Analysis the Reliability of Multilayer Ceramic Capacitor with inner Ni Electrode under highly Accelerated Life Test Conditions

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The reliability of multilayer ceramic capacitor with active thin dielectric layer was investigated by highly accelerated life test at various stress condition. The distribution of multilayer ceramic capacitor failure times is plotted as a function of time from Weibull distribution function. According to the test result, voltage acceleration factor is obtained from 2.24 to 2.96. The acceleration by temperature is much higher than other values of active thick dielectric layer. It is clear that median time to failure is affected by the stress voltage for high volumetric efficiency ceramic capacitors with active thin dielectric layer. The degradation under stress of voltage involves electromigration and accumulation of oxygen vacancy at Ni electrode interface of cathode.

Keywords: BME MLCC, HALT, MTTF, Acceleration factor

1. INTRODUCTION

Multilayer ceramic capacitors (MLCCs) are widely used in the electronic industry for telecommunication applications, data processing, automotive applications and other applications. With the recent tendency in miniaturization of electronic device, electronic component are required to have a larger capacitance and also to be miniaturized. The requirement for high volumetric efficiency and reduced manufacturing costs of MLCCs has the active dielectric thickness to be made more and more thin as well as usage of the nickel (Ni) metal electrodes[1]. The BaTiO$_3$ based ceramics with Ni internal electrodes must be cofired under highly atmospheres to prevent Ni oxidation. In X7R type MLCCs, the temperature coefficient of capacitance (TCC) must be within ±15 % for a -55 °C to 125 °C temperature regime. The temperature stability of capacitance can be created by control of the so-called core shell structure. The core shell structures are the coexistence of ferroelectric structure of tetragonal BaTiO$_3$ and Ferroelectric region by a solid solution of rare oxides in BaTiO$_3$. In a previous study, it was suggested that the substitution of rare earth elements into the shell phase of the BaTiO$_3$-MgO-R$_2$O$_3$(such as Dy, Ho, Er, Y) base system changed from Ba-site (act as a donor) to Ti-site (act as an acceptor) occupation, which is affected high insulation resistance and improved temperature characteristics and reliability[2,3]. The increase in capacitance per volume of MLCCs is mainly due to a reduction in thickness of dielectric layer. With the thickness of dielectric layer less than 0.8 μm, MLCCs are dielectric layer thickness with > 800 active layer have been developed. For MLCCs with Ni internal electrode (Ni –MLCC), The insulation degradation of dielectric materials under temperature and voltage stresses is caused by the oxygen vacancy electromigration toward the cathode due to their positive charge.

The HALT(High Accelerated Life Test) is observed leakage current or insulation resistance of MLCCs as they are subjected to high temperatures and high multiples of rated voltages. The goal of the HALT characteristics is to accelerate wear out effects and extrapolate from the accelerated failure rate to the expected failure in field conditions. The HALT characteristics are important to be able to use the MTTF data as a predictor of time to failure in the field.

Propokoviec and Vaskas[4] are proposed P-V model and then Municoti and Dhar[5], Mogilevsky and Shirm[6] have been demonstrate HALT testing as a proven procedure. The P-V model involved two acceleration factors as the product of voltage and thermal stress functions:

\[
\frac{I_2}{I_1} = \left(\frac{V_2}{V_1}\right)^{\nu} \cdot \exp\left[\frac{E_a}{K} \cdot \frac{1}{T_1} - \frac{1}{T_2}\right]
\]

where, $t_i$ is the time to failure under conditions $i$ of a device, $V_i$ is voltage under conditions, $n$ is the voltage acceleration factor, $E_a$ is the activation energy for dielectric wear out (BaTiO$_3$ based dielectric are typically from 1.3 to 1.5 eV), $K$ is Boltzmann's constant $8.617\text{eV} \cdot \text{K}$, $T_i$ is absolute temperature for conditions $i$. The value for the voltage acceleration factor ($n$) observed may be to varying dielectric thickness. A large number of ceramic degradation mechanisms exist which result in time induced loss of insulation resistance due to migration of material within the ceramic body. The purpose of this paper is to evaluate MTTF characteristics and electrical degradation mechanism for very high volumetric efficiency X5R type Ni-MLCC.
2. EXPERIMENTAL PROCEDURE

2.1 Sample preparation

In the preparation of MLCCs, the main starting material was BaTiO$_3$ with a particle size of 0.3 um synthesized hydrothermal (Sakai Chemical Industry Co., Ltd). The BaTiO$_3$ powders with an organic binder system and addition material (MgO, Y$_2$O$_3$, Er$_2$O$_3$, MnO$_2$, etc) were cast into green sheet. After printing nickel electrodes, green sheet were laminated and pressed to form 380 dielectric layers and then cut into small pieces according to the electric industry alliance(EIA) 2012 standard. The obtained green chips were binder burn out and sintered at 1280 °C for 2 h and cooled to 1100 °C in a reducing atmosphere controlled H$_2$, N$_2$ and H$_2$O, and then to room temperature in a weakly oxidizing atmosphere. After grinding in a barrel, they were terminated with Cu electrode paste, followed by firing at 860 °C in N$_2$-H$_2$ gas mixture. Then, Ni and Sn were electroplated to the end terminals. The characteristic data of final MLCC sample are summarized in Table 1.

Table 1. Characteristic of MLCCs.

<table>
<thead>
<tr>
<th>Electric properties</th>
<th>Physical properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cap. [uF]</td>
<td>10.5</td>
</tr>
<tr>
<td>L × W × T [mm]</td>
<td>2.0 × 1.2 × 1.2</td>
</tr>
<tr>
<td>D.F (%)</td>
<td>5.6</td>
</tr>
<tr>
<td>Dielectric thickness [μm]</td>
<td>1.59</td>
</tr>
<tr>
<td>LR [M-Ohm]</td>
<td>112</td>
</tr>
<tr>
<td>Active layers [Number]</td>
<td>380</td>
</tr>
<tr>
<td>BDV [V]</td>
<td>90</td>
</tr>
<tr>
<td>Active Area [cm$^2$]</td>
<td>6.0</td>
</tr>
</tbody>
</table>

2.2 Electrical and HALT testing

The initial values of capacitance of chips were measured with a LCR meter at 120 Hz with 0.5 V$_{rms}$ at room temperature. In this experiment, HALT test was evaluated using a modified Micro Instruments model PE9051 HALT system. The HALT conditions used in this study were temperature condition of 125 °C, 150 °C, 175 °C, 5 and 7 times rated voltage, for 20 hours. Fifty (50) piece samples were tested and the leakage current of each component was monitored during the test. MLCC failures are indicated when insulation resistance degraded to a value of 500 K-ohm. The MTTF (Mean Time to Failure) was determined from Weibull distribution function.

3. RESULTS AND DISCUSSION

Figure 1 shows the SEM images of the cross sectional view of MLCC. The active layer thickness is about 1.59 um and composed of fine grains of below 0.5 um.

Figure 2 is Weibull statistical plot of failure rate distribution for various temperature biased 34 V (5 X Vr) and 44 V (7 X Vr). It is clear that failure rate is very significantly affected by the change in test temperature. Plots of this type were used to calculated MTTF and shape parameter m.

Table 2 shows a summary of the MLCC tested in the tests, including estimates of Weibull parameters, with 95 % confidence intervals for each of MTTF and m of shape parameter. MLCC test condition subjected 44 V and 150 °C were observed to have significantly higher MTTF than MLCC of 34 V and 150 °C.
Table 2. Summary of MTTF and m (shape parameter) under various stress conditions.

<table>
<thead>
<tr>
<th>Temp</th>
<th>Voltage</th>
<th>MTTF (min)</th>
<th>m (Shape Parameter)</th>
<th>MTTF (min)</th>
<th>m (Shape Parameter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>125 °C</td>
<td>34 V</td>
<td>1596.78</td>
<td>-</td>
<td>894.43</td>
<td>2.076</td>
</tr>
<tr>
<td>150 °C</td>
<td>34 V</td>
<td>610.8</td>
<td>1.988</td>
<td>338.19</td>
<td>2.382</td>
</tr>
<tr>
<td>175 °C</td>
<td>34 V</td>
<td>306.1</td>
<td>2.117</td>
<td>142.53</td>
<td>3.219</td>
</tr>
</tbody>
</table>

Figure 3 shows the MTTF predictions for applied voltage and temperature. The relation between the logarithm of the life time reciprocal of temperature showed linearity as characteristic of Arrhenius-type. Raising the test voltage has significantly decrease the predicted MTTF as Arrhenius-type formula, because the migration of ions and other defects upon a chemical defect reaction.

\[
\frac{t_1}{t_2} = \left(\frac{V_1}{V_2}\right)^n \cdot 2 \left(\frac{T_1}{T_2}\right) \quad (a)
\]

A voltage stress exponent, n, was 2.24 ~2.96 and temperature stress \( \Theta \) was 17.08 ~ 20.05. n value of 2.24 ~ 2.96 is similar to accepted in the industry of ceramic capacitor. However, temperature exponential (\( \Theta \)) is higher than any other values reported earlier[7]. It is clear that \( \Theta \) is significantly affected by the thickness of active layer.

Table 3. Individual voltage exponential (n) and temperature exponential (\( \Theta \)) for each stress condition.

<table>
<thead>
<tr>
<th>n (34 V ~ 44 V)</th>
<th>( \Theta ) (34 V)</th>
<th>( \Theta ) (44 V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.24 (125 °C)</td>
<td>18.03 (125 ~ 150 °C)</td>
<td>17.08 (125 ~ 150 °C)</td>
</tr>
<tr>
<td>2.29 (150 °C)</td>
<td>25.05 (150 ~ 175 °C)</td>
<td>20.05 (150 ~ 175 °C)</td>
</tr>
</tbody>
</table>

Figure 4 shows degradation model of MLCC with thin active layer. When a strong electric field applied to active layer, a tunnel current flows (Fowler-Nordheim electron tunneling). For the insulation resistance degradation behavior with thin active layer, it was found that the tunneling current through grain boundary was dominant at initial stage of a leakage current and then oxygen vacancies are present in significant amount in the core region, migrate towards the cathode[8]. The formation of electrical barriers is attributed to acceptor and doping of the n-type BaTiO\(_3\) dielectric and segregation of the dopants. In general, the large amount of oxygen vacancies in BaTiO\(_3\) varies as a function of the distance from the Ni electrode. When applying dc field to the capacitor, oxygen vacancies electromigrate from the anode to cathode. DC biasing leads to

![Fig. 3. MTTF predictions for applied voltage and temperature.](image)

(a) Stress condition : 34 V, at 125, 150, 175 °C
(b) Stress condition : 44 V, at 125, 150, 175 °C

![Fig. 4. Tunneling schematic of the degradation model.](image)
chemical potential gradients and electromigration of charged defects. The concentration of oxygen vacancies near the cathode of Ni electrode is much higher than within the dielectric layers, leading to local high conductivity. The intrinsic defect of oxygen vacancies in BaTiO$_3$ are related to material imperfections and cause the capacitors to fail in a thermal runaway mode.

4. CONCLUSION

The reliability of MLCC with active dielectric layer was investigated by HALT test:

1. The relation between the logarithm of the life time reciprocal of temperature showed linearity as characteristic of Arrhenius-type.
2. A voltage stress exponent was $n=2.24 \sim 2.96$ and temperature stress was $\Theta=17.08 \sim 20.05$. The value of $n=2.24 \sim 2.96$ is similar to accepted in the industry of ceramic capacitor.

3. The concentration of oxygen vacancies near the cathode of Ni electrode is much higher than within the dielectric layers, leading to local high conductivity.

REFERENCES