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# Effect of nickel electroplating on the electrical properties of PMZNT relaxor ferroelectrics

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**Abstract**

Effect of nickel electroplating on insulation resistance and ferroelectricity of PMN-based relaxor ferroelectrics was investigated by resistivity and hysteresis measurements. Annealing experiments on the degraded specimens in air and argon at high temperature were also conducted. It was found that the insulation resistivity of the specimens and the hysteresis characteristic deteriorated after electroplating. Annealing experiments indicated that the degraded samples can recover totally through air annealing above 600 °C for 1 h while the argon annealing had almost no improvement on the degradation. It suggested that some metal elements in the PMN-based ferroelectrics may be reduced by hydrogen produced during electroplating thereby, oxygen vacancies and free electrons were generated, which led to the electrical degradation of the ceramics. © 2001 Published by Elsevier Science Ltd and Techna S.r.l.

*Keywords:* C. Electrical conductivity; C. Ferroelectric properties; E. Capacitors

## 1. Introduction

Lead magnesium niobate (PMN)-based relaxor ferroelectrics have been intensively studied and widely used in multilayer ceramics capacitors (MLCC) industry due to their high dielectric constants, broad dielectric maxima and low sintering temperatures. Additionally, they are promising materials for utility in microdisplacement devices.

In MLCC fabrication, electroplating is engaged in termination electrode preparation. Firstly, Ag termination electrodes are formed on the MLCC. Secondly, a thin nickel barrier layer is electroplated on the Ag ground. Finally, a tin–lead solder layer is coated on the nickel layer to improve the solderability. As well known, however, the electroplating process can lead to electrical degradation of PMN-based MLCC in some cases. Electrical properties, such as capacitance, dielectric loss and insulation resistance are sensitive to the plating process parameters. It is imperative to find the failure mechanism and improve the reliability of MLCC against electroplating.

Penetration of electroplating solution into the bulk ceramics is generally thought to be the main reason [1] and much research has been carried out. Behm and Anderson have studied the influence of several processing parameters in nickel and tin-lead electroplating on the electrical properties of MLCC [2,3]. Nevertheless, the influence was studied in view of fabrication technology while the mechanism still kept unclear. It was also noted that the some electroplated MLCC could not pass the temperature–humidity-bias (THB) test while the uncoated ones met the quality specification after the THB test easily. Ling ascribed this phenomenon to the solution penetration into the MLCC during electroplating that consequently resulted in easy diffusion of metal ions in the bulk ceramics [4].

In our previous work, hydrogen generation during electroplating has been mentioned and the hypothesis of hydrogen-induced degradation of the ceramics was proposed [5]. In the present study, some experiments were performed to examine the property changes of commercial PMN-based relaxor ferroelectrics after nickel electroplating. It was found that the degradation of the PMN-based ferroelectrics became more and more serious

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with the electroplating. Annealing experiments of degraded specimens in air and argon were conducted to study the recovery process. The results were discussed and reduction of the ceramics by hydrogen during electroplating was emphasized.

## 2. Experimental procedures

Experiments were performed on $0.98Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.01Pb(Zn_{1/3}Nb_{2/3})O_3$-$0.01PbTiO_3$ (PMZNT). This composition can well meet the Z5U and Y5V specifications of Electronic Industries Association (EIA) and has been commercialized [6]. The dielectric powder was prepared by the two-stage calcination method starting from reagent grade oxides. First, two different columbites of $MgNb_2O_6$ and $ZnNb_2O_6$ were prepared. Second, PbO and $TiO_2$ were added to the two previously calcined precursors, and then ball-milled, dried, and calcined. After being ball-milled again, the powders were doped with MgO and $MnO_2$ as additives. Disk samples with diameter of 1cm were formed by dry pressing at 100 MPa and sintered at 970 °C for 4 h. Finally, the specimens were coated with Ag slurry and fired at 600 °C for 10 min.

Before being electroplated, the specimens were cleaned with chemical solvent and activated for 3 min. After being rinsed with distilled water, the specimens were then electroplated with slight mechanical agitation. An annular Ti basket with Ni lumps in it acted as the anode. Composition of the plating solution and the processing parameters are listed in Table 1.

Insulation resistance of the ceramics was measured on a HP 4140B pA meter. Hysteresis loops were obtained at 0 °C on a RT6000 high voltage test system by Radiant Technology. Surface morphology of the ceramics was examined by scanning electron microscopy (SEM). Annealing in air and argon were both conducted at 600 °C for 1 h with a constant heating rate of 300 °C/h.

## 3. Results

The surface morphology graph is shown in Fig. 1. It can be seen that the ceramic is very dense and has very few pores. An immersion experiment of the specimens in the plating solution was conducted in our previous work [5] and the possible influence of solution penetration into the body ceramics had been excluded.

Fig. 2 plots the relationship of resistivity of the PMZNT ceramics and the nickel electroplating time. It can be seen that the insulation resistivity declined nonlinearly with the electroplating time. At the beginning, only a slight decrease occurred. Then, the resistivity declined further with the electroplating and finally an obvious degradation happened. In addition, an interesting phenomenon was found that the color of the specimens turned darker as electroplating time increased while the blank ceramics was brown. For some seriously degraded samples, small parts of the surface near the electrodes even turned black and can be electroplated.

Effect of electroplating on the ferroelectricity of the ceramics was also studied. The hysteresis loop of a blank specimen is plotted in Fig. 3. Because the testing temperature is only a little lower than the Curie temperature of the ferroelectrics, about 16 °C, the loop is slim and the remnant polarization is small. Fig. 4 shows the changes of polarization hysteresis caused by electroplating. The hysteresis loops of plated samples were quite different from that of the initial one. The saturation polarization were suppressed and the whole loops

Table 1
Nickel electroplating parameters and the solution components

| | |
|---|---|
| Nickel sulfamate (g/l) | 60 |
| $NiCl_2$ (g/l) | 15 |
| Boric acid (g/l) | 40 |
| pH | 3.8 |
| Temperature | 55 |
| Cathodic current density ($A/dm^2$) | 1.0 |

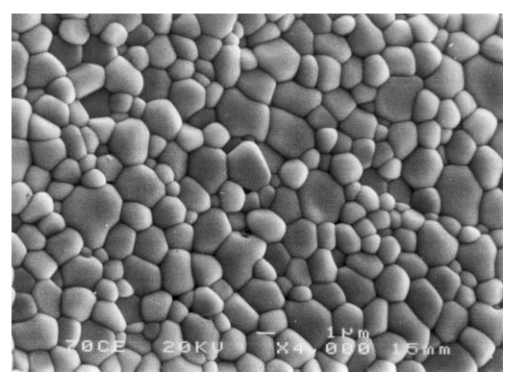


Fig. 1. SEM micrograph of the PMN-based ceramics surface.

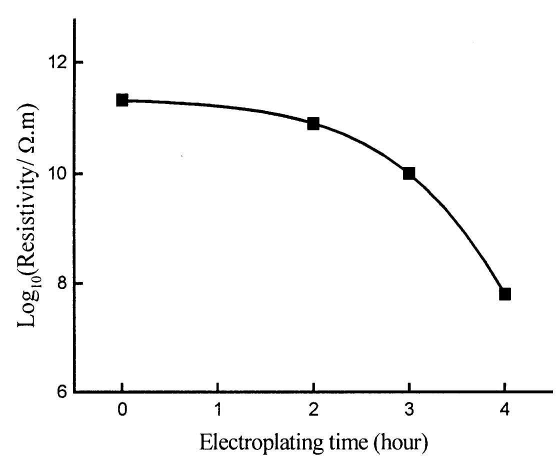


Fig. 2. Resistivity of the ceramics vs. nickel eletroplating time.

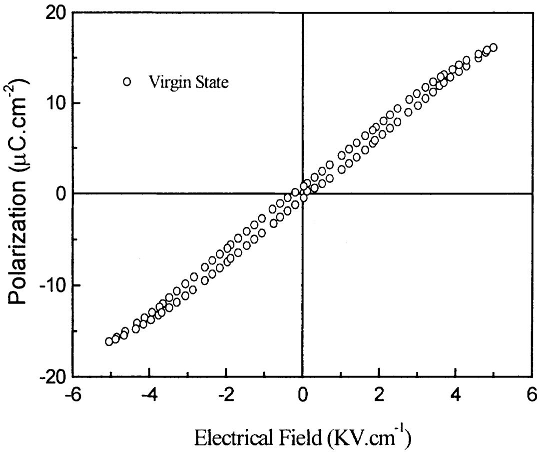


Fig. 3. Hystersis loop of a blank specimen.

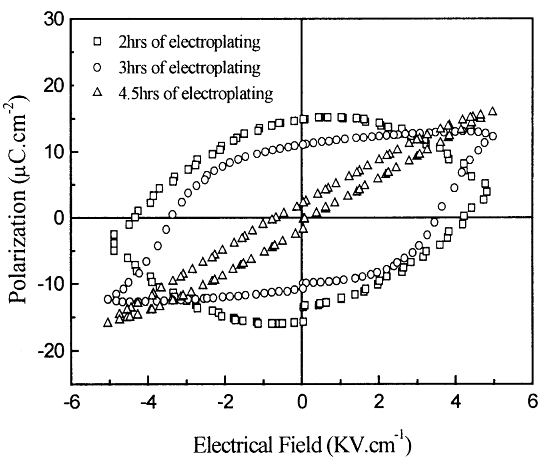


Fig. 4. Hysteresis characteristics after different electroplating time.

became 'blown out', which indicated that the electroplating had led to the ferroelectricity degradation.

In order to study the failure mechanism of the PMN-based ferroelectrics during electroplating, annealing experiments on 4.5 h-plated specimens in air and argon were carried out. It was found that the ceramics turned brown after the air annealing at above 600 °C for 1 h. Also the resistivity and the ferroelectricity of the degraded specimen were restored. Fig. 5 plots the hysteresis characteristics of the plated specimen after air annealing. It can be seen that the ferroelectricity of the annealed ceramics became almost the same as that of a blank one. In contrast, the annealing in argon has almost no influence on the degradation and the color of the specimen did not change.

## 4. Discussion and interpretation for results

In this paper, the effect of electroplating on the electrical properties of PMZNT was clarified. It was found that the dielectric ceramics became semi-conductive

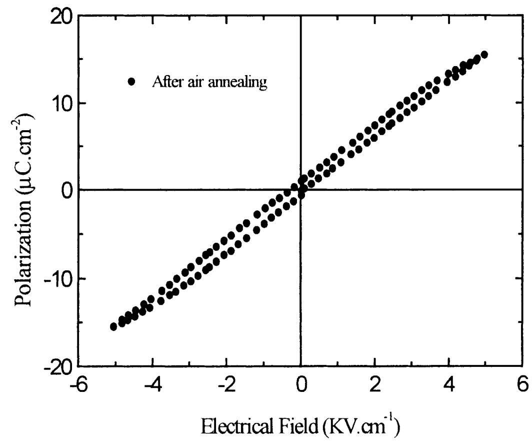


Fig. 5. Hysteresis loop of the plated specimen after air annealing.

after electroplating. For some seriously degraded specimens, even the ceramics can be electroplated with nickel. It strongly indicated that free electrons were produced in the ceramics. Moreover, the degraded specimens can recover completely through an air annealing at high temperature while no improvement was observed after the argon annealing. Based on these results, it was inferred that the ceramics had suffered chemical reduction by hydrogen generated during nickel electroplating.

It is well known that atomic hydrogen can be produced during electroplating process inevitably [7,8]. These active atoms may diffuse along the substrate surface and react with the ceramics. In other words, the electroplating process provides a reducing atmosphere. Metal elements in the ceramics such as Pb and Nb may be reduced according to Eqn.1 and 2, which proves feasible in thermodynamics:

$$H \rightarrow H^{+} + e \tag{1}$$

$$M^{n+} + xe \rightarrow M^{n-x} \tag{2}$$

where $M^{n+}$ represents the metal elements in PMZNT. Meanwhile, oxygen ions were lost from the perovskite type lattice according to Eq. (3).

$$O_{O} \rightarrow \frac{1}{2}O_2 + V_{O}^{\bullet\bullet} + 2e \tag{3}$$

Then oxygen vacancies and free electrons were involved in the failure of PMZNT induced by electroplating, which led to the degradation of resistivity and ferroelectricity.

Consistent with metal element reduction being the cause for the ferroelectricity and resistivity degradation, the electrical properties could be restored to its initial state through an air annealing treatment. Oxygen in the ambient penetrated into the perovskite lattice so that oxygen vacancies and free electrons were minimized. Metal elements of lower valence were re-oxidized to their usual states after air annealing. Hence, ferroelectricity and resistivity of the ceramics were regained. In contrast, the degraded specimens could not recover after the argon annealing. Therefore, we believe that the degraded ceramics had been reduced by hydrogen during electroplating; thereby ionic conduction and electronic conduction were involved, which led to the electrical degradation. To clarify the chemical changes of the ceramics during electroplating, more detailed studies are in progress.

## 5. Conclusions

Resistivity of the PMN-based ferroelectrics declined with nickel electroplating time. The degraded specimens can recover completely after annealed in air at elevated temperature while no improvement was detected after the argon annealing. On the basis of our experiments, it was inferred that some metal elements within the bulk ceramics had been reduced by hydrogen generated during nickel electroplating. Oxygen vacancies and free electrons were produced, which increased the conductivity of the ceramics and changed the hysteresis characteristics.

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