Abstract

There is always the potential for putting a polar, two-terminal device in a circuit, backwards. The reaction for tantalum capacitor manufacturers has been to never, ever allow this to happen, regardless of the level of applied reverse voltage. We have gathered evidence to the point where we can now predict at what levels these reverse voltages are critical, and a theory as to what is taking place as the device decays in a severe reverse voltage application.

Dielectric as Oxide of Base Material

With the tantalum electrolytic capacitor the dielectric is an oxide creation (Ta2O5) of the anode base material (Ta). This film common to all electrolytic capacitors, is created through an electrochemical process that is dependent upon the electrolyte solution and the formation voltage. The formation voltage is usually a multiple of three to four times the final application and the electrolyte is usually a phosphoric acid based solution. In the formation bias, the same as the forward bias of the final capacitor, oxygen (O2) is pulled into the tantalum (Ta5+) and combines to form Ta2O5. The force, or the voltage of formation, controls the depth of penetration into the tantalum metal, or the thickness of the Ta2O5 material created (Figure 1).

Forward Bias

In forward bias applications, the same polarity voltage is applied as that applied during formation. Even with a wet electrolyte, the voltage controls the greatest depth of penetration, and since this application voltage must be fractional to that of the formation voltage, no additional formation should take place. A formation can take place (reformation) at a breakthrough point, but only to a smaller depth than the original. This “reform” ability is utilized in aluminum electrolytic capacitors to “heal” defective sites in the dielectric, appearing while sitting on a shelf. Using a solid electrolyte (the MnO2 in the solid tantalum) in place of the wet, the transfers are inhibited by the loss of molecular mobility in the solid cathode material (Figure 2).

In an unbiased state, the oxygen is stable in the Ta2O5, and will not vacate this arrangement until some force is applied to facilitate this. There are no “shelf-life” degradation characteristics for a solid-state electrolytic device.

Reverse Bias – Oxygen Depletion

In the reverse bias application, with the required destabilization force achieved, the oxygen is pushed out of the compound structure and dissipates into the surrounding voids (Figure 4); thus returning the tantalum element back to lower oxide or more conductive state. This vacancy may be increased at localized, weaker regions of the dielectric, creating tantalum nodes extend-
The variations among different batches to survive the reverse bias application may be an indication of variations of the distribution and magnitudes of fault sites in the dielectric that leads to these nodes.

The production of conductive tantalum regions in the dielectric creates conductive bridges or wedges in the once-insulative region. This development effectively reduces the thickness of the oxide dielectric. As the thickness is minimized, the depletion accelerates as the field in this region increases with thinning dielectric. Near partial faults or crack sites, the acceleration may accelerate further still, creating localized or thinner spots in the dielectric. (If the depletion were uniform, the capacitance would increase as the dielectric got thinner.) There may be some attempt to curb the current through the self-healing mechanism of the MnO₂ material, but this region may create a broad injection of current rather than a localized point, as might be created by a crack.

The leakage current increase as these regions result in effectively reduced dielectric thickness. This leakage aggravates the oxygen vacancy, and a self-consuming failure is in operation. Eventually, the thickness degenerates to the point where the voltage breaks down the remaining insulative material and a “short-circuit” results (Figure 4) [1].

Reverse Bias – Hydrogen Injection

I liked the oxygen depletion theory because it assumes that the dielectric is purely a combination of tantalum and oxygen. There are additional theories of the reverse bias degradation that refers to the infusion of hydrogen as the decaying mechanism. That “protons and hydrogen atoms play an important part” and that they “act at fissures in the oxide, rather than as ‘doping agents’ in a fault free oxide.”[2] There was a symposium conducted in 1967 devoted entirely to this very subject, with much of the evidence presented that defines that hydrogen injection into the Ta₂O₅ structure is the non-insulative converter for the dielectric decay. In support of this there was proof presented where the absence of hydrogen in the system prevented the dual conduction mechanism of the anode and film.[3]

This hydrogen infusion as in Figure 5, could represent a decay mechanism of the insulative properties of the dielectric that works in a direction opposite that shown for the oxygen depletion (Figure 4). It may degrade from the cathode contact in towards the opposite anode edge.

Regardless of the chemical nature of the dielectric decay, the measurable effects of this decay are what I am most interested in – a method of detecting this decay as a measurable revelation of the decay, and a time factored revelation of exposure to reverse voltage.

Reverse Voltage ‘knee’

The conduction current through the dielectric is very much like that effect seen with a diode, but with
opposite conduction references. In a capacitor, which is foreword biased, the conduction through this region acts like a reverse biased diode. The conduction currents behave as if an insulator material is within the current path – very small currents are generated. With the capacitor in reverse bias, it acts like a diode that is forward biased. At very small voltage levels, the conduction through this material remains like an insulative material, but once a specific level is achieved, the conduction increases abruptly (Figure 6).

This action highlights the fact that in a normal or unbiased condition, the oxygen bond to the Ta2O5 is strong, and this compound is normally a stable combination. The sudden increase in current details where the oxygen bond to the Ta2O5 is overcome, and oxygen transport out of the dielectric begins (Figure 4, or in the case of the hydrogen infusion, proton transport as in Figure 5 begins). We refer to this as the ‘knee’ voltage of the capacitor.

Recently we’ve analyzed parts that were in an application, in reverse bias exceeding the ‘knee’ voltage, for an extended period of time. Several pieces were identified from defective circuits, and a control was selected from a “good,” functioning, circuit. The defective piece showed that the ‘knee’ voltage dropped to below 5.5% of the rated voltage, while the “good” piece was over 6% of the rated voltage. (Figure 7 - “Good” and “Bad” were our customers indication of the circuit’s condition.) This indicates that the deterioration of the dielectric existed in all pieces, but the rate of deterioration differed. It was not a question of “if the part will fail,” but “when the part will fail.”

In another application with the applied reverse bias being less than the ‘knee’ voltage, there was no degradation of the ‘knee’ voltage with thousands of hours in field exposure. We have duplicated this by having parts on accelerated life tests at voltages less than the knee voltage, and there is no degradation of the component through thousands of test hours.

**Test Steps**

We were concerned that step application of reverse voltages might have some saturation effects as we moved to larger magnitudes of reverse voltages. In order to overcome this effect, we initially applied a forward bias for each step we incremented, then applied the same voltage in reverse. In order to diminish saturation effects, in between each application, we placed a “short” across the unit.

The procedure started at 0.5 VDC, applied as a forward bias for 30 seconds, and measured at the end of the 30 seconds. We then shorted the unit for 30 seconds before we applied the same voltage in reverse, repeating the 30 second hold and measure. We increment the voltages by 0.5 VDC through 4 VDC, then by 1 VDC to 8 VDC, then by 2 VDC up to the rated voltage.

This became too long of a test as 20 pieces might take all day. We now use the following procedure:

1. Mount 20 pieces to test card or clip 20 leaded pieces to test card.
2. Using a scanner, we test the pieces sequentially.
3. We apply 25% of rated in forward mode for 30 seconds and read the current, followed by 30 second short.
4. We apply 25% of rated in reverse, wait 30 seconds to read the current, then short for 30 seconds.
5. We repeat steps 3 and 4, with 50% of rated voltage.

This allows a much faster determination of the knee, and we compared the results obtained with the streamlined procedure on pieces using the first, elaborate procedures, and there was no difference in the results. The purpose of the forward bias readings is to establish that there is delineation between the reverse bias points and the forward bias points. Without this delinea-

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tion, the device is exhibiting no knee voltage (should calculate to ‘0’).

Reliability in Reverse-Bias Applications

There is none to be established. These are polar devices, with polarity bands indicating proper orientation. The increase in leakage current in reverse bias applications to the point of failure is indeterminate. In many cases, the failure rate is determined by the relative inconsistency of field strength that can be factored by inclusions, cracks, and environmental conditions. The final failure signature is dead short. Some devices fail immediately and others withstand this wrong bias application for thousands of hours. As can be determined by the knee voltage diagram (Figure 6), the magnitude of the reverse bias initially determines the magnitude of leakage current or oxygen depletion current.

This ‘knee’ voltage has some dependency on temperature. As temperature increases, the ‘knee’ moves closer to zero or decreasing reverse bias magnitudes. As leakage current increases and internal heating increases, the ‘knee’ moves lower and the leakage current increases, repeating itself in a continuously self-degrading scenario. At +85°C, we see the knee voltage near 14%, and at +125°C, the knee appears close to 10% of the rated voltage.

If the depletion of the dielectric creates a localized fault site, there is still a possible self-healing mechanism of the MnO\textsubscript{2} trigger. Here, the localized heating of the MnO\textsubscript{2} at the point of high current concentration can cause the temperature to rise enough to convert to a lower oxygen state, of much higher resistance (Mn\textsubscript{2}O\textsubscript{3}).

If the depletion is broad, then there is no localization of the heat in the MnO\textsubscript{2}, and no self-healing conversion. The leakage current increases until the tantalum reaches melting point, and at this point the failure is an absolute, catastrophic, dead short.

Conclusions

There is a measurable indication of pieces that are placed in applications in reverse voltage with the following observations:

1. The magnitude of the reverse voltage must be equal to or above the knee voltage.

2. A catastrophic failure cannot be used to define the knee voltage.
3. ‘Sister’ parts experiencing the same reverse voltage should show some degradation in case one has failed catastrophically.
4. The degradation of the knee voltage is not uniform for all parts within a batch, and from batch to batch.
5. The 15% of rated voltage will show variations from 14.5% up to 21% because the ratio of formation to rated is not a constant, and it is the formation voltage that determines the thickness and the knee voltage.
6. The general observation is that the knee voltage is close to 5.3% of formation voltage.
7. The knee voltage for Al\textsubscript{2}O\textsubscript{3} appears to be in the region of -70% of rated voltage and although the chemistry may differ, I do believe the effects are the same.
8. Results for niobium show the knee voltage to be close to that of the tantalum, or near 15% of rated voltage.

Finding the failure site is still a “needle-in-the-haystack” proposition. Looking for coloration changes indicative of a thinning Ta\textsubscript{2}O\textsubscript{5} would require that the degradation be uniform across the dielectric. If the degradation is uniform across a broad expanse of the dielectric, then a capacitance rise should be apparent.

Acknowledgement

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Bibliography

2. Young, Prof. Lawrence; Anodic Oxide Films; Chapter 11, “Rectification by Valve Metal Electrodes”; pages 141-149; Academic Press; 1961