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Interfacial development and microstructural imperfection of multilayer ceramic chips with Ag/Pd electrodes

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Abstract

The interfacial microstructure between Ag/Pd electrodes and PMN–PZN–PT relaxor ferroelectric ceramics in cofired multilayer ceramic devices was investigated by transmission electron microscopy and scanning electron microscopy. Disadvantageous interfacial defects, such as delaminations, warping, gas holes and exaggerated grain growth, were identified. In addition to the preparation process, the composition of the inner electrode paste and the sintering densification compatibility between the layers played important roles in the interfacial development. The relationship of the interfacial microstructure to the reliability of the device is discussed.

Keywords: A. Tape casting; B. Interfaces; B. Defects; Advanced ceramics

1. Introduction

During the past few years, current trends towards miniaturization and operation at higher frequencies of electronic devices have required electronic components of small size, high volumetric efficiency, high reliability, lost cost, and compact chip configuration [1,2]. Based on advanced tape-casting and surface mounting technologies, multilayer monolithic ceramic devices are promising candidates to meet these requirements. Examples of these types of devices are multilayer ceramic capacitors (MLCC), multilayer piezoelectric ceramic actuators (MPCA), multilayer chip inductors (MLCI), etc. However, the cofiring process of these multilayer devices must be considered because unsuitable sintering processes, structural design, or material compositions can lead to the formation of defects, such as delaminations, interfacial interdiffusion, and chemical reaction [3,4]. Moreover, with increasing thinness of the ceramic layer produced, the volumetric proportion of the inner interfaces of a multilayer device will increase greatly. Thus, study of interfacial problems is important in the preparation of suitable devices. Further, Pb-based complex relaxor ferroelectrics, such as $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN), $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN), etc., have been used extensively for informational functional ceramic devices due to their anomalously large dielectric constant, large electrostrictive strain, broad dielectric maximum, and relatively low firing temperature [5,6]. Consequently, the interfacial problems between PMN–PZN-based relaxor ferroelectric ceramics and Ag/Pd electrodes may be extensive. Concerning interfacial problems in multilayer devices, most research work has been focused on specific material compositions and devices [1-4]. The aim of the present work was to investigate the characteristics of the resultant interfacial microstructures between Ag/Pd alloy electrodes and PMN–PZN-based relaxor ferroelectrics and to correlate these with processing factors and the reliability of multilayer ceramic devices.

2. Experimental procedure

PMN–PZN–PT ($PbTiO_3$ denoted as PT) relaxor ferroelectric ceramic powder was prepared from appropriate amounts of reagent-grade PbO (Beijing Chemical Plant, China), TiO_2 (Beijing Fine Chemical Co., Ltd, China), ZnO (Wenzhou Reagent Chemical Plant, China), MgO

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(Beijing Fine Chemical Co., Ltd, China), and Nb_2O_5 (Beijing Chemical Plant, China) with purities of $>99.5\%$. The modified columbite method [7] was used to synthesize the corresponding ceramic powders in order to eliminate the formation of the pyrochlore-type phase, which is detrimental to the electrical properties [8]. Slurries for tape-casting were made by mixing the calcined powders with a solvent (an azeotropic mixture of methyl ethyl ketone and ethanol, $>97\%$ purity, Xizhong Chemical Factory, Beijing), dispersant (phosphate ester, $>97.5\%$ purity, Nanya Reagent Chemical Plant, Shanghai, China), plasticizer (polyethylene glycol 400, $>96.5\%$ purity, Fine Chemical Plant, Beijing) and binder (polyvinyl butyral, $>95\%$ purity, Xingguang Chemical Plant, Beijing). The slurry was spread by a doctor blade on a flat glass to produce green tapes with thickness ~ 50 μm. The green tapes were cut into smaller sections of $\sim 3\times 3$ cm^2 and then 70Ag/30Pd and 90Ag/10Pd pastes (General Research Institute of Nonferrous Metals, Beijing, China) were deposited onto the tapes respectively by screen-printing. The stacked pads then were warm-pressed at 65°C under 10 MPa pressure for 2 min to develop a good bond between the layers. Before sintering, the binder was burnt out in air by heating the samples at a rate of 0.5°C/min up to a maximum of ~ 500°C, with a soak time of 1 h at this temperature. The samples were heated in a covered alumina crucible at a rate of 3°C/min and sintered between 950 and 1050°C with a soak time of 4 h, followed by a slow cooling process with a rate of 0.5°/min to avoid interfacial cracks due to large thermal stresses during cooling.

The cofired samples were carefully ground on wet grinding paper perpendicular to the interface between the layers, and then polished on a piece of silk cloth coated with diamond abrasive paste with a particle size of 1 μm. The samples were thermally etched in a heating furnace at 100°C lower than the sintering temperature for 1 h. The cross-sectional microstructures were observed by transmission electron microscopy (TEM, H-9000NAR, Hitachi, Japan) and scanning electron microscopy (SEM, S-450 Hitachi, and JSM-6301F, Jeol, Japan) equipped with an energy dispersive X-ray spectroscopy (EDS) detector (Link ISIS300, Oxford). EDS was used to analyze semiquantitatively the compositions at the interface. In order to confirm the cause of interfacial defects, the sintering shrinkage characteristics of the different layers and the burn-out process of the organic additives were determined by thermal analysis (TMA92, DTA/TGA92, SETARAM, France). X-ray diffraction (XRD, Dmax R-13, Rigaku, Japan) was used to identify the chemical reactions of the powder mixture.

3. Results and discussion

Fig. 1 shows a micrograph of the inner interface in a cofired multilayer ceramic sample consisting of PMN–PZN–PT ferroelectric ceramics and 70Ag/30Pd electrodes. It can be seen that a large crack or fissure exists at the interface between the ceramic layer and the electrode layer. Several explanations concerning these interfacial cracks or delaminations have been put forth elsewhere [9], including green-state delaminations, rapid evolution of gas and heat release during burnout, and mismatched physicochemical properties between the electrode and the ceramic. However, it is believed that a mismatch in the sintering densification characteristics between the ceramic and the inner electrode may be responsible for these interfacial defects. Generally, the sintering temperature of the ceramic phase would be expected to be higher than that of the Ag/Pd electrode.

Fig. 2 contrasts the sintering shrinkage behavior of PMN–PZN–PT relaxor ferroelectric and the 70Ag/30Pd electrode. It is to be expected that the sintering of the ceramic occurs more slowly than the electrode and clear sintering mismatch would result. The total sintering process can be divided into three stages, being an initial sintering stage, rapid sintering stage, and final stage. Clearly, the densification of the Ag/Pd alloy paste is nearly completed before the PMN–PZN–PT ceramic begins to densify. The associated differential shrinkage would be expected to establish interfacial stresses, including tensile, compressive, and shear. Since the metal electrodes shrink

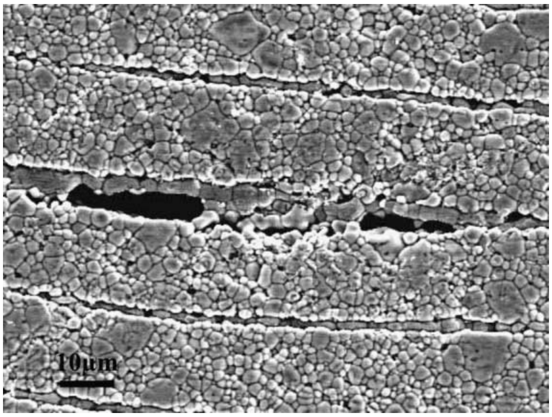

Fig. 1. Cross-sectional microstructure of a multilayer sample.

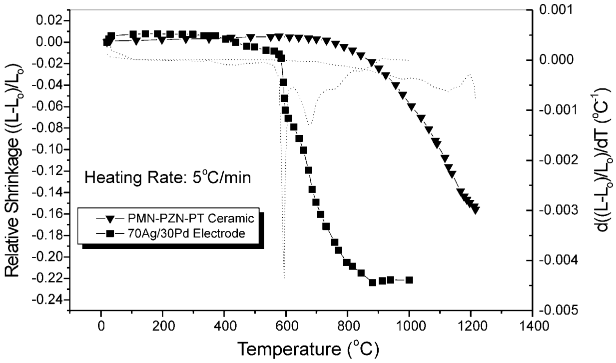

Fig. 2. Densification characteristics of the ceramic and the electrode.

first, they would cause the undensified ceramic to be placed in compression during sintering. Fig. 1 shows that, in addition to this, the ceramic underwent less total shrinkage than did the metal, assuming that the metal volume remained constant at $>1000°C$. Consequently, in the absence of delamination, the ceramic would be placed in a state of permanent compression upon cooling to room temperature. The assumed high coefficient of thermal expansion of the metal relative to that of the ceramic would increase this compression further. Thus, it would be expected that the metal-ceramic interface would be weak due to differential stress resulting from (1) different shrinkage rates during sintering, (2) different amounts of shrinkage during sintering, (3) different thermal contractions during cooling, and (4) the difficulty in joining materials with metallic bonding (metal) and ionic/covalent bonding (ceramic). Fig. 1 clearly shows that the mechanism of stress relief is bending and delamination. This is quite similar to the case of glaze stresses bending the underlying body, followed by peeling. It is unknown if the delamination resulted from bending or shear failure. However, it is clear that the peeling strength of the metal-ceramic interfacial bond is less than the bending strength of the metal and ceramic.

These conclusions are relevant to the issue of reliability of these multilayer devices [1]. Multilayer actuators produce displacement from the repetitive stresses applied to the piezoelectric ceramic layers. A weak metal-ceramic interface would represent a serious risk of delamination in such a device. Also, during electroding, soldering to a substrate, and operation in an electric field, multilayer devices can be subjected to rapid thermal stresses, which could enhance delamination.

In addition to materials defects, an inappropriate sintering process also can lead to another type of interfacial defect. TEM examination of the metal-ceramic interface, as shown in Fig. 3, revealed the presence of spherical pores. It is believed that the spherical shape of these pores suggests that they were formed during the sintering process. Fig. 2 indicates that little sintering shrinkage took place below $\sim 600°C$. Since most organic additives, such as binders and plasticizers, oxidize below $\sim 600°C$, it is important to heat slowly during the initial heating so as to allow the reaction gases to escape. DTA and TGA data for the oxidation (in air) and pyrolization (in nitrogen) of the as-prepared ceramic tape with organic mixtures are shown in Fig. 4. These data indicate that oxidation under high-P_{O2} (air) is complete by $\sim 400°C$ but that, during pyrolization under low-P_{O2} conditions (nitrogen), decomposition is not complete even at 750°C. Thus, when organic particles are placed in low-P_{O2} conditions — as when encapsulated in a ceramic or metal matrix — gas evolution may be hindered owing to the rapid onset of the densification of the metal at $>600°C$.

There are two ramifications of these pores and their contents. First, they may act as points of stress intensity and serve as crack origins [10]. Second, the reducing effect of the pyrolized carbon can affect the sintering behavior and the electrical conductivity of the ceramics [11]. Hence, it is important to use slow initial heating at $<600°C$ to allow complete oxidation of the organic additives.

In addition to microstructural effects, there are compositional issues to consider as well. Fig. 5 shows SEM images of the grain size distributions of the ceramic phases with electrodes of composition (a) 90Ag/10Pd and (b) 70Ag/30Pd. Compared to the latter, the former appears to show more inconsistent grain size. EDS data of two ceramic grains (A and B indicated in Fig. 5) adjacent to the electrode layer are shown in Table 1. It

Table 1
Compositions of the grains adjacent to the Ag/Pd electrode in multilayer samples

At.%		Pb	Mg	Zn	Nb	Ti	O	Ag	Pd
90Ag/10Pd	A	29.13	2.94	1.96	9.79	2.94	52.95	0.28	0.01
	B	29.46	2.90	1.97	9.91	2.99	52.71	0.06	0.00
70Ag/30Pd	A	29.89	2.91	1.90	9.86	2.82	52.59	0.03	0.00
	B	29.74	2.86	1.99	9.71	2.80	52.87	0.02	0.01

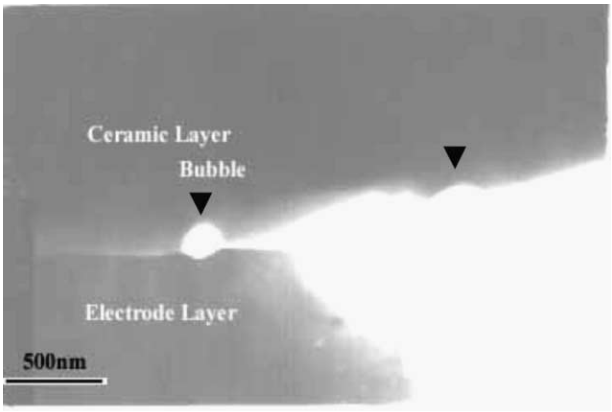

Fig. 3. TEM micrograph of the interface between the 70Ag/30Pd electrode and the PMN–PZN–PT ceramic.

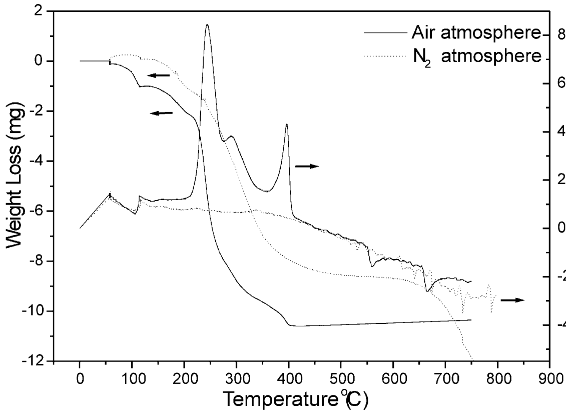

Fig. 4. TGA and DTA data for ceramic tape in different atmospheres (3°C/min).

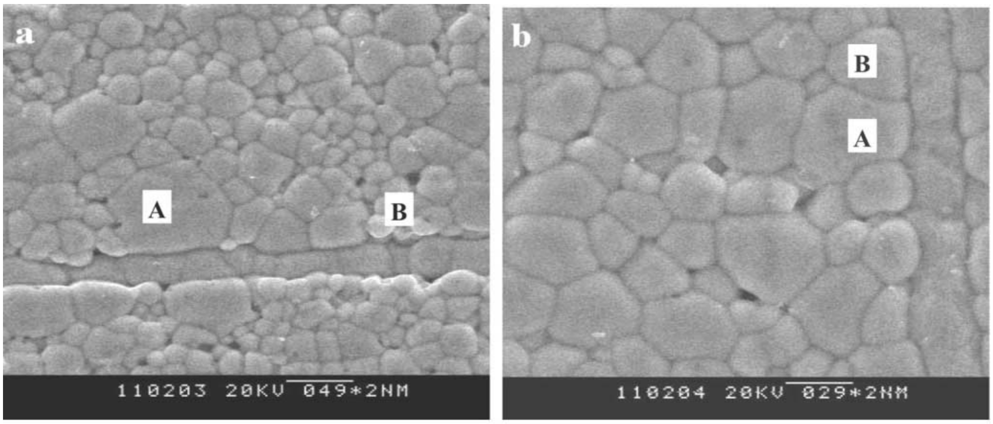

Fig. 5. SEM micrographs of interfaces of two samples with different inner electrodes: (a) 90Ag/10Pd, (b) 70Ag/30Pd.

can be seen that the silver content differs markedly in the grains of the sample with the 90Ag/10Pd electrode, where anomalously large grain (A) has a higher silver content. In contrast, the silver content is very low and is constant for the grains of the sample with the 70Ag/30Pd electrode. Moreover, the palladium content is nearly zero for all samples, which indicates that palladium does not diffuse into the grains. It is well known that the silver in the ceramic grains comes from the inner electrodes [12,13]. Consequently, it is believed that the uneven ceramic grain growth results from the effects of the electrode. Because Ag^+ (0.131 nm) has an ionic radius similar to Pb^{2+} (0.149 nm) [14], Ag^+ is expected to enter into the growing lattice of the ceramic during sintering [15]. The replacement of Ag^+ for Pb^{2+} will produce free electrons in the grains. To remain neutral, $V_{\ddot{o}}$ compensating for free electrons must be produced. The formed lattice defects could accelerate the mass transport process, further promoting grain growth. Further, the melting of silver, which migrates into the ceramic from the electrode, may be helpful for grain growth due to its low melting point (~960°C) owing to the solubility of Pb, Mg, Zn, etc., in the molten silver [16]. So it is concluded that there may be an effect of the electrode composition on the interfacial microstructure due to silver migration. This conclusion is supported by the lower silver migration in the multilayer samples with 70Ag/30Pd electrodes compared to that in the samples with 90Ag/10Pd electrodes.

In fact, not only can silver in the electrode migrate into the ceramic, but metal ions in the ceramic can diffuse into the electrode [17]. As a result of interdiffusion at the interface, a transition layer between the Ag/Pd electrode and the PMN–PZN–PT ceramic formed, as confirmed by TEM, as shown in Fig. 6. EDS analysis identified the composition of the transition layer (the electrode is absent because it was removed by ion milling during preparation). As expected, silver from the Ag/Pd electrode and lead and magnesium from the ceramic layer can be detected simultaneously. This transition layer may change the interfacial bond from a physical bond to a chemical bond, which could enhance the physical integrity of the interface. However, this transition layer may degrade the electric properties of the device. Moreover, silver migration would be expected to have an adverse effect on the dielectric and piezoelectric properties [15,18]. Further, exaggerated grain growth due to silver migration is likely to degrade the mechanical properties of the device.

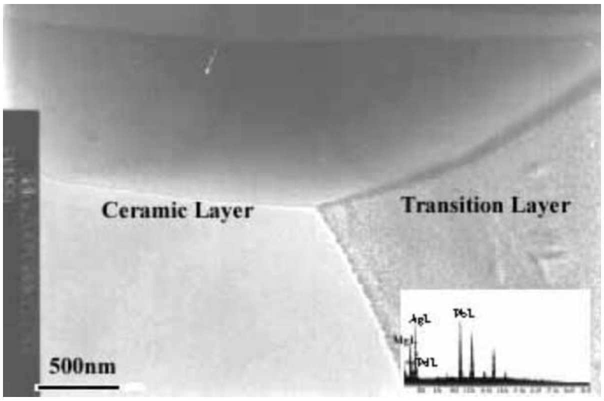

Fig. 6. TEM micrograph of the interface between the electrode and PMN–PZN–PT relaxor ferroelectric ceramic.

4. Conclusions

An investigation of the interfacial development and interfacial imperfections between Ag/Pd electrodes and PMN–PZN–PT ceramics was carried out. Undesired interfacial defects, including delaminations, warping, pores, and exaggerated grain growth were observed. The experimental results showed that these microstructural defects are related to three considerations: (1) mismatched physical and chemical properties, (2) unsuitable preparation process, and (3) different electrode compositions. Careful burnout of the binder, modification of the sintering schedule, and determination of the appropriate Ag/Pd ratio should be achieved in order to obtain a reliable chip device.

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