Observation of the Poole-Frenkel Effect in Tantalum Polymer Capacitors

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Abstract—**I-V and I-time measurements to characterize the Polymer-Dielectric interface of Tantalum/Ta_2O_5/Polymer capacitors were performed. The interface consists of a conducting polymer – PEDOT (poly 3,4-ethylenedioxythiophene) and Ta_2O_5. The leakage current measurements on these capacitors were found to be consistent with Poole-Frenkel Emission in the bulk of the dielectric.**

Keywords- Poole-Frenkel Emission, Tantalum polymer capacitor, PEDOT/PEDT, low ESR.

I. INTRODUCTION

In most electronic applications, tantalum capacitors are preferred over the more standard aluminum and ceramic devices. Tantalum capacitors have a high volumetric efficiency (CV/cc), low equivalent series resistance (ESR), low equivalent series inductance (ESL), and high stability with respect to voltage and temperature. Their reliability and stability make them attractive in military, space, and medical applications [1]. The earliest tantalum capacitors were "wet" capacitors which employed an electrolyte as the cathode. Wet tantalum capacitors have working voltages up to 150V and ESR's of around 1.2Ω. In the 1950's, solid tantalum capacitors which used semiconducting MnO_2 as the cathode material instead of the liquid electrolyte were developed. This change in cathode resulted in the reduction of both ESR and the working voltage. The drawback of using MnO_2 is that under certain conditions, MnO_2 provides oxygen for the tantalum anode to burn and can cause an ignition failure mechanism.

In order to reduce ESR further and circumvent ignition failure mechanisms, the MnO_2 was eventually replaced with a conducting polymer – poly(3,4 ethylenedioxythiophene) (PEDOT) [2], [3]. Because the conductivity of PEDOT is higher than that of MnO_2, the ESR of the capacitor decreased significantly. However, along with the decrease in ESR, the maximum working voltage (WV) of the capacitor decreased [1]. The trend in ESR and working voltages with change in technology over time is illustrated in Fig. 1. It is evident from Fig. 1 that the maximum working voltage has been decreasing steadily along with a decrease in ESR until the 1990s.

The first tantalum polymer capacitors had a maximum working voltage of approximately 20V. By modifying the polymeric cathode, a higher working voltage of 35V was obtained while retaining the low ESR. Further improvements in the polymeric cathodes have resulted in even higher working voltages with almost no increase in ESR. It is anticipated that in the future it will be possible to manufacture tantalum polymer capacitors with higher working voltages.

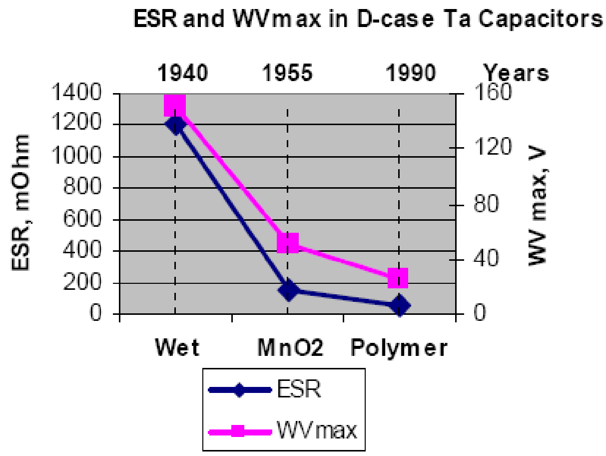

Figure 1. Variation of ESR and Maximum WV [1].

Breakdown voltage of a capacitor is the minimum voltage which will cause an abrupt increase in the current flowing through the dielectric, thus leading to a dielectric damage. The working voltage is the highest voltage guaranteed by the manufacturer at which the capacitor is expected to perform reliably. Typically, a capacitor is rated to work reliably at voltages much lower than its breakdown voltage. If a capacitor has a lower breakdown voltage it will be limited to a lower working voltage. Reliability, performance, and stability of the capacitor decrease significantly when it is operated above its working voltage. It has been shown that capacitors with a lower breakdown voltage have a higher leakage current flowing through them even when operated below the maximum working voltage (WV) [4]. Modeling this leakage current is very important in understanding the mechanisms responsible for the lower breakdown voltage.

The motivation for this research is to determine the underlying cause for the lower working voltage in the tantalum polymer capacitors. Different types of tantalum polymer capacitors were fabricated. Electrical measurements were performed on these devices and the current conduction mechanism in one type of the capacitor was investigated.

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II. FABRICATION OF SAMPLES

In this section we discuss the methods used to fabricate the tantalum polymer capacitors. A tantalum polymer capacitor consists of three major material layers: a tantalum anode, a tantalum pentoxide (Ta_2O_5) dielectric, and a polymer cathode. We will briefly discuss the deposition process of each of these layers. After the cathode is formed, there are additional processes for packaging and aging the capacitors.

A. Fabricating the Anode

Tantalum powder is first pressed into a pellet and sintered in vacuum. The sintering process enhances the electrical connectivity between the tantalum particles, thus obtaining a highly porous structure of well connected tantalum particles. A wire is attached to the pellet which will act as an external contact to the anode in the capacitor. At this stage, we have pure tantalum particles physically and electrically in contact with each other. This process produces the anode of the capacitor. Because of the high porosity, the surface area of the anode is very large. We have calculated the average area of the capacitor to be approximately $400cm^2$. This large area gives the tantalum capacitor a high volumetric efficiency, and therefore maximizes capacitance. Additionally, deoxidizing and decarbonizing processes are used to improve device performance [5].

B. Fabricating the Dielectric

The anode pellet formed in the previous step is placed in an electrolytic bath with a positive voltage on the pellet with respect to the bath. The electrolyte is aqueous phosphoric acid. The tantalum in the anode absorbs oxygen from water in the electrolyte and forms Ta_2O_5. The electrochemically formed Ta_2O_5 is amorphous and becomes the capacitor's dielectric. The thickness of the dielectric is controlled by the magnitude of the positive bias applied to the tantalum pellet and is defined as the "formation voltage". The thickness of the oxide formed is approximately 2nm/V [6]. For our experiments, we formed a dielectric with a thickness of 186nm.

If we were to apply a negative bias to the tantalum metal which has a layer of Ta_2O_5, the oxygen from the dielectric would go in to the solution. This would damage the dielectric and cause the capacitor to be very leaky. Therefore, typical tantalum capacitors are not well suited for normal operation at reverse polarity. Reverse polarity refers to applying a negative voltage at the tantalum metal electrode with respect to the PEDOT electrode.

C. Fabricating the Cathode

The cathode is essentially made of the conducting polymer, poly (3,4-ethylenedioxythiophene) (PEDOT). There are different methods for the deposition of a conducting polymer onto a dielectric. The first method we used was an *in-situ* oxidative polymerization of EDOT (Clevios™ M from H.C. Starck) with iron (III) toluenesulfonate. The second method was the application of pre-polymerized PEDOT particles (Clevios™ K from H.C. Starck) onto the dielectric. This application of PEDOT is achieved by a dip and dry process. PEDOT is a soft material and depositing a current collector contact directly onto the PEDOT is not recommended. A layer of conductive graphite is directly deposited onto the PEDOT to act as an interface layer. To establish an external contact to the cathode, a layer of silver is applied over the graphite.

It has been observed that pre-polymerized cathodes result in capacitors with higher working voltages, higher breakdown voltages, and lower leakage currents compared to devices with the *in-situ* polymerized cathodes [4]. In this paper, we present the results of detailed measurements of leakage current in these polymer tantalum capacitors, along with modeling results, in order to identify the physical mechanisms involved.

III. MEASUREMENT TECHNIQUES

Current versus voltage measurements are often used to model the conduction mechanisms in a material or device. In this research, typical current versus voltage (I-V) measurements were not sufficient. It was observed that the current decays to steady state only after a significant amount of time. This behavior can be attributed to the fact that the charges have to move through the dielectric – which is a good insulator, to reach the cathode from the anode. To provide enough time for the leakage current through the capacitor to reach steady state, we had to conduct current versus time (I-time) measurements. In an I-time measurement, a voltage is applied across the capacitor and the current level is monitored for many hours. Normally, the current level continues to decrease over time until the current reaches a steady state value. When we observe the current to stabilize, we can assume that the device has reached steady state. This final value of current is the actual dc leakage current flowing through the capacitor at the applied voltage. Such I-time measurements were performed at various voltages and the value of the steady state current was determined to produce a single I-V curve. All the current measurements were performed using the Keithley Model 4200-SCS Semiconductor Characterization System. The capacitor itself was placed inside an electromagnetically shielded box to prevent noise from affecting the measurement.

A current versus temperature measurement is performed by applying a constant voltage between the capacitor electrodes and observing the current as the temperature of the capacitor is varied. To perform current-temperature measurements, the device was placed inside a liquid nitrogen cryostat, manufactured by Sula Technology, Inc. (Ashland, OR), in which the temperature can be controlled and adjusted from 400 K to 77 K using a LakeShore 331 Temperature Controller.

IV. RESULTS AND DISCUSSION

Fig. 2 shows the results from an I-time measurement. This I-time measurement was performed at 15V on an *in-situ* polymerized capacitor with a capacitance of about 35μF. The current decreases drastically during the first few hundred seconds and afterwards starts to decrease at a much slower rate. For the first 30 seconds, the measured current varies according to the classical capacitor current discharge equation, $i(t) = \frac{V_0}{R} e^{-t/RC}$, where V_0 is the applied voltage, R is the series resistance and C is the capacitance.

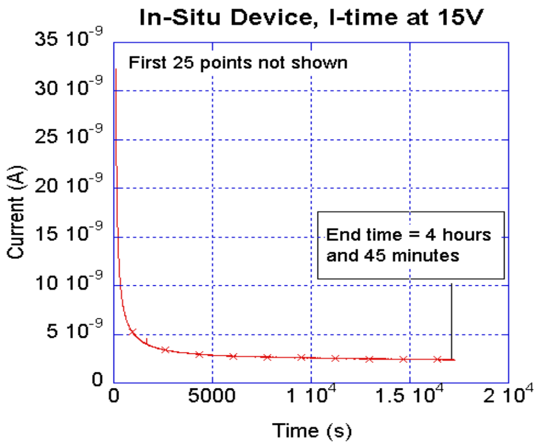

Figure 2. Variation of current with time at 15V.

The steady state current value was determined by averaging the last hundred values of current after 4 hours and 45 minutes. As recommended in [7], a $1M\Omega$ resistor was connected in series with the capacitor to limit the noise. Applying a voltage across the dielectric for long periods of time may stress the dielectric and could lead to dielectric damage. One should watch for degrading performances during an I-time test.

I-time measurements were performed on both the *in-situ* and pre-polymerized samples, both of which had an oxide thickness of 186nm. The data obtained from the I-time measurements were compiled into an I-V plot. The results are shown in Fig. 3 on the same graph for comparison.

It is evident that in the case of *in-situ* type capacitor, the current level was less than 1nA up till 10V, and then it began increasing with increasing voltage. However, for the pre-polymerized capacitor, the current level remained essentially constant at 1.2nA up to 25V. This shows the basic difference between the *in-situ* type capacitor and the pre-polymerized type capacitor. A higher working voltage can be achieved in the pre-polymerized type capacitor because the leakage current is negligible, at least up to 25V. In the case of the *in-situ* capacitor, the current increases significantly with voltage which would ultimately damage the dielectric at higher voltages.

Therefore, to design high working voltage capacitors, it is critical to understand the mechanisms which control the leakage current in these devices. For this, we need to model the leakage mechanism involved in the *in-situ* type capacitor. It is evident from Fig. 3 that the leakage current in the dielectric is significantly higher for the *in-situ* capacitor when compared to the pre-polymerized capacitor. The classical leakage mechanisms often used to explain current conduction in dielectrics are: the Schottky Effect, the Poole-Frenkel Effect, Direct Tunneling, and Fowler Nordheim tunneling.

The Schottky effect is the electric field-induced lowering of the barrier which naturally forms at the interface between a metal and an insulator or semiconductor due to differences in the work function. This effect can strongly influence current transport in some devices. The current flow due to the Schottky effect can be represented by the Richardson-Dushman equation [8],

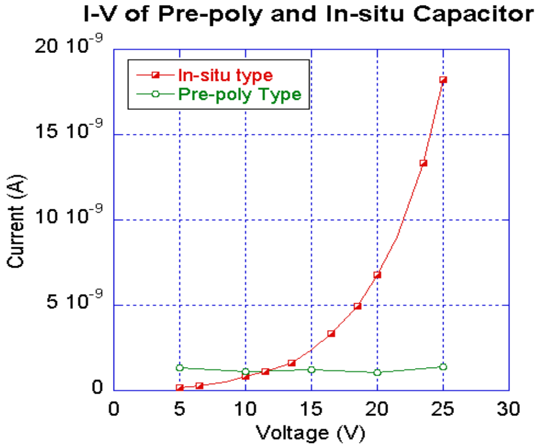

Figure 3. I-V plots of in-situ and pre-poly capacitor

$$J_s = A^*T^2 exp\left[-\frac{q\Phi_s - \frac{1}{2}\beta\sqrt{E}}{kT}\right] \quad (1)$$

where A^* is the Richardson constant, T is the absolute temperature, Φ_s is the barrier height, k is the Boltzmann's constant and β, a material constant as given as,

$$\beta = \sqrt{\frac{q^3}{\pi\epsilon_0\epsilon_r}} \quad (2)$$

In (2) q is the elementary charge, ϵ_0 is the permittivity of free space, and ϵ_r the dielectric constant of the medium. In our case, the dielectric constant of Ta_2O_5 is taken as 25 [9].

Taking the natural logarithm of (1) we can write the characteristic equation for Schottky emission as;

$$\ln(J_S) = \frac{1}{2kT}\beta\sqrt{E} + \left[\ln(A^*T^2) - \frac{q\Phi_s}{kT}\right] \quad (3)$$

The following three conditions should be satisfied in a device that exhibits the Schottky effect. (a) A plot of $\ln(J_S)$ versus $\sqrt{E}$ should yield a straight line. (b) The slope of line should be equal to the theoretically calculated value of $\frac{\beta}{2kT}$ for the dielectric. (c) The variation of current with temperature should be predicted by (1).

The measured data was plotted on a Schottky plot and it fits the characteristic linear Schottky plot quite well. The slope of this fit is 0.00718, but the theoretically calculated slope is 0.0029. Because of the large mismatch between the experimental slope and the theoretical slope, we can rule out the possibility of the leakage current being dominated by the Schottky effect. Another possible leakage mechanism often observed in Ta_2O_5 is the Poole-Frenkel (PF) effect. The PF effect is quite similar to the Schottky effect, but it arises due to the field-assisted emission of electrons from columbic traps in the dielectric. The rate of emission increases when a large enough electric field is applied. The current due the Poole-Frenkel effect is given by [10],

$$J_{PF} = CE\ exp\left[-\frac{q\Phi_s - \beta\sqrt{E}}{\xi kT}\right] \tag{4}$$

where C is a proportionality constant. ξ is called the "slope parameter" of the PF effect [11] and its value depends on the acceptor compensation in the material and can vary between $\xi = 1$ and $\xi = 2$. Taking the natural logarithm of (4), the characteristic equations for PF emission becomes,

$$\ln\left(\frac{J_{PF}}{E}\right) = \frac{1}{\xi kT}\beta\sqrt{E} + \left[\ln(C) - \frac{q\Phi_s}{\xi kT}\right] \tag{5}$$

For evidence of the Poole-Frenkel effect, the following three conditions should be satisfied. (a) A plot of $\ln\left(\frac{J_{PF}}{E}\right)$ versus $\sqrt{E}$ should yield a straight line. (b) The slope of line should be equal to the theoretically calculated value of $\frac{\beta}{\xi kT}$ for the dielectric. (c) The variation of current with temperature should be predicted by (4)

Fig. 4 shows the data presented on a characteristic Poole-Frenkel plot. A good fit is obtained and the correlation coefficient is 0.9935. The slope of the fit is 0.00474. The theoretically calculated value of the slope can vary from 0.0058 to 0.0029 depending on the value of ξ. For our measured data to match the theoretically calculated slope, ξ should be equal to 1.23. This value of ξ falls within the theoretical range and it signifies partial acceptor compensation in the dielectric. To provide further evidence for the Poole-Frenkel effect, we examine the variation of current with temperature.

Taking natural logarithm of (4),

$$\ln(J_{PF}) = \ln(CE) - \frac{1}{T}\left(\frac{q\Phi_s - \beta\sqrt{E}}{\xi k}\right) \tag{6}$$

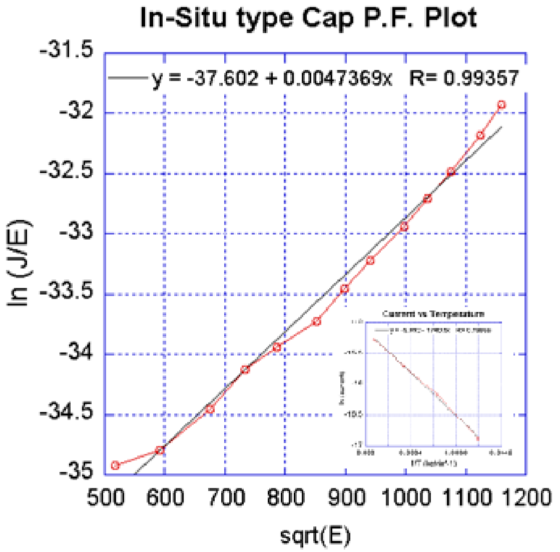

Figure 4. Poole-Frenkel Plot of an in-situ type capacitor and Arrhenius plot of the in-situ capacitor (inset)

Equation (6) implies that at constant electric field (or a constant applied voltage), a plot of the natural logarithm of current should be linear when plotted against 1/T. Measurements were made at 250K, 275K, 300K, and 325K. The measured results are presented on an Arrhenius plot consistent with (6) and is shown as an inset in Fig. 5. We observe a good linear fit with a correlation coefficient of 0.9986. From (6), the slope of the fit should be equal to $-\left(\frac{q\Phi_s - \beta\sqrt{E}}{\xi k}\right)$. All quantities in the slope are known except the Φ_s which is the potential barrier or the "activation energy" of this mechanism. Comparing the slope obtained from the fit with the theoretical slope, the potential barrier was determined to be about 0.2eV. Hence, for the *in-situ* polymerized capacitor, the measured data satisfies all three criteria for the evidence of Poole-Frenkel effect. PF emission appears to be the dominant leakage mechanism in the *in-situ* capacitors.

V. CONCLUSIONS

Based on the experimental data and our analysis, we conclude that the dominant leakage mechanism in the *in-situ* polymerized tantalum polymer capacitors is due to the Poole-Frenkel effect. A Poole-Frenkel effect suggests the presence of traps in the dielectric and implies a lower barrier to leakage current. In the pre-polymerized capacitor, the current is essentially constant in the range of its working voltage, and the leakage mechanism for this type of capacitor is currently being investigated.

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