ELSEVIER

Materials Science and Engineering B95 (2002) 1–5

MATERIALS SCIENCE & ENGINEERING B

www.elsevier.com/locate/mseb

TEM and EDS investigation of heterogeneous interfaces in cofired multilayer ceramic capacitors

Ruzhong Zuo [a,*], Longtu Li [a], Zhilun Gui [a], Takfu Hung [b], Zhengkui Xu [b]

[a] State Key Lab of New Ceramics and Fine Processing, Tsinghua University, Beijing 100084, People's Republic of China
[b] Department of Physics and Materials Science, City University of Hong Kong, Hong Kong, People's Republic of China

Received 21 November 2001; accepted 4 March 2002

Abstract

The interfacial microstructure and cofiring migration between Ag–Pd electrode and Pb-based relaxor ferroelectric ceramics were directly investigated via transmission electron microscope and energy dispersive X-ray spectroscopy (EDS). Different silver migration abilities of 70Ag–30Pd and 90Ag–10Pd electrodes were confirmed by EDS microanalysis. This difference is generally considered to be responsible for different effects of inside electrode on the reliability of multilayer cofired devices. Further, Pb diffusion and new phase formation near the interface were detected, incorporating interfacial microstructural observation. A good consistency of direct experimental evidence to the following theoretic analyses was well combined in this paper. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Interdiffusion; Interface; Cofiring; TEM; EDS

---

1. Introduction

With the rapid development of electrical industry, monolithic ceramic devices with smaller size and laminated structure have been greatly developed and researched. These devices are typically characteristic of multilayer alternate structure of metal layers and ceramics. Moreover, it is known that the interaction between metal electrode and ceramics during cofiring must have badly affected the electronic properties and reliability of the devices [1–5]. This interaction may include not only physical mismatch in sintering densification behavior and various thermodynamic parameters, but also chemical reactions occurred at heterogeneous interfaces. The effect of this interaction on the interfacial microstructure is generally considered as one of the root reasons for the deterioration of electrical properties. Therefore, the research on the cofiring behaviors between different metal electrodes and functional ceramic dielectrics has become an important base of developing many novel multilayer ceramic devices including integrated electronic products. During the past few years a lot of research work was focused on cracks, delamination, and deformation due to mismatched sintering shrinkage [6–8], and on the effect of silver migration on the electrical properties by doping a small amount of silver salt into ceramic dielectrics [9–11]. Thus, there is still a lack of much direct evidence by in-situ measurements or observations via high-resolution electron microscope.

In this paper, a transmission electron microscope (TEM) and energy dispersive X-ray spectroscopy (EDS) were used to directly research the interfacial microstructure between Ag–Pd electrode and Pb-based relaxor ceramics, and to more accurately analyze the interdiffusion characteristics of the elements, compared to the microanalysis via scanning electron microscopy (SEM). This is because EDS in TEM has a much better spacial resolution ($\ll \mu$m) of chemical analysis than that ($\sim \mu$m) of EDS in SEM. This direct and accurate experimental evidence is of great use for confirming the diffusion mechanism of different elements.

---

* Corresponding author. Present address: TU Darmstadt, FB 11, FG Nichtmetallisch-Anorganische Werkstoffe, Petersenstr. 23, Geb. 73a, 64287 Darmstadt, Germany. Tel.: +49-6151-166-312; fax: +49-6151-166-314.

E-mail address: zuo@ceramics.tu-darmstadt.de (R. Zuo).

PII: S0921-5107(02)00094-6

2. Experimental

The cofired multilayer samples (China Guangdong Zhaoqing Fenghua Electronic Ceramic Company, 70Ag–30Pd and 10Ag–90Pd) were composed of alternated Ag–Pd alloy and Pb-based relaxor ferroelectric ceramics. The main composition of ceramic layers is $Pb(Mg_{1/3}Nb_{2/3})O_3$–$Pb(Zn_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PMN–PZN–PT, abbreviated as PMZNT). Specimens for cross-section TEM studies were prepared by mechanical grinding and polishing (~ 10 μm thick) followed by Ar-ion milling using a Gatan Precision Ion Polishing System (PIPS^{TM}, Model 691). Fig. 1 is an optical photomicrograph of as-ion milled cross-section TEM specimen. The microstructures of cross-section specimens were examined by a JEOL2010 TEM equipped with an EDS detector and JEOL JSM-6301F SEM. A 10-nm electron beam probe was used to do chemical analysis.

3. Results and discussion

The typical interfacial morphology of the cofired multilayer ceramic capacitor samples is illustrated in Fig. 2, which are second electron image (a) and backscattered electron image (b) of a cross-section TEM specimen, respectively. Ceramic dielectric and Ag–Pd electrode layers can be more clearly distinguished by backscattered electron image due to their different chemical compositions. The center darker layer in Fig. 2(b) is Ag–Pd electrode layer since it has a smaller average atomic number compared with that of the PMZNT ceramic dielectric layer which is brighter. The Ag–Pd electrode and ceramic dielectric layers are about 4 and 20 μm in thickness, respectively. The electrode line and the ceramic layer are evenly distributed and no clear interfacial delamination and deformation was found. Fig. 3 shows TEM images of two multilayer samples with different electrodes. Ag–Pd alloy and ceramic dielectric during cofiring formed a good bonding and the smooth interface zone was verified from microscopic observation, even though they have greatly different physical properties such as sintering and thermal expansion or contraction. However, different interfacial grain morphology, which maybe came from the effect of various electrode compositions, was hardly found by TEM. This difference was verified previously by SEM [7,9]. This is probably due to the fact that a much smaller area of the sample was examined in TEM compared with that examined in SEM. Inset in Fig. 3(b) is a typical selected area electron diffraction pattern obtained from the Ag–Pd electrode, indicating polycrystalline structure of Ag–Pd. High resolution TEM studies of detailed interfacial microstructure, such as lattice distortion or dislocation in the interface region and thickness of interfacial diffusion zone, are currently underway.

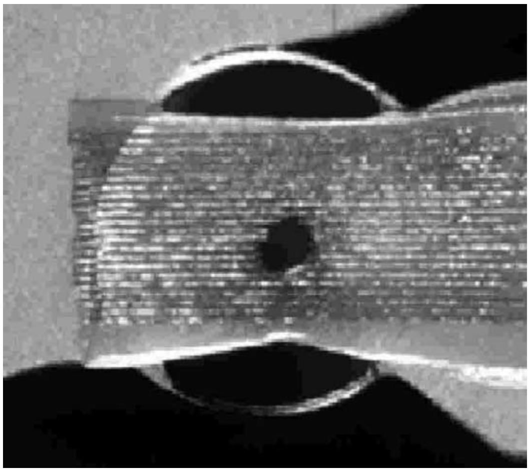

Fig. 1. Optic photomicrograph of as-ion milled multilayer samples for TEM observation.

The interdiffusion of the elements during cofiring was reported previously and many disadvantageous influences on the electronic properties and reliability of multilayer ceramic devices were pointed out, particularly because of the silver migration [2,9]. Most previous research results came from SEM observation and EDS probe in SEM. However, the spacial resolution of chemical analysis by EDS in SEM is only in micrometer range due to the large electron beam-specimen interaction volume for bulk sample used in SEM and thus EDS in SEM will not provide correct information about silver migration if the migration occurs in a submicrometer range. In this work, an electron beam probe of 10 nm was used to collect EDS spectra from a thin specimen of <100 nm in thickness. A much-improved spacial resolution of chemical analysis will help identify the silver diffusion distance in order to account for the effect of electrode compositions on the silver migration. EDS analyses were carried out at different positions away from the interface and the probe was moved along a direction that is perpendicular to the interface, as shown in Fig. 3(a)Fig. 4. These EDS spectra clearly indicate that silver migration occurred during cofiring because the silver element was detected in the ceramic layer and its content decreased with increase of the distance away from the interface. The same EDS measurement was applied to two different multilayer ceramic samples with 70Ag–30Pd and 90Ag–10Pd electrodes, respectively. The plots of relative silver content versus the distance from the interface were drawn in Fig. 5 for comparison. It was verified that 90Ag–10Pd electrode presented a significant interfacial silver migration increase compared to 70Ag–30Pd electrode. A small amount of silver migration in multilayer samples based on 70Ag–30Pd electrode partially accounted for the improved electronic properties and reliability, in contrast to those based

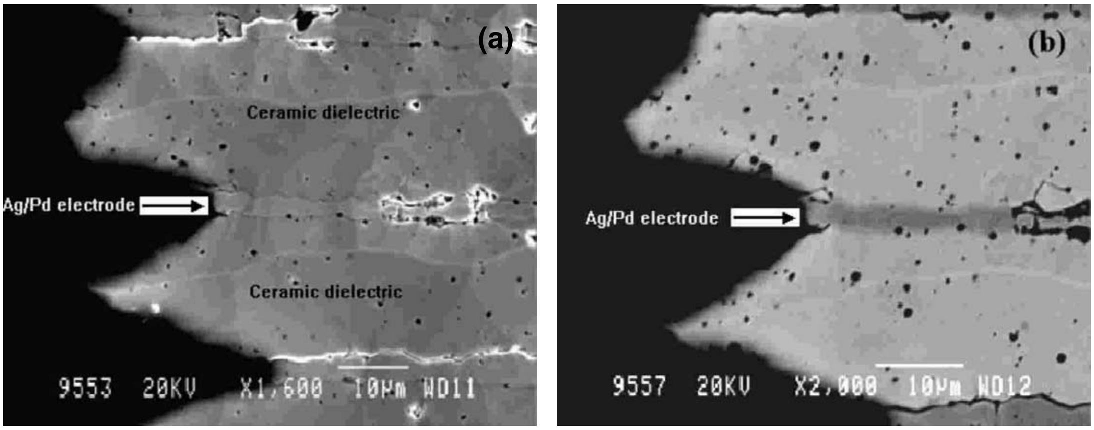

Fig. 2. Typical SEM images of interfacial microstructure for a cofired multilayer ceramic capacitor sample: (a) second electron image; (b) back-scattered electron image.

on 90Ag–10Pd electrode. This is because silver migration into the ceramic layer would change the microstructure and sintering characteristic of the ceramic layers and further degrade the electronic properties of the device. A suitable mechanism of silver migration was put forward in previous work [12], which can be further verified by EDS results for the profile of silver diffusion.

TEM observation in Fig. 6 further examined the phase formation at the interface. In Fig. 6(a), a white triangle particle can be found at the interface. Interestingly, this kind of secondary phase was more often observed at the interface with the electrode region. In Fig. 6(b), an EDS spectrum obtained from the particle shows that this new phase is MgO. The formation of secondary phase at the interface zone to a larger extent confirmed that possible chemical reaction happened during cofiring. In PMN-based multilayer ceramic capacitors with Ag–Pd inner electrode, Eq. (1) can effectively support the formation mechanism of MgO confirmed by EDS.

$$\mathrm{Pb}\left(\mathrm{Mg}_{\frac{1}{3}}\,\mathrm{Nb}_{\frac{2}{3}}\right)\mathrm{O}_3 + \frac{1}{2}\,\mathrm{PdO} \rightarrow \frac{1}{6}\,\mathrm{Pb}_3\mathrm{Nb}_4\mathrm{O}_{13} + \frac{1}{2}\,\mathrm{PbPdO} + \frac{1}{3}\,\mathrm{MgO} \qquad (1)$$

The intrinsic perovskite structural instability of Pb-based relaxor ferroelectric ceramics, such as, PMN, PNN, PZN, etc. and relatively stable Pb–Pb compounds provided a physical base for the interfacial reaction. In previous work, more pyrochlore phases with low dielectric constant at the interface than inside ceramics was also verified by means of series of XRD spectra [10]. Also, the reaction equation clearly explains the process of pyrochlore phase with good consistency with experimental results.

In addition to silver diffusion during cofiring, Pb diffusion from the ceramic to the electrode was also found by EDS in TEM, as shown in Fig. 7, which are two EDS spectra obtained from two samples with different Ag–Pd electrodes. However, it seems different

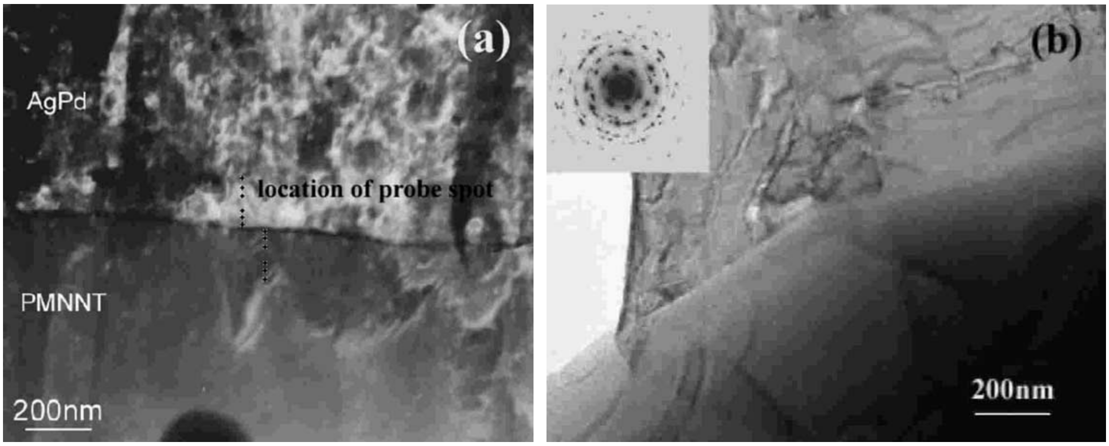

Fig. 3. TEM images of multilayer samples with different electrodes: (a) 70Ag/30Pd (b) 90Ag/10Pd. Inset in (b) is a selected area electron diffraction pattern from the electrode (up half). Note: black dots indicating probe positions in (a) are too small to see!

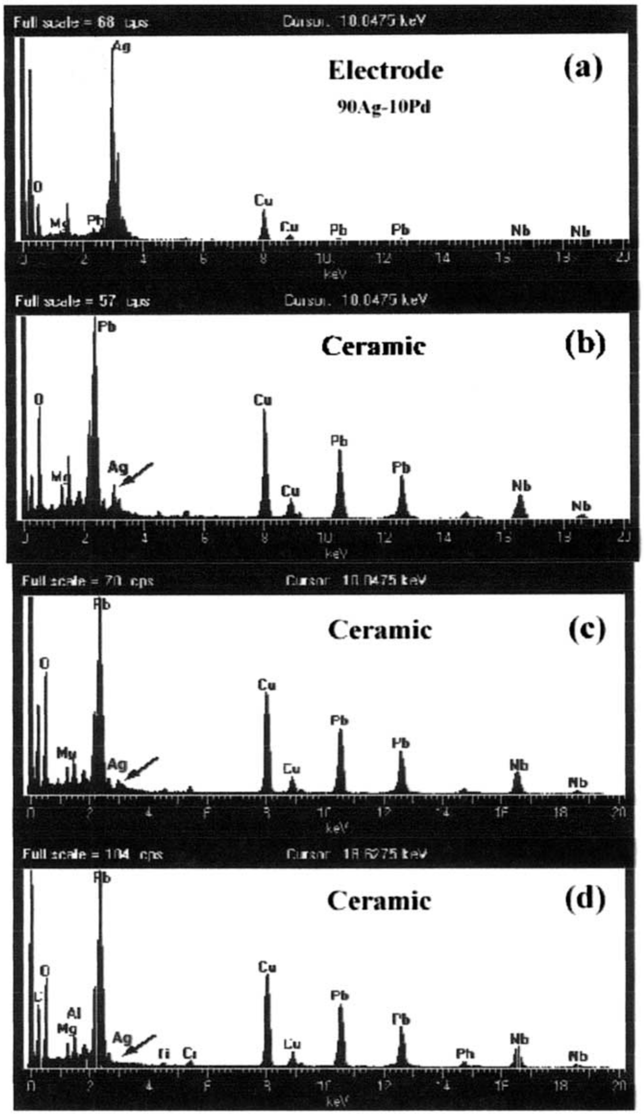

Fig. 4. EDS spectra obtained from different locations near the interface: (a) inside electrode; (b) at the interface; (c) at the position of 25 nm from the interface inside ceramic; (d) 50 nm from the interface inside ceramic.

from the characteristic of silver migration. The different electrode compositions hardly have evident effect on Pb diffusion at the interface. Pb was always detected in the electrode region and Pb diffusion profile has no clear parabolic curve for two samples. Most possibly, this result is correlated to special mass transportation mechanism of Pb, which was generally considered as chemical and physical diffusion but a pure physical one similar to silver migration [12]. The evaporation of Pb at high temperature and Pb–Pd chemical reaction during cofiring will make Pb element detectable in the electrode region.

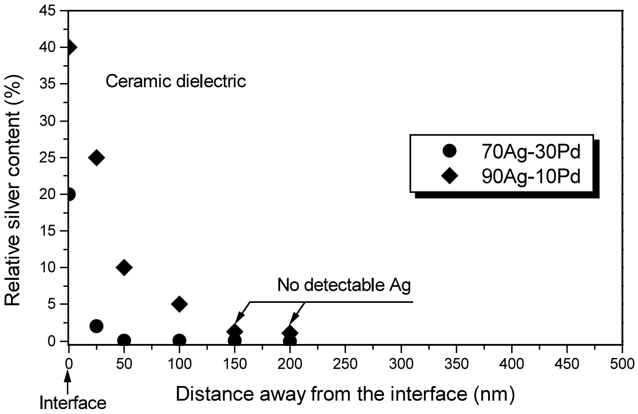

Fig. 5. Interfacial silver migration characteristic of two samples with different electrodes.

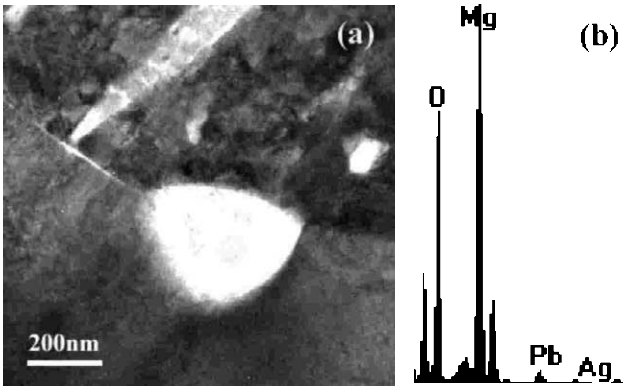

Fig. 6. Secondary phase formed at the interface between Ag–Pd electrode and ceramics: (a) interfacial morphology; (b) EDS spectrum of secondary phase with triangle shape.

4. Conclusions

Compared to SEM analysis, TEM equipped with EDS were a more effective way for investigating the interfacial microstructure and interfacial interdiffusion characteristic during cofiring. Direct evidence from quantitative analyses confirmed the possibility of silver migration during cofiring. 70Ag–30Pd inner electrode paste presented more favorable silver migration feature. Incorporating previous work, the formation of interfacial secondary phase and related reaction equation further verified different diffusion mechanisms of Ag and Pb.

Acknowledgements

This work was supported by National Natural Science Foundation of P.R. China (Serial Number: 59995523). Two of the authors (Z. Xu and T. Hung) would like to acknowledge a grant (No. 7100164) from the City University of Hong Kong for carrying out SEM and TEM works.

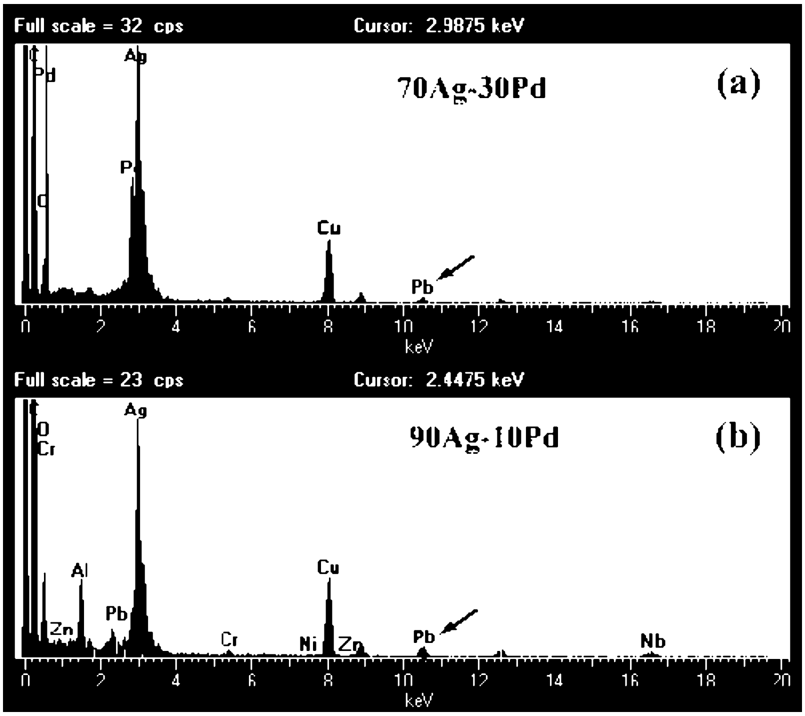

Fig. 7. EDS spectra obtained from electrode region of two samples (a) 70Ag–30Pd and (b) 90Ag–10Pd (at 100 nm away from the interface).

References

[1] M. Villegas, J.F. Fernandez, C. Moure, P. Duran, J. Mater. Sci. 29 (1994) 4999–5004.

[2] W. Wersing, H. Wahl, M. Schnoller, Ferroelectrics 87 (1988) 271–294.

[3] T. Nakamura, Y. Okano, S. Miura, J. Mater. Sci. 33 (4) (1998) 1091–1094.

[4] C.H. Lu, J.Y. Lin, Ceram. Inter. 23 (3) (1997) 223–228.

[5] A.C. Caballero, E. Nieto, J. Mater. Sci. 32 (1997) 3257–3262.

[6] R.Z. Zuo, L.T. Li, Z.L. Gui, J. Mater. Sci.: Mater. Electr. 12 (2001) 117–121.

[7] R.Z. Zuo, L.T. Li, Z.L. Gui, Ceram. Inter. 27 (8) (2001) 889–893.

[8] T. Cheng, R. Raj, J. Am. Ceram. Soc. 72 (1989) 1649–1655.

[9] R.Z. Zuo, L.T. Li, R.Z. Chen, Z.L. Gui, J. Mater. Sci. 35 (2000) 5433–5436.

[10] R.Z. Zuo, L.T. Li, N.X. Zhang, Z.L. Gui, Ceram. Inter. 27 (1) (2001) 85–89.

[11] Y.C. Sato, H. Kanai, Y. Yamashita, J. Am. Ceram. Soc. 79 (1) (1996) 261–265.

[12] R.Z. Zuo, L.T. Li, Z.L. Gui, C.X. Ji, X.B. Hu, Mater. Sci. Eng. B 83 (1–3) (2001) 152–157.