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Structural investigations of the co-fired interface of Pb-based relaxor ferroelectrics and Ag–Pd electrode

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Abstract

With the miniaturization trend of modern electronic devices and increasing demand for multilayer ceramic chip components, a full understanding of the role of the co-fired ceramic/electrode interface in the performance and long-term reliability of the components becomes very important. In the present work, the inter-diffusion and structure of the co-fired interface of Pb-based relaxor ferroelectrics and Ag–Pd metal electrode were investigated by scanning electron microscopy (SEM) and transmission electron microscopy–energy dispersive analysis of X-rays (TEM–EDAX). No strong structural distortions were observed at the co-fired ceramic/electrode interface except for a thin interfacial layer of 1.5 nm thick on each side of the interface. The ceramic near the interface retains the perovskite lattice structure. It is suggested that the diffused electrode compositions could be incorporated into the perovskite lattice.

Keywords: B. Interfaces; C. Diffusion; D. Perovskites; E. Electrodes

1. Introduction

Multilayer ceramic chip devices are in great demand due to the rapid development of surface mounting technology. These devices are generally fabricated using tape-casting method. The ceramic layers and internal electrode layers, normally Ag or Ag–Pd pastes, are tape-cast and screen-printed alternately and then stacked, followed by high-temperature sintering to form a monolithic structure. Pb-based ferroelectrics have been used in multilayer ceramic capacitors (MLCC) and multilayer chip transformers owing to their high dielectric constants, high piezoelectric coefficients and low sintering temperatures [1–3]. With the miniaturization trend of the chip devices, the ceramic layer becomes thinner in order to sustain the high capacity. Accordingly, the volumetric ratio of the ceramic/electrode interfaces in the devices increases inevitably. It is imperative to investigate the structures and properties of the interfaces since these interfaces generally play an important role in the service performance and reliability of these ceramic components.

Many studies have been dedicated to the interfacial reactions between Pb-based ferroelectrics and Ag–Pd electrode during high-temperature sintering [4–8]. It was proposed that Ag or Pd could react with the ceramics, through which the structure and electrical properties of the ceramics can be altered. Especially, Ag can diffuse into the ceramics in the form of Ag^+ and substitute for Pb^{2+} at the A site of the ABO_3 lattice [6–8]. However, these studies were mainly carried out using Ag or Pd doping experiments for simulation. The structure and chemical reactions at the co-fired interface have not been well understood. In the present study, the structure and inter-diffusions at the co-fired interface of Pb-based ferroelectrics/Ag–Pd alloy electrode were characterized using scanning electron microscopy (SEM), and transmission electron microscopy and energy dispersive analysis of X-rays (TEM–EDAX).

2. Experimental details

2.1. Preparation of specimens

The reference ceramic composition used in this study was commercial $x\mathrm{Pb}(\mathrm{Mg}_{1/3}\mathrm{Nb}_{2/3})\mathrm{O}_3$–$y\mathrm{Pb}(\mathrm{Zn}_{1/3}\mathrm{Nb}_{2/3})\mathrm{O}_3$–$z\mathrm{PbTiO}_3$ ($x + y + z = 1$, $0.90 \leq x \leq 0.95$, $0 \leq y \leq 0.05$, $0 \leq z \leq 0.1$)

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(Guangdong Fenghua Advanced Technology Co. Ltd., China). This composition can meet the specifications of EIA Y5V and Z5U. The dielectric powders were prepared through a two-stage calcination method using all reagent grade oxides [9]. The capacitor specimens were made through tape-casting method with internal electrode of Ag–Pd 90/10 with a melting point of about 1030 °C. Sintering was carried out at 955 °C for 4 h followed by cooling down in the furnace.

2.2. *SEM and TEM observations*

Fractured profile of the multilayer capacitors was examined using SEM (KYKY-2800). Element diffusions at the interface of Pb-based ferroelectrics/electrode were examined using TEM–EDAX (JEOL-2010F). The interface structure was characterized on nanometer scale using high-resolution transmission electron microscopy (HRTEM). Cross-sectional samples for TEM and HRTEM observations were prepared using a standard technique. Firstly, the specimen was mechanically polished to a thickness of less than 40 μm, and then etched by argon ion-beam milling to electron transparency.

3. Results and discussion

3.1. *Study of the co-fired interface through SEM and TEM–EDAX*

Fig. 1 gives a SEM micrograph of the fractured profile of a multilayer capacitor. It can be seen that the ceramic is dense and there are hardly any pores. It is interesting to find that the bulk of the ceramic is fine-grained. By contrast, the ceramic becomes coarse-grained and the ratio of transgranular fracture increases towards the electrodes. In the present case, it is suggested that this structure gradient should be attributed to the diffusion of the electrode composition and its promotion to the densification of the ceramic during the sintering, as revealed by previous silver doping simulation experiment [10].

Fig. 2(a) shows a cross-sectional bright-field TEM image of the co-fired ferroelectrics/electrode interface. The metal electrode is bonded to the ceramic closely and no voids are observed along the interface. The inset gives the selected area electron diffraction (SAED) pattern of the ceramic near the interface. There is only the lattice pattern of the ceramic in the image and no observable secondary phase can be seen.

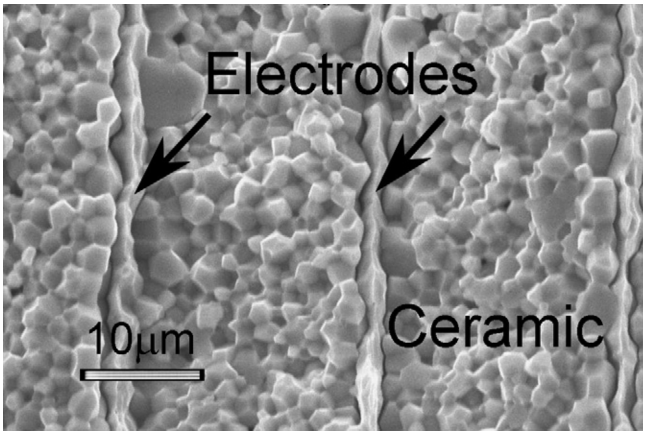

Fig. 1. SEM micrograph of the fractured profile of the Pb-based ferroelectrics/electrode multilayered structure.

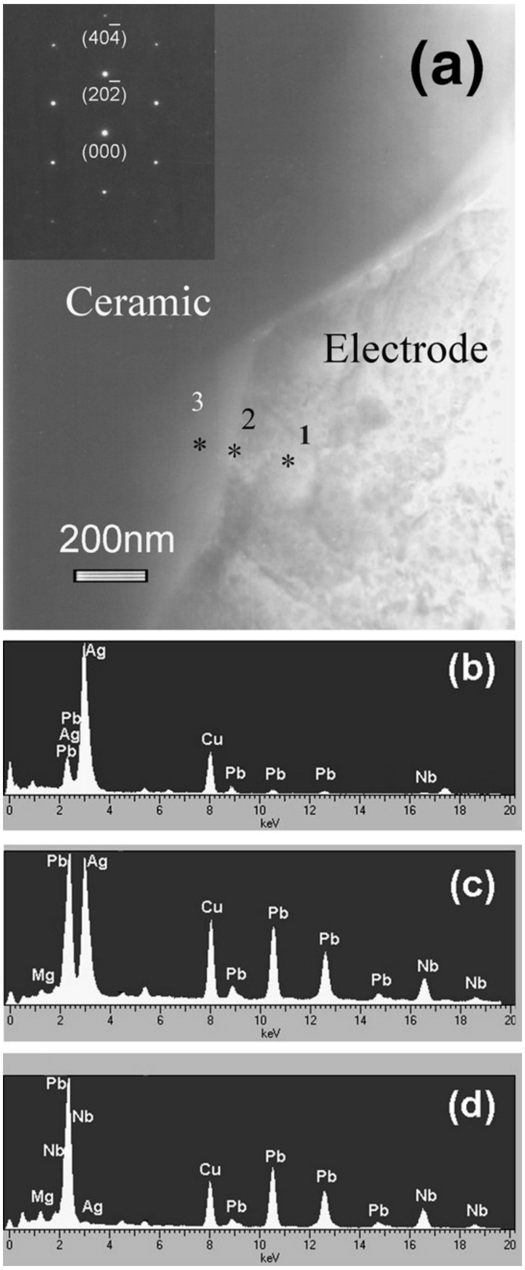

Fig. 2. TEM analyses. (a) TEM micrograph of the co-fired interface of ferroelectrics/electrode. The inset gives the SAED pattern of the ceramics near the interface. EDAX spectra of (b) point 1, (c) point 2 and (d) point 3.

The EDAX spectra at the points 1–3 in Fig. 2(a) are shown in Fig. 2(b)–(d), respectively. The Cu peaks at 8 keV in the EDAX spectra are caused by the contamination from the copper grid support during the TEM sample preparation. The ceramic compositions such as Pb and Nb are detected in the electrode at point 1 which is 150 nm away from the interface. At point 2 across the interface, both the ceramic compositions and electrode compositions are detected. A small amount of electrode compositions is found at point 3, 100 nm away from the interface. It suggests a weak inter-diffusion between the ceramic and electrode during the high-temperature sintering. No obvious structural transition is observed at the interface in spite of the inter-diffusion. Therefore, we further examined the interface structure of the Pb-based ferroelectrics/electrode through HRTEM on nanometer scale.

3.2. Structure of the interface on nanometer scale

Fig. 3(a) gives a HRTEM image of the ceramic/electrode interface. The area in the black square is enlarged in Fig. 3(b). The image in Fig. 3(a) can be divided into four parts, as designated as A–D from left to right. They correspond to the ceramic, the interfacial layer on the ceramic side, the interfacial layer on the electrode side, and the electrode, respectively. There is a rotational misorientation of 45° between the main bodies of the ceramic and electrode. On the ceramic/electrode interface, there is an interfacial layer on each side of the ceramic/electrode interface. These two interfacial layers are both about 1.5 nm thick that are distinct from the main bodies of the ceramic and electrode areas. It is proposed that the structural distortions in the interfacial layers accommodate the strong chemical disorders caused by the interfacial diffusion. By contrast, the main bodies of the ceramic and electrode areas are less affected. This confirms the SAED result that the ceramic area consists of only one phase.

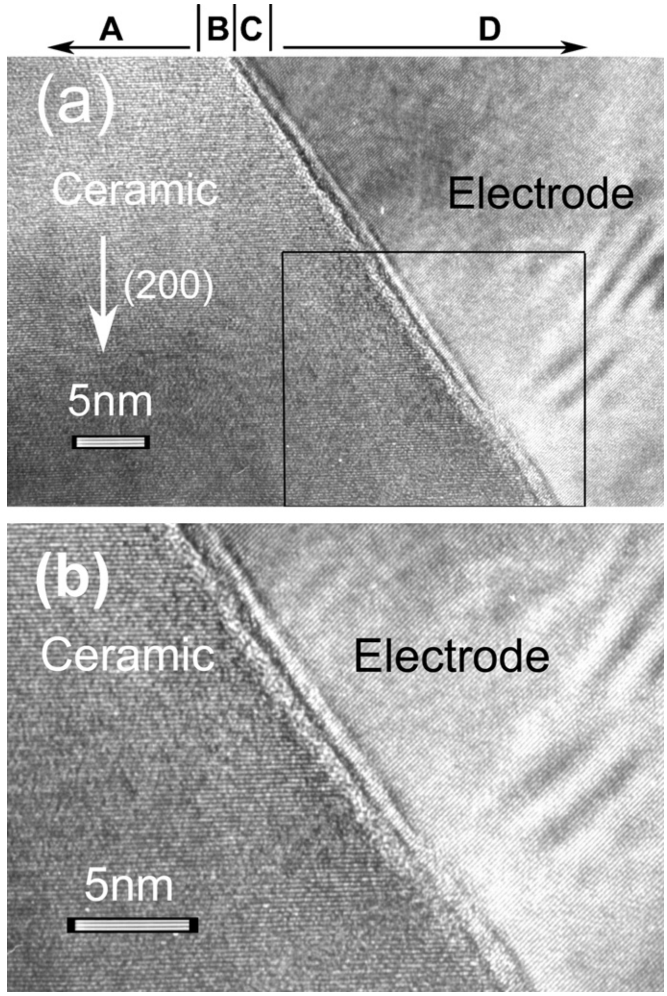

Fig. 3. HRTEM observations. (a) HRTEM lattice image of the co-fired ferroelectrics/electrode interface and (b) the enlarged area in the black square of (a).

Previously, it was suggested that Ag could be incorporated into the perovskite lattice while Pd mainly reacted with the ceramics to form new products such as $PbPdO_2$ and PdO [5,11,12]. In the present study, since the main body of the ceramic near the interface remains the lattice structure, it is reasonable to expect that the diffused Ag and Pd could be incorporated into the perovskite structure. Furthermore, it can be inferred that Ag tends to substitute for A-site of the perovskite structure because of the similar radii of Ag^+ and Pb^{2+} [13]. Then according to defect chemistry, oxygen vacancies will be generated [10], as shown in the equation as below:

$$Ag_2O\xrightarrow{\text{A-site}}2Ag'_{Pb}+O_O+V_O^{\bullet\bullet}$$

By contrast, Pd^{2+} may substitute for the compositional elements at B-site in the ceramic due to their similar ionic radii [13].

4. Conclusions

The inter-diffusion between the electrode and Pb-based ferroelectrics was examined. A gradient structure of the ceramic was observed near the co-fired interface and could be ascribed to the slight diffusion of the electrode composition into the ceramic. However, no excessive structural change was observed in the ceramic and electrode areas except for an interfacial layer of about 1.5 nm thick on each side of the ferroelectrics/electrode interface. The main bodies of the ceramic and the electrode retained the periodic lattice configurations, which is distinct from the interfacial layers. This indicates that the diffused Ag and Pd in the ceramic could be incorporated into the perovskite structure.

References

[1] S.L. Swartz, T.R. Shrout, Fabrication of perovskite lead magnesium niobate, Mater. Res. Bull. 17 (1982) 1245–1250.

[2] M. Lejeune, J.P. Boilot, Low firing dielectrics based on lead magnesium niobate, Mater. Res. Bull. 20 (1985) 493–499.

[3] D.J. Voss, S.L. Swartz, T.R. Shrout, Effects of various B-site modification on the dielectric and electrostrictive properties of lead magnesium niobate ceramics, Ferroelectrics 50 (1983) 203–208.

[4] A. Caballero, E. Nieto, P. Duran, C. Moure, Ceramic–electrode interaction in PZT and PNN–PZT multilayer piezoelectric ceramics with Ag/Pd 70/30 inner electrode, J. Mater. Sci. 32 (1997) 3257–3262.

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

[6] H.C. Ling, Diffusion of sputtered vanadium, nickel and silver in lead magnesium niobate ceramics, J. Am. Ceram. Soc. 72 (5) (1989) 770–774.

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

[8] H. Kanai, O. Furukawa, S. Nakamura, Y. Yamashita, Effects of silver doping on the reliability of $(Pb_{0.875}Ba_{0.125})[(Mg_{1/3}Nb_{2/3})_{0.5}(Zn_{1/3}Nb_{2/}$

$_3)_{0.3}Ti_{0.2}]O_3$ relaxor dielectric ceramics, J. Am. Ceram. Soc. 78 (5) (1995) 1173–1178.

[9] Z.L. Gui, Y. Wang, L.T. Li, Lead-based relaxor ferroelectric ceramics for high performance low firing MLCs, in: Proceedings of the 10th IEEE International Symposium on Applications of Ferroelectrics, 1996, pp. 409–412.

[10] J.L. Cao, X.H. Wang, N.X. Zhang, L.T. Li, Direction current–voltage failure of lead-based relaxor ferroelectrics with silver doping, J. Am. Ceram. Soc. 86 (2003) 1856–1860.

[11] S.F. Wang, Y.F. Hsu, Electrical conductivity and thermal expansion coefficient of internal phases occurring in multilayer ceramic structures, Ceram. Int. 26 (2000) 669–671.

[12] R.Z. Zuo, L.T. Li, N.X. Zhang, Z.L. Gui, Interfacial reaction of Ag/Pd metals with Pb-based relaxor ferroelectrics including additives, Ceram. Int. 27 (2001) 85–89.

[13] R.D. Shannon, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, Acta Cryst. A 32 (1976) 751–767.