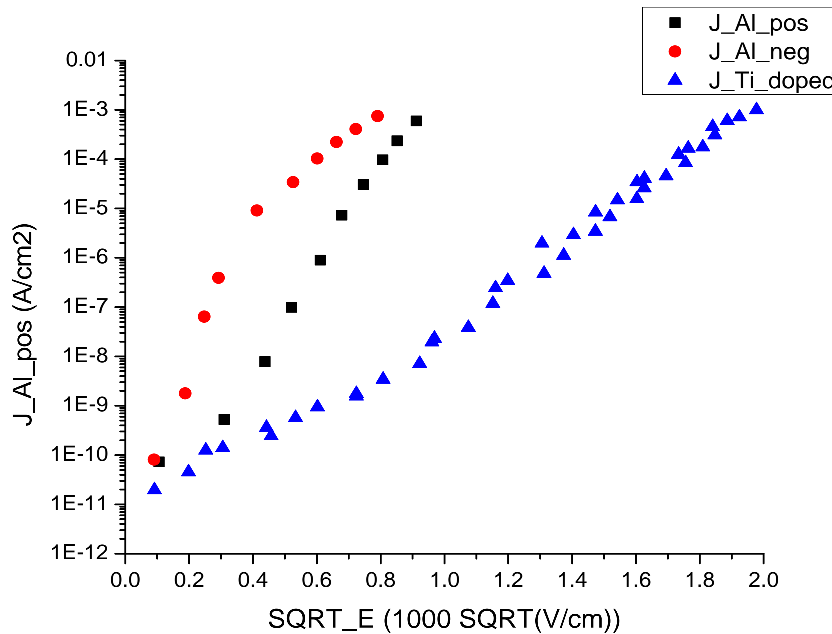

Fig. 2 The leakage current density plotted against the square root of the electric field for $Al/Ta_2O_5/n^+$-Si capacitors with (a) Al gate positive (squares), (b) Al gate negative (circles) and for $Al/Ta_2O_5/n^+$-Si capacitors with Ti doping with (c) Al gate positive and negative. With Ti doping, the I-V characteristics became independent of the polarity of the bias voltage. The original data came from Fig. 5 and Fig. 8 of Saitoh et al. 1986 (3).

Lau et al. pointed out that Ti doping can suppress defect states in tantalum oxide, resulting in significantly lower leakage current (4). Let us name this mechanism of I-V symmetry by suppression of defect states as Mechanism A I-V symmetry. Furthermore, Lau et al. pointed out that post-metallization annealing (PMA) sometimes can suppress defect states in tantalum oxide, resulting in significantly lower leakage current (5).

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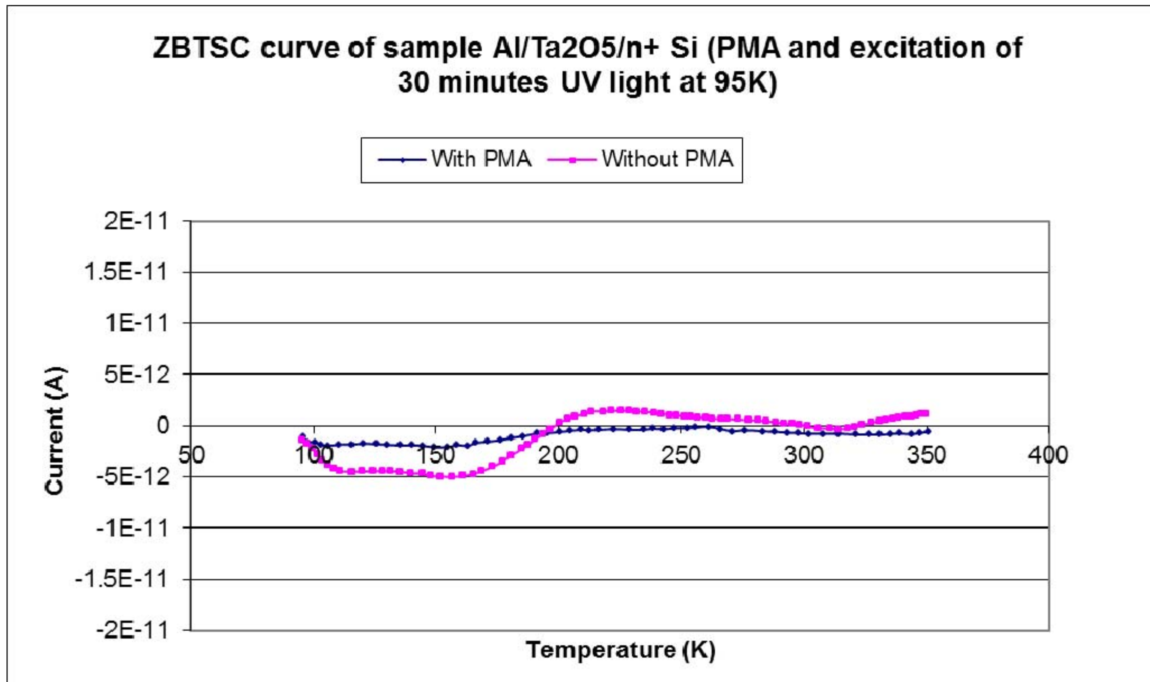

Fig. 3 Zero-bias thermally stimulated current (ZBTSC) spectra of an $Al/Ta_2O_5/n^+$-Si sample with and without post-metallization annealing (PMA).

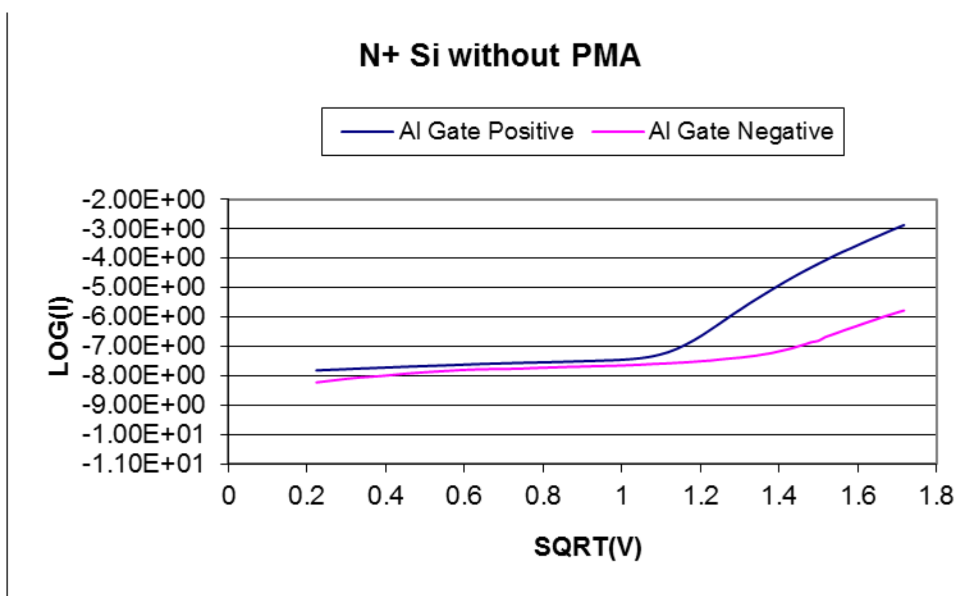

Fig. 4 A plot of the logarithm of current against the square of bias voltage for an $Al/Ta_2O_5/n^+$-Si sample without post-metallization annealing (PMA).

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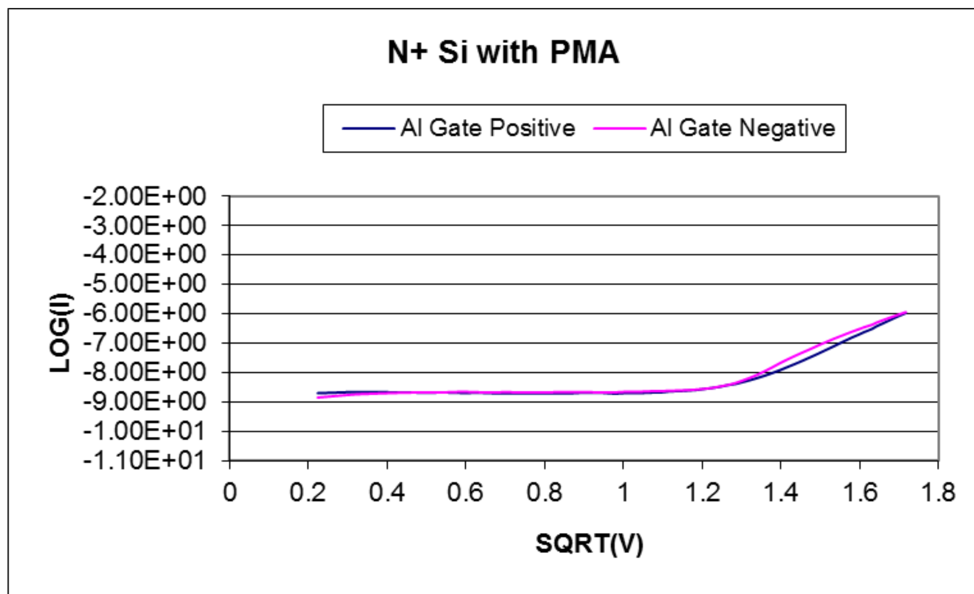
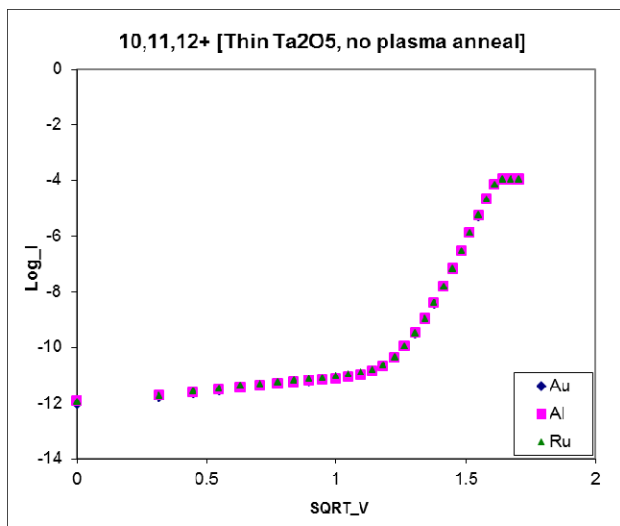


Fig. 5 A plot of the logarithm of current against the square of bias voltage for an $Al/Ta_2O_5/n^+$-Si sample with post-metallization annealing (PMA).

Mechanism B Symmetry

When the insulating film in an M_1IM_2 capacitor is very thin or when it has a lot of defect states, the I-V characteristics is expected to be asymmetrical because RNL in Fig. 1 becomes less insulating than D1 and D2. In reality, the author experimentally observed that the I-V characteristics of an M_1IM_2 capacitor can be symmetrical even when the insulating film is very thin or when it has a lot of defect states.



(a)

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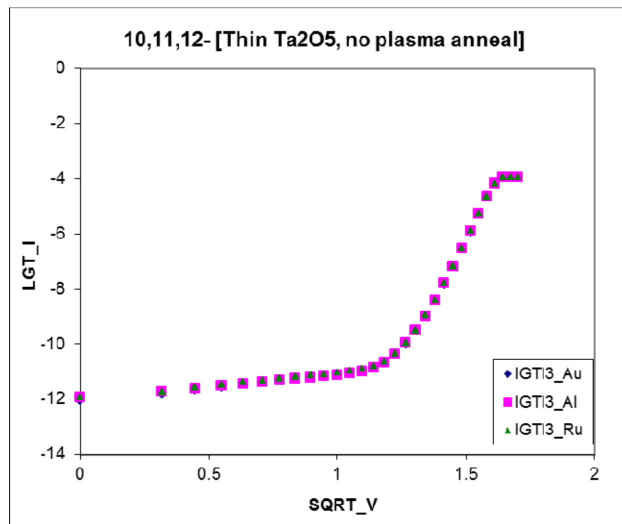

(b)

Fig. 6 The logarithm of current plotted against the square root of voltage for a M/Ta_2O_5/n-Si capacitor. The physical thickness of the Ta_2O_5 film was about 8 nm. Measurement was done at room temperature. (a) Positive bias applied to the metal M while (b) negative bias applied to the metal M.

As shown in Fig. 6, the I-V characteristics is independent of the bias voltage polarity and also the choice of metal (Au, Al or Ru) for M. The insulating film was an ultrathin tantalum oxide film as deposited without any annealing and so highly defective. The author's explanation is that there are an unusually high interface state density at the two metal-insulator interfaces when the insulating film itself is highly defective, resulting in Schottky barrier height pinning for both interfaces such that the two Schottky barrier heights at the two interfaces become equal, resulting in a symmetrical I-V characteristics. Let us name this mechanism of I-V symmetry by generation of defect states as Mechanism B I-V symmetry.

In Fig. 5 of the paper by Shinriki and Nakata, it can be seen that the I-V characteristics of $W/Ta_2O_5/n^+$-poly-Si capacitors tend to be much more symmetrical for as-deposited Ta_2O_5 than for Ta_2O_5 after annealing (7). (Note: Ta_2O_5 was prepared by CVD or sputtering in this work.) Hirai et al. proposed to use a heat treatment to improve the symmetry of the I-V characteristics of their $Ti/Ta_2O_5/Ta$ structures; the penalty was that the leakage current was also increased (1). This approach was further studied by Lee et al. (7). In Fig. 5 of the paper by Lee et al., it can be seen that the I-V characteristics of $Ti/Ta_2O_5/Ta$ capacitors tend to be much more symmetrical after annealing the whole $Ti/Ta_2O_5/Ta$ capacitor structure in vacuum (7). (Note: Ta_2O_5 was prepared by anodization of Ta in this work.) This can be explained by the reaction of Ti and Ta with Ta_2O_5 to generate a lot defect states at the Ti/Ta_2O_5 and Ta/Ta_2O_5 interfaces and also in the Ta_2O_5 bulk. A lot of defect states generated in the bulk can make the Ta_2O_5 bulk leaky, resulting in the I-V characteristics dominated by the Schottky effect at the Ti/Ta_2O_5 and Ta/Ta_2O_5 interfaces. A lot of defect states generated at the Ti/Ta_2O_5 and Ta/Ta_2O_5 interfaces can make the Schottky barrier heights at the Ti/Ta_2O_5 and Ta/Ta_2O_5 interfaces equal because of "pinning" as discussed above, resulting in a symmetrical I-V characteristics. Fermi-

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level pinning at the interface between high-k dielectric and metal or a semiconductor, for example, silicon, is known (8-10). The defect states at the interface are quite likely to be interfacial oxygen vacancies. There is probably a correlation between the interfacial oxygen vacancies and the bulk oxygen vacancies; that is, when there are a lot of bulk oxygen vacancies, it is likely that there are also a lot of interfacial oxygen vacancies. There is probably a correlation between the interfacial defect states and the bulk defect states; that is, when there are a lot of bulk defect states, it is likely that there are also a lot of interfacial defect states. Pulfrey et al. applied a strong electric field to their tantalum oxide capacitor ($Au/Ta_2O_5/Ta$ or $In/Ta_2O_5/Ta$) and the I-V characteristics, which were originally asymmetrical, became much more leaky and symmetrical (11). This can be explained as follows. The strong electric field broke down their tantalum oxide capacitor, resulting in the generation of a lot of defect states in the bulk and also at the two interfaces.

Tsai et al. reported their work on $Ta/Ta_2O_5/Ta$ capacitors (12). The I-V characteristics are symmetrical for as deposited Ta_2O_5; a $Ta/Ta_2O_5/Ta$ capacitor with as deposited Ta_2O_5 is leaky. However, once annealing was done to reduce leakage current, the I-V characteristics become less symmetrical. The experimental results of Tsai et al. can be explained by the theory explained here. As deposited Ta_2O_5 is highly defective and the I-V characteristics is symmetrical for $Ta/Ta_2O_5/Ta$ capacitor with as deposited Ta_2O_5 by Mechanism B. Once annealing is done to suppress defects, the I-V characteristics become less symmetrical. Joo et al. reported their work on $Pt/(BaSr)TiO_3/Pt$ capacitors with sputtered $(BaSr)TiO_3$ (13). The I-V characteristics are asymmetrical for as deposited $(BaSr)TiO_3$; a $Pt/(BaSr)TiO_3/Pt$ capacitor with as deposited $(BaSr)TiO_3$ is highly insulating. However, once annealing was done; the leakage current becomes high and the I-V characteristics become symmetrical. The experimental results of Joo et al. can be explained by the theory explained here. As deposited $(BaSr)TiO_3$ is relatively free of defects and the I-V characteristics is asymmetrical for $Pt/(BaSr)TiO_3/Pt$ capacitor with as deposited $(BaSr)TiO_3$. Once annealing is done to create defects, the I-V characteristics become symmetrical by Mechanism B. These two examples also show that using the same metal for both electrodes of MIM capacitor is not sufficient to ensure symmetry of I-V characteristics. On possible reason that the I-V characteristics are asymmetrical for MIM capacitors with the same kind of metal for both top and bottom electrodes is that the interface roughness for the top metal-insulator interface and that for the bottom metal-insulator interface are not the same, resulting in two different effective Schottky barrier heights for the two interfaces. Hashimoto et al. pointed out that the leakage current of $Mo/Ta_2O_5/Mo$ capacitor is sensitive to the morphology of the bottom Mo electrode (14). Kim et al. pointed out that the I-V characteristics of MIM capacitors are sensitive to interface roughness if the conduction process is controlled by the Schottky emission mechanism (15). Similarly, Gaillard et al. also shared similar opinion (16). The author's opinion is that the effective Schottky barrier height is lowered by interface roughness. This is similar to the experimental observation of Mulyukov who pointed out the work function of tungsten depends on the nanocrystalline structure of tungsten (17). (Note: The Schottky barrier quite frequently depends on work function.) Therefore using the same metal for both electrodes of MIM capacitor is not sufficient to ensure symmetry of I-V characteristics. However, it appears that a large quantity of defect states help to produce the same effective Schottky barrier heights, resulting in Mechanism B I-V symmetry. Chen et al. pointed out Fermi level pinning by a chemical reduction process on lead zirconate titanate (PZT) (18).

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The same situation can be found in silicon nitride. It is believed that the main type of defect states come from the silicon dangling bond in silicon nitride (19-20). The I-V characteristics are asymmetrical for nitrogen-rich silicon nitride which has a small density of silicon dangling bonds; however, the I-V characteristics are symmetrical for silicon-rich silicon nitride which has a large density of silicon dangling bonds according to Lau et al. (21).

Conclusion

In conclusion, the author points out there are two mechanisms of I-V symmetry. Mechanism A happens when the Poole-Frenkel effect is the dominant mechanism for current transport. Mechanism B happens when the Schottky effect is the dominant mechanism. Using the same metal for both electrodes may not ensure I-V symmetry. Fermi-level pinning due to a large quantity of defect states can produce I-V symmetry. This happens for both oxide based or nitride based insulators. Finally, the author would like to point out that Mechanism A I-V symmetry and Mechanism B I-V symmetry are not mutually exclusive but may happen simultaneously; this is because reduction of defect states in the bulk and generation of defect states at the two interfaces can happen simultaneously without conflict. In addition, a lot of defect states at the interface probably make the Schottky energy barrier smaller. Schaeffer et al. reported that the effective work function of platinum on hafnium oxide becomes larger when the amount of oxygen vacancies becomes less (22); larger effective work function implies larger Schottky barrier height and so the effective Schottky energy barrier becomes larger when the amount of defect states at the interface becomes smaller. In other words, the Schottky energy barrier probably becomes smaller when the amount of defect states at the interface becomes bigger.

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