Radiation Characterisation for New Tantalum Polymer Capacitors

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Abstract—Polymer tantalum capacitor technology was developed in response to demands from the market to lower the ESR of tantalum capacitors while preserving their small case size and high reliability. The technology is promising in several aspects. The higher quality interface between the dielectric and the polymer cathode increases the breakdown voltage of the device, as well as reducing its DC leakage current, even at extreme radiation exposure conditions.

I. INTRODUCTION

Passive parts and particularly capacitors offering for space applications have evolved significantly during past few years. New materials and structures aiming to offer advanced electrical performance and improving the ratio capacitance per volume of these components have been introduced recently.

Additionally, future missions approved by ESA where high levels of radiation are involved, and the lack of experimental data corresponding to these new technologies in families traditionally considered as radiation immune, require users and industry to agree on the need of radiation characterizations of devices able to comply with the radiation requirements of these missions. Attention has focused on discrete semiconductors and integrated circuits due to the complexity of their structures. However, an important part of the PCBs are formed by passive parts, historically listed as radiation immune devices but not taking into account these new materials and structures.

New EEE parts manufacturing process and technologies can require the radiation characterisation before using them in radiation severe environment where high accumulated doses are received during the mission.

KEMET and ALTER TECHNOLOGY have performed a radiation characterisation of new tantalum polymer capacitors based on the conductive polymer PEDT

(polyethylenedioxythiophene), with same successful results than standard manganese dioxide tantalum capacitors [1].

The radiation test has been performed at RadLab [2] [3] radiation facility from ALTER TECHNOLOGY, which is awarded with ISO-17025 accreditation to perform radiation test according to ESCC 22900, MIL-STD-750 and MIL-STD-883 TM1019, including the dosimetry process; and the laboratory suitability for MIL-STD-883 and MIL-STD-750 provided by the Defense Logistics Agency (DLA). These accreditations make this state-of-the-art radiation facility one of a kind.

II. DESCRIPTION OF THE DEVICES UNDER TEST

A. Solid-electrolyte tantalum capacitors

Solid-electrolyte tantalum capacitors were first developed and commercially produced in the 1950s. They represented a quantum leap forward in miniaturization and reliability over existing wound-foil wet electrolytic capacitors. While the solid tantalum capacitor has dramatically improved electrical performance versus wet-electrolyte capacitors, especially at low temperatures, today's electronic circuits require even better performance. In response to this need, steady improvements in the equivalent series resistance (ESR) of tantalum capacitors have been made.

Tantalum electrolytic capacitors, just like other electrolytic capacitors, are consisted of an anode, some electrolyte and a cathode. The anode is isolated from the cathode so only a very small leakage DC current may flow through the capacitor. The anode is made of pure tantalum metal. The metal is ground into a fine powder, and sintered into a pellet at high temperatures. This forms a very porous anode with a high surface area. A high surface area directly translates to an increased capacitance value.

The anode is then covered with a layer of insulating oxide, which acts as a dielectric. This process is called anodization. This step must be precisely controlled to reduce tolerances and ensure correct capacitance values as the extent of oxide growth determines the dielectric thickness.

Electrolyte is added to the anode by means of pyrolysis in the case of solid tantalum capacitors. Solid tantalum capacitors are then dipped into a special solution and baked in an oven to produce a manganese dioxide coat. The process is repeated until a thick coating is present on all internal and external surfaces of the pellet. Finally, the pellet used in solid

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tantalum capacitors is dipped into graphite and silver to provide a good cathode connection.

B. Low equivalent series resistance (ESR)

Low ESR is the most important attribute of capacitors used to filter and decouple power for high-speed digital electronics. While the first patented tantalum capacitor was claimed to have ESR of roughly 2.0Ω , a similar capacitor today has ESR of about 0.1Ω .

Any defect causing increased current flow in localized areas results in heating that promotes conversion of MnO_2 into manganese oxide (Mn_2O_3) which has lower conductivity and effectively heals the fault site and prevents further deterioration.

C. Manganese dioxide (MnO₂) versus conductive polymer

A substantial fraction of the ESR of a tantalum capacitor comes from cathode plate material, manganese dioxide (MnO₂). While MnO₂ is substantially more conductive than almost all wet electrolytes, especially at low temperatures, capacitor manufacturers search for higher conductivity materials to replace MnO₂.

Today's cathode plate material of choice is the conductive polymer PEDT (polyethylenedioxythiophene) which has up to 100 times MnO₂'s conductivity and has generally acceptable compatibility with tantalum pentoxide, the tantalum capacitor's dielectric.

Counter electrode structure detail with both technologies (MnO₂ and polymer) is presented in Fig. 1 and Fig. 2 [12].



Fig. 1. Cross-section of a Moulded Chip Surface Mount Tantalum Capacitor.



Fig. 2. Schematic representation of sintered tantalum electrolytic capacitor structure with solid electrolyte and cathode contacting layers.

ESR can best be described as the cumulative effect of various forms of resistance in the finished capacitor. Losses from resistance in a tantalum capacitor come from the various sub-components that make up the capacitor, most notably from the resistance of the material contacting the negative side of the tantalum dielectric.

The cathode of polymer tantalum devices is many times more conductive than the manganese dioxide traditionally used for this part of the device. The high conductivity of the polymer gives the capacitor its low ESR; the polymer's conductivity is also very temperature stable, meaning the ESR is temperature stable (Fig. 3) and the devices can withstand high ripple current as a result [12].



Fig. 3. ESR typical behavior in temperature and frequency (MnO₂ vs Polymer).

These desirable characteristics have made polymer tantalum capacitors very popular for commercial low-voltage electronics systems, but historically, DC leakage and low breakdown voltage have held back adoption in high-voltage and high-reliability applications such as defence, aerospace and space.

It was therefore desirable to develop a high-voltage version of the tantalum polymer capacitor, keeping its low ESR properties and high reliability whilst improving its DC leakage current and breakdown voltage properties.

D. F-Tech tantalum manufacturing technology

In combination with several proprietary cutting-edge KEMET developments, these technology advances have made the T540/T541 Polymer COTS and T550/T551 series possible.

Compare to the known formed dielectric defects located in the traditional process (Fig. 4) when the tantalum pentoxide is formed on the pure tantalum metal: cracks, pores and crystalline oxide (Fig. 5), the new technology based on PEDT is expected to be free from those defects.

The scanning electron microscope (SEM) pictures show a clear distinction between the older technology, which resulted in tantalum node material with cracks, pores and other defects, and the F-Tech anode which is practically free-defect Fig. 6. [4].



Fig. 4. The traditional process of manufacturing the tantalum anode material resulted in cracks [4].



Fig. 5. SEM of T492 tested device shows dislocation and cracks (solid MnO₂ technology). SEM by Francisco J. Aparicio at Nanotechnology on Surfaces Lab. Materials Science Institute of Seville - Spain

The technology actually comprises multiple processes which minimize the anode's carbon and oxygen content, as these contaminants can lead to crystallization of the anodic oxide dielectric [5]. Another process strengthens the mechanical connection between the tantalum lead wire and the anode, enhancing reliability [6].



Fig. 6. SEM of T541 tested device shows a free-defects structure (Polymer). SEM by Francisco J. Aparicio at Nanotechnology on Surfaces Lab. Materials Science Institute of Seville - Spain

The organic conductive polymer cathode promotes a more benign failure mode, as the conductive polymer, unlike MnO_2 , is not an oxidation agent. Also, the conductive polymer has a different self-healing process. The failure site is insulated within the defect site that stops further current flow through the failure sites (Fig. 7).



E. Breakdown voltage and DC leakage current

Another discovery relates to the interface between the dielectric and the polymer cathode. This interface is important because any defects here can greatly affect the capacitor's electrical properties. A pre-polymerized PEDOT is applied to the dielectric, which meant that an in-situ chemical reaction to create the interface was not required. Bi-products of this insitu reaction, which lead to contamination, were therefore avoided, resulting in a higher quality interface. This higher quality interface between the dielectric and the polymer cathode helps increase the breakdown voltage of the device, as well as reducing its DC leakage current [4].

III. EXPERIMENTAL SETUP AND TEST CONDITIONS

A. Test samples

Two different series of tantalum polymer capacitors were submitted to radiation tests. The specific component numbers are shown in TABLE I. On each of them, nine samples of each series were irradiated: five parts with bias condition specified in Fig. 6. And four unbiased parts (connected to ground).

As a control lot, the comparison was made using data from on a standard- MnO_2 tantalum capacitor, T492 style, [8].

Style	Part Number	Technology	Qty.	
T492	T492D106K025DH4215	Solid MnO2	5 ^{ON} +4 ^{OFF} +1	
T541	T541X337M016AH	Polymer	5 ^{ON} +4 ^{OFF} +1	
T551	T551B107K060AH	Polymer	$5^{ON+4OFF+1}$	

B. Radiation source

The radiation source used for the test was the field of a Cobalt 60 gamma source, in compliance with ESCC 22900.

This isotope is produced in a reactor by neutron bombardment of the ⁵⁹Co stable isotope. With a half-life of 5.26 years, the ⁶⁰Co nucleus decays to become ⁶⁰Ni by beta emission and two associated gamma rays with energy of 1.17 and 1.33 MeV. The medium value (1.25 MeV) is usually established for testing purposes.

In RadLab facility, the Cobalt-60 source is housed in a Gammabeam ® X200 irradiator manufactured by Best Theratronics Ltd. Company shown in Fig. 8 [2].



Fig. 8. Gammabeam ® X200 irradiator at RadLab radiation facility.

C. Dose rate and dose steps

The three series of tantalum capacitors were irradiated at a dose rate within the low rate window specified in ESCC 22900 [7][8][9]. The standard-MnO2 tantalum capacitor was considered as reference data [8] for comparison purposes. Summary of irradiation conditions is displayed on TABLE II.

The dose steps of the three tantalum capacitors were practically the same, up to a maximum test level of 212krad(Si), with intermediate steps around 25krad(Si), 50krad(Si), and 100krad(Si), as shown in TABLE II.

	TABLE 1	п.		
Dose steps and c	lose rate for	each ca	pacitor	style.
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Style	Technology	Ste	Dose rate			
		1	2	3	4	rad(Si)/h
T492	Solid MnO ₂	25.267	46.039	98.779	211.749	224.9
T541	Polymer	25.267	46.039	98.779	211.749	224.9
T551	Polymer	25.379	46.244	99.218	212.691	225.9

D. Radiation biased circuit

The pins for the biased parts were connected in accordance with the radiation bias circuit shown in Fig. 9.



Fig. 9. Radiation biased circuit.

The resistance value was $10k\Omega$ in all cases. The voltage applied on each case was the following: 25V for T492, 16V for T541 and 60V for T551.

The pins for the unbiased parts were short circuited and connected to ground.

E. Electrical parameters, conditions and limits

The electrical parameters which were measured prior, during and after the radiation test of the tantalum capacitors are the capacitance, C, the dissipation factor, DF, the equivalent series resistance, ESR, and the DC leakage current, IL, [7][8][9].

For the purpose of these investigations, ALTER focused on the degradation of the polymer conductivity induced by the ionization radiation. Any alteration of this material may affect the performance of the capacitors, due to the fact that the equivalent series resistance (ESR) summarizes all resistive losses of the capacitor: the line resistance of the electrodes, the electrolyte resistance, the dielectric losses in the dielectric oxide layer, etc. TABLE III shows test conditions and limits for ESR.

TABLE III. ESR test conditions and limits for each capacitor style.

Style	Cap (uF)	ESR Test conditions	ESR Limits		Unit
Style	(µ1)	ESK Test conditions	Min	Max	Unit
T492	10	f=100kHz, 1Vrms, Vbias=2.2Vdc		1.2	Ω
T541	337	f=100kHz, 1Vrms, Vbias=2.2Vdc		25	mΩ
T551	100	f=100kHz, 1Vrms, Vbias=2.2Vdc		100	mΩ

Note: In order to evaluate if the different types may have different behaviour, three different references were selected. This is the reason why the three candidates have also three different ESR limits.

F. Annealing conditions

After irradiation exposure, the irradiation samples were submitted to annealing 24 hours at 25°C, and after that accelerated ageing of 168 hours at 100°C, with electrical measurements between them. The maximum operating temperature is 125°C for T492, T541 and T551 styles.

IV. EXPERIMENTAL RESULTS

A. ESR results over accumulated dose and annealing

The results of the electrical measurements of the equivalent series resistance (ESR) in function of the accumulated dose associated to each dose step for the three tantalum capacitors used on this analysis are shown in Fig. 10 and Fig. 11.

The measurements of all biased (ON) samples of each style have been averaged so only one value is shown per style at each dose step in Fig. 10, and same for unbiased (OFF) samples in Fig. 11.

Considering the different values of the ESR of the three styles due to the size differences, the vertical axis represents the variation of the parameter value respect to the value obtained at 0krad(Si), that is, the results have been normalized respect to the electrical measurements carried out before starting the radiation test.

The horizontal axis represents the accumulated dose, and after total dose the two annealing steps described in paragraph III.F.



Fig. 10. ESR over accumulated dose, biased (ON) samples.



Fig. 11. ESR over accumulated dose, unbiased (OFF) samples.

The test results show that for all capacitor styles involved, standard MnO_2 T492 and conductive polymer -T541 & T551, the ESR values are within limits after radiation exposure. 'Polymer capacitors' do not show any enhanced response to accumulated dose compared to 'MnO₂ capacitor'.

V. CONCLUSIONS

In comparison with semiconductor devices, MnO₂-based tantalum capacitors are generally considered to be insensitive to radiation. Small shifts of roughly 10mV/krad(Si) are observed in the open-circuit voltage of previously discharged capacitors, but this effect is transient and generally only of interest in high impedance, small-signal circuits. However, tantalum capacitors are rarely used in such circuits, even when radiation is not of concern.

Moreover, radiation-generated oxide defect concentrations for doses in excess of 10Mrad(Si) are estimated to be orders of magnitude lower than intrinsic defect levels and are not thought to significantly impact long-term performance or reliability. Since the same dielectric and dielectric thickness are employed in tantalum polymer capacitors, these devices were expected to be similarly insensitive to radiation effects.

Effectively, these test results suggest that 'polymer capacitors' preserve their ability to operate properly under such environment as well as 'MnO₂ capacitors' and thus can be considered immune to radiation to the levels typically experienced in space.

In order to better evaluate the degradation of the polymer during on irradiating samples, a complementary Life Test is being performed. This will provide more information about the reliability of these materials and its contribution to ESR. But taken into account that ESR depends on temperature and the reliability of the polymer, it would be desirable to complement this work, with an evaluation of the polymer behaviour after long periods at low temperature. This would help to assess how the polymer properties may be affected by extreme temperatures in combination with TID exposure that may occur during long extremely low temperatures interplanetary missions.

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