Kinetics of Moisture Sorption and Reverse Bias Degradation in Chip Tantalum Capacitors

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Abstract

Exposure of chip MnO2 tantalum capacitors to humid environments might result in increased ESR, leakage currents, and first turn-on failures. However, there is a lack of literature data on the effect of moisture on reverse bias behavior of the parts. The presence of moisture can also result in pop-corning when a high water vapor pressure develops when moisture absorbed in pores of tantalum slugs vaporizes instantly during soldering process resulting in damage to capacitors. A study of kinetics of moisture ingress to and release from active elements of capacitors would allow a better understanding of degradation mechanisms and is important for preventing failures. In this work, a technique for investigation of moisture sorption and desorption in solid chip tantalum capacitors that employs tantalum slugs as a humidity sensor have been developed and kinetics of the process analyzed for different types of capacitors at temperatures from room to 125 °C. A model that relates diffusion characteristics of polymer cases and size of the slugs to characteristic times of moisture sorption has been developed. A strong effect of moisture on long-term degradation of reverse bias currents in MnO2 cathode capacitors has been demonstrated and physical mechanisms discussed.

Introduction

Chip tantalum capacitors are encapsulated in epoxy materials, and like most plastic encapsulated electronic components are sensitive to moisture. An adverse effect of moisture on reliability of chip tantalum capacitors has been reported by many authors [1-4]. The degrading effect of moisture might increase due to soldering-related stresses [5] and by intermittent power on/off cycling [6].

An increase in the probability of scintillation breakdowns with time under bias for parts after exposure to humid environments was reported in our previous study [7]. The effect was explained by the "sleeping cells" model. In dry conditions, some areas on the surface of Ta2O5 dielectric that are not covered by MnO2 are isolated. These cells remain in a dormant state until they are activated by absorbed moisture which increases capacitance and might raise leakage currents or cause local breakdown. Another type of sleeping cell is related to the self-healed areas of capacitors where conductive MnO2 had been converted into high-resistive Mn2O3 or Mn3O4 oxides due to local overheating caused by breakdown. Moisture can oxidize these areas increasing conductivity of the manganese oxide by two to three orders of magnitude [8] and reactivate defective sites.

Analysis of failures of chip tantalum capacitors caused by first power turn-on after soldering showed that the probability of failures depends strongly on preconditioning before soldering, suggesting an important role of absorbed moisture [9]. The effect was explained by local internal damage to the dielectric during soldering of the parts that contained moisture (internal pop-corning). It was shown that even a relatively small amount of moisture that is absorbed in capacitors stored at room conditions can result in post-soldering failures.

Although an important role of moisture in degradation of tantalum capacitors has been demonstrated by multiple studies, the kinetics of moisture ingress and the rate of desorption during bake-out has not been sufficiently investigated. The lack of experimental data and absence of models creates uncertainty in determining moisture sensitivity levels of capacitors and does not allow for adequate assessments of bake-out times.

A specific feature of reverse bias behavior of chip tantalum capacitors is substantial, up to three orders of magnitude increase of leakage currents with time. In our previous work [10] this behavior was explained by migration of positively charged oxygen vacancies in the dielectric and their accumulation with time at the Ta/Ta2O5 interface. This accumulation raises electric fields at the interface, enhances injection of electrons, and increases reverse currents. Investigations of conduction asymmetry and degradation of currents with time in polymer tantalum capacitors by Y. Freeman and co-workers [11] showed that reverse currents remained stable in dry conditions, but increased with time in the presence of

moisture. The effect was attributed to proton diffusion toward the Ta/Ta2O5 interface and oxygen migration into the Ta anode. The humidification was carried out at 85 °C and 85% RH, and it was not clear whether moisture at room conditions would affect behavior of the capacitors. The possibility of protonic currents in anodic grown Ta2O5 dielectrics was considered earlier by D. A. Vermilyea [12, 13] and J. Prymak [14].

In the first part of this work, a model, technique, and experimental data on kinetics of moisture sorption and desorption in solid chip tantalum capacitors are discussed. Investigations of the long-term (up to 3000 hours) degradation of leakage currents under reverse bias at different levels of humidity in the environments and mechanisms of degradation are described in the second part of the paper.

Experiment

Two types of conformal coated (CC) and one types of molded case (MC) 10 μ F 25 V tantalum capacitors were used in this study. Characteristics of the cases and slugs for these parts are shown in Table 1. Capacitance and dissipation factors were measured at 120 Hz using Agilent 4294A impedance analyzer. The thickness of polymer case walls, *d*, and sizes of the slugs were determined by X-ray analysis and cross-sectioning. Variations of reverse leakage currents with time were monitored using a PC-based system and Agilent scanners that measured voltage drop across 10 ohm resistors connected in series with each capacitor. Reverse bias stress (RBS) testing was carried out at different temperature and humidity conditions using groups of samples with 7 to 13 pcs in each group.

Part	case size	case LxWxH, mm	weight, g	<i>d</i> , mm	slug LxWxH, mm
CC1	F	5.6x3.4x1.8	0.137	0.2	4.2x2.2x0.8
CC6 (CWR06)	G	6.7x2.8x2.8	0.275	0.2	5.5 x 2 x 2
MC1	С	6x3.2x2.5	0.14	0.39	2.9x2.2x1.1

Table 1. Characteristics of used capacitors

Examples of capacitance variations with time after changes in environmental conditions are shown in Fig.1. For moisture sorption experiments CC1 capacitors were baked and then monitored with time after exposure to 85% humidity at room temperature. Desorption kinetics was determined by measurements at 125 °C after capacitors were preconditioned in the humidity chamber at 85 °C and 85% RH. Results show that C(t) dependencies are reproducible and can be characterized by two characteristic times: the time during which capacitance remains stable, t_D , and the time that characterizes variation of capacitance with time, τ . The physical meaning of these times is discussed below.



Figure 1. Variations of capacitance in CC1 parts with time after bake (a) and during the bake (b).

Simulation of moisture sorption

Variations of capacitance with time clearly indicate the presence of a certain induction period during which capacitance does not change and remains at a minimal, C_{min} , or maximum, C_{max} , value for moisture sorption and desorption conditions respectively. These periods indicate times when moisture content in the slug is not changing and correspond to a so-called diffusion delay that is determined by the moisture diffusion coefficient, D, and thickness of the encapsulant, d:

$$t_D = \frac{d^2}{6 \times D} \tag{1}$$

After diffusion delay, the rate of moisture accumulation in the slug is controlled by the moisture permeability coefficient \tilde{p} that is defined as the amount of moisture passing through a unit area of the barrier layer having a unit thickness per unit time at a unit difference in moisture pressure inside and outside of the case. Assuming the external and internal moisture pressures are P_o and P_i , and the surface area through which diffusion occurs, S, the rate of moisture increase in the slug can be expressed as:

$$\frac{\Delta m(t)}{\Delta t} = \tilde{p} \frac{S}{d} \left[P_o - P_i(t) \right]$$
⁽²⁾

In the first approximation, we can assume that the amount of moisture accumulated in the slug, $\Delta m(t)$, increases capacitance and internal pressure linearly:

$$MC(t) = \alpha \times \Delta m(t), \text{ and } P_i(t) = \gamma \times \Delta m(t) = (\gamma/\alpha) \times \Delta C(t),$$
 (3)

where $\Delta C(t) = C(t) - C_{min}$ for moisture sorption process, α and γ are constants, and C_{min} is the capacitance value for a dry capacitor.

With these substitutions Eq.(2) can be presented as:

$$\frac{\Delta C(t)}{\Delta t} = \tilde{p} \times \frac{S}{d} \times \alpha \times P_o - \tilde{p} \times \frac{S}{d} \times \gamma \times \Delta C(t) = A - \frac{\Delta C(t)}{\tau} , \qquad (4)$$

where constant $A = \tilde{p} \times (S/d) \times \alpha \times P_o$, and τ is the characteristic time of moisture sorption in the capacitor:

$$\tau = \frac{d}{\gamma \times \tilde{p} \times S} \tag{5}$$

Note that in the system SI γ is in N/m²_kg, \tilde{p} is in sec, *d* is in m, and *S* is in m², so $[\tau] = \frac{m \times m^2 \times kg}{N \times \sec m^2} = \sec r$.

A solution to Eq.(4) can be written in a form

$$\Delta C(t) = \frac{\alpha}{\gamma} \times P_0 \times \left[1 - \exp\left(-\frac{t}{\tau}\right)\right] = \Delta C_{\max} \times \left[1 - \exp\left(-\frac{t}{\tau}\right)\right], \quad (6)$$

where ΔC_{max} is the difference in steady-state values of capacitance with and without moisture.

At $t = \tau$, $\Delta C(t) = 0.63 \times P_0 \times (\alpha/\gamma) = 0.63 \Delta C_{max,.}$

Values of the coefficients α and γ , can be determined based on Eq.(3) if the amount of moisture absorbed in the slug at a steady-state condition, Δm_{max} , is known:

$$\alpha = \Delta C_{max} / \Delta m_{max}, \qquad \gamma = P_0 / \Delta m_{max} , \qquad (7)$$

Variations of capacitance with time of exposure to a changed environmental conditions can be described as follows. For moisture sorption:

$$C(t) = C_{\min} , \qquad \text{at } t \le t_D$$

$$C(t) = C_{\min} + \left(C_{\max} - C_{\min}\right) \times \left[1 - \exp\left(-\frac{\left(t - t_D\right)}{\tau}\right)\right], \quad \text{at } t > t_{Ds} \qquad \} \qquad (8a)$$

and for moisture desorption:

$$C(t) = C_{\max} , \qquad \text{at } t \le t_D$$

$$C(t) = C_{\min} + \left(C_{\max} - C_{\min}\right) \times \exp\left(-\frac{\left(t - t_D\right)}{\tau}\right), \qquad \text{at } t > t_d \qquad \} \qquad (8b)$$

To simulate variations of capacitance with time using Eq.(8), Eq.(1), and Eq.(5), we need to evaluate moisture sorption and diffusion coefficients of polymers used for encapsulation, thicknesses of polymer cases, and the amount of moisture that can be absorbed in the slug, Δm_{max} , at a moisture pressure P_0 .

Sorption isotherms for molding compounds used for manufacturing of tantalum capacitors and temperature dependences of the diffusion coefficients measured earlier [7] showed that moisture uptake is a linear function of the relative humidity and coefficients of diffusion have activation energy of 0.42 eV. The linearity between relative humidity and moisture uptake in a wide range of RH variations allows for characterizing molding compounds with a single moisture sorption coefficient, σ .

Assuming that the amount of moisture, Δm_w , which is absorbed at a steady-state condition in epoxy of volume V, is proportional to the moisture pressure, P_0 , the sorption coefficient can be determined as

$$\sigma = \frac{\Delta m_w}{V \times P_0} = \frac{\Delta m_w}{m_0} \frac{\rho}{P_0} \quad , \tag{9}$$

where m_0 is the mass of the encapsulant in volume V and ρ is its density.

The moisture permeability coefficient \tilde{p} is a product of the moisture sorption coefficient, σ , and coefficient of diffusion, D:

$$\tilde{p} = \sigma \times D \tag{10}$$

For epoxy materials σ has a weak temperature dependence, while *D* increases with temperature exponentially according to Arrhenius law:

$$D = D_a \exp(-U/kT) \tag{11}$$

where D_o is a constant, U is the activation energy, T is the absolute temperature, and k is the Boltzmann's constant.

Based on our measurements and literature data, $D_o = 3.6 \times 10^{-6} \text{ m}^2/\text{sec}$ and U = 0.42 eV for molding compounds and $D_o = 4.8 \times 10^{-6} \text{ m}^2/\text{sec}$ and U = 0.4 eV for low-filled epoxy materials [15].

Typically, at 85% humidity and room temperature that corresponds to moisture pressure $P_0 = 2000$ Pa, moisture sorption in unfilled epoxies is $\Delta m_w/m_0 \approx 2$ to 3%. Considering that the density of unfilled epoxies is $\rho \approx 1.1$ g/cm³ (1100 kg/m³), the sorption coefficient, σ is in the range from 1.1×10^{-2} to $1.7 \times 10^{-2} \sec^2/m^2$. For molding compounds used to manufacture cases for tantalum capacitors $\rho \approx 1.8$ g/cm³ (1800 kg/m³) and $\Delta m_w/m_0 \approx 0.5$ to 0.7%, so $\sigma \approx 4.5 \times 10^{-3}$ to $6.3 \times 10^{-3} \sec^2/m^2$. Moisture diffusion coefficient in epoxies at room temperature is $D \sim 2$ to 6×10^{-13} m²/s [16], and for molding compounds $D \sim 1$ to 3×10^{-13} m²/s [15]. Respectively, the permeability coefficients are $\tilde{p} \sim 2.2 \times 10^{-15}$ to 9×10^{-15} sec for low-filled epoxy polymers that are used in CC capacitors and $\tilde{p} \sim 4.5 \times 10^{-16}$ to 1.8×10^{-15} sec for compounds used in molded case capacitors.

Estimations showed that the total amount of moisture in capacitors is in the range from 0.6 to 1.5 mg. The amount of moisture in active elements of capacitors is comparable with the amount of moisture absorbed in polymer cases.

Variation of capacitance with time in different environments

Variations of capacitance in humid environments (85% RH) at room temperature and during baking at 125 °C for different types of capacitors are shown in Fig.2. Based on experimental data, characteristic times were determined and calculations per Eq.(8) are shown as dashed lines in the charts. Results show that the suggested model allows for adequate approximation of the experimental data. Different part types have substantially different characteristic times. Values of t_D for CC capacitors at room temperature are a few hours and decrease almost 10 times at 125 °C, whereas for the MC capacitor these times are approximately 10 times greater.



Figure 2. Variations of normalized capacitance with time of storage at room temperature and 85% RH after baking (a) and decrease of capacitance during bake (b). Dashed lines are calculations per Eq.(8a) and (8b).

To evaluate capacitance variations during moisture sorption and desorption processes, the parts were tested after baking at 125 °C in humidity chamber first at 85 °C 85% RH, then during bake at 85 °C, and finally during moisturizing at 65 °C and 85% RH. Results of these measurements allowed for calculations of t_D and τ at different temperatures. These times

are plotted against temperature in Arrhenius coordinates in Fig.3. Approximations with straight lines indicated activation energy of t_D of 0.5 eV and 0.43 eV for MC and CC capacitors respectively. These data are close to the values of activation energy of moisture diffusion in the encapsulating epoxies. For characteristic times the values of activation energies were somewhat lower, 0.36 and 0.33 eV. At all temperatures both values, t_D and τ , are almost an order of magnitude lower for CC compared to MC capacitors, which is mostly due to a much thinner polymer cases for conformal coated parts compared to parts in molding compounds.



Figure 3. Temperature dependencies of diffusion delays measured during moisture sorption (a) and characteristic times measured during moisture desorption (b) for different types of capacitors.

Effect of moisture on reverse bias behavior of tantalum capacitors

To assess the effect of preconditioning on reverse bias behavior, one group of CC1 capacitors was baked at 125 °C for 40 hours, while another was stored in humidity chamber at 85 °C 85% RH also for 40 hours. Both groups were tested at room conditions and under 2 V reverse bias stress (RBS) for 340 hours. After one hour of testing currents in dehydrated capacitors were substantially, up to two orders of magnitude, lower than in moisturized capacitors (see Fig. 4a). However, by 340 hours this difference reduced to ~ 2 times only, which is likely due to drying of "wet" and moisturizing of "dry" capacitors at room condition humidity (~ 35 % RH). After 100 hours of testing the parts were depolarized for 1000 sec and then the testing continued. Depolarization resulted in reduction of currents by more than two orders of magnitude, but after the bias was reapplied the currents increased rapidly and in approximately one hour reached the same level as previously measured. The parts were depolarized again after 340 hr testing and leakage currents were measured at 25 V forward bias for one hour. Comparison with initial DCL measurements showed a relatively minor, less than two-fold increase in forward leakage currents. Similar effects were observed before [10] and were explained by charge accumulation under RBS at the Ta/Ta2O5 interface that practically does not affect Ta2O5/MnO2 interface that is responsible for forward leakage currents.

Following RBS at 2 V the parts were tested for 600 hours at 5 V RB that resulted in currents increasing to more than 10 mA by the end of testing (see Fig. 4b). Pre-moisturized capacitors had ~ 50% higher leakage currents up to ~10 hours, but then no substantial difference in currents was observed. Results show that preconditioning of the parts strongly affects their RB behavior, and the lasting effect can be observed for a much longer period than the characteristic time of moisture sorption (~ 40 hr at room temperature). Another interesting feature of *I*-*t* characteristics at 5 V is the presence of maximum at 0.4 to 0.6 mA after ~0.6 hours of testing. It appears that a second maximum at much higher currents might happen after thousands of hours of testing. Post 5 V RBS measurements of DCL at 25 V forward bias showed that leakage currents increased approximately an order of magnitude, but had a tendency of decreasing with time under bias.

Two other groups of CC1 capacitors were preconditioned by baking and one group was tested at 75 °C in a regular temperature chamber and another in vacuum, 4×10^{-6} torr. After 1000 hours of testing capacitors in vacuum had currents below 2 mA, whereas capacitors tested in air had currents from 12 to 25 mA and continue growing. Note that at room conditions of 23 °C and humidity 50% RH, the relative humidity in the temperature chamber at 75 °C is ~ 3.4%. This means that even relatively minor variations in humidity, ~3%, can cause substantial difference in degradation of reverse currents.



Figure 4. Degradation of leakage currents in CC1 10 μF 25 V capacitors preconditioned by 40 hr bake at 125 °C (red lines) and by 40 hr storage in humidity chamber at 85C 85% RH (blue lines) at 2 V (a) and 5 V (b, c) reverse bias. All parts tested at 75 °C (c) were preconditioned by bake at 125 °C.

The next experiment with CC1 capacitors was carried out for 100 hours at 4 V RB at room temperature in dry box (7% RH), in humidity chamber (85 % RH), and at room conditions (35% RH). Before dry box testing, the parts were preconditioned by baking at 125 °C for 100 hours, and before humidity chamber testing preconditioning was at 85 °C 85% RH also for 100 hours. The level of currents after 100 hours of testing in humid environments was approximately 20 times greater than in dry conditions (Fig.5). A significant difference, ~ 3 times was found between leakage currents at 7% and 35% RH (Fig. 5b). Variations of median current with relative humidity can be approximated with exponential function: $I_{st} \sim exp(0.04 \times RH)$.



Figure 5. Effect of humidity on variations of leakage currents with time at 4 V RB (a) and distribution of currents after 100 hours of testing (b) for CC1 capacitors.

Testing of prebaked CC1 capacitors in dry conditions at 5 V for 420 hours (Fig. 6a) resulted in increasing leakage currents that could be approximated with linear functions. This allowed assessments of degradation rates, *R*, for each sample and characterization of parts and test conditions by distributions of *R*. Calculations based on RBS at room temperature and different voltages resulted in distributions shown in Fig. 6b. Increasing voltage from 2 to 5 V raised the rate by almost three orders of magnitude. Estimations using Weibull inversed power law model showed that voltage variations of *R* can be approximated with a power function, $R = 1.1 \times 10^{-10} \times V^{6.9}$.



Figure 6. Degradation of leakage currents in CC1 capacitors during RBS. a) Testing in dry conditions at 5 V. b) Distributions of R at different voltages. Straight lines show calculations Based on Weibull inversed power law model.

Testing of CWR06 (CC6) and MC1 capacitors at 5 V reverse bias and different humidity for 3000 hours resulted in leakage currents increasing up to 4 orders of magnitude (Fig. 7a, b). Similar to conditioning of CC1 capacitors, parts tested in the dry chamber were preconditioned by baking and parts for humid testing were preconditioned in humidity chamber. Parts tested at room conditions (RC) were used as is. Below, these conditions are referred to as "dry", "RC", and "HUM".

In all cases, a hump on *I*-*t* curves was observed within a few hours of testing. The currents continued increasing and at room and dry condition parts had a tendency to saturate after 3000 hours. Variations of currents with time between ~100 and 2000 hours could be approximated with linear functions thus allowing for calculations of degradation rates. Distribution of *R* (Fig. 7c) showed that for both part types the median value is increasing approximately two times as RH increasing from 7% to ~30%, and more than two orders of magnitude for CWR06 and ~ 50 times for MC1 capacitors as humidity is increasing to 85%.



Figure 7. Degradation of leakage currents for MC1 (a) and CWR06 (b) capacitors at 22 °C and 5 V reverse bias at different levels of humidity. Fig.c shows distributions of degradation rates calculated using linear approximations between 100 and 2000 hours.

Variations of leakage currents for different types of capacitors in dry conditions at room temperature for 2000 hr, and for 1000 hr at 55 °C and 75 °C are shown in Fig. 8. To assure dry conditions at 55 °C, the testing was carried out with dry N2 purging. In all cases, a two stage degradation process with a hump on *I-t* curves within 0.1 to 30 hours of testing was clearly observed. Comparison of the curves shows that the character of degradation is similar for all part types and temperatures; however, the level of degradation can differ by more than an order of magnitude.



Figure 8. Degradation of leakage currents for three part types in dry conditions at 22 °C (a), 55 °C (b), and 75 °C (c).

The time to the first maximum, τ_l , and relevant current amplitude, I_{max} , were determined for each part type, and their temperature dependencies are plotted in Arrhenius coordinates in Fig. 9. Activation energies for τ_l were 0.6 to 0.66 eV, and for I_{max} in the range from 0.39 to 0.44 eV. The range for I_{max} is within the area typical for forward leakage currents in MnO2 capacitors, from 0.32 to 0.5 eV. Additional testing of CWR06 capacitors, but having different lot date code, LDC2, at temperatures 22 °C, 35 °C, 55 °C, and 75 °C showed a similar activation energy for τ_l , 0.61 eV.

Distributions of long-term degradation rates at different temperatures determined based on linear approximations of *I*-t curves after ~ 10 hours of testing are shown in Fig. 9c. Assuming that the rates follow Arrhenius law, activation energies, E_a , for CWR06 and MC1 capacitors are 0.74 eV and 0.67 eV respectively. The data indicate that the long-term degradation rate in the presence of humidity has activation energy ~ 0.7 ±0.4 eV. RBS testing at 5V and 55 °C and 75 °C temperatures in 4×10⁻⁶ torr vacuum during more than 1000 hours showed that activation energies of the rates were 0.96

eV and 1.1 eV for CC1 and CWR06 capacitors respectively. Apparently, the presence of moisture reduces activation energy of the degradation process.



Figure 9. Temperature dependencies of the times to first maximum (a) and maximum currents (b). Fig. c) shows distributions of degradation rates in CWR06 capacitors measured at 25 °C, 55 °C and 75 °C.

Discussion

The major result of this study is that the presence of moisture increases substantially reverse leakage currents in tantalum capacitors. Considering that in humid environments conductivity of MnO2 is due to protons [8] and protons can migrate through Ta2O5 dielectrics [17-19], the simplest explanation of the excessive reverse currents would be by ionic conduction caused by protons injected from the MnO2 cathode. According to this model, diffusion of moisture through the polymer case creates a flow of water molecules that generate protons in MnO2 by dissociation (H2O \rightarrow H⁺ + OH⁻) and then the protons are injected in Ta2O5 dielectric. In this case, the flow of protons cannot exceed the flow of water molecules.

The flow of moisture can be estimated based on the moisture sorption model discussed above. The permeability coefficients of epoxies that are used in CC capacitors, \tilde{p} , is in the range from ~ 2×10⁻¹⁵ to 9×10⁻¹⁵ sec, and the maximum flow of moisture into an initially dry capacitor can be expressed as

$$\frac{\Delta m(t)}{\Delta t} = \tilde{p} \frac{S}{d} P_0 \tag{12}$$

Assuming that all water molecules will dissociate forming protons, the maximum ionic current can be calculated as

$$I_{i_{-}\max} = \frac{\Delta m(t)}{\Delta t} \frac{qN_A}{M} = \frac{qN_A}{M} \tilde{p} \frac{S}{d} P_0$$
(13)

At room temperature and ~40%RH moisture pressure, P_0 , is ~1000 Pa and considering that for a 10 µF 25 V CWR06 capacitor the surface area is $S = 44 \text{ mm}^2$ and the thickness of polymer d = 0.2 mm, $\Delta m/\Delta t = 1.2 \times 10^{-12} \text{ kg/sec}$. This corresponds to $I_{i_max} = 6.5 \text{ µA}$. The microampere range currents might explain leakages at low voltages (~ 2 V) and currents observed at higher voltages within first several hours of testing. However, the maximum calculated current is far below (more than 3 orders of magnitude) the level of reverse currents observed experimentally after long-term testing at 5 V. Also, according to this model the moisture flow through epoxy, hence leakage currents, should stabilize after time ~ t_D , which is less than a few hours. However, degradation of reverse currents at room conditions continues for more than thousands of hours. In calculations per Eq.(13) we have neglected diffusion through MnO2 in pores of the slug and through cathode layers (silver epoxy and MnO2), so the actual ionic currents should be smaller, likely in the submicroampere range.

Due to thermodynamic instability of anodic oxide films [20], Ta2O5 dielectric has a large concentration of positively charged oxygen vacancies, $V_o^{\bullet\bullet}$ in Kröger–Vink notations. Migration of these vacancies to Ta/Ta2O5 interface under reverse bias will result in the buildup of a surface charge, Q_s , reduction of the Schottky barrier and increasing injection of electrons from tantalum cathode. Accumulation of $V_o^{\bullet\bullet}$ should stabilize with time, and Q_s might eventually decrease due to charge compensation processes. This mechanism explains degradation of reverse currents in in the absence of moisture.

It is also possible that conductive filaments created either by oxygen vacancies aligned by electric field in the oxide as it is assumed in resistive random access memories based on TaOx dielectrics (anion-based switching memories) or by

electrochemical migration of ions (Cu^{++} or Ag^+) from the cathode electrode of the memory cells (cation-based switching memories) [21]. In our case, the source of Ag^+ is silver-epoxy used for attachment of pellets to lead-frames. The formed filaments are not stable and can be destroyed electrochemically, by reversing polarity, or by Joule heating that might result in erratic variations of leakage currents.

In humid environments, concentration of positively charged ions in the dielectric increases substantially due to injection of protons and reactions of water molecules with oxygen vacancies. Protons are active species and are strongly associated with oxygen in metal oxides. However, there are evidences that two states of hydrogen can be present in metal oxides [22]. One as protons covalently bonded to oxygen ions and forming relatively stable OH groups, while the other one is "free" isolated protons (interstitial mobile protons, H_{im}^{\bullet}) capable of fast moving in the oxide lattices. These mobile

protons are not stable and their concentration can be reduced substantially by ageing during a few hours at room temperatures resulting in gas H2 generation. For this reason, highly mobile protons are unlikely to participate in reverse bias degradation observed in dry conditions and in vacuum.

It is generally accepted that protons can migrate through oxides by two different mechanisms [23]. First, is a free transport, or Grotthuss mechanism, when protons spend most of the time localized at an oxygen ion, but from time to time can jump from one site to a neighboring one and second, as passengers on oxide ionic complexes by the vehicle mechanism. Oxygen vacancies are typically considered as such transport vehicles. Water molecules forming hydronium ions, H_3O^+ , may also serve as vehicles for protonic diffusion in relatively open structures. Similar to oxygen vacancies, positively charged hydroxyl vacancies, V_{OH}^{\bullet} might be formed in hydrated metal oxides and participate in conduction process [24].

Reaction of free water molecules with oxygen vacancies can result in formation of interstitial protons, H_i^{\bullet} , and neutral oxygen anions in normal lattice sites, O_o^x , [25]:

$$H_2 O + V_0^{\bullet \bullet} \longrightarrow 2H_i^{\bullet} + O_0^x, \tag{14}$$

Another reaction of water with oxygen vacancies can partially fill the vacancies and form movable protonic species [26]:

$$H_2 O + V_0^{\bullet} + O_0^{\chi} \longrightarrow 2OH_0^{\bullet}, \tag{15}$$

The presence of different types of oxygen vacancies that is based on their location in the lattice [27] and protonic species with different mobility can explain the two-stage degradation process in capacitors under reverse bias conditions. Species with higher mobility travel faster resulting in a hump on *I*-*t* curves during the first stage of degradation. At mobility of the species, μ , the time of travel across dielectric of thickness *d* under voltage *V* can be estimated as

$$\tau = \frac{d^2}{\mu \times V},\tag{16}$$

For CWR06 capacitors $d \sim 0.15 \,\mu\text{m}$ and $\tau I \sim 30$ hr at room temperature. This corresponds to $\mu \sim 4 \times 10^{-16} \,\text{cm}^2/(\text{V}\times\text{sec})$. Considering that the characteristic time of the second stage of the process is more than two orders of magnitude greater, the mobility for "slow" species is less than $4 \times 10^{-18} \,\text{cm}^2/(\text{V}\times\text{sec})$. A faster time transfer in commercial 194D and 293D capacitors might be partially due to thinner dielectrics used in these parts. Variations in the oxide structure, concentration of oxygen vacancies and protonic species formed during manufacturing processes are also factors contributing to the difference in the rate and level of degradation in capacitors from different lots.

The mobility of oxygen vacancies reported by Manceau and co-workers [28] is ~ 1.7×10^{-16} cm²/(V×sec), which is close to our estimations for the fast species. Analysis of electrochemical impedance spectroscopy on tantalum oxide films indicated the presence of two types of charges with diffusion coefficients that differ by more than two orders of magnitude, ~ 5×10^{-17} and 2×10^{-20} cm²/s [24]. These charges were attributed to the oxygen and hydroxyl vacancies respectively. Using Einstein-Smoluchowski equation, $\mu = D \times q/(kT)$, these diffusion coefficients correspond to mobilities of 2.1×10⁻¹⁵ and 4×10⁻¹⁹ cm²/(V×sec), which are within an order of magnitude of our results.

The most likely species for fast charge transport during RBS testing are oxygen vacancies and protonic complexes OH_o^{\bullet} formed by reaction Eq.(15). Higher values of I_{max} and smaller times to the first maximum in humid environments compared to dry conditions (see Fig. 7a, b) are due to a greater concentration of ionic charges in humid environments and likely somewhat greater mobility of protonic species compared to oxygen vacancies.

Protonic species can be reduced at the cathode and hydrogen atoms can relatively easily enter into the lattice of tantalum. The diffusion coefficient of hydrogen in tantalum at room temperature is relatively large ~ $(1-2)\times10^{-6}$ cm²/sec, and the activation energy is relatively low, 0.14 eV to 0.18 eV [29-31], so hydrogen will travel a distance of dozens of micrometers within a few seconds. Considering a large solubility of protons in tantalum [32], this process can explain saturation of the degradation process and decreasing currents after long-term operation under reverse bias.

When a part is left unbiased in the presence of moisture, concentration of protonic species in the oxide is increased according to reactions Eq.(14, 15), and repeat application of reverse bias results in currents exceeding the level that had been reached during previous stresses. In dry conditions the situation is different and because discharging of accumulated charge continues during unbiased storage, it might result in lower currents when testing continues.

Anodic oxidation goes along with saturation of the oxide with moisture and hydrogen resulting in formation of different protonic complexes. Most of these complexes can be expelled only in vacuum at temperatures exceeding 200 °C, and for this reason they are present in oxides even in dry conditions. This explains why the two-stage degradation process can be observed even in vacuum. However, in the absence of hydrogen supply from environments, the degree of degradation is much less. Also, RBS at high temperatures or voltages might "clean-up" the oxide by sweeping most oxygen vacancies and protonic species to the Ta/Ta2O5 interface, so a repeat reverse bias testing at lower voltages or temperatures in vacuum would result in more stable leakage currents.

Conclusion

- 1. Slugs in tantalum chip capacitors can be used as moisture sensors. Variations of capacitance with time after exposure to environments with different humidity depends on the moisture content in the slug and allows for evaluation of the kinetics of moisture sorption or desorption in capacitors.
- 2. Variations of capacitance with time after change in the humidity of environments can be characterized by two time constants: diffusion delay, t_D , and characteristic time of variations between minimal and maximal values, τ . A simple model that describes *C*-*t* variations using moisture characteristics and sizes of plastic packages and tantalum slugs has been developed.
- 3. Degradation of leakage currents in tantalum capacitors under reverse bias strongly depends on pre-conditioning and the presence of moisture in environments. Pre-history has a long lasting effect exceeding substantially the characteristic times of moisture diffusion. At room temperature, variations of relative humidity from 7% to 85% can increase currents more than 2 orders of magnitude. There is also a substantial difference in the degradation rates between vacuum and dry air conditions.
- 4. Estimations based on the permeability of plastic cases show that experimental reverse leakage currents are orders of magnitude greater than the ionic currents calculated based on the moisture flow into the slug. The effect of moisture is explained by increased concentration of positively charged protonic species in oxide. Migration of these species acts similar to migration of oxygen vacancies resulting in reduction of the barrier at the Ta/TaO5 interface and increasing Schottky injection of electrons.
- 5. Reverse bias degradation of leakage currents is a two-stage process with the first maximum observed within a few hours of testing at room temperature, and the second appears after hundreds and thousands of hours. This is attributed to the presence of ionic species with high, $\sim 4 \times 10^{-16} \text{ cm}^2/(\text{V}\times\text{sec})$, and low, less than $4 \times 10^{-18} \text{ cm}^2/(\text{V}\times\text{sec})$, mobility. The first one likely corresponds oxygen vacancies and the vehicle transport mechanism of protons migration, while the second one to protonic species with strong bonds to oxygen ions.

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