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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.

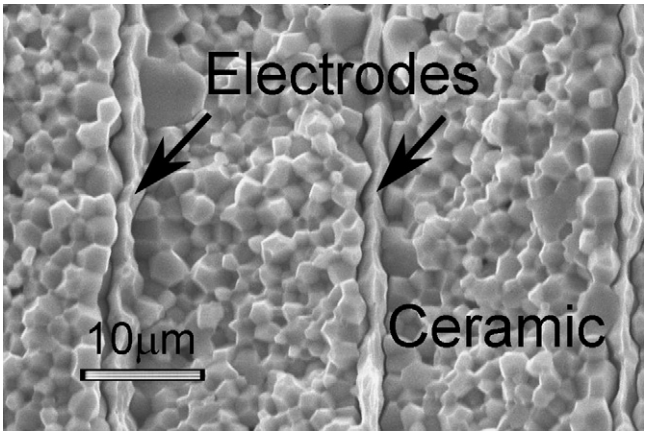

Fig. 1. SEM micrograph of the fractured profile of the Pb-based ferroelectrics/electrode multilayered structure.

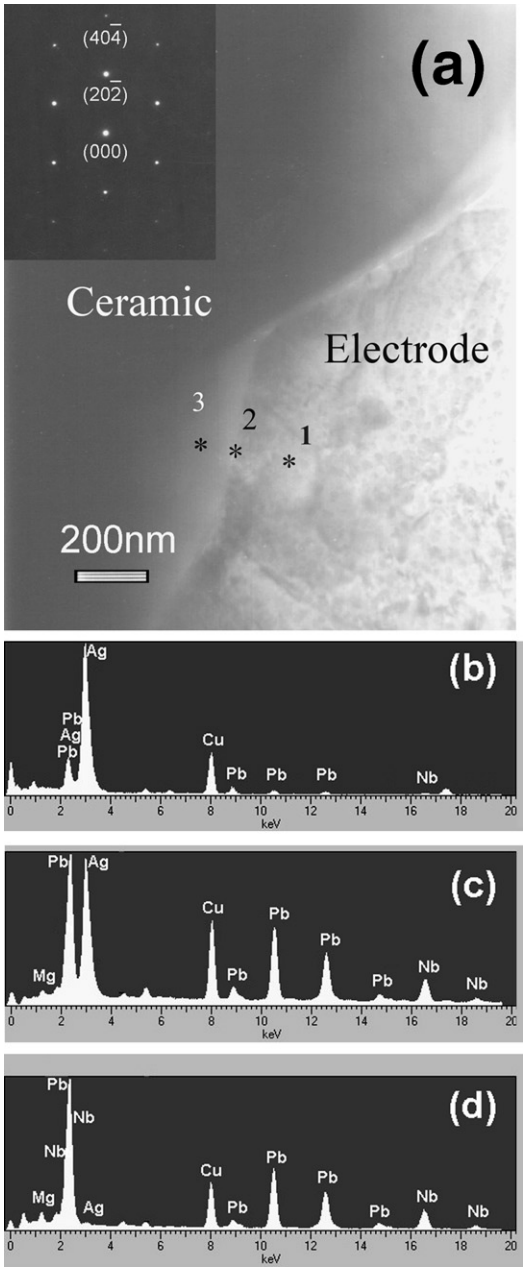

Fig. 2. TEM analyses. (a) TEM micrograph of the co-fired interface of ferroelectrics/electrode. The inset gives the SAED pattern of the ceramics near the interface. EDAX spectra of (b) point 1, (c) point 2 and (d) point 3.

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