



Effect of Interactions at the Cofired Interface of Electrode/Ceramics on the Reliability of Lead-Based Multilayer Ceramic Capacitors

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Abstract. The increase of silver content in the internal electrodes was found to have a negative influence on accelerated-test life of lead magnesium niobate-based multilayer ceramic capacitors under direct current-voltage. Transmission electron microscopy (TEM) and auger electron spectroscopy (AES) analyses were carried out on the cofired electrode/ceramics interfaces to demonstrate the effect of Ag content in the electrode on the reliability of capacitors. The result showed that Ag could diffuse into the ceramic layers for more than one micrometer. We designed Ag-doping experiments to study the interactions between the ceramics and Ag. Temperature-humidity-bias (THB) tests on Ag-doped disc specimens revealed that the failure rate of the specimens increased with the Ag content in the ceramics. Based on these results, it was inferred that the deterioration of the multilayer ceramic capacitors with the increase of Ag content in the electrodes should be attributed to the Ag diffusion from the electrodes into the oxide ceramics.

Keywords: ferroelectrics, interface, diffusion, electrical properties, reliability

1. Introduction

Lead magnesium niobate (PMN)-based relaxor ferroelectrics have become one of the most important material systems in multilayer ceramic capacitors (MLCC) owing to their valuable properties such as low sintering temperatures and high dielectric constants. The low sintering temperatures allow the use of palladium/silver (Pd/Ag) alloy electrodes, which effectively lowers the product cost. In addition, the high dielectric constants make it possible to reduce the number of ceramic layers and thereby meet miniaturization demands. However, it was found that some PMN-based MLCC suffered direct current (DC)-voltage failure under working conditions with the increase of Ag content in the electrodes. Understanding the failure mechanism is very important for achieving reliability improvement.

Attempts have been made to find clues related to degradation by examining microstructural defects such

as flaws, voids and cavities [1, 2], and chemical inhomogeneities in oxide ceramics [3, 4]. The common conclusion, however, is that the migration of metal atoms from the electrodes bring about conductive paths in the ceramics or on the ceramics surface. Ling and Jackson suggested that metallic silver migration under temperature-humidity-bias (THB) conditions at 85°C was the cause of electrical short-circuit paths, leading to subsequent failure of MLCC [1]. Chen and Yeung believed that the electromigration of end termination metals such as silver and tin on the moisturized surface under DC-voltage is the major mechanism for the resistance failure of MLCC [2]. H. Kanai reported that triple points and grain boundaries of the ceramics dissolved during the life test, and then migration of Ag ions through the dissolved grain boundaries led to the degradation [3, 4]. In summary, they took into consideration the electrodes and ceramics respectively and put emphases on the chemical or physical reactions to the electrodes under THB condition.

In fact, Ag and Pd can not only diffuse into the ceramics [5–8], but also be incorporated into the oxide lattice during the high-temperature sintering, thereby

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changing the properties of the materials [9–11]. As to PMN-based ferroelectrics, the effects of Ag and Pd doping on the sintering characteristics and electrical properties of the oxides have been extensively studied. However, the interactions between the electrodes and ceramics during sintering and their effects on the reliability of MLCC received much less attention.

In the present paper, the reliability of PMN-based MLCC with different internal electrodes was compared through THB tests. The results revealed that the reliability of MLCC deteriorated with increasing the Ag content in the internal electrodes. Therefore, the microstructure and chemical reactions at the cofired interface of the Ag/Pd electrode and ceramics were studied using TEM and AES techniques. The effects of the interfacial reactions on the reliability of PMN-based ceramics are discussed in light of Ag-doping experiment results.

2. Experimental Procedures

2.1. Specimen Preparation

The studied material composition was $x\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}y\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}z\text{PbTiO}_3$ ceramics (PMZNT, $x + y + z = 1$, $0.90 \leq x \leq 0.95$, $0 \leq y \leq 0.05$, $0 \leq z \leq 0.1$) [12]. The MLCC samples were made by the tape-casting method with internal electrodes of 1/9 or 3/7 Pd/Ag (designated as 1/9 MLCC and 3/7 MLCC respectively). The MLCC (size 0.08 inch \times 0.05 inch) obtained had a capacitance of 100 nF and dielectric loss below 100×10^{-4} at 25°C. The thickness of the ceramic layers was 20 μm in average while that of the internal electrode was about 2 μm . For the fabrication of Ag-doped specimens, firstly AgNO_3 was added to the ceramics powders at 0, 0.1, 0.2, 0.4, 0.8, 1.5 and 3.0 mol% of Ag contents respectively. Secondly, the powders were dry-pressed into pellets with a diameter of 1 cm after water ball-milling and drying. Then all specimens were sintered at 955°C for 4 hours followed by cooling down in the furnace.

2.2. AES, SEM and TEM Analyses

AES analysis (PHI-610/SAM, by Perkin-Elmer) was used to examine the interactions at the cofired electrode/ceramics interface. The focused electrons were directed on the sample with an angle of 30°.

Light Ar^+ sputtering cleaning and depth profile composition analysis were conducted by a scanning Ar^+ gun which permitted an etching area of 1 mm^2 . Auger spectra were taken from a focused spot of about 2.3 μm^2 near the center of the sputtered area. The etching rate was 25 nm/min, which was calibrated to the heated SiO_2/Si .

Microstructure analyses were carried out using scanning electron microscopy (SEM, JEOL-6301F) and TEM (H-800). Specimens for SEM observation were firstly polished down to grit 2000 with water grinding paper, then cleaned in alcohol and heat-etched at 800°C for 20 minutes. Specimens for TEM observation were prepared using standard techniques.

2.3. THB Experiments

10-day THB tests at 85°C and 95% relative humidity (RH) were carried out with DC fields of 0.1 and 0.25 $\text{V} \cdot \mu\text{m}^{-1}$ for disc specimens and MLCC respectively. MLCC with resistance below $10^9 \Omega$ after the THB test was designated to have failed. The disc samples with resistivity below $10^8 \Omega \cdot \text{m}$ were designated to have failed. The insulation resistance was measured at room temperature using an HP 4190B pA meter by applying a DC voltage of 10 V on specimens for 1 minute.

3. Results

THB tests on MLCC showed that the failure rate of 1/9 MLCC reached about 50% while that of 3/7 MLCC was merely 5%. As described in Section 2.1, these two kinds of MLCC were made from the same ceramics powders. The only difference between them was the Pd/Ag ratio in the internal electrodes. This result strongly suggested that the electrode composition had played an important role in the DC-voltage failure of the MLCC.

3.1. TEM and AES Analyses on the Cofired Interface

In order to demonstrate the effect of internal electrode composition on the reliability of MLCC, microstructure and chemical reactions at the cofired interface of electrode/ceramics were studied through TEM and AES analyses. Figure 1 gives a TEM micrograph of the cofired interface. It can be seen that the electrode was well bonded with the ceramics and the interface

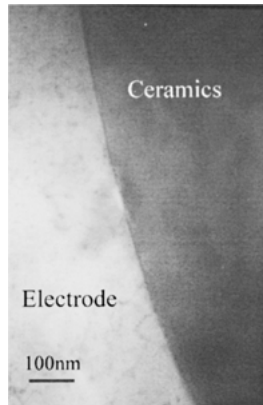


Fig. 1. TEM micrograph of the cofired interface of electrode/ceramics in a 1/9 MLCC.

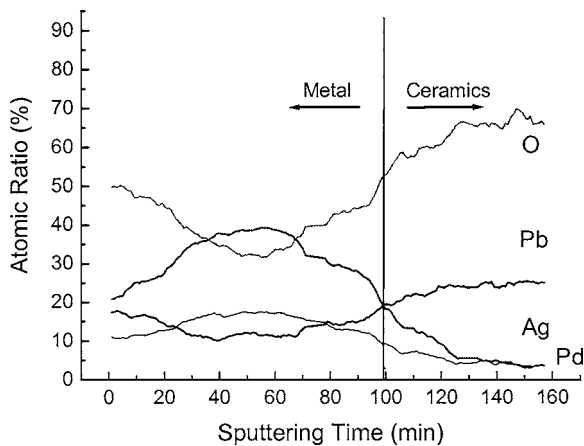


Fig. 2. AES depth profile analysis across the cofired interface of electrode/ceramics in a 3/7 MLCC.

was very clear. No excessive chemical reaction in the ceramics was observed.

Figure 2 shows the atomic concentration ratios of Ag, Pd, O and Pb across the interface of electrode/ceramics in a 3/7 MLCC. The sputtering started from the electrode layer and continued in the direction from the metal to the ceramics. It can be seen that there were gradual changes of concentration for all the elements studied, which revealed the interdiffusion between the electrode and the ceramics during the sintering. Elements from the oxide, e.g., Pb, could be found across the entire metal electrode layer. We assumed that the electrode/ceramics interface was located where the concentrations of the diffused elements reached their average values, corresponding to the sputtering time

of 99 min. Then the diffusion depths of the electrode elements into the ceramics layer were estimated to be more than 1 μm .

3.2. SEM Observation of Ag-Doped Ceramics

As mentioned above, the deterioration of the MLCC resulted from the increase of Ag content in the internal electrodes. Therefore, we designed Ag-doping experiments to evaluate the effects of Ag diffusion on the reliability of MLCC.

Figure 3(a) gives a SEM micrograph of a 3.0% Ag-doped specimen. Distributions of Ag, Pb and O in the same area as Fig. 3(a) were shown in Fig. 3(b)–(d) respectively. It can be seen that these elements were uniformly distributed in the ceramics. This suggested that all of the silver was in the form of Ag^+ and was incorporated into the perovskite solid solution.

Figure 4 shows the relationship between the Ag content and DC-resistivity of the doped ceramics. As the Ag content increased initially, the resistivity of the ceramics increased and then decreased after the Ag content reached 0.4%. However, the effect of Ag addition on resistivity of the material can be neglected in the range of Ag contents studied. This suggests that Ag additions have little effect on the DC-conduction of the ceramics.

3.3. THB Experiments

THB tests were conducted on Ag-doped specimens to examine the effect of Ag diffusion into the ceramic oxide on the reliability of the MLCC. Figure 5 shows that the failure rate of the specimens increases significantly after the Ag content reaches 0.2%. This result revealed that Ag dopant damaged the reliability of the PMN-based ferroelectrics under long-term DC-voltage.

4. Discussion

In the present paper, the effect of electrode composition on the reliability of PMN-based MLCC was studied. It was found that the failure rate of 1/9 MLCC became much higher than that of 3/7 MLCC after the 10-day THB test. This indicated the important role of the electrode composition in the DC-voltage failure of MLCC. We combined AES and TEM to investigate the interdiffusion between the electrode and the

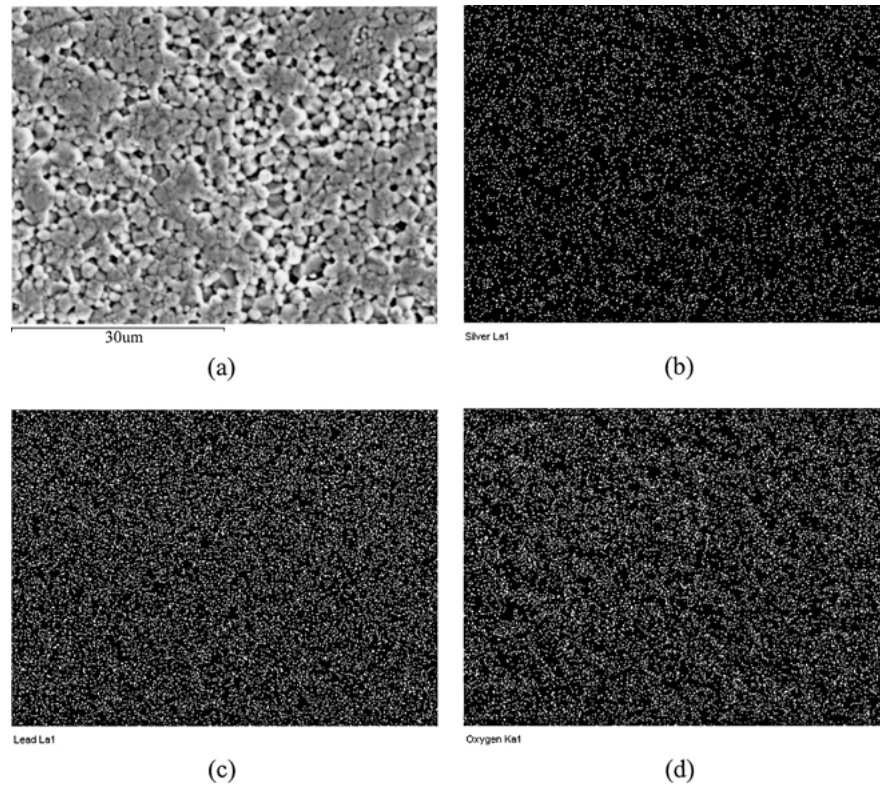


Fig. 3. SEM observations on the 3.0% Ag-doped ceramics (a) topography of the specimen and surface distribution of (b) Ag, (c) Pb and (d) O in the same area as (a).

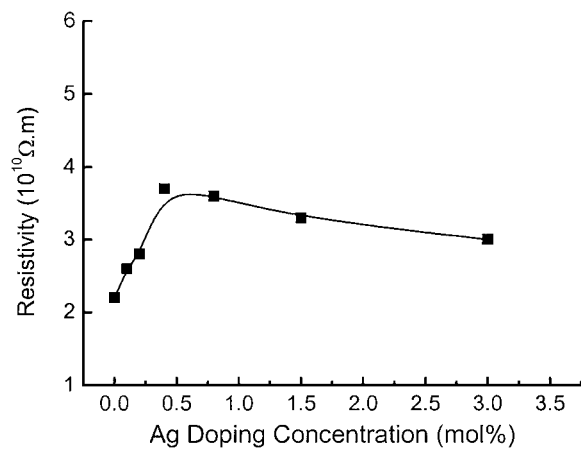


Fig. 4. The effect of Ag dopant on the DC-resistivity of the ceramics.

ceramics. Based on the results obtained, we designed Ag-doping experiments to simulate the Ag diffusion into the ceramics layer. THB tests showed that Ag addition damaged the reliability of the ceramics at high Ag contents.

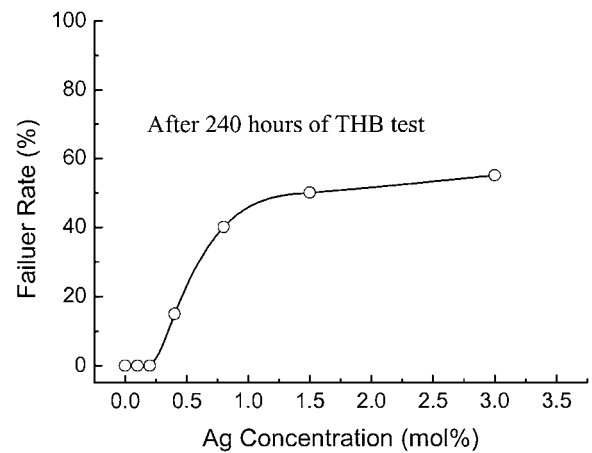
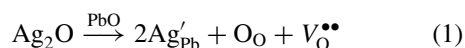


Fig. 5. Failure rate of the specimens at different Ag doping levels after THB test.

In a previous study [14], an inner bias field was observed in the resistance-degraded MLCC using hysteresis property measurement. In the present paper, we further studied the effect of Ag diffusion on the

reliability of MLCC through Ag-doping experiments. As to the state of Ag in the ceramics of MLCC, however, TEM observation suggested that no new phase was formed in the ceramics near the interface though the diffused Ag concentration was rather high. Moreover, the interface was very clear, as shown in Fig. 1. SEM observations on Ag-doped samples suggested that all the Ag has been incorporated into the ceramics as Ag^+ in the range of the Ag contents studied. Meanwhile, it was found that Ag^+ incorporation affected the DC-resistivity of the materials only slightly.

Because of the similar radii of Ag^+ and Pb^{2+} , Ag^+ tends to substitute for Pb^{2+} and occupies the A site of ABO_3 lattice. Then according to defect chemistry and the results obtained, it was inferred that oxygen vacancies would be generated to keep electroneutrality because of the Ag substitution, as shown in Eq. (1).



Oriented migration of oxygen vacancies under external DC-bias and subsequent generation of electronic defects led to the DC-voltage failure of MLCC [13, 14].

According to Fick's first law, Ag diffusion into the ceramics will increase with the Ag content in the internal electrodes. Reliability of the specimens became worse with increasing Ag concentration in the ceramics, including the disc samples and MLCC.

It is interesting that no excessive chemical reaction was observed in the ceramics grains at the cofired interface by using TEM though AES analysis revealed significant element interdiffusions. More detailed studies on the structure and chemical reactions at the cofired interface of PMN-based ferroelectrics/electrode are needed.

5. Conclusions

1. AES analysis revealed the significant interdiffusion between the electrode and the ceramics at the cofired interface.

2. Ag addition could damage the accelerated-test life of the PMN-based ferroelectrics.
3. Deterioration of PMN-based MLCC with internal electrodes of higher Ag content is attributed to the Ag diffusion across the cofired interface.

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