Electrical Characterization of Polymer Tantalum Capacitors with Poly (3,4-ethylenedioxythiophene) Cathode

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Electrolytic tantalum (Ta) capacitors are broadly used in modern electronics due to their high volumetric efficiency, stability and reliability. Recently introduced to the market Polymer Ta capacitors also provide low equivalent series resistance (ESR) due to higher conductivity of the conductive polymer cathode in comparison to conventional manganese dioxide cathode. Another feature of Polymer Ta capacitors is their non-burning failure mode, which is an important safety feature, especially in low ESR circuit applications. Most of Polymer Ta capacitors use either polypyrole (PPy) or poly(3,4-ethilenedioxythiophene) (PEDT) as their cathode.[1-3]

Since their introduction to the market, working voltages (WV) of Polymer Ta capacitors were limited to WV ≤ 25 V, while WV of Ta capacitors with MnO_2 cathode reached 50 V or even higher voltages. This prevented application of Polymer Ta capacitors in high voltage circuits, where low ESR and non-burning failure more are the most critical. What limited WV in Polymer Ta capacitors was a rapid increase in dc leakage (DCL) and the breakdown of the dielectric at about 50 V even with relatively thick dielectric Ta_2O_5 film formed to 100 V and higher voltages.[4] To provide long term stability and reliability to Ta capacitors, the BDV at room temperature should be at least twice as large as the WV.

A significant increase in the BDV and WV of Polymer Ta capacitors was achieved when the traditional method of in-situ PEDT polymerization by chemical reaction between oxidizer and monomer was replaced by the using of a pre-polymerized PEDT suspension.[5,6] This resulted in a significant increase in the BDV and, thereby, the WV of Polymer Ta capacitors.

According to [5], the differences between Polymer Ta capacitors with in-situ and pre-polymerized PEDT were related to defects in the Ta_2O_5 film near to its interface with PEDT, caused by chemical reaction of in-situ polymerization on the Ta_2O_5 surface. With pre-

polymerized PEDT, no chemical reaction took place and, thereby, no defects in the Ta_2O_5 film were created. This model was supported by the fact, that BDV was decreasing with an increasing the number of in-situ polymerization cycles. Oxygen vacancies in the Ta_2O_5 film near to the Ta_2O_5/PEDT interface as well as damage to Ta_2O_5 surface could be the defects caused by in-situ polymerization.

The effect of oxygen vacancies in Ta_2O_5 film on electrical properties of Ta capacitors was described in [7]. According to [7], thermal treatment results in Ta_2O_{5-x} layer enriched with oxygen vacancies near to Ta_2O_5/Ta interface due to oxygen migration from Ta_2O_5 film into Ta anode. Since oxygen vacancies contribute free electrons to the dielectric, the Ta_2O_{5-x} layer has higher conductivity than the stoichiometric Ta_2O_5 film. This lowers effective thickness of the dielectric and, therefore, causes capacitance (C) to increase. Furthermore, C becomes strongly dependent on bias voltage at normal polarity, when free electrons are pulled from the dielectric, increasing its effective thickness and reducing C. That's why C(V) measurements can be indicative of oxygen vacancies in Ta_2O_5 film

Another model explaining the differences between Polymer Ta capacitors with in-situ and pre-polymerized PEDT was developed in [6]. According to [6], these differences were related to macro defects in the anodic Ta_2O_5 film such as cracks and pore. Molecules of PEDT, which were created during in-situ polymerization, penetrate these defects in the dielectric, reducing its BDV. On the contrary, PEDT particles in the pre-polymerized suspension are larger than the typical size of the macro defects in the dielectric. Therefore, they stay on the Ta_2O_5 film surface and do not affect its dielectric properties.

The purpose of this paper is to investigate the structure of the dielectric in Polymer Ta capacitors with in-situ and pre-polymerized PEDT cathode as well as to electrically characterize these capacitors using I(V) and C(V) measurements. The resulting experimental data did not support the models presented in literature models. An alternative model is proposed to explain the differences in electrical properties between the capacitors with in-situ and pre-polymerized PEDT. This model is based on classical metal- insulator -semiconductor (MIS) theory. With regard to Polymer Ta capacitors M stands for the Ta anode, I stands for the dielectricTa_2O_5 film, and S stands for PEDT, which is p-type semiconductor.

Experimental Details

Tantalum powder with an average primary particle size of 2.74 μm was pressed into rectangular pellets 4.5 mm x 3.1 mm x 1.3 mm with 5.5 g/cc green density. The pellets were sintered in vacuum at 1350° C for 10 min, then Ta lead wire was welded in argon to the pellet, and additional sintering was performed at under the same conditions as those at the initial sintering. Chemical analysis by a LECO analyzer showed 90 ppm of carbon and 6200 ppm of oxygen in the sintered anodes (control sintering). Besides control sintering, test sintering was performed, which included de-carbonizing and de-oxidizing techniques. The

test sintering resulted in 18 ppm of carbon and 2500 ppm of oxygen in the sintered Ta anodes.

The Ta anodes were anodized at 80° C at formation voltages in the range 9V ≤ V_f ≤ 100 V in an aqueous solution of 0.01 mol. % phosphoric acid. This resulted in variation of the Ta_2O_5 film thickness from 18 nm to 200 nm. In-situ polymerization of PEDT was performed by chemical reaction between iron-based oxidizer and 3,4-ethilenedioxythiophene monomer. A Baytron PEDT suspension was used as pre-polymerized PEDT. With both in-situ and pre-polymerized PEDT, multiple cycles were performed to provide maximum coverage of the Ta_2O_5 film with the PEDT cathode.

The microstructure of the anodic oxide films on Ta anodes was studied by field emission scanning electron microscopy (SEM) using Hitachi S4500 model electron microscope. Electrical characterization of the Polymer Ta capacitors was performed using a Hewlett Packard 4156B Semiconductor Parameter Analyzer for I(V) measurements and an Agilent E4980A Precision LCR Meter for C(V) measurements.

Results and Discussion

Fig. 1 shows SEM images of the 200 nm anodic oxide film on Ta anodes with control sintering (a,b), test sintering (c), and test sintering, in-situ PEDT deposition, and PEDT stripping (d).

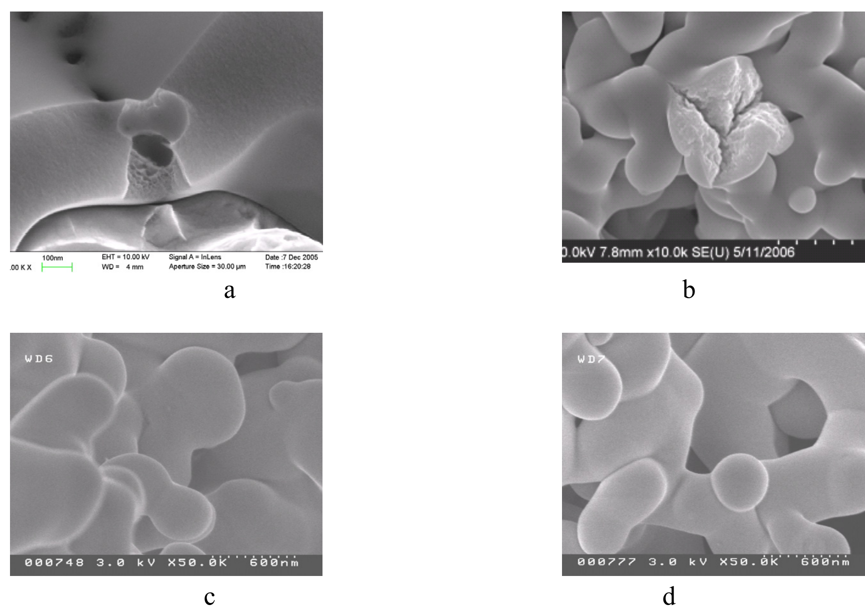

Fig. 1. SEM images of anodic oxide films on control anodes (a,b), test anode (c), and test anode after in-situ deposition of PEDT and its subsequent stripping (d).

As one can see, local pores (Fig. 1a) and cracks (Fig. 1b) were found in anodic oxide film on control anodes. These defects are typical for relatively thick anodic oxide films formed on Ta anodes enriched with carbon and oxygen.[7] At the same time, anodic oxide films formed on test anodes with low carbon and oxygen contents were practically flawless (Fig. 1c). No defects were detected in anodic oxide films on test anodes after in-situ PEDT deposition on their surface and its subsequent stripping in diluted solution of nitric acid (Fig. 1d). Similar to Fig. 1d images of the flawless anodic oxide film on test anodes were obtained after deposition of pre-polymerized PEDT and its subsequent stripping.

Fig. 2 shows I(V) characteristics of Polymer Ta capacitors with either control or test anodes, 200 nm Ta_2O_5 film, and either in-situ or pre-polymerized PEDT cathodes. SEM images of the anodic oxide films in these capacitors were shown in Fig. 1

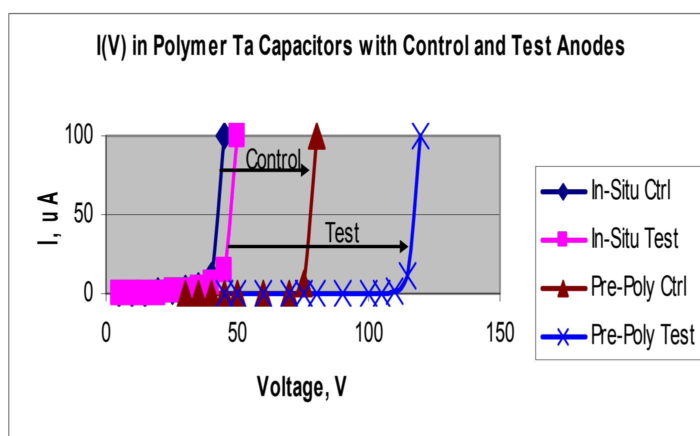

Fig. 2. I(V) characteristics of Polymer Ta capacitors with either control or test anodes and either in-situ or pre-polymerized PEDT.

From the Fig. 2, threshold voltage at which the current begins to increase rapidly leading to breakdown of the dielectric is higher in the capacitors with pre-polymerized PEDT vs. that with in-situ PEDT. The shift in threshold voltages between pre-polymerized and in-situ PEDT is larger for test anodes with the flawless dielectric vs. that for control anodes having macro defects in the dielectric. This provides evidences that the differences between Ta capacitors with in-situ and pre-polymerized PEDT are not related to macro defects in dielectric of these capacitors. All subsequent experiments were performed with test anodes.

Fig. 3 presents C(V) characteristics of Polymer Ta capacitors with test anodes, 200 nm Ta_2O_5 film, and either in-situ or pre-polymerized PEDT cathode. The C(V) characteristics were measured at room temperature.

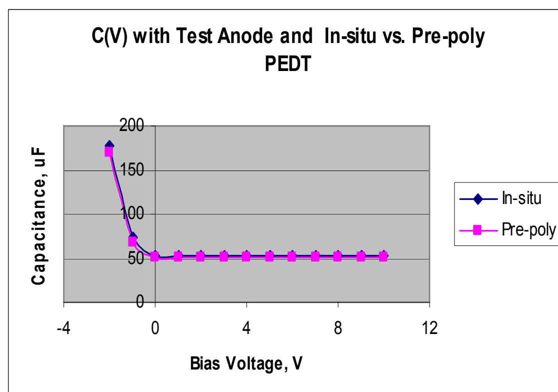

Fig. 3. C(V) characteristics of Ta capacitors with test anodes, 200 nm anodic oxide film, and either in-situ or pre-polymerized PEDT cathode

As one can see, Polymer Ta capacitors with both in-situ and pre-polymerized PEDT have practically identical capacitance with very low capacitance dependence on bias voltage at normal polarity. This result provides evidences that Ta_2O_5 film is stoichiometric, without layers enriched with oxygen vacancies, for both in-situ and pre-polymerized PEDT. The in-situ polymerization process also does not cause any damage to the Ta_2O_5 film surface (Fig. 1d).

Fig. 4 shows the breakdown voltage dependence on formation voltage (dielectric thickness) in Polymer Ta capacitors with in-situ and pre-polymerized PEDT.

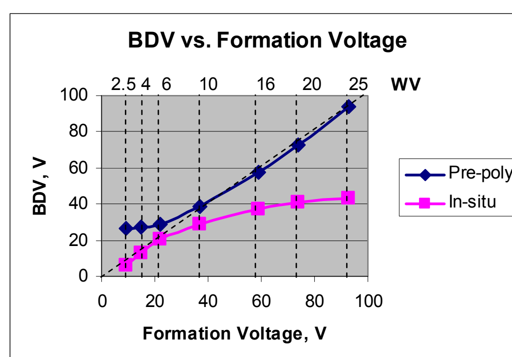

Fig. 4. BDV dependence on formation voltage in Polymer Ta capacitors with in-situ and pre-polymerized PEDT

From the Fig. 4, BDV with in-situ PEDT is approximately equal to V_f at $V_f \leq 20$ V and then gradually saturates at $V_f \approx 100$ V with increasing V_f. In the case of pre-polymerized PEDT, BDV exceeds formation voltage at $V_f \leq 20$ V and then stays practically equal to formation voltage with increasing V_f. The difference between BDV with in-situ and pre-polymerized PEDT increases with increasing formation voltage, achieving maximum at $V_f \approx 100$ V, which corresponds to WV = 25 V.

Besides large difference in BDV, 25 WV Polymer Ta capacitors with in-situ and pre-polymerized PEDT have large difference in I(V) characteristics measured at room temperature (Fig. 5).

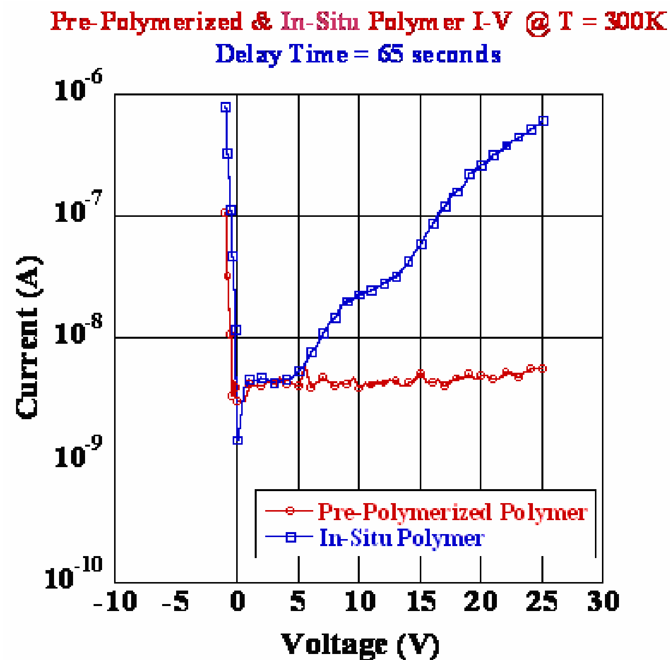

Fig. 5.Room temperature I(V) characteristic of 25 WV Polymer Ta capacitors with either in-situ or pre-polymerized PEDT.

As one can see, Ta capacitors with pre-polymerized PEDT have almost ideal diode-like I(V) characteristic at room temperature with very low current at normal polarity and rapidly increasing current at reverse voltage. In comparison to that, Ta capacitors with in-situ PEDT have gradually increasing current at normal polarity and $V \geq 5V$, while the current at reverse voltage is similar to that of the pre-polymerized PEDT.

These two types of I(V) characteristics can be explained within classical MIS theory, which has been experimentally confirmed on broad range of semiconductor devices such as Al-SiO_2-Si.[8] According to this theory, current flow through the MIS structure at normal polarity can be caused by field and temperature induced emission of current carriers from the semiconductor into the insulator. A potential energy barrier on the IS interface limits the emission. This barrier increases with applied voltage, which keeps the current low. At reverse voltage the barrier at the IS interface reduces with increasing applied voltage, which results in a rapid current increase. This ideal diode-like behavior can be hampered if surface charge is accumulated on the IS interface. The surface charge "pins" the barrier on the IS interface, preventing its increase with applied voltage at normal polarity, which results in high current and low BDV.

Polymer Ta capacitors also have an MIS structure, with the Ta anode as a metal, Ta_2O_5 film as an insulator, and PEDT as a p-type semiconductor. At normal conditions, dc leakage in Ta capacitors can be limited by a barrier at the Ta_2O_5/PEDT interface. Residuals of the oxidizer and monomer from in-situ PEDT polymerization can cause surface charge on the Ta_2O_5/PEDT interface, affecting the barrier. Increasing the number of in-situ polymerization cycles, results in a higher density of the surface charge and, thereby, a higher DC leakage current and lower BDV. In contrast to that, pre-polymerized PEDT does not cause surface charge on the Ta_2O_5/PEDT interface. In this case, the barrier increases with applied voltage limiting the current flow, which results in a low DCL and high BDV.

A characteristic feature of the classical MIS structures is a capacitance increase and gradual saturation with increasing reverse voltage. This is because reverse voltage attracts majority carriers in the semiconductor to the IS interface, reducing the thickness of the depletion region in the semiconductor. Eventually, only the insulator thickness contributes to the capacitance. Due to the series connection of the semiconductor and insulator capacitances, this effect is stronger in MIS structures with thin insulator vs. that with thick insulator. This type of C(V) behavior was observed in Polymer Ta capacitors with PEDT cathode (Fig. 6a). The C(V) curve was measured at liquid nitrogen temperature, where I(V) characteristic becomes practically non-polar (Fig. 6b).

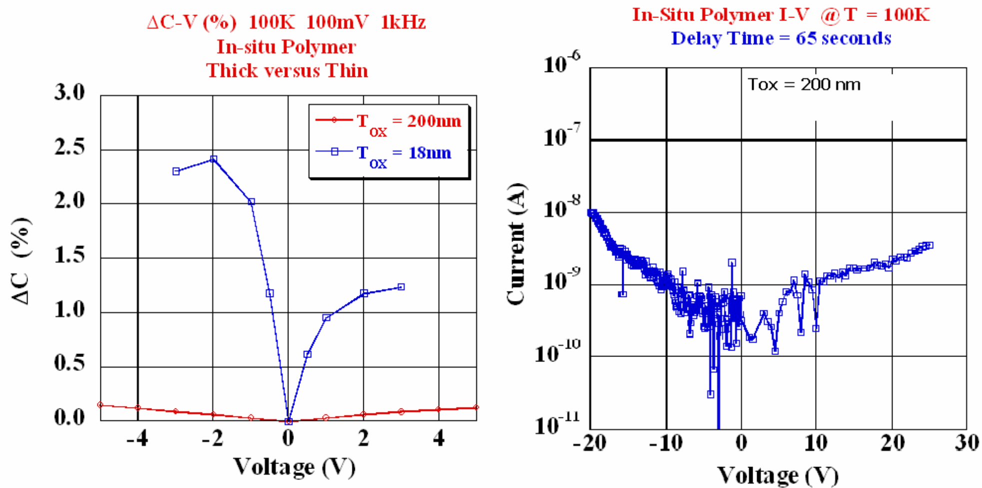

Fig. 6. C(V) (a) and I(V) (b) characteristics of Polymer Ta capacitors at T = 100 K

Recent results showed that at $V_f \geq 100$ V BDV in Ta capacitors with pre-polymerized PEDT becomes higher than that not only in Ta capacitors with in-situ PEDT, but also in Ta capacitors with MnO2 cathodes (Fig. 7). For this analysis, Ta anodes with 3,500 CV/g powder and test sintering were used at $V_f \geq 150$ V

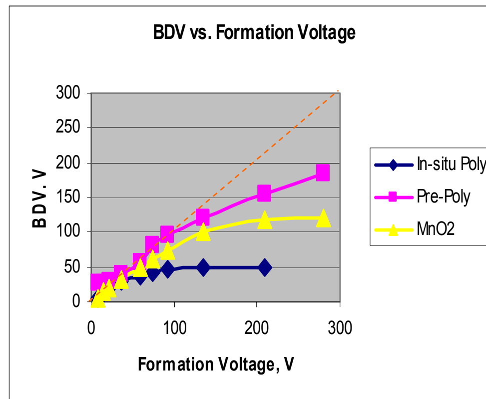

Fig. 7. BDV vs. formation voltage in Ta capacitors with different cathodes

As one can see from the Fig. 7, BDV in Ta capacitors with pre-polymerized PEDT is constantly growing in given range of formation voltages, while BDV in Ta capacitors with MnO2 cathodes reaches its maximum at $V_f \approx 200$ V and doesn't increase after that with increasing formation voltage.

Conclusion

Experimental data presented in this paper, show that Polymer Ta capacitors with pre-polymerized PEDT have lower DCL and higher BDV vs. Polymer Ta capacitors with in-situ PEDT. The difference in DCL and BDV becomes greater with increasing formation voltage (thickness of the dielectric Ta_2O_5 film). This difference also becomes greater when the Ta_2O_5 film doesn't have macro defects like pores and cracks. This provides evidences that macro defects in dielectric do not cause the differences between the capacitors with in-situ and pre-polymerized PEDT. No evidence of damage to the Ta_2O_5 film surface by in-situ PEDT polymerization was found.

There is little difference in capacitance between Polymer Ta capacitors with either in-situ or pre-polymerized PEDT and the same Ta_2O_5 film thickness. The capacitance has very little dependence on bias at normal polarity, especially, with thick Ta_2O_5 film, when there is a large difference in BDV and DCL between the capacitors with in-situ and pre-polymerized PEDT. Thus there is a lack of evidence for a model that postulates oxygen vacancy creation in the Ta_2O_5 film during in-situ polymerization process.

According to the measured I(V) and C(V) characteristics, the differences between Polymer Ta capacitors with in-situ and pre-polymerized PEDT can be explained within the classical MIS model, where M (metal) stands for the Ta anode, I (insulator) stands for the Ta_2O_5 film, and S (semiconductor) stands for the p-type PEDT. At normal conditions (plus on Ta anode and operating temperatures), current flow through the capacitor can be limited by a barrier at the Ta_2O_5/PEDT interface. In the case of in-situ PEDT, residuals of the oxidizer and monomer involved in the polymerization reaction can cause surface charge on the Ta_2O_5/PEDT interface, affecting the barrier, which results in high DCL and low BDV. Repetitions of the polymerization cycles increase the density of the surface charge, making the barrier less efficient in limiting the current. In contrast to that, using pre-polymerized PEDT does not cause surface charge on the Ta_2O_5/PEDT interface. This allows the barrier to increase with applied voltage, which results in low DCL and high BDV.

At the moment, this is a qualitative model. Additional experiments are in progress, which will allow calculation of the height of the barrier on Ta_2O_5/PEDT interface as well as other parameters of the conduction process in Polymer Ta capacitors with in-situ and pre-polymerized PEDT. An attempt at direct analysis of the Ta_2O_5/PEDT interface using Auger electron spectroscopy is also in progress.

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