

Effect of Reverse Bias Stress on Leakage Currents and Breakdown Voltages of Solid Tantalum Capacitors

Alexander Teverovsky

Dell Perot Systems
Code 562, NASA GSFC, Greenbelt, MD 20771
Alexander.A.Teverovsky@nasa.gov

I. Introduction

The majority of solid tantalum capacitors are produced by high-temperature sintering of a fine tantalum powder around a tantalum wire followed by electrolytic anodization that forms a thin amorphous Ta_2O_5 dielectric layer and pyrolysis of manganese nitrite on the oxide to create a conductive manganese dioxide electrode. A contact to tantalum wire is used as anode terminal and to the manganese layer as a cathode terminal of the device. This process results in formation of an asymmetric $Ta - Ta_2O_5 - MnO_2$ capacitor that has different characteristics at forward (positive bias applied to tantalum) and reverse (positive bias applied to manganese cathode) voltages. Reverse bias currents might be several orders of magnitude larger than forward leakage currents so I-V characteristics of tantalum capacitors resemble characteristics of semiconductor rectifiers.

Asymmetric I-V characteristics of $Ta - Ta_2O_5$ systems have been observed at different top electrode materials including metals, electrolytes, conductive polymers, and manganese oxide thus indicating that this phenomenon is likely related to the specifics of the $Ta - Ta_2O_5$ interface. There have been multiple attempts to explain rectifying characteristics of capacitors employing anodic tantalum pentoxide dielectrics:

- Analysis of photoeffects and variations of capacitance with applied voltage allowed Sasaki [1] to conclude that the oxide film can be presented as a p-i-n junction. A thin n-type layer is formed at the Ta interface due to excess of Ta atoms, and a p-type layer is formed at the external oxide surface due to excess of oxygen atoms.
- Vermileya [2] suggested that rectification in $Ta - Ta_2O_5$ systems occurs at flaws in the oxide layer by at least two mechanisms, one involving the opening of physical holes and the other an electronic junction that is formed by electrodes with different contact potentials resulting in an asymmetric barrier.
- Bishop and Jill [3] also assumed that reverse currents are due to the presence of defects in oxide resulting in current densities high enough to form tiny hot spots that enhance conversion of amorphous Ta_2O_5 dielectric into a more conductive crystalline form.
- Sikula and co-workers [4-5] considered $MnO_2 - Ta_2O_5$ contact as a n - p heterostructure formed by the n-type MnO_2 semiconductor and P-type Ta_2O_5 isolator.
- Loh [6] regarded $Ta - Ta_2O_5 - MnO_2$ capacitor as a metal-insulator-metal structure with two blocking contacts. The conduction mechanism in the reverse direction was described as electron trap-filling at relatively low voltages followed by space-charge-limited process at high voltages.
- Primak [7] explained high level of reverse currents as a result of oxygen depletion that forms local thinning of the dielectric and causes local breakdowns. Another possible mechanism was related to injection of hydrogen (protons) at high enough reverse voltages.
- Extensive studies of thermal and photoconductive charge transport in Ta_2O_5 metal-oxide-metal capacitors fabricated by different techniques, including anodization, have been carried out by Fleming and co-workers [8]. In all cases diode-like, asymmetric I-V characteristics were observed and increased currents in forward direction were explained by electron emission from tantalum anode into a defect band formed by high concentration of defects in the oxide.

A brief review of works related to reverse bias (RB) behavior of tantalum capacitors shows that the mechanism of conduction in $Ta - Ta_2O_5$ systems is still not clear and more testing and analysis is necessary to understand the processes involved.

If tantalum capacitors behave just as rectifiers, then the assessment of the safe reverse bias operating conditions would be a relatively simple task. Unfortunately, these parts can degrade with time under reverse bias significantly [1, 9], and this further complicates analysis of the I-V characteristics and establishing safe operating areas of the parts. On other hand, time dependence of reverse currents might provide additional information for investigation of the processes under reverse bias conditions.

In practice, there were instances when, due to unforeseen events, the system operated at conditions when capacitors experience periodically a relatively small reverse bias for some time followed by normal, forward bias conditions. In such a case an assessment should be made on the degree to which these capacitors are degraded by application of low-voltage reverse bias, and whether this degradation can be reversed by normal operating conditions.

In this study, reverse currents in different types of tantalum capacitors were monitored at different reverse voltages below 15% VR and temperatures in the range from room to 145 °C for up to 150 hours to get better understanding of the degradation process and determine conditions favorable to the unstable mode of operation. The reversibility of RB degradation has been evaluated after operation of the capacitors at forward bias conditions. The effect of reverse bias stress (RBS) on reliability at normal operating conditions was evaluated using highly accelerated life testing at voltages of 1.5VR and 2 VR and by analysis of changes in distributions of breakdown voltages. Possible mechanisms of RB degradation are discussed.

II. Degradation of reverse currents

Fourteen types of commercial and military-grade chip tantalum capacitors rated to voltages from 35V to 63V have been tested at reverse bias voltages in the range from 3% VR to 15% VR and temperatures from room to 145 °C. Four groups of low-voltage capacitors were added to this study to address common features in the degradation process. Each tested group of parts had from five to twenty samples.

II.1. Effect of voltage at room temperature

Figure 1 shows variations of RB currents with time for three types of capacitors rated to 35V at voltages from 1 V (2.8% VR) to 2.5 V (7.1% VR) in 0.5 V increments. In all cases, the currents decreased initially and then increased with a rate decreasing with time, indicating a trend to stabilization. An on-set of current degradation is ~ 1hr at 1.5 V (4.3% VR) and decreases to approximately one minute at 2.5 V. RBS testing at 2 V (5.7% VR) for 20 hrs resulted in currents increasing more than two orders of magnitude. The level of current stabilization increases and time to stabilization decreases with applied voltage.

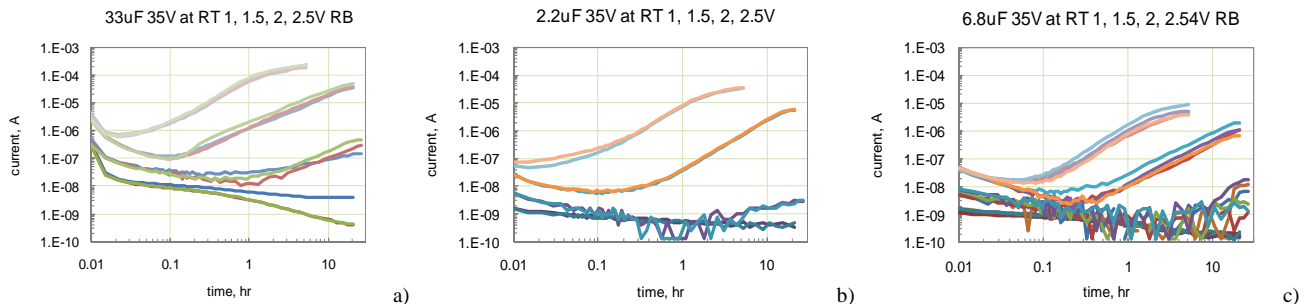


Figure 1. Degradation of reverse currents with time for 33 uF (a), 2.2 uF (b), and 6.8 uF (c) 35 V capacitors at voltages from 1 V to 2.5 V in 0.5 V increments.

Contrary to the 35 V capacitors, erratic behavior was observed in one out of 20 Mfr.C_T 4.7 uF 50 V capacitors tested at 3 V (6% VR) and in three out of four parts tested at -5 V (see Figure 2). Similar to the previous case, reverse currents start degrading at voltages as low as 1.5 V (3% VR) and increase 3 to 4 orders of magnitude at 6% VR (3V). The on-set of current increase at 1.5 V occurs after approximately 10 hours of testing and after ~0.1 hr during testing at 3 V. After reaching maximum at 10 to 20 hours, the currents are decreasing with time and apparently stabilize at somewhat lower levels.

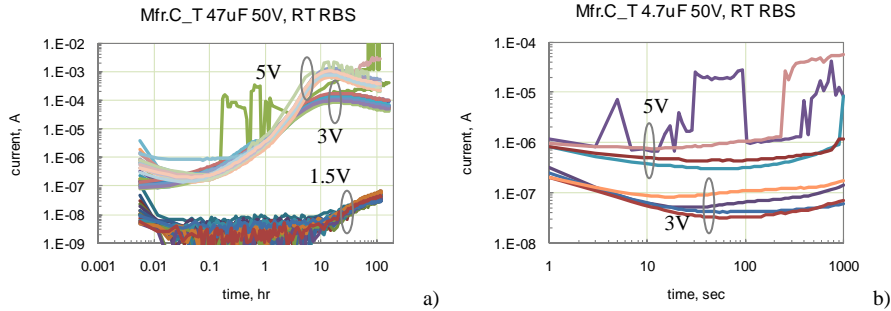


Figure 2. Time-dependence of reverse currents in 4.7 uF 50 V capacitors at 1.5 V, 3 V, and 5 V during 150 hrs of RBS testing (a) and at 3 V and 5 V during 15 min test (b). Note erratic behavior for some parts at 5V.

Long-term degradation of reverse currents in three other types of 4.7 uF 50 V capacitors at 3 V, 5 V, and 7 V is shown in Figure 3 and indicates that, for different part types, the level of stabilized currents varies up to two orders of magnitude. Reverse bias stress at 6% VR for 140 hours results in more than 4 orders of magnitude of currents increase for Mfr.I_R3 parts, more than 2 orders of magnitude for Mfr.A_S parts, and approximately 3 orders of magnitude for Mfr.I_3 parts. One out of 10 samples was in the unstable mode with erratically changing currents after ~20 hour of testing at 5 V for Mfr.A_S lot of parts and after ~30 hours of testing for Mfr.I_3 parts.

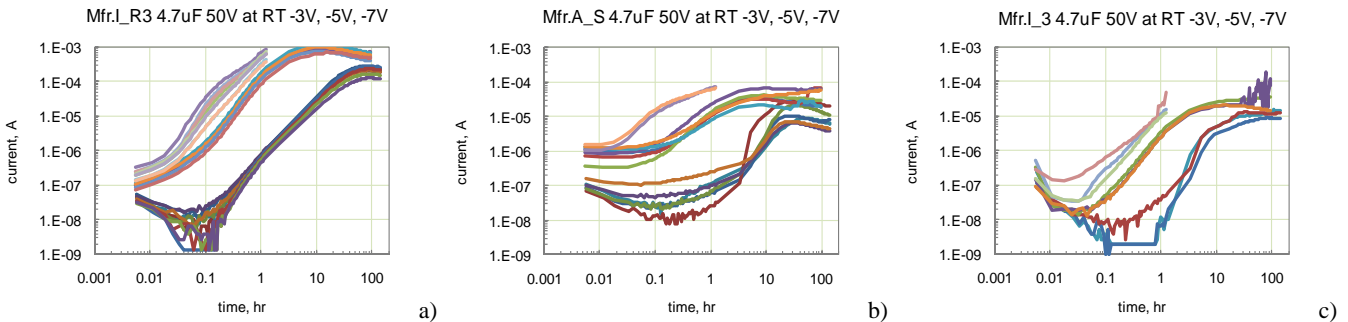


Figure 3. Reverse currents in three types of 4.7 uF 50 V capacitors at 3 V, 5 V, and 7 V.

Figure 4 presents more data on long-term (100 hr) reverse bias stress testing in capacitors rated to 50 V. These data confirm that degradation in different part types at low RB voltages (3% VR) begins after ~10 hrs to ~50 hrs of testing. Erratic behavior of currents and oscillations were not observed at 1.5 V, but was detected in some part types at 5 V and in all part types at 7 V. The results show that erratic behavior might be not observed initially after RB application, but can happen after a few hours of testing at RB ~ 10% VR.

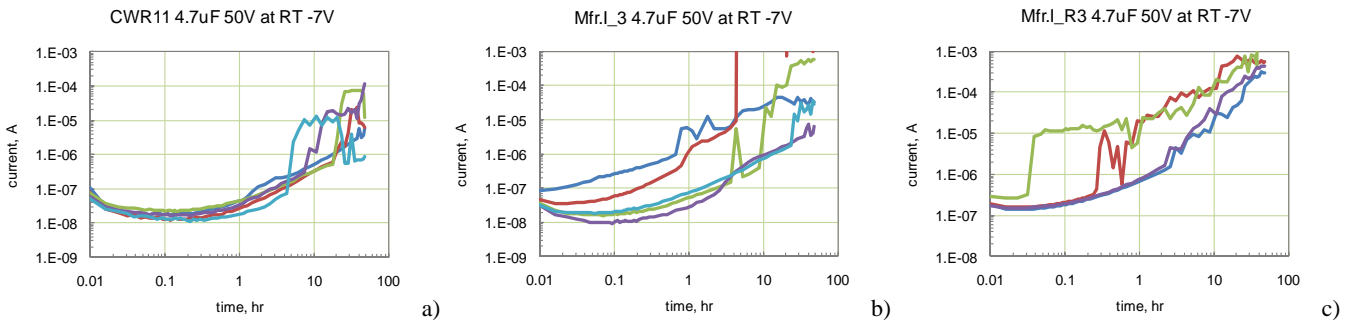


Figure 4. Degradation of reverse currents with time at 7 V reverse bias for five samples of different types of 4.7 uF 50 V capacitors.

The probability of capacitors to become unstable and cause erratic changes of the current is lot-dependent and can occur at voltages as low as 6% VR. The observed current variations did not exceed a few mA and appeared as a noise rather than high current spikes. However, this is likely due to a relatively low sampling rate of the data acquisition system used, so the real current spikes are likely similar to scintillation breakdowns, have a duration in the micro- or milli-second range, and can reach a few amperes in the amplitude. In circuits with inductances these spikes can generate

significant voltage transients and cause damage to other components. This erratic behavior in capacitors can occur after hours under reverse bias, and the probability of its occurrence increases with reverse voltage. For the tested lot of Mfr.C_T 4.7 uF 50 V capacitors, the proportion of samples manifesting erratic behavior increases from ~5% of the lot during 3 V testing to ~50% at 5 V and to >75% at 7 V. Approximately 50% of parts rated to 63V were unstable at a voltage as low as 4 V RB (6.3% VR).

II.2. Effect of temperature.

Results of RBS testing at 1 V and temperatures from room to 125 °C for different types of 10 V capacitors showed that temperature accelerates current degradation and reduces the onset of current increase from 0.1 hr to 1 hr at room temperature to 0.02 hr to 0.1 hr at 50 °C and to less than 0.01 hr at temperature of 85 °C and higher. This indicates an effective activation energy of the degradation process $E_d \sim 0.75$ eV.

Typical variations of reverse currents with time of stress testing for of 35 V capacitors at voltages from 1 V to 2.5 V and temperatures of 22 °C, 85 °C, and 105 °C are shown in Figure 5. Similar results were obtained for five types of 35V capacitors. Different part types have similar kinetics of current variations, but different levels of degradation that apparently increases with the capacitance value. An increase in temperature accelerates degradation processes and makes stabilization of currents after large enough duration of stress more obvious. The level of current stabilization increases with voltage, and at 2.5 V, the time to stabilization decreases from approximately 10 hrs at room temperature to 0.1 hr at 85 °C and to ~ 0.01 hr at 105 °C thus indicating $E_d \sim 0.74$ eV, which is close to the value estimated for 10 V capacitors.

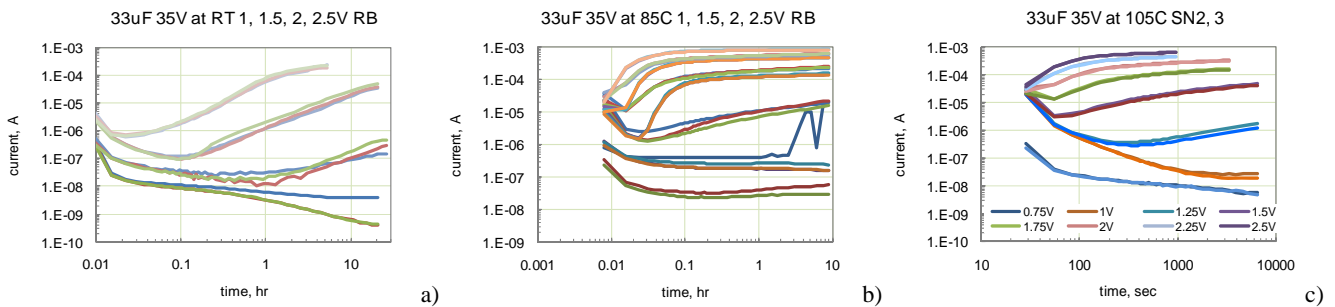


Figure 5. Degradation of reverse currents in 33 uF 35 V capacitors at different voltages and temperatures of 22 °C (a), 85 °C (b), and 105 °C (c).

For 33 uF 35 V capacitors reverse currents at 85 °C and 3 V RB increased from less than 0.1 mA initially to approximately 0.04 A after 0.5 hours of stress testing (see Figure 6). After that the currents remained stable for up to ~ 40 hour of testing and then start increasing again. This indicates a two-stage degradation process with significantly different characteristic times and likely different activation energies.

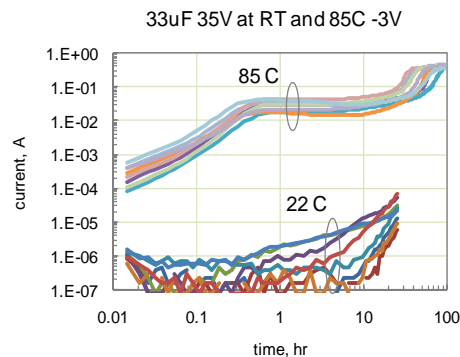


Figure 6. Comparison of room temperature and 85 °C degradation of reverse currents in 33 uF 35 V capacitors at 3 V RB. Note, that the effective resistance of the power supply was 1.7 ohm, so the current stabilization at 85 °C below 0.05 A is not related to possible variations of the stress voltage during the testing, whereas stabilization at ~ 0.5 A is likely due to the reduction of the voltage drop across the capacitors.

Results of RBS testing of Mfr.C_T 4.7 uF 50 V capacitors at temperatures from 85 °C to 145 °C in 20 °C increments and voltages varying from 2% VR to 6 % VR are shown in Figure 7. Analysis shows that at 1.5 V an increase in

temperature reduces drastically the time to beginning of degradation. This time decreases from ~10 hrs at 22 °C to ~0.1 hr at 85 °C, 0.04 hr at 105 °C, and to ~0.02 hr at 125 °C, indicating $E_d \sim 0.7$ eV.

At 145 °C and voltage as low as 2% VR reverse currents are increasing up to two orders of magnitude after ~ 1 hr of testing and then stabilize after a few hours. Test results at 105 °C (see Figure 7b), similar to 33 uF 35 V parts, indicate the presence of at least two degradation processes with different characteristic times. The first process results in current stabilization after ~1 hour at 3 V and probably after ~ 3 hours at 1.5 V. The onset of the second process is clearly seen after ~ 50 hours of testing at 3 V.

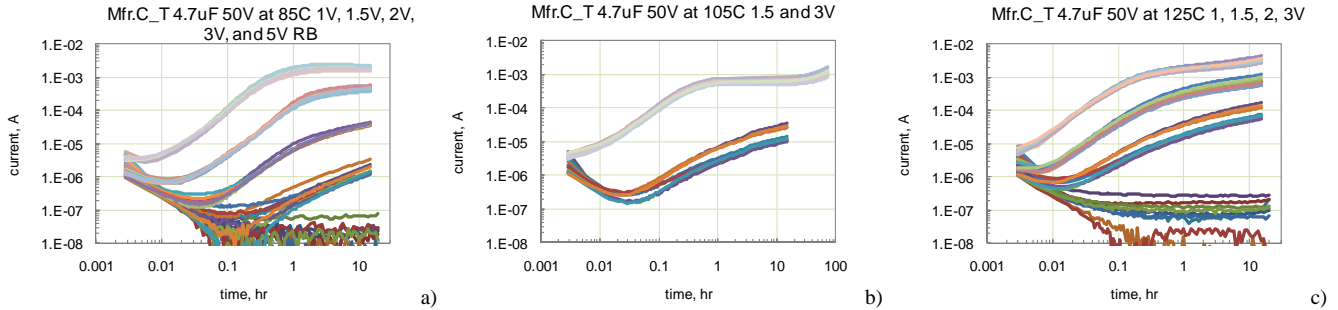


Figure 7. Degradation of reverse currents in 4.7 uF 50 V Mfr.C_T capacitors at different voltages and temperatures of 85 °C (a), 105 °C (b), 125 °C (c).

II.3. Reproducibility of RB degradation after operating at forward bias conditions

Results of measurements of reverse currents in 220 uF 10 V capacitors at room temperature and 1.5 V for 80 hours are shown in Figure 8. The currents degraded more than an order of magnitude and stabilized after approximately 20 hours of testing. Repeat measurements after three days of storage at unbiased conditions resulted in a similar behavior indicating the reversibility of the degradation process.

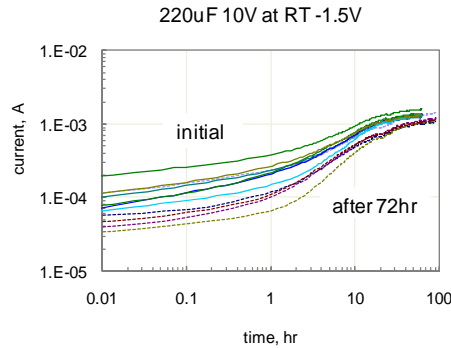


Figure 8. Reverse currents in 220 uF 10V capacitors at 1.5V initially (solid lines) and after storing for 3 days (dashed lines).

Similar results were obtained for Mfr.C_T 4.7 uF 50V capacitors (see Figure 9). After initial RBS testing at room temperature and 3 V for 140 hours the currents increased almost three orders of magnitude, from ~0.1 uA to ~0.1 mA. Exposure of these parts to normal operating conditions at 50 V for 15 minutes restored initial currents and resulted in currents increasing with time similar to what was observed initially. RBS testing at 5 V for 120 hours (Figure 9 b) increased currents by approximately four orders of magnitude. In this case, testing at 50 V of forward voltage for 30 minutes was not sufficient to restore initial conditions completely, and repeat reverse bias testing occurred somewhat faster than initially.

An increase of time of testing at normal conditions after RBS results in a more complete recovery of the initial currents and in a better reproducibility of the RB degradation process. Figure 9c shows that 5 minutes of testing at 50 V resulted in only partial restoration of degradation at 85 °C, whereas this process was close to the initial after testing at 50 V for 60 minutes.

Results of repeat room temperature RBS testing for three types of 4.7 uF 50 V capacitors at 3 V following 100 hour testing at 100V forward bias conditions are displayed in Figure 10. A comparison with the results of the initial RBS test at the same conditions that are shown in Figure 3 indicates almost complete reproducibility of the process. However, the rate of current increase was somewhat slower and the incubation period before the on-set of degradation was greater

than initially. For example, for the Mfr.I_R3 part type the level of 1×10^{-6} A was reached after ~ 1 hour during the initial RBS and after ~ 4 hours after forward bias stress (FBS) testing. For Mfr.I_3 parts these times were ~ 6 hours initially and 10 to 20 hours after FBS.

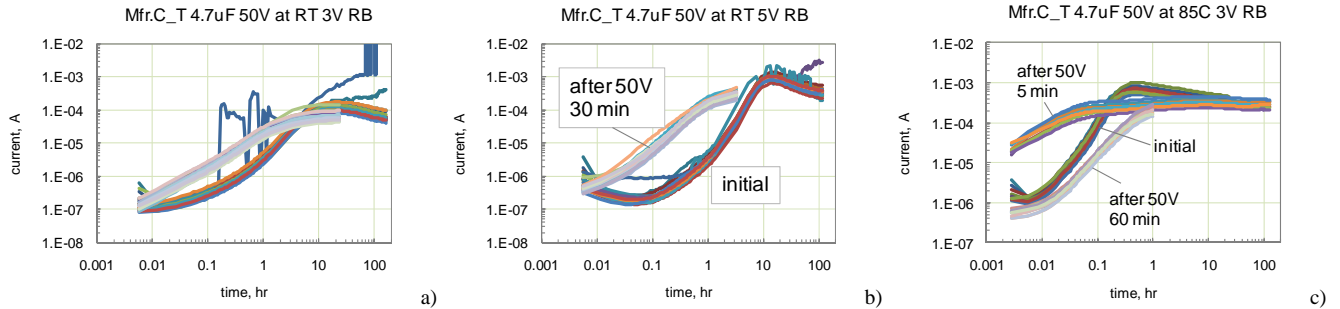


Figure 9. Reproducibility of degradation of reverse currents in 4.7 uF 50 V capacitors at room temperature (a, b) and at 85 °C (c).

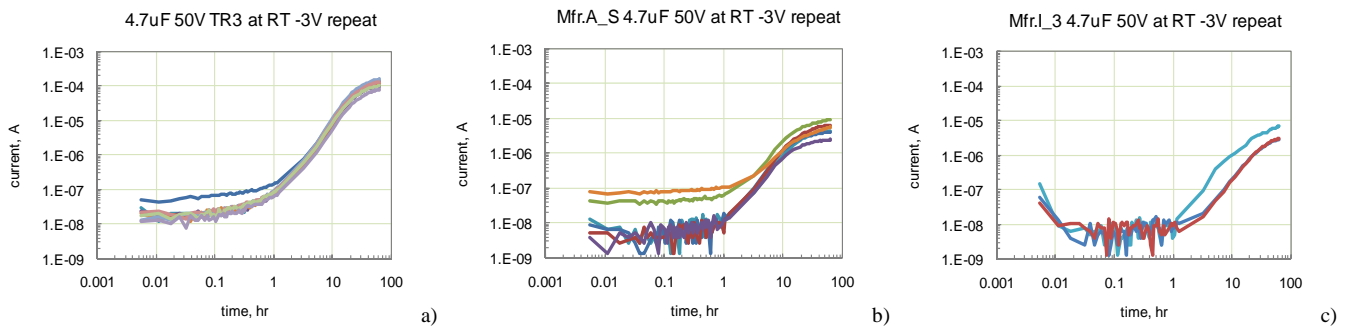


Figure 10. Repeat degradation of reverse currents in different types of 4.7 uF 50 V capacitors at room temperature and -3V after testing the parts at 100 V forward bias for 100 hr. Initial results of RBS testing are shown in Figure 3.

III. Effect of reverse bias stress on forward leakage currents

To assess the effect of reverse bias stress on leakage currents, four types of 10 V capacitors were stressed at 2 V RB for 3 hours at temperatures of 85 °C, 105 °C, and 125 °C. The values of Direct Current Leakage (DCL) were measured at 10 V and relevant temperatures before and after RBS testing. A correlation between the initial and post-RBS values of DCL is shown in Figure 11 and indicates that in spite of substantial, from one to two orders of magnitude degradation of reverse currents, forward currents in these capacitors remain unchanged.

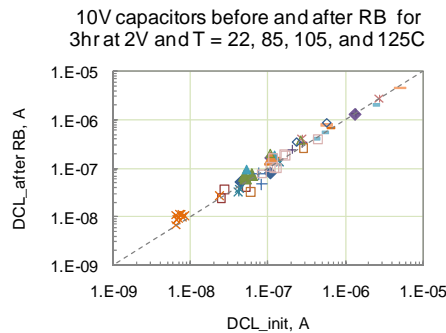


Figure 11. Correlation between initial and post-reverse-bias-stress forward leakage currents measured at 10 V for 15 uF, 22 uF, 47 uF, and 100 uF 10 V capacitors stressed at -2 V for 3 hr and temperatures varying from room to 125 °C. Different marks correspond to different groups of capacitors. A dashed line corresponds to no-change values.

Similar results (see Figure 12) were obtained for various 35 V capacitors after RBS testing at different conditions varying from 1 V for 24 hrs at room temperature to 2 hrs at 2.5 V and 105 °C. A substantial, more than 2 orders of

magnitude increase in DCL was observed in two samples out of 25 parts stressed by 10-hour RB testing at 85 °C; however, leakage currents in the rest of the group remained stable.

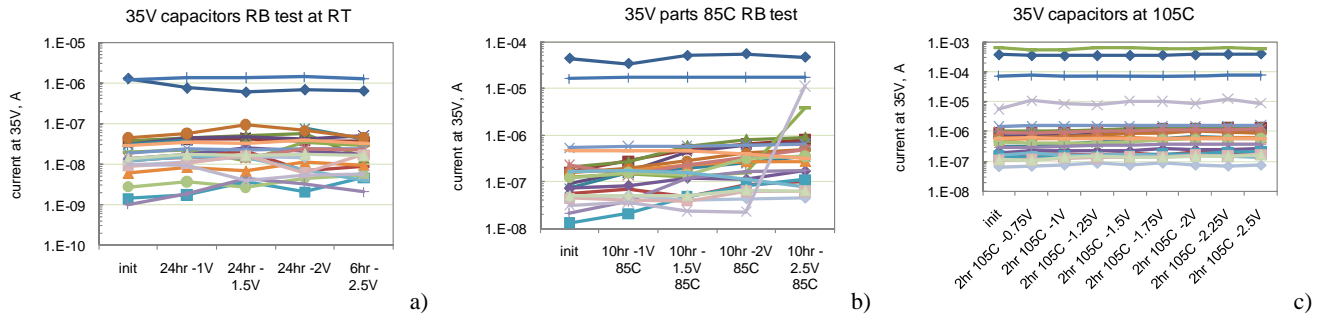


Figure 12. Variations of forward leakage currents measured at VR in various types of 35 V capacitors (2.2uF to 33uF) after different reverse bias stresses at room temperature (a), 85 °C (b), and 105 °C (c).

Forward leakage currents in Mfr.C_T 4.7 uF 50 V capacitors were measured at the rated voltages following RBS testing at different voltages, temperatures, and stress duration. Results of these measurements are shown in Figure 13 and indicate that leakage currents for a majority of the parts remain stable in spite of the increase in reverse currents by three to four orders of magnitude. Test results for other types of 4.7 uF 50 V capacitors confirm stability of leakage currents after RBS testing. In some cases, the values of DCL decrease slightly as the level of reverse bias stresses increases from one group of testing to another.

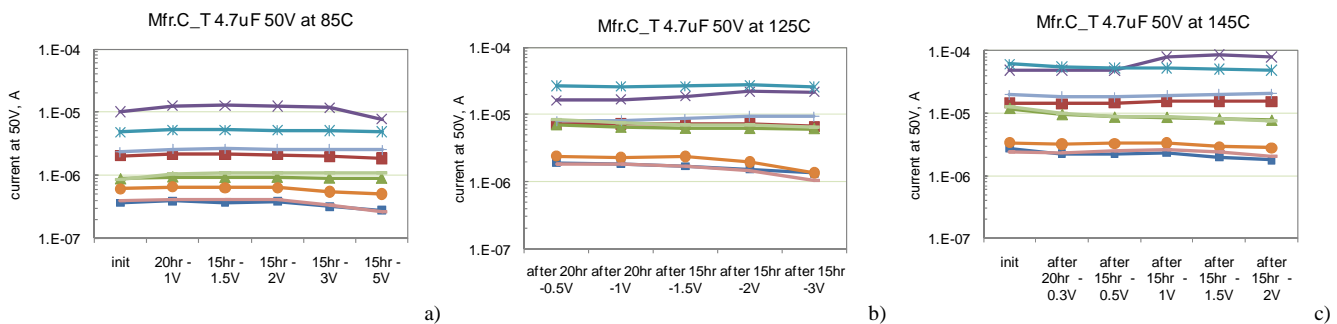


Figure 13. Variations of forward leakage currents measured at VR in 4.7 uF 50 V Mfr.C_T capacitors after different reverse bias stresses in the range from 22 °C to 125 °C.

To evaluate the effect of RB on reliability, several groups of 4.7 uF 50 V capacitors after reverse bias stress testing at 22 °C and 3 V for 140 hours were tested for 100 hours at room temperature and voltages of 1.5VR and 2VR. No failures were observed during 100-hour 75 V testing and two out of 10 tested Mfr.I_R3 samples failed during the 100 V test. A similar proportion of failures for testing at twice the rated voltage is expected for these part types based on additional experiments with virgin samples, which suggests that RBS likely did not cause any significant increase in the failure rate of the parts. However, post-RBS failures were observed in another two groups of 4.7 uF 50 V capacitors that were stress tested at 3 V reverse bias at 85 °C for 6 hours and then at the same temperature at 50 V forward bias for 90 hours. Most of the capacitors had scintillations, and one out of four parts failed after 40 hours of testing. This indicates that, at relatively high temperatures, RB degradation at voltages as low as 6% VR can compromise reliability of the parts.

IV. Effect of reverse bias stress testing on breakdown voltages

Distributions of scintillation breakdown voltages were measured in various groups of capacitors after RB and forward bias (FB) stress testing. Out of ten tested part types, eight were high-voltage capacitors: two part types were rated to 63 V, five to 50V, and the rest were rated to 35 V, 10 V, and 6V. Each group had from 10 to 20 samples. Comparison of distributions with the results of measurements for virgin parts was used to assess the effect of stress testing on breakdown voltages.

For low-voltage capacitors (parts rated to 6 V and 10 V), testing at a relatively high level of reverse voltages (from 20% to 30% VR) for 18 hours did not cause substantial degradation of breakdown voltages. Median VBR decreased ~15%

for 6 V capacitors and practically did not change for 10 V parts. Similarly, 73-hour forward bias stress (FBS) testing of 10 V capacitors at 2VR and 125 °C did not cause any changes in the distributions of VBR.

Results of testing of 4.7 uF 50 V capacitors are shown in Figure 14 and are summarized in Table 1. RBS testing was typically carried out at 85 °C and 3 V (6%VR) for 72 hours and FBS at 150 °C and 50 V for 100 hours. In all cases long-term stress at forward bias conditions resulted in a significant (from 20% to 50%) increase in breakdown voltages. Contrary to that, median VBR decreased by 10% to 20% in three out of five part types after RBS and remained the same for two other lots. Typically, RBS resulted in a decrease in the slope of distributions due to increased proportion of samples with substantially degraded VBR. For this reason, values of VBR that correspond to the first quantile of distributions, VBR_1%, decreased by 20% to 80% in four out of five part types, and no effect of RBS on VBR was observed for a lot of Mfr.A_S parts. Two part types, Mfr.A_J and Mfr.C_T, that are shown in Figure 14 were tested after different levels of FB stress testing indicating that the higher the level of stress the more significant the change of VBR is.

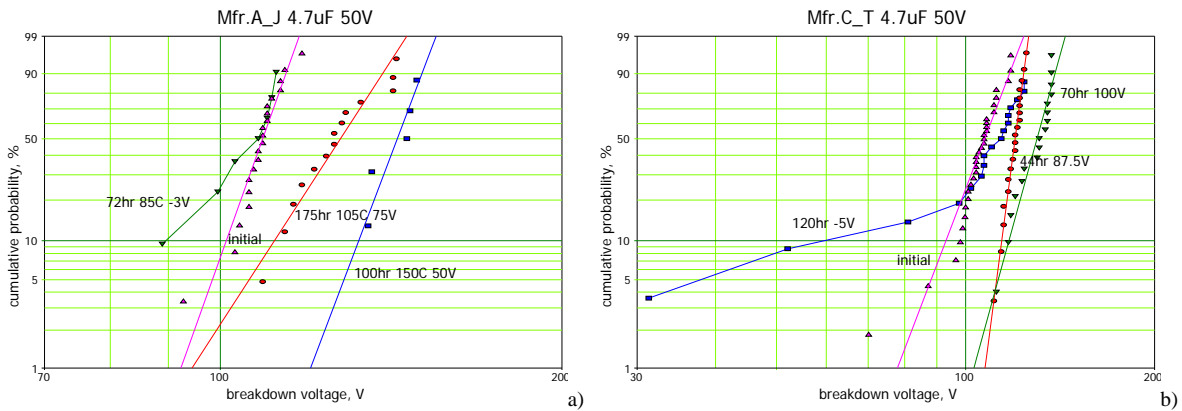


Figure 14. Weibull distributions of scintillation breakdown voltages for different types of 4.7 uF 50 V capacitors.

Breakdown voltages in two types of 22 uF 63 V capacitors have been tested after BRS at room temperature and 5 V for 54 hours and after FBS after 100 hrs and 100 V. Similar to 50 V parts, these capacitors decrease VBR after reverse bias and increase after forward bias stresses. The median value decreased after RBS by 17% to 50% and VBR_1% values decreased by 20% to 85%. An increase of VBR after FBS was ~ 15% for median values and from 17% to 41% for the first quantiles.

Table 1. Effect of reverse and forward bias stress on breakdown voltages in 4.7 uF 50 V capacitors

Part	median VBR					first quantile				
	Init, V	RBS, V	%	FBS, V	%	Init, V	RBS, V	%	FBS, V	%
Mfr.I_3	134	106	79			105	20	19		
L1YF	154	121	82			106	75	70		
Mfr.A_J	112	104	92	143	128	92	77	83	120	130
Mfr.C_T	107	109	101	130	121	78	31	40	107	137
Mfr.A_S	96	96	100	148	153	84	85	100	122	145
average			90.8		134.0			62.4		137.3
stdev			10.1		16.8			32.7		7.5

V. Discussion

The most important experimental results of this study that require explanations can be summarized as follows:

- Reverse leakage currents significantly (up to four orders of magnitude) increase and then stabilize with time under bias. This process is reversible after long-term storage and/or operation of the part under forward bias conditions.
- An increase in temperature and reverse voltage reduces the time to the onset of degradation and the time to current stabilization. Based on temperature variations of the onset times, the effective activation energy of degradation is ~ 0.75 eV. Long-term RBS testing at temperatures of 85 °C and above clearly indicate the presence of a second degradation process that have much larger characteristic times (~ 30 hrs at 85 °C compared to ~ 0.3 hr for the initial process), and respectively, larger (>0.75 eV) activation energies.

- In spite of significant degradation of currents under RBS (several orders of magnitude), there is minimal or no variations of forward currents for the majority of samples from different part types.
- RBS in the majority of tested high-voltage capacitors resulted in a substantial decrease of breakdown voltages.

As it has been shown in our previous work [10], breakdown voltages in tantalum capacitors can be considered as a characteristic that is directly related to long-term reliability of the parts, so the reduction of VBR after RBS testing indicates a higher probability of failures during operation. Post-RBS life testing at 85 °C showed a significant proportion of failures and thus confirms that a long-term stress at relatively low RB voltages (6%) can degrade reliability of the capacitors at normal operating conditions.

Experimental data discussed above can be explained considering solid tantalum capacitors as asymmetric metal-insulator-semiconductor (MIS) structures with a defect-related band gap formed in the tantalum pentoxide insulator. In this structure, tantalum is the metal and manganese dioxide is a narrow-band n-type semiconductor [4, 6] (see Figure 14). High concentration of defects and associated electron traps in anodic Ta₂O₅oxide results in formation of a defect band across the thickness of the dielectric and to the pinning of the Fermi level near the defect band [8]. The presence of a defect band gap, E_g, allows consider conduction through Ta₂O₅dielectric as electron transport in a semiconductor with two blocking contacts at the tantalum and MnO₂ interfaces [6] with the barrier at the Ta interface being much lower than at MnO₂.

At normal voltage polarity (Figure 14a) when a negative bias is applied to manganese cathode, electrons are emitted into the band gap over a barrier Φ_B between MnO₂ and Ta₂O₅ layers. Forward currents are controlled by surface conditions and depend on the value of electric field at the surface that reduces the barrier according to Schottky mechanism. At reverse polarity (Figure 14c), the current depends on the barrier V_B that exists between tantalum and quasi-semiconductor Ta₂O₅ oxide. Electrons from the tantalum cathode are injected into oxide either by direct tunneling through a thin barrier layer or by the indirect, trap assistant tunneling [11]. As was shown in ref. [11], for insulators containing a high density of traps and at relatively low voltages, the currents increase nearly exponentially with voltage, and the conduction process changes from electrode-limited to bulk-limited as voltage increases. In this case, the current is controlled by transport through the defect conduction band and the activation energy of temperature dependence of reverse currents can be used to assess the value of E_g. Based on our data, E_g is in the range from 0.75 eV to 0.95 eV.

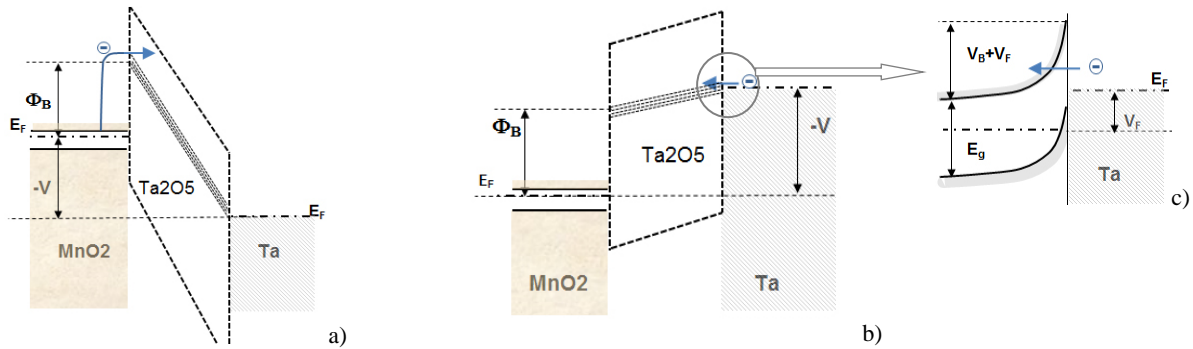


Figure 14. A simplified schematic of Ta – Ta₂O₅ – MnO₂ structure under forward (a) and reverse (b, c) bias conditions.

The presence of movable positively charged oxygen vacancies, V_O⁺⁺, in anodic Ta₂O₅ dielectrics results in accumulation of positive charges at the Ta – Ta₂O₅ interface with time under reverse bias. This raises electric field at the interface, enhances injection of electrons, and increases reverse currents with time under bias. Redistribution of oxygen vacancies is stabilizing with time resulting in leveling off of the currents. Electron trapping and neutralization of positive charges reduce electric field at the surface and might cause some decrease in reverse currents with time after stabilization of V_O⁺⁺ distribution. Migration of V_O⁺⁺ is a thermally activated process with high activation energy and is rapidly accelerating with temperature, whereas electron trapping, that is a tunneling related process, has weak temperature dependence. For this reason charge neutralization is more likely to occur at relatively low temperatures. This explains why maximum on the variation of reverse currents with time of stress is typically observed during room temperature testing, while a clear stabilization of the current is observed at 85 °C and higher temperatures.

Based on our estimations, activation energy of the RB degradation process is ~ 0.75 eV, which is lower than the activation energy of forward current degradation (~ 1.1 eV) [10]. This apparent discrepancy can be explained considering the presence of at least two RB degradation processes with more than an order of magnitude different characteristic times and respectively substantially different activation energies. These two processes might be related to the two ionization states of oxygen vacancies suggested by Lau [12] or to the presence of different types of movable ionic charges. It is also possible that due to a large concentration of defects and vacancies and relatively loose oxide structure, the mobility of V_o^{++} is greater, and the activation energy of transport is lower at the areas of the oxide close to Ta – Ta₂O₅ interface compared to the bulk of the oxide.

The similarity of degradation processes during forward and reverse stresses was also confirmed by analysis of spectrums of thermally stimulated depolarization (TSD) currents measured after forward and reverse bias polarizations. Results of these experiments for two types of 4.7 uF 50V capacitors showed the presence of two peaks with maximum at ~ 75 °C (peak B) and ~ 150 °C (peak C) for both FBS and RBS test conditions. Position of peak B remains stable and corresponds to relaxation processes with activation energy of ~ 0.95 eV. The temperature corresponding to peak C is decreasing with the level of stress voltage and the effective activation energy of the corresponding processes is more than ~ 1.1 eV. As it was suggested in [10], this peak is likely related to migration of oxygen vacancies in anodic tantalum pentoxide dielectrics.

Accumulation of oxygen vacancies at the Ta – Ta₂O₅ interface increases concentration of donor states and conductivity of oxide near tantalum cathode [6]. This accumulation occurs not evenly along the surface, but mostly at the irregularities where the electric field is larger, thus further reducing the effective thickness of the oxide. This explains a reduction of breakdown voltages and increased number of failures for capacitors that experience long-term RB stresses even at relatively low reverse voltages. Considering that the total surface area of the spots with decreased effective thickness of the oxide is minute, the additional current gathered from these spots can be negligibly small in spite of high local current density. In this case, no variations of forward-bias DCL would be observed.

The process of decreasing of the effective thickness of Ta₂O₅ dielectric that results in reduction of local breakdown voltages is likely responsible also for the unstable behavior of reverse currents in tantalum capacitors. Local overheating associated with breakdown might convert manganese dioxide into lower oxide state that has much larger resistance and can terminate breakdown by the self-healing mechanism.

Accumulation of positive charges near tantalum cathode increases electrical field at the Ta – Ta₂O₅ interface but does not affect the field at the MnO₂ – Ta₂O₅ interface. This explains insensitivity of forward leakage currents to the processes causing substantial degradation of breakdown voltages and reverse currents.

VI. Conclusion

- 1 At room temperature, degradation of reverse currents in capacitors rated to 50 V occurs at voltages as low as 1.5 V after dozens of hours of stress. At 6% VR reverse currents can increase with time up to four orders of magnitude and stabilize after dozens and hundreds of hours of testing. The level of degradation is lot-related and varies up to two orders of magnitude for different part types.
- 2 An increase in voltage and temperature drastically reduces the time for the on-set of degradation and raises the level of reverse currents nearly exponentially. At 145 °C, reverse currents in 50 V capacitors start degrading at 1 V after ~ 1 hr and increase up to two orders of magnitude after a few hours of testing. Based on temperature variations of the onset times, the effective activation energy of degradation is ~ 0.75 eV.
- 3 The probability of capacitors to become unstable and cause erratic changes of reverse currents is lot-dependent, increases with voltage and time under bias, and can occur in high-voltage capacitors at voltages as low as 6% VR. Capacitors operating in this mode can cause damage to other elements in the circuit, and this possibility should be considered if a reversely installed capacitor is to be replaced.
- 4 Results of RBS testing at high temperatures (85 °C and above) indicate the presence of at least two degradation processes with substantially different characteristic times and activation energies. The activation energy of the second process is likely much larger than 0.75 eV.
- 5 Reverse bias degradation is reversible and can be reproduced by exposure to forward bias and/or long-term (a few days) storage at room temperature conditions. Even a long-term (100-hour and greater) degradation of reverse currents at $\sim 10\%$ VR that results in more than 3 orders of magnitude of current increase can be reversed after a few hours of exposure to the forward bias conditions at rated voltages.

- 6 A long-term (hundreds of hours at room temperature or a few hours at 85 °C) exposure of solid tantalum capacitors to relatively low reverse voltages, below 10% VR, might not change substantially leakage currents of the parts at forward bias conditions, but can result in a significant decrease of breakdown voltages. This suggests that sufficiently long RBS at low voltages can compromise the reliability of capacitors, weaken the parts, and result in increased probability of failures under rated voltages. However, considering a significant (~50%) voltage derating, a relatively short-term (minutes and hours at room temperature) exposure of the parts to reverse bias below ~ 10% VR most likely will not cause failures of the parts during operation at normal, forward bias conditions.
- 7 Mechanisms of degradation in solid tantalum capacitors have been discussed. The experimental data can be explained assuming that forward currents are controlled by surface conditions at the MnO₂ – Ta₂O₅ interface and by Schottky emission of electrons over the surface barrier, and reverse currents depend on the potential barrier between tantalum and quasi-semiconductor formed in the dielectric by defects at Ta – Ta₂O₅ interface.
- 8 Degradation of reverse currents can be explained similar to degradation at forward bias conditions and is likely due to migration of oxygen vacancies and accumulation with time of positive charges at the Ta – Ta₂O₅ interface. This raises electric field at the interface, enhances injection of electrons, and increases reverse currents with time under bias, but does not affect the field at the MnO₂ – Ta₂O₅ interface and, respectively, does not affect forward currents.
- 9 Accumulation of oxygen vacancies at the Ta – Ta₂O₅ interface increases concentration of donor states and conductivity of the oxide near tantalum cathode. This accumulation occurs mostly at irregularities where the electric field is larger, reduces the effective thickness of the dielectric, decreases breakdown voltages, and increases the probability of failure during normal operating conditions.

VII. Acknowledgment

This work was sponsored by the NASA Electronic Parts and Packaging (NEPP) Program. The author is thankful to the Program Manager Michael Sampson for support and discussions and appreciates the help of manufacturers of tantalum capacitors for providing data and samples for this study.

VIII. References

- [1] F. C. Aris and T. J. Lewis, "Steady and Transient Conduction Processes in Anodic Tantalum Oxide," *Journal of Physics D-Applied Physics*, vol. 6, pp. 1067-1083, 1973.
- [2] D. A. Vermilyea, "Conduction and Rectification in Anodic Oxide Films," *J. Appl. Phys.*, vol. 36, pp. 3663-3671, 1965.
- [3] I. Bishop and J. Gill, "Reverse voltage behavior of solid tantalum capacitors," *AVX Technical information*, 2004.
- [4] J. Sikula, *et al.*, "The tantalum capacitor as a MIS structure in reverse mode," in *CARTS'01*, 2001, pp. 289-292.
- [5] J. Pavelka, *et al.*, "Noise and transport characterisation of tantalum capacitors," *Microelectronics Reliability*, vol. 42, pp. 841-847, 2002.
- [6] E. Loh, "DC conduction mechanism in tantalum chip capacitors," *Journal of Physics D-Applied Physics*, vol. 13, pp. 1101-1111, 1980.
- [7] J. D. Prymak, "A theory of reverse voltage failures in SMT Tantalum/Electrolytic capacitors," in *22 Capacitor And Resistor Technology Symposium*, 2002.
- [8] R. M. Fleming, *et al.*, "Defect dominated charge transport in amorphous Ta₂O₅ thin films," *Journal of Applied Physics*, vol. 88, pp. 850-862, Jul 15 2000.
- [9] A. Teverovsky, "Reverse bias behavior of surface mount tantalum capacitors," in *Capacitor and Resistor Technology Symposium, CARTS*, New Orleans, LA, 2002, pp. 105-123.
- [10] A. Teverovsky, "Degradation of Leakage Currents in Solid Tantalum Capacitors under Steady-State Bias Conditions " in *60th Electronic Components and Technology Conference*, Las Vegas, NV, 2010.
- [11] J. G. Simmons, "Transition from Electrode-Limited to Bulk-Limited Conduction Processes in Metal-Insulator-Metal Systems," *Physical Review*, vol. 166, pp. 912-920, 1968.
- [12] W. S. Lau, "Similarity between the first ionized state of the oxygen vacancy double donor in tantalum oxide and the first ionized state of the cadmium vacancy double acceptor in cadmium sulfide," *Applied Physics Letters*, vol. 90, May 2007.