The mechanism of lifetime improvement through vanadium addition to multilayer ceramic capacitor with nickel electrode

Kazumi KANEDA¹,³, Yoshiki IWAZAKI¹ and Yukihiro KONISHI¹

¹Materials Research and Development Department, R&D Laboratory, TAIYO YUDEN CO., LTD., 5607-2 Nakamuroda-machi Takasaki, Gunma 370–3347, Japan

One of the methods to improve the lifetime of a multilayer ceramic capacitor with Ni electrode (Ni-MLCC) is vanadium addition. With the addition of vanadium, insulation resistance deteriorates and reliability improves. The resistance elements of the three resistor-capacitor electrical equivalent circuit: dielectric-electrode interface, grain boundary, and grain, all deteriorated. In particular, the interface resistance significantly deteriorated with the increase in vanadium. The experimental results suggest that the high interface resistance is not always necessary to improve reliability of Ni-MLCCs. It is deduced that oxygen vacancy formation is suppressed with vanadium addition from the first principles calculation and the thermally stimulated depolarization current analysis. Therefore, the decrease in oxygen concentration is the main factor for improving reliability with vanadium addition.

Key-words : Ni-MLCC, Vanadium, TSDC, IS, Oxygen vacancy, Reliability

[Received March 29, 2018; Accepted August 29, 2018]
and sintering aid oxides, namely V$_2$O$_5$, Ho$_2$O$_3$, MgO, SiO$_2$, and MnCO$_3$, were weighed and ball-milled with BaTiO$_3$ in an aqueous system and then dried. The formulations are listed in Table 1.

The powders mixed with an organic binder system were cast into green sheets. A Ni internal electrode was printed onto the green sheets approximately 6 $\mu$m thick. Eleven green sheets with Ni electrodes and protective sheets on the upper and lower sides were stacked and pressed into a bar, and then cut into small pieces. Terminal Ni electrodes were formed on both ends of the chips. The chips were fired at 1280°C for 2 h followed by cooled to 900°C in a reducing atmosphere controlled by H$_2$, H$_2$O, and N$_2$ ($P_{O_2} = 10^{-11}$ MPa at 1280°C), soaked for 2 h at 900°C, and then further cooled to room temperature in a low oxidizing atmosphere ($P_{O_2} = 10^{-6}$ MPa at 900°C).

The microstructures were observed using a HITACHI S-4300 scanning electron microscope operated at 10 kV. HALT was performed at 150°C applied at 20 V/$\mu$m. IS measurement was performed from 325 to 425°C under air atmosphere applied at 1 Vdc using an impedance analyzer (Solartron Instruments SI1260). First principles calculations were performed based on density functional theory (DFT). The projector augmented wave method with plane wave basis set and generalized gradient approximation for exchange-correlation functional implemented in Vienna ab initio simulation package code were employed. The stabilization of oxygen vacancy and substitution of vanadium into barium and titanium sites were evaluated with formation energies based on the total energy differences of each system. The host crystals used for the formation energy calculations were composed of 3 $\times$ 3 $\times$ 3 rhombohedral phase BaTiO$_3$ unit cells. The Monkhorst-Pack special k-point grid for Brillouin-zone sampling was taken as 2 $\times$ 2 $\times$ 2, and the cutoff energy for the plane wave basis was 550 eV. We adopted rhombohedral-phase structure of BaTiO$_3$ because DFT calculations are performed under 0 K condition, and the lowest temperature phase of BaTiO$_3$ is rhombohedral phase. An O$_2$ molecule, TiO$_2$ and V$_2$O$_5$ crystals were used for the chemical potentials of $\mu_{O_2}$, $\mu_{TiO_2}$, and $\mu_{V_2O_5}$ respectively. TSDC measurement was performed with polarization at 150°C under 20 V/$\mu$m for 30 min, followed by heating from 150 to 350°C with ramp rate of 10°C/min under helium atmosphere using a Rigaku thermally stimulated femtoampere electron trap tracer.

### Table 1. Sample compositions (mol %)

<table>
<thead>
<tr>
<th>Number</th>
<th>BaTiO$_3$</th>
<th>MgO</th>
<th>MnO</th>
<th>V$_2$O$_5$</th>
<th>Ho$_2$O$_3$</th>
<th>SiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>V000</td>
<td>100</td>
<td>0.5</td>
<td>0.1</td>
<td>0</td>
<td>0.75</td>
<td>1.5</td>
</tr>
<tr>
<td>V005</td>
<td>100</td>
<td>0.5</td>
<td>0.1</td>
<td>0.05</td>
<td>0.75</td>
<td>1.5</td>
</tr>
<tr>
<td>V010</td>
<td>100</td>
<td>0.5</td>
<td>0.1</td>
<td>0.10</td>
<td>0.75</td>
<td>1.5</td>
</tr>
<tr>
<td>V015</td>
<td>100</td>
<td>0.5</td>
<td>0.1</td>
<td>0.15</td>
<td>0.75</td>
<td>1.5</td>
</tr>
</tbody>
</table>

3. Results and discussion

The active layer thickness of all the fired Ni-MLCCs was approximately 4.5 $\mu$m. The mean grain size of the all samples was approximately 0.65 $\mu$m, and no abnormal grain growth was observed. The grains were found to have a core–shell structure. Permittivity of V000 was 3300, which decreased slightly with vanadium addition up to V015 of V015. The temperature coefficient of capacitance improved with vanadium addition, and both V000 and V005 were consistent with X7R characteristics. Figure 1 shows the mean time to failure (MTTF) of HALT measured at 150°C under 20 V/$\mu$m. It is confirmed that MTTF improved with the increase in vanadium up to V010.

The current density–electric field ($J$–$E$) characteristics were measured at 150°C, as shown in Fig. 2. The insulation resistance at high electric field was comparable despite the difference in the amount of vanadium added. On the other hand, the insulation resistance at low electric field deteriorated with the increase in vanadium. That is to say, the conduction mechanism changed with vanadium addition, as the previous paper addressed.

To understand the detailed conduction mechanisms, IS analysis and SBH measurements were performed. Figure 3 shows Nyquist plots measured at 350°C under 1 Vdc. Distorted semicircles were observed, whose shapes
changed with the increase in vanadium. This implies that the microstructure and/or conduction mechanism could change with vanadium addition. In this study, a three resistor-capacitor (RC) section electrical equivalent network was adopted, which gave excellent fitting results. Each RC element was considered as a grain (G), grain boundary (GB), and dielectric-electrode interface (IF), respectively. The resistance change and activation energy of each R element were extracted and compared.16)–18)

Figure 4 shows the variations of each three-R elements with vanadium addition, \( R(G) \) is resistance of the grain, \( R(GB) \) is that of the grain boundary, and \( R(IF) \) is that of electrode-dielectric interface.

Insulation resistances along with the \( J–E \) characteristics, it is deduced that the increase in mobile carrier (electron) concentration caused by the substitution of vanadium into titanium sites acting as a donor caused the insulation resistance deterioration expressed as,

\[
2\text{BaO} + \text{V}_2\text{O}_5 \rightarrow 2\text{Ba}^{\text{II}} + 2\text{V}^{\text{IV}}_\text{Ti} + 6\text{O}_\text{O}^{\cdot} + \frac{1}{2}\text{O}_2 \uparrow + 2e^{-}
\]

It is considered that this is a main factor of decrease in \( R(G) \) and \( R(GB) \). Another important point obtained from the IS analysis is the significant decrease in interface resistance. Here, SBH was estimated according to the study by Samantaray et al.19) SBH decreased with the increase in vanadium from 1.5 eV (V000) to 0.50 eV (V015). This trend is consistent with the decrease in \( R(IF) \) obtained in the IS analysis, which explains the overall trend changes of the high resistance element in Fig. 4.

From the results mentioned above, it was deduced that low interface resistance does not always mean that the reliability of the Ni-MLCCs will deteriorate as shown in Fig. 1. However, reliability could deteriorate as shown by V015 sample in Fig. 1, because MLCC is heated due to high leakage current when \( R(IF) \) is too low.

Furthermore, degradation of Ni-MLCCs is generally explained by the migration of oxygen vacancies to the cathode region during reliability testing, e.g. HALT.18)–21) Therefore, the investigation of the change in oxygen vacancy concentration with vanadium addition becomes important.

To investigate the substitution energy of vanadium into Ba and/or Ti sites and the valence state of vanadium, first principles calculations were performed. Furthermore, the oxygen vacancy formation energy was estimated. Figure 6 shows the calculated substitution energy of vanadium (a) into the Ba site and (b) Ti site of BaTiO_3.

The substitution energy of vanadium into Ba site is greater than 4 eV, on the other hand, that of vanadium into Ti site is less than 4 eV. Comparing the substitution energy of each
valence state of vanadium, the case of +5 is the lowest substitution energy between -1 and 2 eV. This means that substitution of vanadium into Ba site is difficult, whereas substitution of vanadium into Ti site is possible. Moreover, vanadium tends to incorporate into BaTiO₃ with the valence state of +5. This reaction is shown in Eq. (1). This means that the experimentally observed insulation resistance (IR) degradation mentioned above is due to the increase in mobile carrier electrons (n), as shown in Eq. (1).

Figure 7 shows the oxygen vacancy formation energy to BaTiO₃. It was deduced that the valence state of oxygen vacancy tends to be +2, and formation was suppressed under n-rich conditions. In other words, when vanadium was incorporated into BaTiO₃ as a donor, n increased and the next reaction could shift to the right,

\[
\text{BaTiO}_{3-\delta} + \frac{\delta}{2} \text{O}_2 \uparrow + 2\delta e^- + \frac{\delta}{2} \text{V}_0 \rightarrow \text{BaTiO}_3
\]  

(2)

This reaction means that oxygen vacancy concentration decreased with vanadium addition.

The electronic charge transfer level of oxygen vacancy is just below conduction band minimum at 2.40 eV position from valence band maximum, whereas that of vanadium at Ti site of BaTiO₃ is 2.18 [from V(V) to V(IV)] and 2.39 [V(IV) to V(III)] eV. These results indicate that the vanadium does not act as an effective donor species compared to the oxygen vacancy. Considering our experimental results, these theoretical results indicate that these kinds of non-effective donor species are effective for the improvement of the lifetime of MLCCs by the suppression of oxygen vacancy with a slight deterioration of insulating properties.

To investigate the actual oxygen vacancy concentration of the MLCCs, TSDC measurement was performed. Figure 8 shows the TSDC spectra, which was polarized at 150°C under 20 V/µm for 30 min and measured from 150 to 350°C with heating rate of 10°C/min. One noticeable difference is the rising current above 250°C. The rate of increase is almost proportional to the amount of vanadium added, implying that the number of carrier electrons is increasing and easily thermally excited from the trapped state with the increase in vanadium. As a result, insulation resistance deteriorates. Therefore, the current above 250°C was increased by the effects of the electro-
motive force of the TSDC measurement device. Another noticeable difference is TSDC peaks related to oxygen vacancy which are generally considered to originate from defect dipole rotation at approximately 150°C (peak \( \alpha \)), in-grain migration at approximately 200°C (peak \( \beta \)) and across-grain boundary migration at approximately 250°C (peak \( \gamma \)). It is considered that peak \( \gamma \) has been decrease and then disappear with the increase in vanadium addition, however it is difficult to compare because the current of the samples increases drastically with vanadium addition as mentioned above. On the other hand, peak \( \alpha \) and peak \( \beta \) are comparable each other and were lowered with the increase in vanadium, implying the decrease in oxygen vacancy concentration with vanadium addition. It was deduced from TSDC analysis that the main factor behind the improvement of Ni-MLCC reliability is the decrease in the oxygen vacancy concentration with vanadium addition.

Generally, incorporated site of rare-earth element into BaTiO\(_3\) changes by means of composition, firing condition and re-oxidation condition; as a result, that electrical properties and reliability of Ni-MLCCs changes as reported by Kishi et al. and Sakabe et al.\(^{25,26}\) On the other hand, in this study we simply discussed the effect of vanadium addition on the electrical property and reliability change mechanism of Ni-MLCCs. Therefore, further study should be performed in order to well understand the reliability improvement mechanism of Ni-MLCCs.

4. Conclusions

The effects of vanadium addition on the lifetime of Ni-MLCCs and the lifetime improvement mechanisms were investigated. Insulation resistance deteriorated and MTTF (reliability) improved with vanadium addition as reported by previous studies.

The resistance elements of the three-RC electrical equivalent circuit: dielectric-electrode interface, grain boundary, and grain, all deteriorated. In particular, the significant deterioration of interface resistance could be correlated with the decrease in SBH. The insulation resistance deterioration of Ni-MLCC was attributed to the increase in the amounts of mobile carriers (electrons) and decrease in the interface resistance. On the other hand, reliability improved with vanadium addition. Therefore, to improve reliability, the high interface resistance is not always necessary.

The first principles calculation and the TSDC analysis showed that oxygen vacancy formation was suppressed with vanadium addition. Thus, the decrease in oxygen vacancy concentration is the main factor for improving reliability with vanadium addition.

Acknowledgement The authors would like to thank Dr. T. Atsumi, TAIYO YUDEN CO., LTD. for performing the first principles calculations and helpful discussions.

References