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Influence of silver migration on dielectric properties and reliability of relaxor based MLCCs

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Abstract

In order to study the micro-mechanism of silver migration which influences the reliability of relaxor based multilayer ceramic capacitors (MLCCs), micro-silver-doped PMN-PZN based relaxor ferroelectric ceramics were investigated for their microstructural and dielectric properties. SEM observations showed that the microstructure near the interface of MLCCs was greatly changed by the action of the inner silver/palladium electrode. The results indicate that silver migration causes grain growth, changes dielectric properties and decreases insulation resistance. Defect chemistry principles were used to explain the micro-mechanism of action of the silver dopant.

Keywords: C. Ferro electric properties; Migration

1. Introduction

To keep up with the trend in miniaturization of electronic equipments and related components, particularly with the rapid development of integrated circuit and surface mounting technology, the demand for MLCCs is steadily increasing. The use of modified $BaTiO_3$ is widely recognized. However, its high sintering temperature implies the adoption of high melting point internal electrodes, such as Pd, Pt and so on. An high-performance Pb-based relaxor ferroelectric has been developed for the fabrication of MLCCs. Because of its sintering temperature lower than conventional ceramics, silver/palladium alloys can be used as inner electrode in the metal-ceramic co-firing step of the fabrication process. Compared with $BaTiO_3$ based MLCCs, in addition to delaminations, cracks, chemical interaction like Pd–Pb and Pd–Bi reaction [1,2], silver migration into ceramics in the co-firing process of relaxor based MLCCs is another important reason which influences reliability and dielectric characteristics. Even though silver migration has been yet reported [3–5], micro-mechanism of action of silver on MLCCs reliability has been poorly investigated. In this paper, authors attempt to use micro-silver-doped PMN–PZN based relaxor ceramic and cofired multilayer ceramic samples with 30Pd/70Ag electrode to study the mechanism of silver migration. PMN and PZN as the typical candidates for relaxor ferroelectrics can be modified by suitable dopants, to meet Y5V and Z5U characteristic (EIA specification) and to be commercially applied in MLCCs, so the results may prove to be significant for other relaxor based MLCCs.

2. Experimental procedure

2.1. Sample preparation

xPMN–yPZN–zPT (PMZNT) modified by a small amount of MnO_2, MgO and other dopants was used as the main constituent of the studied samples. The detailed ceramic powder preparation process has been described elsewhere [6]. In order to eliminate pyrochlore formation, the columbite method was used to synthesize the PMZNT ceramic powder. The calcined ceramic powder and silver salt were weighed and mixed by ZrO_2 ball-milling in deionized water for 24 h, obtaining an homogeneous distribution of silver element. Ten-mm

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diameter disk pellets were pressed and then sintered in a closed Al_2O_3 crucible using a protective Pb atmosphere.

Using 30Pd/70Ag paste and the ceramic powder mixed with suitable binder, solvent, dispersant, and plasticizer, multilayer ceramic samples were prepared through tape-casting, screen printing and laminating.

2.2. Experimental methods

The temperature dependence of the dielectric properties was measured with a HP4192A impedance analyzer equipped by a Delta 2300 automatic temperature control box and a computer-monitoring system. One-hundred V voltage was applied to specimens for 1 min to measure their insulation resistance at room temperature. X-ray analysis on powder specimens was used to identify phase formation.

The fracture morphology of silver-doped samples and the microstructure near the interface in the multilayer ceramic specimens were observed by SEM (JEOL6301F).

3. Results and discussion

As seen from Fig. 1, the dielectric characteristics of PMZNT ceramic were changed in the presence of small amounts of silver salt. The dependence of dielectric properties on silver content was more complex, not simply monotonically rising or falling, than previously reported [7]. When silver dopant was less than 0.2 mol%, the dielectric constant slightly increased. The reason for this may be that the low melting point of silver leads to transient liquid sintering and then promotes grain growth, which further causes the reduction of grain boundary phases. Generally speaking, the larger grains in the samples, the less amounts of grain boundary. According to our past experiments, silver can effectively promote the sintering of relaxor ceramics. In Pb-based relaxor ceramics, the secondary phases at grain boundary or triple angle are known to be among the main reasons for degradation of the dielectric properties. According to the series mixing model, the following equation can be applied:

$$\frac{D}{K_s} = \frac{D_g}{K_g} + \frac{D_{gb}}{K_{gb}} \tag{1}$$

where K_s is the dielectric constant of the sample, K_g the dielectric constant of the perovskite PMZNT grain, K_{gb} the dielectric constant of the grain boundary phases, and D the grain boundary thickness. Being K_{gb} much lower than K_g, the dielectric constant of the samples decreases greatly. So this equation can be used to explain the effect of higher amounts of silver dopant on the dielectric properties, as indicated in Fig. 1. On the other hand, the effects of grain growth or density increase also lead to the appearance of the micro-peak in the curve of Fig. 2.

It is well known that the cations at A-site and B-site of Pb-based complex perovskite can be replaced by many other cations. The substitution is mainly determined by the difference of valence and ionic radius. The size of Ag^+ is almost the same as for Pb^{2+}(about 0.149 nm), and much larger than for B-site cations, such as Nb^{5+}(0.064 nm) and Zn^{2+}(0.074 nm) [8]. So Ag^+ may enter into A-site, substituting for Pb^{2+}. The non-equivalent replacement of Ag^+ for Pb^{2+} will produce free electrons in the grains. To keep neutral, $V_o^{\cdot\cdot}$ compensating for this will be produced. This process may be explained as follows:

$$2Ag^+ + 2Pb^{2+} \rightarrow 2Ag'_{Pb} + V_o^{\cdot\cdot} \tag{2}$$

$$PbBO_3 + \frac{x}{2}Ag_2O \rightarrow \left[\left(Ag_xPb_{1-x}\right)BO_{3-\frac{x}{2}} + e'\right] + \frac{x}{2}V_o^{\cdot\cdot} + xPbO \tag{3}$$

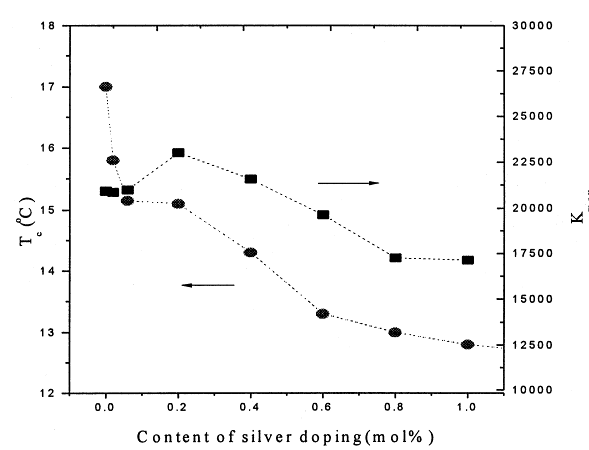

Fig. 1. Effect of silver doping on the dielectric properties of relaxor ceramic.

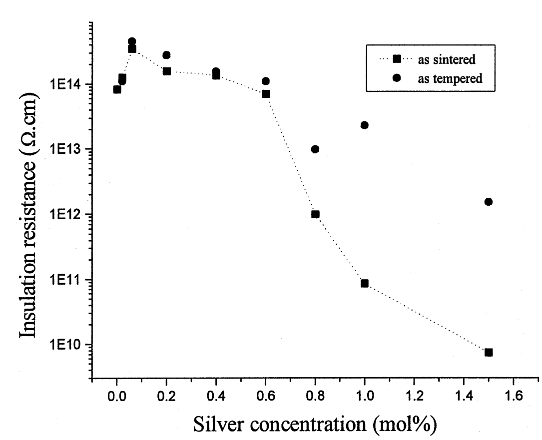

Fig. 2. Insulation resistance of silver-doped relaxor ceramic for different heat-treatments.

The free electrons and $V_O^{\cdot\cdot}$ will form a weakly-bonded relationship. When the electric field was applied, these electrons could give rise to leakage currents due to their transition form one place to another, so that the electrical insulation resistance of the samples evidently decreased. In addition, the existence of $V_O^{\cdot\cdot}$ in the crystal can be identified by comparing the electrical resistance of silver-doped samples before or after heat-treatment because of the oxidation reaction, as shown in Fig. 2. The electrical insulation resistance of silver-doped samples can be improved through an annealing treatment.

The X-ray spectra in Fig. 3 shows that due to the addition of silver, the typical diffraction peaks of perovskites move to higher angles. As previously stated, this is thought to be the result of the contraction of cells on account of the formation of $V_O^{\cdot\cdot}$. X-ray data also further confirm that Ag^+ enters A-site to a certain extent. According to this assumption, the substitution of silver ion for lead ion will inevitably expel the Pb from the lattice, forming a Pb-rich grain boundary glass phase. This procedure can be presented with the Eq. (3). The grain boundary glass phase with low K can account for the degradation of the dielectric properties of specimens to a large extent, as indicated in Fig. 1 and explained in Eq. (1). Moreover, the rich-Pb grain boundary phases can explain the decline of life performance of Ag/Pd electrode-based MLCCs in the humid atmosphere and the intergranular fracture near the interface inside MLCCs [9]. Because the Pb-rich grain boundary phases slightly dissolve into water, the ionized electrode, such as silver/palladium, may migrate to another pole through grain boundary channels because of the applied field. The fracture morphology of silver-doped specimens also presents more distinct intergranular fracture than that of un-doped specimens. Furthermore, the abnormal growth of ceramic grain near the electrode in Fig. 4 tends to cause paste leakage into the inside of parts when electroplating the end electrode. All these factors will influence the reliability of MLCCs.

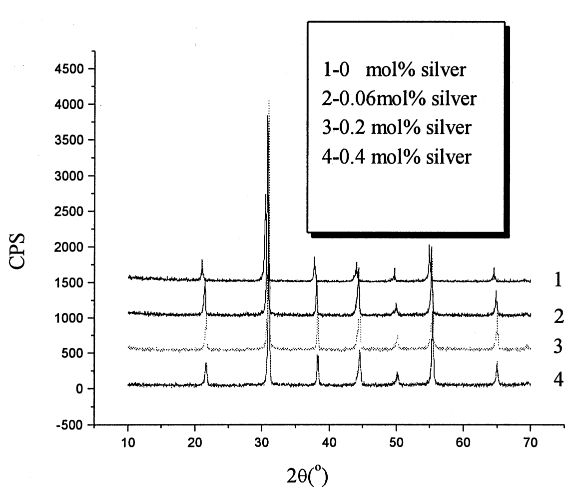

Fig. 3. XRD spectra for silver-doped relaxor ferroelectric ceramic.

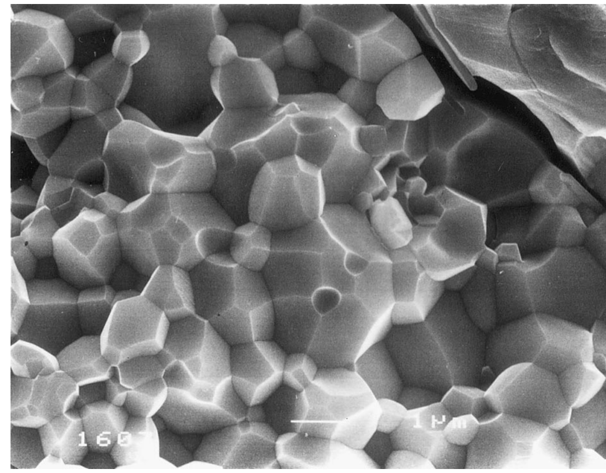

Fig. 4. SEM graph at the internal interface of MLCC with 70Ag/30Pd electrode.

In addition to the effect of silver migration on the dielectric constant, electrical insulation resistance and failure mode of devices, a change in the Curie temperature (T_c) was observed because of silver addition. However, there are many different reports about this [10], an effect which may be determined by the silver concentration, kind of ceramic and sintering conditions. Generally, the drift of T_c was thought to contribute to atomic replacement of A-site or B-site. In this paper, the micro-silver addition into A-site of PMZN ceramic is helpful to the falling of T_c. The reduction of 0.5°C in T_c is attributed to 0.1 mol% silver addition.

4. Conclusions

Through many experiments and analyses, the micromechanism of silver migration into ceramic influencing the dielectric properties and reliability of MLCCs may lead to the following:

1. silver addition can change the dielectric properties and microstructure evolution of relaxor ferroelectric ceramic. Very little amount of silver can increase the dielectric constant and resistance values, but more silver will degrade its performance;
2. the migration of silver into the growing ceramic grain produces $V_O^{\cdot\cdot}$ and forms Pb-rich grain boundary phases during cofiring. This may be an important reason for the degradation of dielectric properties and reliability of relaxor based MLCCs with Ag/Pd inner electrode;

3. the intrinsic low melting point of silver may account for the microstructure change and abnormal grain growth of the ceramic near the interface.

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References

[1] S.F. Wang, Interaction of silver-palladium electrode with lead and bismuth based electroceramics, J. Am. Ceram. Soc. 76 (2) (1993) 474–480.

[2] S.F. Wang, W. Huebner, Interaction of Ag/Pd metallization with lead and bismuth oxide based fluxes in multilayer ceramic capacitors, J. Am. Ceram. Soc. 75 (9) (1992) 2339–2352.

[3] C.H. Lu, J.Y. Lin, Interaction between lead iron niobate/tungstate ceramics and silver/palladium metals, Ceramics International 23 (3) (1997) 223–228.

[4] W. Wersing, H. Wahl, M. Schnöller, PZT-based multilayer pizeoelectric ceramics with AgPd-internal electrodes, Ferroelectrics, 87 (1998) 271–294.

[5] S.S. Cole, W.H. Payne, J. Miller, V. Venkatessin, Silver loss in multilayer capacitors, in: Proceedings of the 81st Annual Meeting of the American Ceramic Society, Cincinnati, OH, May 1979.

[6] Z.L. Gui, P.S. Cui, Y. Wang, L.T. Li. Advanced Structural Materials. Elaevier Science Publisher, 1991, pp. 463–468.

[7] Y.C. Sato, H. Kanai, Y. Yamashita, Effects of silver and alladium doping on the dielectric properties of 0.9 $Pb(Mg_{\frac{1}{3}}Nb_{\frac{2}{3}})O_3$–$0.1PbTiO_3$ ceramic, J. Am. Ceram. Soc. 79 (1) (1996) 261–265.

[8] R.D. Shannon, Revised effective ionic radii and systematic studies of interatomic distances in halids and chalcogenides, Acta Crystallogr., Sect. A. Found. Crystallogr. 32 (1976) 751–767.

[9] H. Kanai, O. Furukawa, S.I. Nakamura, Effect of stoichiometry on the dielectric properties and life performance of $(Pb_{0.875}Ba_{0.125})\ [(Mg_{\frac{1}{3}}Nb_{\frac{2}{3}})_{0.5}(Zn_{\frac{1}{3}}Nb_{\frac{2}{3}})_{0.3}Ti_{0.2}]O_3$ relaxor dielectric ceramics, J. Am. Ceram. Soc. 76 (2) (1993) 459–464.

[10] H.J. Hwang, T. Nagai, T. Ohji, M. Sando, Curie temperature anomaly in lead zirconate titanate/silver composites, J. Am. Ceram. Soc. 81 (3) (1998) 709–712.