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Mechanisms of Difficulty to Correlate the Leakage Current of High-k Capacitor Structures with Defect States Detected Spectroscopically by the Thermally Stimulated Current Technique

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Historically, it has been difficult to correlate the leakage current of capacitor structures involving high-k dielectric materials and defect states detected spectroscopically by the thermally stimulated current (TSC) technique. Four mechanisms are proposed and solutions are explained with tantalum oxide as an example. One of the mechanisms is the limitation of the TSC technique itself because of the presence of a parasitic current due to the bias voltage used. This can be solved by migrating to more advanced versions of TSC like zero-bias TSC or zero-temperature-gradient zero-bias TSC. In addition, another possible mechanism is that some defect states may have an electron repulsive energy barrier. Furthermore, another possible mechanism is that the leakage current may be insensitive to the presence of defect states under some situations; a unified Schottky-Poole-Frenkel model is proposed by the author to explain such a situation. Finally, another mechanism is due to the non-uniform distribution of defect states. Sometimes, this can be solved by using a 2-zone model proposed by the author.

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Intuitively it can be imagined that the leakage current of high-k capacitor structures may arise from some defect states in the high-k dielectric material, which can be detected by thermally stimulated current (TSC) spectroscopy. However, it has been difficult to make a successful correlation between the leakage current and defect states detected by TSC. For example, Dr. Y. Nishioka, who was a pioneer working on high-k dielectric material, pointed out to the author that no correlation can be seen between leakage current and defect states detected by TSC in tantalum oxide through a private communication.¹ However, the author strongly believes that there is a correlation. Since Dr. Nishioka and his co-workers never publish their work on defect states detected by TSC in tantalum oxide, this problem has become some sort of mystery. In this paper, the author would like to point out that the correlation of the leakage current with defect states detected by TSC can really be difficult but this problem may not be really so mysterious. Besides TSC, other techniques have been tried. For example, Alers et al. used photoluminescence (PL) for the detection of defect states in tantalum oxide;² they pointed out that the defect band detected by PL could be significantly reduced by a nitrogen/oxygen plasma annealing process. However, photoluminescence is not convenient for failure analysis of practical capacitor structures which involve both a top metal electrode and a bottom metal electrode. Furthermore, there is another family of techniques based on the shift of the I-V characteristics because of charge trapping by defect states. For example, Zhao et al.^{3,4} applied this approach to study ultrathin HfO₂/SiO₂ structure; they pointed out a shortcoming of this technique is that if the defect state causes leakage, then the defect state is not efficient to cause charge trapping and vice versa. The problem of this approach is to use the I-V characteristics to detect defect states and then correlate the detected defect states with the I-V characteristics. Another variant is to use the shift of the C-V characteristics due to charge trapping by defect states.⁵ This approach can also suffer from the problem that the defect states responsible for leakage may not be able to cause significant charge trapping and vice versa. The author's approach is to use TSC to detect defect states and then correlate with the I-V characteristics and so there is no such problem.

Theory

Mechanism A.— In the 1910's, Poole reported his experimental observations on mica insulators.⁶ In 1938, Frenkel followed up on Poole's work and proposed his theory that an electric field can enhance the ionization of defect states in a semiconductor.⁷ According

to standard solid state theory, there is no basic difference between a semiconductor and an insulator except that the bandgap energy is larger for an insulator compared to a semiconductor. Hence, the Poole-Frenkel (P-F) effect can be observed in both semiconductors and insulators. For the P-F mechanism, the leakage current through an insulator is given by

$$J_{PF} = BE \exp\{[\phi_B - ((qE)/(\pi\epsilon_0 K))^{1/2}]/(kT/q)\} \quad [1]$$

In Equation 1, B is a constant while E, ϕ_B , k, T, q, ϵ_0 and K are the electric field, barrier height of defect state, Boltzmann constant, absolute temperature, electronic charge, vacuum permittivity and dielectric constant.

Beside the P-F effect, leakage current can also be due to Schottky emission. For the Schottky emission mechanism, the leakage current through an insulator is given by

$$J_{SK} = A^{**} T^2 \exp\{[\phi_B - ((qE)/(4\pi\epsilon_0 K))^{1/2}]/(kT/q)\} \quad [2]$$

In Equation 2, A^{**} is Richardson constant while ϕ_B is the barrier height at the metal-insulator interface.

In general, it is not easy to distinguish between the P-F mechanism and the Schottky emission mechanism because for both cases the logarithm of leakage current plotted against the square root of voltage is a straight line. In addition, there is also a controversy whether the dielectric constant in Eqs. 1 and 2 is the dielectric constant at low frequency or that at optical frequency.^{8,9} The author would like to point out that this problem arises because Equations 1 and 2 are used to fit the same I-V characteristics, resulting in two different values of K; then these two different values of K will be compared with the known value of K in order to see whether equation 1 or equation 2 fits better. Then there is a controversy whether the measured value of K is the known DC dielectric constant or the dielectric constant at optical frequencies. In this paper, the author would like to point out a different approach: Equations 1 and 2 can be used to fit two different portions of the same I-V characteristics. For example, the I-V characteristics may show a forward characteristics with current rising faster as a function of voltage compared to the reverse characteristics; then equation 1 can be used to fit the forward I-V characteristics while equation 2 can be used to fit the reverse I-V characteristics.

As discussed above, there is a controversy regarding the leakage current versus voltage relationship is governed by the Schottky mechanism or by the Poole-Frenkel mechanism for several decades. The Schottky mechanism does not involve defect states in the bulk of the high-k dielectric; however, the Poole-Frenkel mechanism involves defect states in the bulk of the high-k dielectric. In this paper, the author points out that these two mechanisms actually can happen simulta-

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Figure 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. The high- k dielectric is usually a metallic oxide with oxygen vacancy type of defect states. An oxygen vacancy is a deep double donor; a high- k dielectric can be considered as a very weakly n-type large bandgap semiconductor such that D1 and D2 are drawn for metal to n-type semiconductor Schottky diodes. D1 and D2 actually represent the two interfacial regions of the capacitor and RNL represents the bulk region of the high- k dielectric.

neously and a unified Schottky-Poole-Frenkel model, as shown in Fig. 1, can be used to explain observed experimental data.

The unified Schottky-Poole-Frenkel model shown in Fig. 1 is actually similar to a model involving two back-to-back Schottky diodes suggested by Lai and Lee in 1999.¹⁰ The only difference is the author's addition of a non-linear resistor RNL, which can be used to represent the Poole-Frenkel effect. Lai and Lee analyzed capacitor structures involving an as-deposited tantalum oxide film which is very leaky;¹⁰ according to the model shown in Fig. 1, RNL is approximately zero for their work. If a high- k dielectric has oxygen vacancies, which are deep double donors, as the dominant type of donors, the high- k dielectric can be considered a very slightly n-type large bandgap semiconductor. The model shown in Fig. 1 is drawn assuming that the high- k dielectric behaves like a very slightly n-type large bandgap semiconductor. The physical origin of the model shown in Fig. 1 is the author's hypothesis that the distribution of oxygen vacancies in a high- k dielectric is non-uniform; for an MIM capacitor, it can be easily imagined that the concentration of oxygen vacancies is greatest at the two metal/high- k interfaces because the high- k dielectric, which is usually a metallic oxide, is chemically reduced by the metal. As discussed above, oxygen vacancies are deep double donors. It is well known that when the concentration of donors is very large, the donors will appear as much shallower donors compared to the situation when the concentration of donors is small according to Pearson and Bardeen;¹¹ the same situation is true for acceptors. Thus near the interface between the metal and the high- k dielectric, the high- k dielectric can behave like an n-type large bandgap semiconductor.

As discussed above, one basic difficulty to correlate the leakage current with defect states (Mechanism A) is the difficulty to distinguish whether the leakage current follows the Schottky mechanism which does not depend on bulk defect states or the Poole-Frenkel mechanism which depends on bulk defect states. This problem can be solved in the following manner. The analysis of the structure shown in Fig. 1 can be very greatly simplified if one of the two Schottky diodes D1 and D2 has a significantly lower barrier height than the other one such that it can be considered an Ohmic contact. According to the theoretical analysis by Robertson,¹² this is the case if the metal is n^+ -Si and the high- k dielectric is tantalum oxide (Ta_2O_5) or titanium oxide (TiO_2). As shown in Table I, the calculated conduction

band (CB) offset on Si for Ta_2O_5 or TiO_2 is quite small and so the Schottky barrier height of n^+ -Si on Ta_2O_5 or TiO_2 is quite small. As shown in Table I, the CS offset for Ta_2O_5 on Si is 0.36 eV according to theoretical calculation; experimentally, Miyazaki¹³ reported a value of 0.28 eV, which is quite close. Similarly, as shown in Table I, the CS offset for TiO_2 on Si is 0 eV according to theoretical calculation; experimentally, Perego et al.¹⁴ reported a negative value. As shown in Table I, the bandgap of TiO_2 is significantly smaller than that of Ta_2O_5 and CB offset on silicon is so low such that the leakage current of TiO_2 capacitors on silicon is expected to be much higher such that quite frequently Ta_2O_5 may be more suitable for microelectronics applications. Thus, in this paper, we will concentrate on $\text{M}/\text{Ta}_2\text{O}_5/n^+$ -Si capacitors where M stands for "metal". If D2 is the Schottky diode with the metal n^+ -Si and the high- k dielectric Ta_2O_5 , then D2 is like an Ohmic contact and so it can be ignored such that the model is Fig. 1 has only D1 and RNL left. When the metal M is positively biased, D1 is forward biased and RNL is likely to dominate over D1 such that the Poole-Frenkel mechanism dominates over the Schottky mechanism. Conversely, when the metal M is negatively biased, D1 is reverse biased and D1 is likely to dominate over RNL such that the Schottky mechanism dominates over the Poole-Frenkel mechanism. (Note: According to basic MOS theory, applying positive bias to $\text{M}/\text{Ta}_2\text{O}_5/n^+$ -Si capacitors will lead to "accumulation"; applying negative bias to $\text{M}/\text{Ta}_2\text{O}_5/n^+$ -Si capacitors may lead to "depletion" or "inversion", resulting in the formation of a depletion region or an inversion layer such that the model shown in Fig. 1 has to be modified to include the effect of a depletion region or an inversion layer. Thus, in order to see the Schottky mechanism dominating over the Poole-Frenkel mechanism when M is negatively biased, the magnitude of the negative bias voltage cannot be too big. Alternatively, the doping concentration of the n^+ -Si can be made larger such that it is not so easily depleted or inverted.) Experimental evidence to support the above theory can be found in the work by Matsushashi and Nishikawa for Ta_2O_5 .¹⁵ Similarly, experimental evidence to support the above theory can be found in the work by Sun and Chen for TiO_2 .¹⁶ Thus it is more likely to have a correct correlation of the leakage current with bulk defect states if the $\text{M}/\text{Ta}_2\text{O}_5/n^+$ -Si capacitors are biased positively on the metal M than when the capacitors are biased negatively on the metal M.

The above discussion shows that $\text{M}/\text{Ta}_2\text{O}_5/n^+$ -Si capacitors with positive voltage applied to M can be more easily understood because of the small CB offset of Ta_2O_5 on Si. The same theory with some modification can be applied to $\text{M}/\text{Ta}_2\text{O}_5/p^+$ -Si capacitors with positive voltage applied to M. It appears to the author that there may be some positive charge in tantalum oxide due to ionized donors such that $\text{M}/\text{Ta}_2\text{O}_5/p^+$ -Si capacitors are quite frequently inverted. (Note: In the absence of a large positive charge in Ta_2O_5 , $\text{M}/\text{Ta}_2\text{O}_5/p^+$ -Si capacitors can also be inverted because of a large enough positive voltage applied to M.) In this way, sometimes, an $\text{M}/\text{Ta}_2\text{O}_5/p^+$ -Si capacitor can be weakly inverted or even strongly inverted; it can behave like $\text{M}/\text{Ta}_2\text{O}_5/n^+$ -Si/ p^+ -Si or even like $\text{M}/\text{Ta}_2\text{O}_5/n^+$ -Si/ p^+ -Si. In other words, an $\text{M}/\text{Ta}_2\text{O}_5/p^+$ -Si capacitor can behave like an $\text{M}/\text{Ta}_2\text{O}_5/n$ -Si capacitor in series with an "induced" n -Si/ p^+ -Si p-n junction or even an "induced" n^+ -Si/ p^+ -Si tunnel diode. There is some voltage drop across the n -Si/ p^+ -Si p-n junction or n^+ -Si/ p^+ -Si tunnel diode such that usually $\text{M}/\text{Ta}_2\text{O}_5/p^+$ -Si capacitors are less leaky than $\text{M}/\text{Ta}_2\text{O}_5/n^+$ -Si capacitors for the same positive voltage applied to M. For the author, the significance of the $\text{M}/\text{Ta}_2\text{O}_5/p^+$ -Si capacitor structure is that he only managed to perform ZBTSC on an $\text{M}/\text{Ta}_2\text{O}_5/p^+$ -Si capacitor structure for as deposited CVD Ta_2O_5 , which is very leaky; this is because even ZBTSC has some sort of very small parasitic voltage (probably of the mV level) applied to the sample.¹⁷ It was observed that ZBTSC on an $\text{M}/\text{Ta}_2\text{O}_5/p^+$ -Si capacitor structure for as deposited CVD Ta_2O_5 sometimes can be significantly easier than ZBTSC on an $\text{M}/\text{Ta}_2\text{O}_5/n^+$ -Si capacitor structure for as deposited CVD Ta_2O_5 . In order to make a study of the defect states after high temperature annealing compared to the defect states for an as deposited sample using ZBTSC, the $\text{M}/\text{Ta}_2\text{O}_5/p^+$ -Si capacitor structure sometimes can be the better choice.

Table I. Calculated conduction band (CB) offset on Si for Ta_2O_5 and TiO_2 .

Insulator	E_g (eV)	Electron affinity (eV)	Calculated CB offset on Si (eV)
SiO_2	9	0.9	3.5 (experimental)
Si_3N_4	5.3	2.1	2.4 (experimental)
Ta_2O_5	4.4	3.2	0.36
TiO_2	3.05	3.9	0

Note: The values of the experimental conduction band offset on Si for SiO_2 and Si_3N_4 are shown in Table I for the purpose of comparison. Data in Table I originate from Robertson.¹²

Mechanism B.— Another difficulty to correlate the leakage current with defect states arises from a basic shortcoming of the TSC technique (Mechanism B): for an insulating film with finite thickness, the physical location of the defect states detected by TSC cannot be distinguished. Naturally, the greatest quantity of defect states occur at the two interfacial regions of the high- k dielectric capacitor but RNL is only controlled by the defect states in the bulk. Thus the defect states detected by TSC represent both the bulk and the interfacial region. Careful interpretation of TSC spectrum is therefore necessary to handle this issue.

Mechanism C.— There is a third mechanism (Mechanism C). TSC may have a limited range such that only some of the defect states can be detected while some important defect states may be out of range. This situation is particularly serious if the high- k dielectric is in the form of an ultrathin film. This problem can be partially solved by using a novel zero-bias thermally stimulated current (ZBTSC) spectroscopy technique.^{17–19} The purpose of zero bias is to get rid of a parasitic leakage current that can interfere with the measurement. Experience shows that even ZBTSC may not be sufficient such that a more sophisticated technique like zero-temperature gradient ZBTSC has to be used,^{20,21} as shown in Fig. 2.

Sometimes the high- k dielectric thin film can be quite leaky. For example, as deposited CVD Ta_2O_5 thin film is quite leaky. For such a situation, even ZBTSC may run into problem. One way to solve this problem is to modify the sample structure. It turns out that $\text{M}/\text{Ta}_2\text{O}_5/\text{p}^+\text{-Si}$ tends to be much less leaky than $\text{M}/\text{Ta}_2\text{O}_5/\text{n}^+\text{-Si}$. For as deposited CVD, usually, the $\text{M}/\text{Ta}_2\text{O}_5/\text{p}^+\text{-Si}$ structure is used instead of the $\text{M}/\text{Ta}_2\text{O}_5/\text{n}^+\text{-Si}$ structure. This case will be discussed in more detail subsequently in this paper.

Mechanism D.— There is a fourth mechanism (Mechanism D). The TSC family of techniques involves two steps in general: Step 1) filling up of defect states in the sample by carriers (electrons or holes) usually at a relatively low temperature by electrical injection or optical injection and Step 2) heating up the sample from the filling temperature to a higher temperature. During Step 2, the current due to carriers released from the defect states is recorded as a function of temperature, resulting in a spectrum. There is a possibility that it may be difficult to fill up the defect states during Step 1. Previously, the author pointed out the first ionization level of the oxygen vacancy double donor (Defect D) has an electron repulsive energy barrier such that Defect D is quite difficult to be filled by electrons at low temperature.²¹ Another possibility is that the carrier lifetime may be small. For example, in as deposited Ta_2O_5 , the carrier lifetime may be quite small such that the filling of defect states by optical injection is quite inefficient. Shining light may generate “electrons” and “holes”; shining light can also excite electrons captured by the defect states

Figure 2. Defect D (first ionization state of the oxygen vacancy) detected by a novel zero-temperature-gradient ZBTSC technique in an ultrathin Ta_2O_5 capacitor structure. A TO-5 metal can was used to house the sample when zero-temperature-gradient ZBTSC was performed.

Table II. A comparison between the 23 kT_m method and the initial rise method.

Defect level	E_T by the 23 kT_m method (eV)	E_T by the initial rise method (eV)
B'	0.373	0.332
C'	0.522	0.499

back into the conduction band. Thus it is possible that the defect states measured may be significantly lower than the actual amount of defect states present. After a high temperature annealing, the carrier lifetime may be significantly improved such that the filling of defect states by optical injection becomes significantly more efficient. Because of this, there may be difficulty to compare the defect states spectrum of as deposited Ta_2O_5 with that of annealed Ta_2O_5 .

Experimental

Ta_2O_5 was deposited onto (100) $\text{n}^+\text{-Si}$ or $\text{p}^+\text{-Si}$ wafers by low-pressure metal-organic chemical vapor deposition (LP-MOCVD), as discussed before.^{17–22} The precursor used was tantalum ethoxide with the chemical formula of $\text{Ta}(\text{OC}_2\text{H}_5)_5$. As deposited Ta_2O_5 film is amorphous and very leaky. A post-deposition annealing in an oxidizing environment is necessary to lower the leakage current. Then Al dots with a diameter of 1 mm were evaporated through a shadow mask onto the front side of the wafer to form an $\text{Al}/\text{Ta}_2\text{O}_5/\text{n}^+\text{-Si}$ or $\text{Al}/\text{Ta}_2\text{O}_5/\text{p}^+\text{-Si}$ capacitor structure. The film deposited on the back side was removed by chemical etching and then Al was evaporated to form a back side contact.

ZBTSC (zero-bias thermally stimulated current) measurements were performed at a ramp rate of 0.5 K/s as before.^{17–22} Conventional TSC technique suffers from a serious parasitic current problem because of the need to apply a bias voltage to the sample. The purpose of “zero bias” is to solve this parasitic current problem. The energy level of the defect was estimated using $E_T = 23 kT_m$, where T_m is the peak temperature and k the Boltzmann constant. The validity of this equation was checked for Ta_2O_5 by comparison with the initial rise method, as shown in Table II.

Defect States in Tantalum Oxide

Various types of defect states have been detected by the ZBTSC technique as shown in Table III. People have been speculating that the oxygen vacancy is an important type of defect in tantalum oxide. As discussed above, the precursor was $\text{Ta}(\text{OC}_2\text{H}_5)_5$ and naturally CVD

Table III. Various defect states in Ta_2O_5 identified by our previous ZBTSC study.

Defect state	Peak temperature (K)	Estimated energy level (eV)	Remark
A, B, B'	~100,150,200	~0.2, 0.3, 0.4	Tentatively identified as the Si/O vacancy complex shallow single donor in slightly different configurations
C'', C', C	~250,270,290	~0.49,0.53,0.57	Tentatively identified as the C/O vacancy complex shallow single donor in slightly different configurations
H	~250	~0.49	C'' or C' may be a H_2O related defect H
D	~380	~0.8	Tentatively identified as the first ionization level of the O vacancy deep double donor.

Figure 3. ZBTSC spectra of as deposited CVD Ta₂O₅ film on p⁺-Si with 15 min. UV excitation (thin line) and 30 min. UV excitation (thick line).

tantalum oxide will be contaminated by carbon and hydrogen. In addition, as discussed above, the substrate used for deposition was silicon and so it is not too difficult to imagine that tantalum oxide may be contaminated by silicon from the silicon substrate by thermal diffusion²³ or by recombination enhanced diffusion.²⁴ The author believes that hydrogen contamination can be eliminated relatively easily by heating but carbon contamination is relatively difficult to remove. This can be seen by the SIMS (Secondary Ion Mass Spectrometry) data presented by Shinriki and Nakata in their Fig. 14 in 1991;²⁵ annealing in an oxidizing ambient quite frequently only removes the carbon contamination near the surface for a thick tantalum oxide film while hydrogen can be removed relatively easily throughout the whole film. Thus the author believes that tantalum oxide is usually only contaminated by carbon and silicon, which can be expected to substitute for tantalum, resulting in acceptors in tantalum oxide. In the presence of a large quantity of oxygen vacancies, which are deep double donors, it is not too difficult to imagine that carbon and silicon can complex with oxygen vacancies. As shown in Table III, the author believes that the defect states detected by the TSC family of techniques are silicon oxygen vacancy complex, carbon oxygen vacancy complex and the first ionization level of the oxygen vacancy. Please note the defect states discussed above are all donor states. However, silicon oxygen vacancy complex and carbon oxygen vacancy complex are relatively

shallow single donors while the oxygen vacancy is a relatively deep double donor.

Results and Discussion

As explained above, there is some sort of mystery regarding how to correlate the leakage current of tantalum oxide with defect states detected by TSC. The author would like to point out that once the nature of the defect states is understood this sort of mystery can be solved as follows. Furthermore, as discussed above, a basic shortcoming of the TSC technique (Mechanism B) is that for an insulating film with finite thickness, the physical location of the defect states detected by TSC cannot be distinguished. It is not too difficult to imagine that the correlation between leakage current and defect states detected by TSC is easier when the insulator film is very thin. However, as discussed above, TSC may have a limited range (Mechanism C) and this problem becomes more serious when the insulator film is very thin; this problem is partially solved by using ZBTSC. ZBTSC also suffers from Mechanism B but it suffers less from Mechanism C.

Relatively thick tantalum oxide capacitor on silicon.— Fig. 3 shows the ZBTSC spectra of as deposited CVD Ta₂O₅ on p⁺-Si. Fig. 4 shows the ZBTSC spectra of Ta₂O₅ film on p⁺-Si after anneal-

Figure 4. ZBTSC spectra of CVD Ta₂O₅ on p⁺-Si after annealing in O₂ at 800°C for 1 hour with 15 min. UV excitation (thin line) and 30 min. UV excitation (thick line).

Figure 5. ZBTSC spectra of CVD Ta₂O₅ film on p⁺-Si (a) as deposited (thin line) and (b) after annealing in O₂ at 800°C for 1 hour (thick line) with 15 min. UV. The thickness of the Ta₂O₅ film was 98.6 nm thick.

ing in O₂ at 800°C for 1 hour. It is interesting to note that 15 min. UV excitation produces a stronger signal than 30 min. UV excitation. The thickness of the Ta₂O₅ film was 98.6 nm thick.

Fig. 5 shows the comparison of ZBTSC spectra for as deposited sample and annealed sample. By examining Fig. 5 with the help of Table III, it can be easily seen that the carbon oxygen vacancy complex single donor (peak at about 300 K) is slightly reduced by annealing but the silicon oxygen vacancy complex single donor (peak at about 150 K) is strongly enhanced by annealing. In terms of leakage current, it is significantly reduced by the annealing, as seen in Figs. 6 and 7. As explained above, as deposited CVD Ta₂O₅ film on silicon suffers from strong carbon contamination but not much silicon contamination. Strong carbon contamination comes from using an organo-metallic compound Ta(OC₂H₅)₅ as precursor for CVD; strong silicon contamination comes from using silicon substrates for CVD and silicon diffusion during high temperature annealing. Annealing in an oxidizing ambient at high temperature results in a reduction of the carbon contamination near the exposed Ta₂O₅ surface and silicon can diffuse from the Ta₂O₅/Si interface into the Ta₂O₅ film. A 2-zone model can be proposed as follows. The high-k dielectric can be divided into a bulk region and two interfacial regions. The bulk region can be further divided into Zone I and Zone II as follows. Zone I is a region near the exposed Ta₂O₅ surface with carbon contamination depleted by annealing in an oxidizing ambient at high temperature. Zone II is a region between Zone I and the Ta₂O₅/Si interface with

strong carbon contamination not removed by annealing in an oxidizing ambient at high temperature. For a thick CVD Ta₂O₅ film, Zone I can be much smaller than Zone II. If Zone II is large enough such that most of the silicon contamination coming from the silicon substrate resides in Zone II, the silicon contamination may not be able to cause any leakage current. It can be easily imagined that Zone II has a lot of carbon oxygen vacancy complex and silicon oxygen vacancy complex single donors such that it is highly leaky whereas Zone I does not have much carbon oxygen vacancy complex and silicon oxygen vacancy complex single donors such that it is highly insulating such that the leakage current is controlled by Zone I instead of by Zone II. However, our experience shows that annealing in an oxidizing ambient at high temperature only slightly reduces the ZBTSC signal from the carbon oxygen vacancy complex but strongly increases the ZBTSC signal from the silicon oxygen vacancy complex while the leakage current is strongly reduced. This may appear difficult to understand without the 2-zone model. The strongly reduced leakage current is actually correlated with the strongly reduced carbon oxygen vacancy complex in Zone I. However, the TSC family technique measures essentially the total quantity of defect states regardless of physical location such that the ZBTSC spectrum only shows a small reduction of carbon oxygen vacancy complex. The justification of the 2-zone model can be seen in Fig. 8. As shown in Fig. 8, carbon concentration as a function of distance from the tantalum oxide surface was measured by SIMS (Secondary Ion Mass Spectrometry). Fig. 8 was modified from Fig. 7 in Aoyama et al.²⁶ It can be seen that as deposited CVD tantalum oxide

I-V characteristics of Al/Ta₂O₅/p⁺-Si with Al gate

Figure 6. I-V characteristics of CVD Ta₂O₅ film on p⁺-Si (a) as deposited (thin line) and (b) after annealing in O₂ at 800°C for 1 hour (thick line) with 15 min. UV. Al metal was biased positively.

I-V characteristics of Al/Ta₂O₅/p⁺-Si with Al negatively

Figure 7. I-V characteristics of CVD Ta₂O₅ film on p⁺-Si (a) as deposited (thin line) and (b) after annealing in O₂ at 800°C for 1 hour (thick line) with 15 min. UV. Al metal was biased negatively.

Figure 8. Carbon concentration in tantalum oxide measured by SIMS (Secondary Ion Mass Spectrometry) modified from Fig. 7 of Aoyama et al. 1996.²⁶ The thickness of the tantalum oxide was 40 nm. Annealing in an oxidizing ambient only removes the carbon contamination near the surface. This is probably because carbon probably diffuses slowly in tantalum oxide. Zone I is the region where carbon contamination is suppressed while Zone II is the region where carbon contamination is not suppressed. In this figure, Zone I is the first 10 nm while the rest is Zone II. It can be expected the concentration of oxygen vacancies is probably also lower in Zone I than in Zone II. Thus the concentration of carbon oxygen vacancy complexes is probably much lower in Zone I than in Zone II.

tends to be strongly contaminated by carbon. Annealing in an oxidizing ambient only removes the carbon contamination near the surface. Zone I is the region where carbon contamination is suppressed while Zone II is the region where carbon contamination is not suppressed. It can be expected the concentration of oxygen vacancies is probably also lower in Zone I than in Zone II. Thus the concentration of carbon oxygen vacancy complexes is probably much lower in Zone I than in Zone II. During annealing, silicon diffuses from the silicon substrate into tantalum oxide. It can be expected the concentration of silicon oxygen vacancies is probably also much lower in Zone I than in Zone II.

An analogy of this situation is like ten $10\ \Omega$ resistors in series with a 100 V applied to them, resulting in a current of 1 A. If just one out ten resistors is burnt, resulting in a 1 G Ω resistor in series with nine $10\ \Omega$ resistors, the current will drop to $100\text{ V}/1\text{ G}\Omega = 10^{-7}\text{ A}$. If the total number of undamaged resistors is counted, the change is just a decrease from 10 to 9; however, the change of current is a decrease from 1 A to 10^{-7} A . Using the 2-zone model, it is possible to explain the observation that a small decrease in the concentration of carbon oxygen vacancy complexes (peak near 300 K in Fig. 5) can result in a very large decrease in the leakage current as shown in Figs. 6 and 7. Using the 2-zone model, it is possible to explain the observation that a huge increase in the concentration of silicon oxygen vacancy complexes (peak near 150 K in Fig. 5) does not cause a huge increase in the leakage current.

As discussed above, it can be difficult to distinguish between the Schottky mechanism, which does not involve bulk defect states, or by the Poole-Frenkel mechanism, which involves bulk defect states (Mechanism A). This problem can be solved as explained above by using the I-V characteristics of $\text{M}/\text{Ta}_2\text{O}_5/\text{n}^+\text{-Si}$ capacitors with M positively biased. As discussed above, for $\text{M}/\text{Ta}_2\text{O}_5/\text{p}^+\text{-Si}$ capacitors in the inverted state, they can be considered similar to $\text{M}/\text{Ta}_2\text{O}_5/\text{n}^+\text{-Si}$ capacitors with some voltage drop in the silicon substrate.

Ultrathin tantalum oxide capacitor on silicon.— It is not too difficult to imagine that an ultrathin Ta_2O_5 film is quite different from a thick Ta_2O_5 film. Experimental observation shows that carbon contamination can be relatively easily suppressed throughout an ultrathin

Figure 9. I-V characteristics of $\text{Al}/\text{Ta}_2\text{O}_5/\text{n}^+\text{-Si}$ capacitors with O_2 RTA at 800°C for 30 s with RTN (thick line) and without RTN (thin line). The thickness of Ta_2O_5 film was 8.4 nm. Diameter of metal contact = 1 mm. (a) Al was biased positively (b) Al was biased negatively. (c) ZBTSC spectra of $\text{Al}/\text{Ta}_2\text{O}_5/\text{n}^+\text{-Si}$ capacitors with O_2 RTA at 800°C for 30 s with RTN (thick line) and without RTN (thin line). The thickness of Ta_2O_5 film was 8.4 nm. RTN = rapid thermal nitridation.

Ta_2O_5 film by a short annealing in an oxidizing ambient at high temperature²⁷ such that carbon oxygen vacancy complex simply disappears and the 2-zone model discussed above is not necessary. As shown in Fig. 2, there are only two kinds of defect states left: silicon oxygen vacancy complex and simple oxygen vacancies. Thus interpretation of experimental data can become much more straightforward. As shown in Fig. 9, the leakage current is obviously reduced because of RTN (rapid thermal nitridation) of silicon substrate before deposition. This can be correlated with the suppression of the silicon oxygen vacancy complex seen in ZBTSC spectra. RTN helps to prevent sil-

icon diffusing into the tantalum oxide film because silicon nitride is a diffusion barrier and so suppress oxygen vacancy formation by the reaction between silicon and tantalum oxide.

Conclusions

Four mechanisms regarding why it is difficult to correlate the leakage current of high-k dielectric capacitor structures with defect states detected by the TSC family of techniques have been discussed. Methods to handle the three types of problems have been discussed above. Mechanism A is that it is possible that only part of the I-V characteristics is related to the presence of bulk defect states. Therefore it is necessary to identify which portion of the I-V characteristics is sensitive to the variation of bulk defect states. Mechanism B is that the defect states may not have a uniform distribution in the high-k dielectric. This problem can only be handled on a case-to-case basis. There is no general outline for solving this problem. Sometimes, this problem can be solved by the 2-zone model proposed in this paper by the author. Mechanism C is that the TSC technique may have a limited range because of the presence of a parasitic current. This problem can be solved by migrating to ZBTSC or even ZTGZBTSC. Mechanism D is that it may be difficult to fill some defect states at low temperature. This problem can be handled by a two-scan TSC technique: one scan is used for defect states with this problem while the other scan is used for defect states without this problem. In conclusion, it is possible to make a successful correlation between the leakage current of high-k dielectric capacitor structures with defect states detected by the TSC family of techniques even though it is difficult in general.

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