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Study on the interdiffusion in base-metal-electrode MLCCs

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Abstract

The co-firing techniques of base-metal-electrode (Ni) and dielectric oxides in reducing atmosphere were widely studied by many researchers. In this paper, the metal-oxide interface in BME-multilayer ceramic capacitors (MLCCs) have been investigated using AES, STEM, EDX, and HRTEM. It was found that the element inter-diffusion took place along the metal-dielectric layer interface and nickel element migration towards the dielectric ceramic dominated this process. One reactive co-firing model was proposed according to the experiment results, and the influence of the element inter-diffusion through the phase boundary on the component performances was discussed as well.

Keywords: B. Interfaces; C. Diffusion; D. $BaTiO_3$ and titanates; E. Capacitors

1. Introduction

During the past decades multilayer ceramic capacitors (MLCCs) occupied the highest position both in production and in sales figures among fine-ceramic products. Driven by the enormous market demands, researchers paid great attention in novel MLCCs with higher performance, smaller size and lower producing cost by searching for high dielectric ceramic compositions, developing thin-layer tape-casting techniques, and adapting base-metals or base-metal alloys as the electrodes [1,2]. Ni-electrode MLCCs, characterized by the co-firing of internal nickel electrode and anti-reducing dielectric ceramics, were widely studied aiming on the performance enhancing and the reliability improving. Great effort has been devoted to optimizing the sintering process and adjusting the ceramic composition which are considered as two key factors leading to the unwanted failures, etc. resistance degradation and breakdown [1–4]. The interaction and diffusion between the internal electrode and the dielectric ceramic layer in BME-MLCCs during high temperature co-firing, however, has not been fully understood although it was demonstrated to play an important role in the degradation of MLCCs with precious metal as internal electrode [5,6,8]. In this paper, the diffusion of nickel element towards the dielectric ceramic layer was studied using AES, STEM, EDX, and HRTEM. The element inter-diffusion around the electrode-dielectric interface was revealed, and was discussed with a reactive co-firing model. It was demonstrated that the element inter-diffusion between nickel electrode and dielectric ceramics is of great importance in reliability controlling for the BME-MLCCs.

2. Experimental

The main composition of the anti-reducing dielectric material was $Ba_m(Zr_yTi_{1-y})O_3$, where $y = 0.10$–0.18 and $m = 1.005$, of which the dielectric properties satisfied EIA Y5V specifications. The MLCC specimens were prepared via a conventional tape-casting technique. The chips are subjected to a two-stage firing program: firstly at 1210–1250 °C for 2 h in a reducing atmosphere of $P_{O_2} = 10^{-11}$ to 10^{-13} MPa, and then annealing in a weak oxidizing atmosphere ($P_{O_2} = 10^{-8}$ to 10^{-10} MPa) at 1050 °C for 3 h to form monolithic compacts. Finally, copper slurry is employed to form external electrodes and to finish the preparation of MLCC specimens.

TEM samples were prepared by grinding the monolithic chips along the direction perpendicular to the internal electrodes to a thickness of $\sim$20 μm. A H800 analytical transmission electron microscope was used to conduct STEM observation and EDX analyzing. HRTEM was conducted

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with a JEM-2010F field emission transmission electron microscope. For Scanning Auger Microprobe (SAM) experiments, the monolithic chips were ground and polished along the direction parallel to the internal electrode plane to expose the nickel electrode. The surface of the metallic electrode was cleaned by the Ar ion gun for 30 min before SAM analysis to eliminate the absorbed light atoms. A PHI-610 scanning Auger microprobe instrument was employed to determine the nickel distribution along the thickness direction of the dielectric layers.

3. Results and discussion

The STEM micrograph of the interface between the co-fired nickel electrode and the ceramic layer was shown in Fig. 1. The boundary between the different phases is characterized by a straight and thin line and no intergranular phases or impurities were found nearby. This point was demonstrated by HRTEM observation, as was shown in Fig. 2(a). The metallic nickel lattice kept continuity until it was broken by the boundary line. It was hardly to obtain a common crystallology direction for the two co-fired different phases so that the two lattices could be visible in one micrograph. Although, the case in the ceramic side was revealed to have the same nature as the nickel side by carefully tilt the specimen. Fig. 2(b) and (c) exhibited the electron diffraction pattern for the two phases, and also no third phase was found at the very nearby of the boundary line. The careful refinement of the nickel lattice revealed that around 5–10 nm away from the interface the lattice was distorted and some dislocation regions appeared, whereas the perovskite lattice showed a stronger lattice distortion (expansion of around 2%) in a larger region (hundreds of nanometers away from the boundary) than the nickel side.

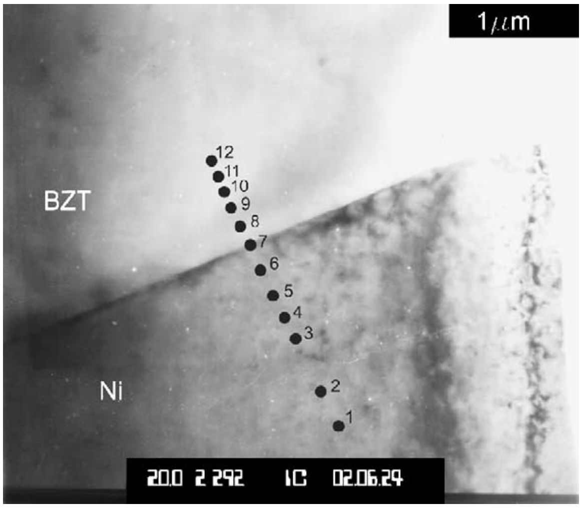


Fig. 1. Micrograph of the interface between the co-fired nickel electrode and the perovskite ceramic layer.

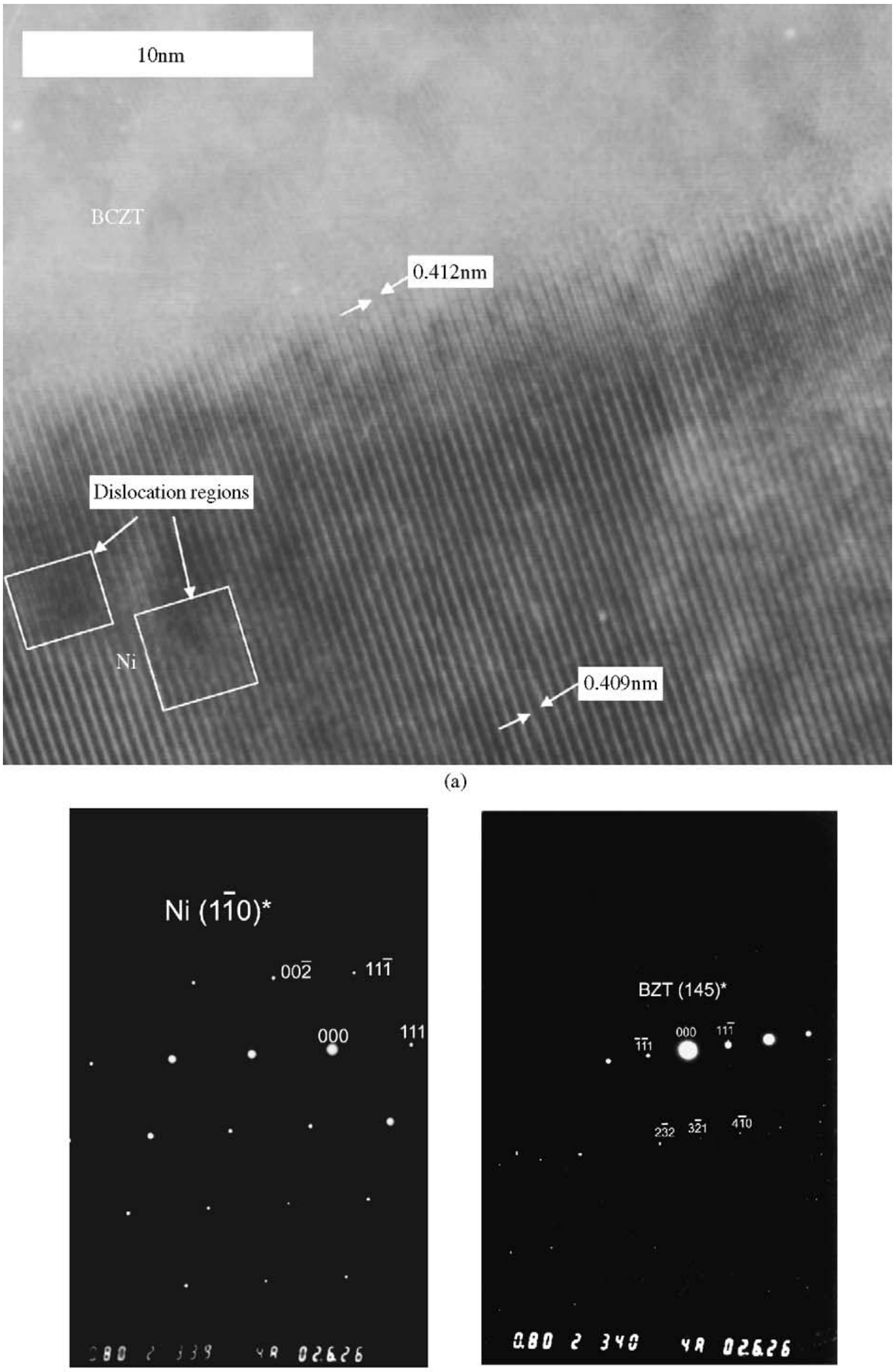
The EDX analysis was carried out at a series of points along the normal direction of the boundary line, as were marked by the solid dark circles (Fig. 1). The relative concentrations of the metal elements in question were illustrated as a function of the distance to the boundary line (see Fig. 3). Apparently there existed a diffusion region in which the element concentrations varied gradually. The extent the nickel element diffused into the ceramic phase was quite stronger than that the ceramic constituting elements into the metallic phase. The concentration profile for the related elements by SAM was illustrated in Fig. 4 as a function of sputtering time. The deepness of the inter-diffusion region was estimated by the thinning rate of ∼20 nm/min for a SiO_2/Si reference. The position of the interface in SAM profile was estimated according to a SEM observation on the section of the same specimen after SAM experiment. Again the element diffusion as well as the different extent in either phase was demonstrated. It seems that for nickel atoms it was fairly easy to enter and diffuse into perovskite lattice, whereas it was difficult for ceramic containing elements to enter and diffuse into the nickel lattice. The absence of a third phase and the perovskite distortion hinted the strong solution ability of nickel in BZT ceramics.

Fig. 5 shows the partial Auger spectrum for the nickel electrode and for the BZT ceramic in the inter-diffusion region. The chemical shift was evidently observed on the curve for the ceramic layer [7]: the peak for NiO_x–MNN (∼52.5 eV) was greatly strengthened in contrast to the curve for nickel electrode. This means that the nickel element that diffused into the perovskite lattice was provided with a higher valence rather than metallic state, and the diffusion of nickel atoms into perovskite lattice was accompanied with an oxidization procedure during high temperature co-firing.

Combining the microstructure observation and composition analysis, it was clarified that during sintering and annealing, the nickel electrode layer and the ceramic dielectric one were co-fired into a monolithic. The element inter-diffusion between the two phases played an important role in the forming as well as migrating of metal-oxide interface. Nickel atoms were able to easily enter and diffuse into the BZT perovskite lattice without introducing a new phase but lattice distortion, and the ceramic constituting elements into electrode was limited to a lower level. The diffusion of nickel dominated the whole inter-diffusion procedure. The incorporation of nickel atoms into BZT was accompanied with the valence change (from 0 to +2 or +3) and most probably performed a B-site substitution. Accordingly, the interaction between metallic nickel and the perovskite ceramic could be formulated as:

$$\mathrm{Ni} + \tfrac{1}{2}\mathrm{O}_2 \rightarrow \mathrm{Ni}_{\mathrm{B}}'' + \mathrm{O}_0 + \mathrm{V}_0^{\bullet\bullet} \qquad (1)$$

Considering the oxygen partial pressure during sintering and annealing should be lower enough to ensure the conductivity of the internal electrode, the reaction could not take place spontaneously. There existed near the metal-oxide



(a)

(b)

(c)

Fig. 2. The micro morphology of the metal-oxide interface (a) and the electron diffraction pattern for the two phases (b) for Ni electrode and (c) for BZT ceramic layer, respectively.

interface, however, a large gradient of the nickel concentration, which brought about chemical potential and facilitated the incorporation and diffusion of nickel atoms into BZT ceramic layers. Therefore, the extent of nickel diffusion was in close relation with the temperature, the dwelling time, and oxygen partial pressure during densification of the monolithic chips according to this model.

It is widely accepted that a certain extent of element inter-diffusion is benefit for the monolithization procedure and can enhance the mechanical strength and improve the breakdown resistance of multilayer components by eliminating the micro cracks due to thermal mismatch between the different co-firing layers [8]. Excess incorporation of electrode elements into the dielectric layer, however,

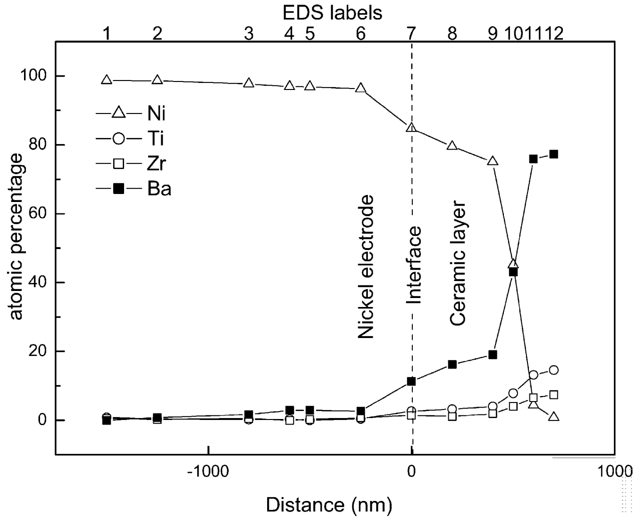


Fig. 3. The relative concentrations of the considered metal elements as a function of the distance to the boundary line by EDX results.

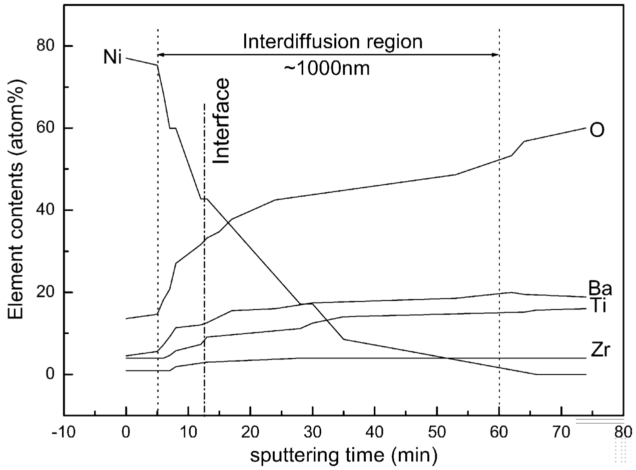


Fig. 4. The concentration profile for the related elements by SAM.

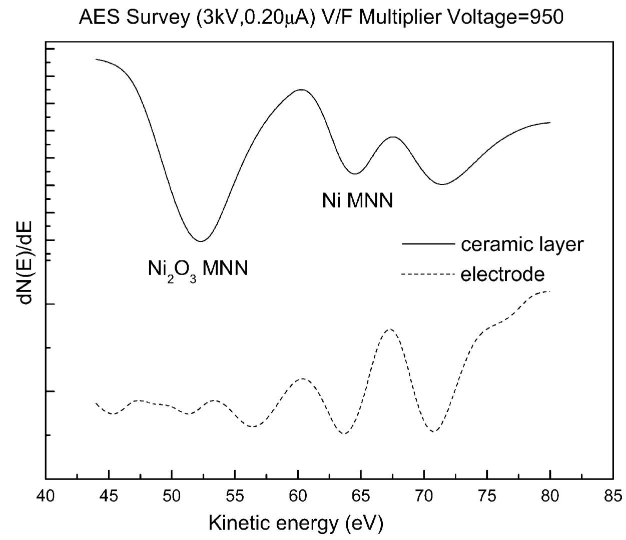


Fig. 5. The chemical shift of nickel in the diffusion region of ceramic layers.

usually introduced some lattice defects, etc. oxygen vacancy, and was harmful for the reliability and aging resistance of MLCCs [5,6]. Therefore, to design and optimize the process parameters for BME-MLCCs in the view of controlling element inter-diffusion between electrode and dielectric ceramic layers should be critical in obtaining high performance, low cost MLCCs. It was expectable that lower sintering temperature, shorter dwelling time, lower oxygen partial pressure, and adopting nickel contained dielectric compositions could efficiently depress the nickel diffusion.

4. Conclusions

Microstructure and compositional analysis were carried out on the interface of nickel electrode and dielectric ceramic layer in BME-MLCCs. Nickel incorporation and diffusion were found to be the key factors on the interface forming and migrating during high temperature procedure. A reactive co-firing model was proposed to interpret the experimental results. Controlling of the nickel diffusion into dielectric ceramic layer should be of great significance in BME-MLCC producing.

Acknowledgements

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