High Temperature Ta/MnO_2 Capacitors

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Abstract:

The paper presents results on high temperature stability of tantalum capacitors with MnO_2 cathodes (Ta/MnO_2 capacitors). The critical role of silver migration on high temperature stability of these capacitors was demonstrated. Replacing of silver in the top coating with electrochemically plated nickel provides a radical improvement in the high temperature stability of the Ta/MnO_2 capacitors. Nickel plating was performed on top of transition multilayer comprising two carbon layers separated by hydrophobic blocking layer. We discuss possible mechanisms of the improvement in the high temperature stability of Ta/MnO_2 capacitors due to the new technology.

Introduction:

Increasing electronic component operating temperatures above 200^o C is desirable for applications like gas and oil drilling and jet engine monitoring. These applications also involve strong vibration and shocks, which require mechanical robustness in addition to ability to operate at high temperatures. To withstand these harsh application conditions, all the materials involved in the electronic components and all the interfaces between different materials should have sufficient thermal and mechanical strength. With regard to Ta capacitors, these applications rule out traditional Wet Ta capacitors with liquid electrolyte cathodes due to excessive electrolyte pressure inside hermetic cans as well as Polymer Ta capacitors with conductive polymer cathodes due to possible decomposition or dedoping of the polymer at these temperatures.

Solid Ta capacitors with manganese dioxide (MnO_2) cathodes potentially can withstand these harsh application conditions. Their most sensitive layer, thin anodic oxide film of Ta employed as a dielectric, undergoes numerous heat treatments at temperatures equal or exceeding 270^o C during deposition of MnO_2 cathode by dipping formed anodes in manganese nitrite and its subsequent pyrolysis. The external layers of carbon and silver, packaging, and terminations of these capacitors can be also made with materials capable of working at high operating temperatures and under mechanical stress. In this situation the critical question becomes how long these capacitors can work safely before inherent degradation mechanisms cause their parametric or catastrophic failures.

The major thermally activated degradation mechanisms in Ta capacitors are oxygen migration from the dielectric into the Ta anode and crystallization of amorphous matrix of the dielectric.[1] At normal operating conditions, MnO_2 cathode, employed as solid electrolyte, replenishes oxygen deficiency in the dielectric caused by oxygen migration into Ta anode, and, thereby, prevents dc leakage (DCL) increase. At extreme temperatures oxygen migration from the dielectric can exceed MnO_2 ability to provide oxygen to the dielectric. The oxygen misbalance can begin in some local areas of the dielectric, resulting in local current increase, overheat, and thermal runaway. Crystallization process is also intensified exponentially with the increase of temperature. Solid Ta capacitors with thicker dielectrics are more prone to crystallization in comparison to the capacitors with the thinner dielectrics. Despite of the fact that most of high temperature applications require relatively low voltages, typically in the range 3.3 V to 5.5 V, the capacitors for temperatures exceeding 200^o C should have

relatively high rated voltage (thick dielectrics). This is due to the 70% - 75% voltage de-rating requirements at these high temperatures. Crystalline inclusions in grow faster in thicker dielectrics eventually causing cracks in the dielectric and catastrophic failure of the capacitor.

One more degradation mechanism, which is common to all the electronic components containing silver , is silver migration.[2] The mechanism of silver migration as it is viewed in literature includes three steps: electro dissolution, ion transport, and electro deposition. These three steps are activated by temperature and presence of humidity. Typical outcome of silver migration in electronic components is forming of silver shunts in some areas of the circuit boards and shortening the circuits. In the case of Ta/MnO_2 capacitors, silver can migrate through the pores in carbon and MnO_2 cathode and deposit on the dielectric surface.[3] According to [3], local MOM structures $Ta\text{-}Ta_2O_5\text{-}Ag$ cause DCL increase when silver deposits on the defect areas in the dielectric. According to [4] breakdown voltage of these $Ta\text{-}Ta_2O_5\text{-}Ag$ structures is relatively low even in the defect free areas of the dielectric and practically independent of the dielectric thickness when it exceeds about 100 nm. This is because Ta_2O_5-Ag interface does not form potential barrier for the current carriers and does not provide self-healing to the dielectric. That's why deposition of even small amount of silver on the dielectric surface can cause catastrophic failure of the capacitors even with defect free dielectric. Depending on the capacitors structure and working voltage, silver migration can become dominant degradation mechanism which defines actual failure rate in these capacitors.

The paper presents data on high temperature behavior of Ta/MnO_2 capacitors with traditional silver layer on top of the carbon layer and also with nickel layer plated on top of transition multilayer, which includes layers of carbon with hydrophobic blocking layer between the carbon layers.[5] A radical improvement in thermal stability of Ta/MnO_2 capacitors with Ni plating on transition multilayer in comparison to Ta/MnO_2 capacitors with traditional top coating is demonstrated and possible applications are discussed.

Experimental

Tantalum powder with 50k μC/g specific charge was pressed into rectangular pellets of 2.5 mm x 2.5 mm x 4 mm with 6 g/cc green density. The pellets were sintered in vacuum at 1400^{o} C for 15 min. The anodes were anodized in an aqueous solution of phosphoric acid to the formation voltage $V_f = 35$ V. Manganese dioxide cathode was applied by dipping the formed Ta anodes in manganese nitrate and subsequent heat treatment in air at approximately 270^{o} C for 5 min. These steps were repeated several times to provide full impregnation of the porous anodes with MnO_2 cathode. Control capacitors were manufactured with carbon layer (or several layers) on top of the MnO_2 cathode, which comprised graphite dispersion in acrylic solution. Subsequent silver layer was applied by dipping of the pellets into silver paste, which comprised Ag particles, an acrylic binder, and DE acetate as solvent. The solvent was evaporated by heat treatment in air at 150^{o} C for about 1 hour. Test capacitors were manufactured with the same anodes, dielectrics and cathodes as these in Control capacitors; however, top coating in Test capacitors was manufactured with Ni plating on top of transition multilayer according to [5]. In the first group of Test capacitors a Ni plated layer formed on the first carbon layer. In the second group of Test capacitors a hydrophobic blocking layer was applied on the first carbon layer. A second carbon layer comprising a mixture of carbon black and graphite dispersion in a polyester binder was applied on the hydrophobic layer. A Ni plated layer was formed on the second carbon layer by electroplating. Both Control and Test capacitors were finished and tested as D-case Ta/MnO_2 capacitors with capacitance 220 μF and rated voltage 10 V.

Results and Discussion

Table 1 presents results of the 100 hours storage test at 200° C of non-capsulated Control capacitors with different number of carbon layers and with or without silver layer.

Layers of Carbon	Silver	% of Failures
1	Yes	17
2	Yes	7
3	Yes	3
1	No	0

Table 1. Results of the 100 h storage test at 200° C of the D-case Ta/MnO2 capacitors 220 uF – 10 V

As one can see from the Table 1, there were shorts in Ta/MnO_2 capacitors with silver layer in the top-coating. Even three carbon layers beneath silver layer couldn't prevent these failures, while in the absence of silver layer there were no shorts or even noticeable DCL increases. These results demonstrate critical impact of silver migration on long-term stability of Ta/MnO_2 capacitors at high temperatures. It's obvious that silver layer can't be eliminated all together without a replacement providing a connection between the cathode and lead-frame and external termination. Nickel is a good candidate for such a replacement due to its high conductivity, good solderability, and high stability in presence of moisture and at high temperatures.

Table 2 presents DCL and equivalent series resistance (ESR) in Ta/MnO_2 capacitors manufactured with control top coating (one carbon layer and silver layer), Test1 top coating (one carbon and plated nickel) and Test2 top coating (multilayer of two carbon layers separated by hydrophobic blocking layer).

Top coating	DCL, uA	ESR, mOhm
Control: one C and Ag	1.3	57.6
Test1: one C and Ni	536	115
Test2: transition layer and Ni	1.25	42.8

Table 2. End-of-line DCL and ESR in D-case Ta/MnO_2 capacitors with different top coatings.

Presented in Table 2 data show that nickel layer on top of one carbon layer (Test1) results in drastic DCL and ESR increase in comparison to these in control capacitors. This is obviously due to nickel ion migration during the plating process toward the dielectric on external anode surface through the single carbon layer and MnO_2 cathode. Similarly to silver, direct deposition of nickel on the dielectric surface causes high DCL and capacitor failures. Red-ox reaction between MnO_2 and nickel causes nickel oxidation and high ESR. In contrast to that, Test2 capacitors demonstrated low DCL and ESR, which evidences that transition multilayer with two carbon layers separated by hydrophobic blocking layer prevents Ni diffusion toward the dielectric. Low ESR values in the Test2 capacitors also evidence about high conductivity of plated nickel layer and relatively high conductivity of the thin blocking layer in transition multilayer in comparison to the conductivity of the MnO_2 cathode.

Figure 1 shows DCL distribution in Control and Test2 capacitors before and after 100 h test at 200° C and -1 V applied to the Ta anode. Applying reverse voltage to Ta anode intensifies migration of positively charged metallic ions through the cathode toward the dielectric.

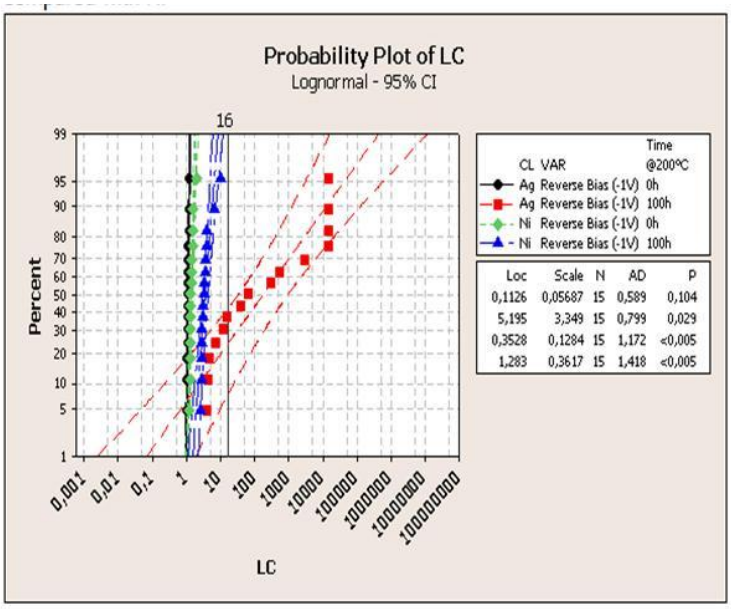

Fig. 1. DCL (Leakage Current) before and after 100 h life test at 200° C and -1 V in D-case Ta/MnO_2 capacitors 220 uF – 10 V with Control and Test2 top coatings.

As one can see from Fig. 1, there is practically no difference in initial DCL between control capacitors with silver layer and Test2 capacitors with nickel layer. At the same time, DCL values after the test DCL increased significantly in most of the capacitors and 30% of the control capacitors became shorts, while no significant change in DCL occurred in Test2 capacitors. These results indicate a possibility of long-term operating at high temperatures when Ta/MnO_2 capacitors are manufactured with nickel layer plated on the transition multilayer with hydrophobic blocking layer. As an example, Fig. 3 demonstrates 1000 h storage test of Test2 capacitors at 215° C.

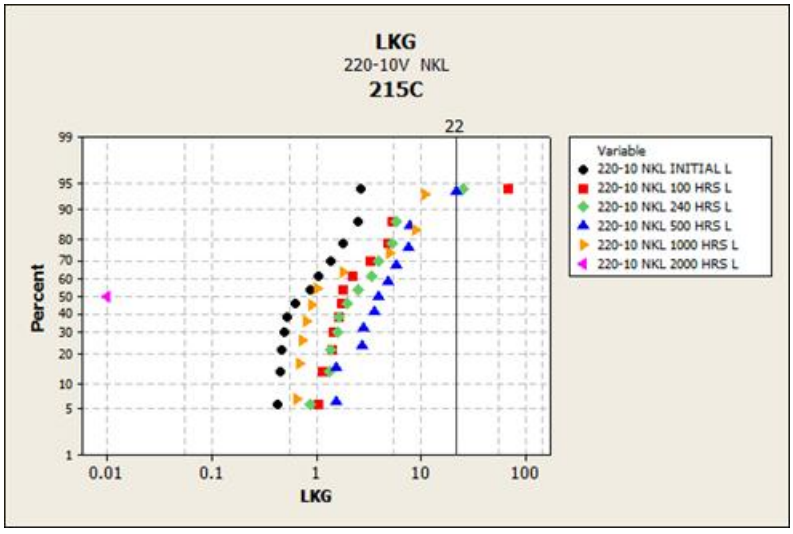

Fig. 2. DCL distribution in D-case Ta/MnO_2 capacitors 220 uF – 10 V with Test 2 top coating during storage test at 215° C.

According to Fig. 2 there were some DCL fluctuations during the test; however, the capacitors remained functional even after 1000 h testing at such a high temperature.

Conclusions

Results presented in this paper demonstrate the critical role of silver migration in high temperature applications of Ta/MnO_2 capacitors and a possibility of radical improvement of high temperature stability in these capacitors by replacing silver layer in the top coating with electrochemically plated nickel layer on top of transition multilayer comprising two carbon layers separated hydrophobic blocking layer. This is due to the much lower migration activity of nickel vs. silver and also due to the fact that nickel provides a barrier for silver migration from the external adhesive silver layer through the cathode toward the dielectric. The work on further increasing of operating temperatures of Ta/MnO_2 capacitors and their longevity and operating voltages is in progress. This work includes technological means to suppress degradation mechanisms inherent to these capacitors such as oxygen migration and crystallization of the dielectric as well as forming dense and uniformly thick cathode and top coating on external surface of tantalum anodes and special casing and terminations techniques

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References

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