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Re-oxidation of Ni-MLCs

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Abstract

Ni-electrode based multilayer ceramic capacitor (MLC) have been successfully introduced in the market since 1992. One essential step in the processing of the MLCs is the so called re-oxidation step, where the reductively fired parts are heat treated in an atmosphere containing a higher oxygen partial pressure as the reductive firing atmosphere. This causes a modification of the defect chemistry of the doped $BaTiO_3$ and guaranties the reliability of the device. In order get a deeper understanding of the re-oxidation process and its kinetics in MLC experiments with different re-oxidation conditions will be presented and the observed effects will be explained by the help of model calculations.

Keywords: $BaTiO_3$; Capacitors; Diffusion; Ferroelectric properties; Re-oxidation

1. Introduction

Multilayer ceramic capacitors (MLC) based on $BaTiO_3$ dielectrics suitable for Ni internal electrodes (BME = base metal electrode) have to be fired under reducing conditions in order to avoid an oxidation of the Ni. Therefore the ceramics has to be acceptor doped and thus oxygen vacancies are formed during the reductive firing. These oxygen vacancies were identified to be the root cause for the degradation of the insulation resistance of perowskite ceramics[1,2] and the number of the oxygen vacancies has to be reduced in order to improve the reliability of the device in the application under DC bias or for the highly accelerated life test (HALT). For some material compositions also the insulation resistance is increased by this so called re-oxidation treatment.[3,4]

The re-oxidation of Ni electrode based multilayer ceramic capacitors (MLC) has been subject to several investigations. Basic studies on the Ni-oxidation embedded in $BaTiO_3$ were done by Weiss,[5] who observed that Ni embedded in $BaTiO_3$ is oxidized in the temperature range from 950 to 1300 °C by a parabolic rate law; controlled by the diffusion in the NiO layer. The ceramic materials investigated by Weiss where not designed for the reducing conditions (donor doped material), and thus not fully comparable with modern BME-MLC formulations. Yamamatsu et al.[4] report a significant increase in the reliability of MLCs by re-oxidation at partial pressures $>10^{-9}$Pa at 1000 °C, and state that the upper limit for the Ni-oxidation is given by 1 Pa, which is caused by Ni-oxidation and thus insufficient electrical contact. Shoji et al.[3] show that good electrical properties may also be obtained in air for temperatures between 600 and 800 °C, again at 800 °C Ni-electrode oxidation caused undesired properties.

In order to get a deeper understanding of the MLC re-oxidation conditions a few additional experiments have been performed and a model has been set up to simulate the re-oxidation behavior of the ceramics in the presence of the Ni-inner-electrodes. The model is based on the assumption that the re-oxidation should be controlled by the oxygen diffusion, while the diffusion of the cations is neglected. It does not include a description of the Ni-electrode oxidation, but is taking the presence of the Ni-electrodes into account for the oxygen migration. A two dimensional finite element method was developed to describe a quarter of the active and passive (electrode free margin) part of the MLC as illustrated in Fig. 1.

2. Experimental

In order to illustrate the influence of different re-oxidation (or annealing) conditions MLCs (Y5V, Ferro

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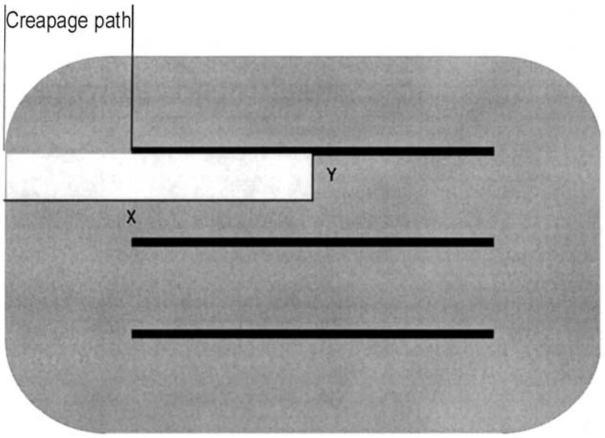

Fig. 1. Area simulated by the model calculation.

dielectric AD143N) were fired without oxidation treatment in moistened (18 °C) N_2 with 1% H_2 and later re-oxidized for 2 h under different conditions in moist N_2: A: 1000 °C without Ni-getter ($PO_2 = 3$Pa from N_2), B: 1000 °C with Ni-getter (Ni-ink layer burned out on a ZrO_2 setter plate in reducing atmosphere; 4.4×10^{-6} Pa–Ni–NiO equilibrium) . In order to get well defined conditions, only 5 MLCs were re-oxidized at one run with an gas flow of 1 l/min; the partial pressures were confirmed by measurements with a ZrO_2 sensor (Ametek). In a second experiment, the insulation resistance of BME-X7R MLCs (Ferro, AD342N) was determined for two different re-oxidation conditions.

3. Model

The driving force for all diffusion processes is a gradient of the chemical potential of the mobile species. For the re-oxidation of the ceramic and the oxidation of the Ni-inner electrode the chemical potential of the oxygen would be the interesting value. It is, e.g. on the surface of the Ni-electrode (when Ni-metal is still present) equal to the Ni/NiO equilibrium partial pressure. The oxygen activity (partial pressure) in the ceramic is not known. For simplification of the model calculation the respective partial pressure of the reductive firing of the ceramic has been selected as state for the ceramics. This means that, e.g. a ceramic cooled down from the firing temperature (1300 °C) to 1000 °C in a moist N_2 1%H_2 mixture should exhibit an oxygen activity proportional to the partial pressure of this gas mixture, which is equal to 10^{-9} Pa.

This partial pressure is considered as starting point of the oxygen chemical potential and depending on the change of the outside atmosphere conditions, oxygen will diffuse into the structure. The model now considers the presence of the Ni-inner-electrode in such a way, that if the partial pressure of oxygen in the ceramic by diffusion is higher as 4.4×10^{-6} Pa at 1000 °C a diffusion towards the Ni will occur simultaneously. No passivation or total oxidation of the Ni is taken into account and the partial pressure at the electrode surface is considered to be at this equilibrium value for all times of the modulation. This results in the fact that the electrodes are a continuous drain for oxygen at partial pressures higher than 4.4×10^{-6} Pa.

The finite element calculation based on Fick's second law were done with a program described elsewhere.[6] The diffusion constant for oxygen used was based on diffusion data obtained by Wernicke[7] for low ($<10^{-5}$ Pa) oxygen partial pressures and acceptor doped $BaTiO_3$ and may be described by: $D = 1.51\times10^{-3}$ exp-(1.6 eV/kT) [m^2/s]. All model calculations were done for 1000 °C and the described segment of the MLC with a passive margin of 200 and 750 µm active layer depth for dielectric layers with different thickness.

4. Results and discussion

The two micro-graphs at the left hand of Fig. 2 show that the top Ni-electrode (top picture) is oxidized, while electrodes inside the stack show no oxidation; a little is present at the second electrode. It further illustrates that also the tips of the electrodes (lower picture) are oxidized as well. Ca. 30 µm in-between the electrodes the detectable oxide layer vanishes. The micro-graphs at the right hand side show no visible oxide layers when the MLCs are heat treated in the same gas with a Ni-getter in front of the MLCs.

Fig. 3 shows cracking of an MLC with many layers (>150) close to the termination caused by the expansion of the Ni-electrode tips during re-oxidation at 3 Pa. No such cracks are observed when a Ni-getter is present. In order to illustrate the effect of the Ni-inner-electrode on the diffusion oxygen as described by the presented model the conditions in the MLC are simplified in Fig. 4. The following conditions where chosen for this plot in order to visualize the effects.

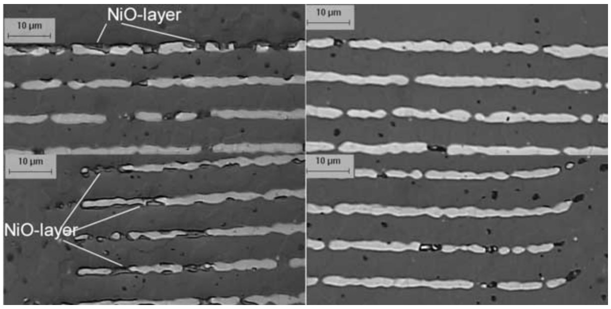

Fig. 2. Left Photos: Oxidized top Ni layer and electrode tips after 2h re-oxidation at 1000 °C in moist N_2 without Ni-Getter $PO_2 = 3$Pa. Right Photos: No observable Ni-oxide layers for MLCs re-oxidized at 1000 °C in the presence of a Ni-getter.

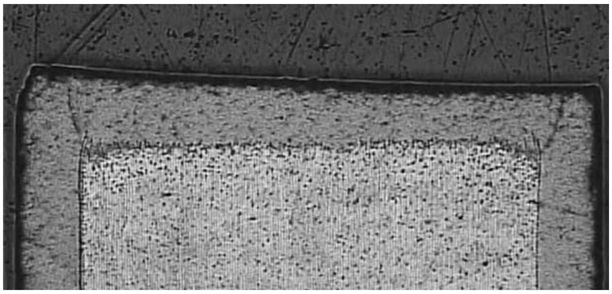

Fig. 3. Cracks in the MLC caused by oxidation of Ni-electrodes.

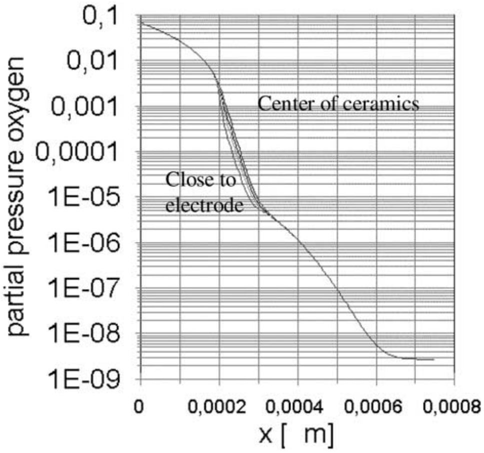

Fig. 5. Oxygen partial pressure–concentration distribution after 10 s for a 45 μm simulated MLC.

A: Constant partial pressure at the surface = 1.
B: Creepage path (= electrode free ceramic margin) 200 μm.
C: The constant (Ni-electrode) potential starts at 200 μm and is set to 0.2.
D: The dielectric layer thickness is 750 μm.

The resulting oxygen distribution after 10 s shows the inrush of the oxygen into the material as obtained by the calculation based on Fick's second law. As the "oxygen partial pressure" in the vicinity of the Ni-electrode is below the "level" governed by the metal the diffusion profile is undisturbed by the electrode. After 100 s the concentration front has moved further into the device and the concentration close to the electrodes is higher than 0.2 and a flow to the drain electrode occurs as well. After 1000 s a steady state is obtained and the influence of the electrode is clearly visible. Even for these very thick dielectrics of 750 μm the influence of the inner electrode in the model as a continuous drain, does not allow a higher concentrations as 0.43 in the center of the part. If the layers are considered closer to the commercial range, e.g. 45 μm, and the border conditions are set to those discussed for the MLC oxidation with a surface partial pressure of 0.67 Pa (equilibrium partial pressure of moistened N_2, from water decomposition) the following partial pressure distribution (Fig. 5) is obtained. In this two-dimensional plot the partial pressure distribution is shown after 10 s simulated diffusion time.

The variation of the oxygen partial pressure is shown as a package of lines representing the respective oxygen concentration from next to the electrode towards the middle between the electrodes. In the center of the MLC the initial low partial pressure is still present, while an area influenced by the electrodes is only observable for ca. 130 μm into the active area. This effect is even more clear for a 45 μm dielectric, after 1000 s diffusion time, when no more changes in the diffusion profile are observable and the partial pressure in the center of the MLC is equal to the Ni-NiO value (Fig. 6).

For thin layered MLCs with 5.6 μm dielectric layer thickness the area with a higher oxygen partial pressures nearly vanishes totally, and is narrowed down to 15 μm (Fig. 7).

Just like for the thicker dielectric layers the model indicates no concentration variation between the electrodes (center of the MLC) after 1000 s. The described model shows that the oxidation of the ceramic between the electrodes is mainly obtained by diffusion of oxygen

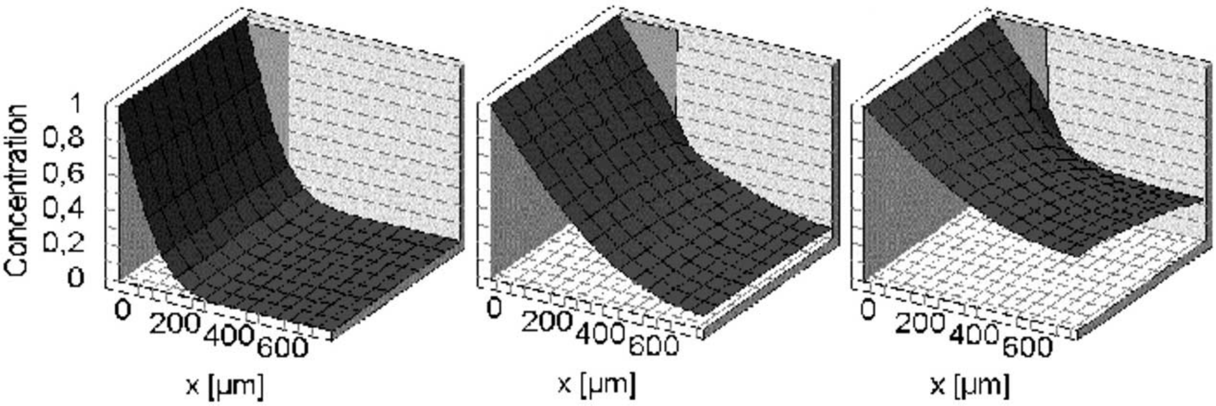

Fig. 4. Simplified diffusion model, relative concentration evaluation for a 750 μm dielectric layer for 10, 100 and 1000 s.

parallel to the electrodes towards the center of the MLC, an oxidation perpendicular to the electrodes should only be possible, if gaps in the electrodes are present (not considered in the model). Fig. 8 shows a section of the micro-graph of the MLCs where the electrodes are less continuous and also a little Ni-oxide is detectable for lower layers in the MLC.

Even though the model itself does not consider any Ni-oxidation, for ca. three times the dielectric layer thickness an oxygen flow towards the electrodes is calculated if the re-oxidation takes place at partial pressures higher than the Ni–NiO equilibrium value. This is in the same order as the experimental observation shown in Fig. 2 lower left picture. Where the oxide layers are detectable up to ca. 30 μm for 6 μm thick dielectric layers. Thus the calculation allows a prediction of oxidation zones as long as the Ni-oxide formation is faster than the oxygen consumption of the dielectric body and no total oxidation of the Ni takes place; which seems to be the case for 1000 °C.

The next theoretical calculations were done for an oxygen partial pressure outside the MLC equal to the Ni–NiO equilibrium value at 1000 °C. As the "partial pressure of oxygen" in the ceramic is never going to be higher than this outside value, no diffusion in the direction of the Ni will occur and no Ni-oxidation is observed in MLCs re-oxidized under these conditions (see Fig. 2). The model calculation shows no differences for segments close to the electrodes or for the center of the dielectric layers. The oxygen partial pressure distribution in the MLC for different annealing times is given in Fig. 9.

Besides the effect that no influence of the Ni-electrode is observable in the calculation it can be seen that the time to reach an equilibrium for the oxygen partial pressure in the center of the MLC (at 750 μm) is twice as long as for the higher outer partial pressure. This is caused by the fact, that for smaller concentration differences the driving force for the diffusion process is lower (several orders of magnitude) and thus the rate of oxygen "flow" especially in the margin area is lower as well. Nevertheless the final oxidation state in the center of the MLC reached is identical to that of the model calculations with higher outer partial pressures. This

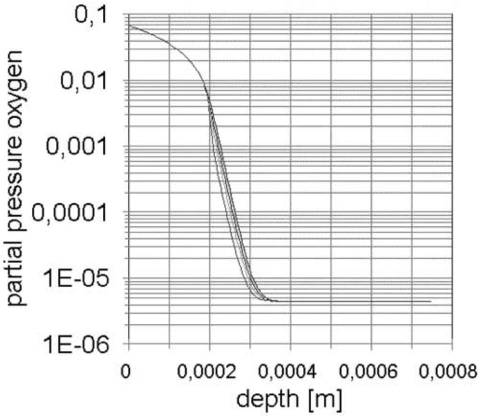

Fig.6. Oxygen partial pressure distribution after 1000 s for 45 μm dielectric layer.

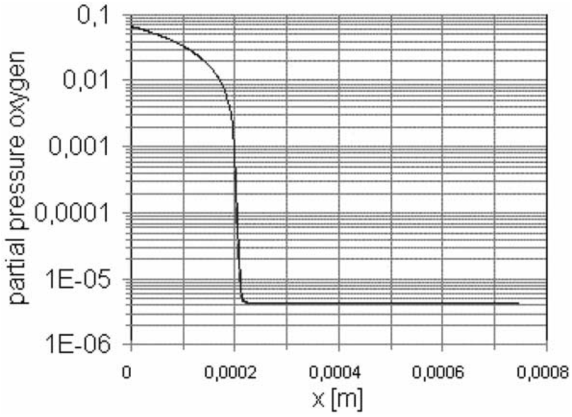

Fig. 7. Oxygen partial pressure distribution after 1000 s for 5.6 μm dielectric layers.

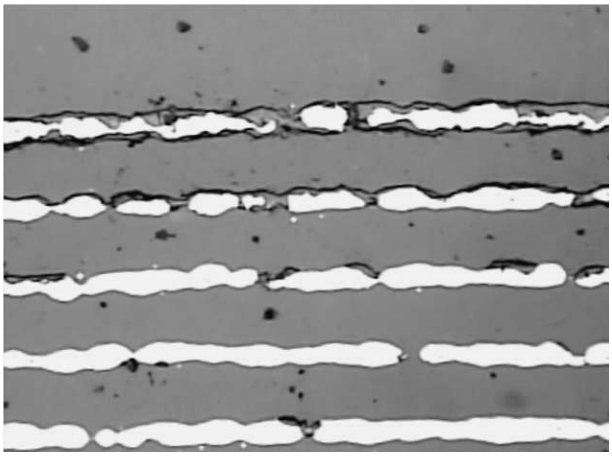

Fig. 8. Partial oxidation of "lower" Ni-electrodes by oxygen diffusion via gaps in the Ni layers, from electrode 4 on no Ni-oxidation is visible.

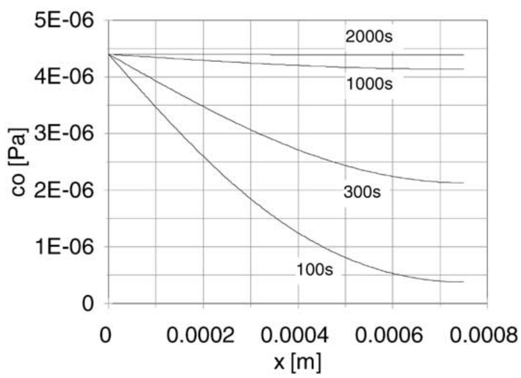

Fig. 9. Simulation of the oxygen partial pressure distribution for different annealing times for MLCs annealed in an atmosphere equal to the Ni–NiO equilibrium partial pressure.

Table 1
Insulation resistance of X7R MLCs after different re-oxidation conditions

	No-re-oxidation	1 Pa	4.4×10^{-6} Pa
IR (MΩ)	43	14 500	13 600
Standard deviation (MΩ)	7	2050	1830

means that the same electrical properties should be obtainable. In order to check this, MLCs made from Ferro AD342N were re-oxidized under two conditions: (a) in moist N_2 with ca. 3 Pa O_2 and (b) at 4.4×10^{-6} Pa, generated by a big plate of Ni in front o the MLCs in the gas stream and checked by an oxygen sensor. AD342N is sensitive to the re-oxidation state and the insulation resistance of MLC increases several orders of magnitude in the re-oxidation step. Thus if the model calculation given before are correct similar insulation resistances should be obtainable for both re-oxidation conditions. The insulation resistances values for 49 MLCs of each annealing condition are given in Table 1.

Within the statistical error margins the insulation resistances are identical and confirm the assumptions of the model.

5. Summary

A finite element diffusion model has been build to describe the re-oxidation of Ni-based MLCs. The model implies an oxygen diffusion parallel towards the electrode layers. The influence of the Ni-inner electrodes in the MLCs is simulated by a constant partial pressure for the Ni electrodes. The achievable "oxygen partial pressure" in the center of the MLC is independent from the layer thickness, governed by the Ni–NiO equilibrium value. Experimental observations for re-oxidation experiments at 1000 °C are in accordance with the model.

With respect to the re-oxidation atmosphere in mass production of MLCs, the model description and the experimental data indicate, that the time to reach the "oxygen partial pressure" in the center of the MLC is equivalent for different dielectric layer thickness' and mainly depending on the width of the MLC. It further indicates that a re-oxidation at higher partial pressures than the Ni–NiO equilibrium will not give any improvement of properties with respect to the defect chemistry of the ceramic between the electrodes. Crack formation due to Ni-oxidation especially for high layer count MLCs is promoted by higher oxygen partial pressures (Fig. 3). These findings may be different for lower temperatures when the oxidation speed of the Ni electrodes is lower and the kinetics are different (e.g. passivated Ni-electrode).

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