ADHERENCE ENHANCEMENT OF METALLIC FILM ON PZT TYPE CERAMIC USING NITROGEN PLASMA IMPLANTATION*

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Abstract

PZT (Lead zirconate titanate) type ceramics used as piezoelectric sensors have electrodes made by metallic film deposition on the ceramic substrate, which has low adherence on substrate surface. During the welding process in electronic component manufacture, the metallic film releases from surface due to the electrode delamination caused by the large difference in thermal expansion gradients between the film and ceramic [1]. Delamination is a serious problem found in the manufacture of ceramic capacitors since the metallic electrode is split into several layers, leading to a component failure as the electrode is not in contact with the ceramic surface anymore. Therefore, in order to increase the film adherence on the ceramic it is proposed in this work to treat the PZT samples covered with silver metallic films by means of plasma immersion ion implantation (PIII) technique using a high voltage 100 kV/1μs stacked Blumlein pulser. By using this technique, it is shown that the mechanical adherence of the electrode metallic silver film is increased, which allows the welding process of terminals for the piezoelectric device manufacture without film release failure. Thermal stress relief treatment known as annealing process was also used in this work as an alternative to the PIII method for increasing the film anchoring on ceramic substrate.

I. INTRODUCTION

Metal-ceramic junction requires special attention because it involves very large differences in chemical and mechanical affinities between both surfaces, causing great tensile stress which may lead to component failures. Nowadays, technological advances have allowed the use of metal-ceramic materials in various hybrid systems such as in electronic components, light bulbs, electrical insulation for vacuum monitoring devices and other applications in precision engineering industry [2]. In electronic components because of the non-linear characteristics of ferroelectric ceramics these applications include nonlinear ceramic capacitors used in the construction of non-linear transmission lines (NLTLs) for the soliton-type wave RF wave generation [3]. As alternative nonlinear dielectric material of lower losses (dissipation factor on the order of 0.01), PZT ceramics can be a good choice for use in high power NLTLs. However, for the NLTL construction, the process of soldering the PZT sample capacitor electrodes to the printed circuit board (PCB) revealed to be a problem because the metallic film deposited by the manufacturer to form the electrodes on surface sample (see Fig. 1) has low adherence to the ceramic substrate. As a result, the metallic film is released from surface due to the electrode delamination caused by the thermal stress at the ceramic-metal junction. The thermal stress can be explained taking into account the significant difference between the expansion of both surfaces at the interface region due to the different temperature gradients of the metallic film and ceramic.

Figure 1. Commercial PZT piezoelectric sensors.

The contents of this paper are given as follows. In the next section it is shown a background discussion on film deposition, scratching test and soldering process. Section III shows the experimental set-up used for PIII and annealing treatments. Section IV shows the experimental results for pristine and treated samples using both techniques. These results include scratch/soldering thermal shock tests, and surface diagnostics such as energy-dispersive spectroscopy (EDS) and scanning electronic microscopy (SEM). Finally, section V presents a short summary on the work.

II. BACKGROUNDS

For the deposition of metallic electrodes on commercial PZT ceramic sensors a paste containing a thick layer (25- 50 μm) of metallic particles (normally Ag or Au, etc) and seal glass bonding are applied on both

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sides of the ceramic disk. To complete the sintering process the dielectric ceramic disk is heated. Then the seal glass melts during the heat treatment, improving adhesion of the metallic electrode on the ceramic surface under a low processing temperature [4]. In our case, this has been confirmed by the scratch test using a pristine sample. This test consists of generating a scratch on the sample surface by moving linearly a loaded sharp tip with an increasing force on a selected area. The results from this test give three important parameters: the applied normal force, the friction coefficient and the critical loads determined by an acoustic sensor along the track. Any failures of the film release or debris found on the scratch track are detected through noticeable peaks on the waveforms of the testing parameters. This analysis is also completed with a full examination of track scratch image from a built-in optical microscope.

On the other hand, thermal stress worsens the surface film adhesion during soldering process. The melt point of solder used in PCBs is on the order of 220 ° C. When the melted solder is in contact with the silver film of the PZT electrodes, the heat exchange occurs in a fast way, since silver is an excellent thermal conductor. As a result the silver film goes under thermal expansion in a short time. On the contrary, ceramic is a refractory material with little dilatation at the solder melt point. Therefore, the surface adhesion between ceramic and metal film is weak, basically kept by Van der Waals forces and surface mechanical grip. Since the film layer expands much faster than ceramics, the soldering process is compromised causing delamination on the film with subsequent crack of the film/ceramic junction.

III. PIII TREATMENT SET-UP

Commercial PZT samples covered with electrodes of silver metallic films have failures of adhesion on ceramic surfaces when heated. For use as capacitors in nonlinear transmission lines or in general applications in electronics it is necessary to solder the PZT sample electrodes to the printed circuit board. As previously commented, with the heating caused by the use of a soldering tool, film metallic delamination occurs on the surface sample, disabling the component. To solve this problem, PZT circular samples as shown in Fig. 1 were treated by plasma immersion ion implantation (PIII) technique. For this process, a high voltage 100 kV/1μs stacked Blumlein pulser [5] was used. As demonstrated in literature [5], PIII processing is quite adequate for treating different type of materials to improve their mechanical, physical, chemical and tribological surface properties without changing the bulk and dimensions of substrate.

Fig. 2 shows a schematic diagram of the high voltage PIII system used in this work, which includes a vacuum chamber with working pressure of 7×10^{-3} mTorr where the nitrogen plasma is formed previously by a glow discharge using a 600V DC plasma source. The samples to be treated are placed on a support inside the chamber and during PIII process they are immersed in the nitrogen plasma and involved with a layer of ions known as plasma sheath where the electrons are displaced by the negative high voltage potential from the pulser applied on the surface sample. As this region expands towards chamber walls during pulse application ions are accelerated and implanted on treated sample surfaces. More details of the PIII principle of operation are discussed elsewhere [6], [7].

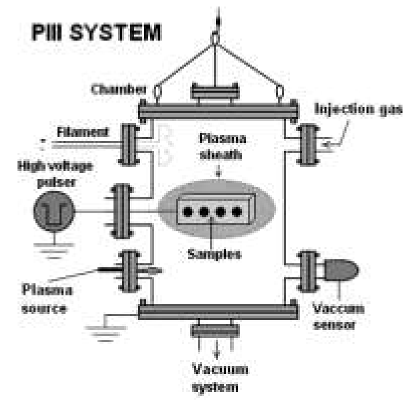

Figure 2. Schematic drawing showed for the whole PIII system.

Before sample implantation, the vacuum chamber and sample support were submitted to glow discharge cleaning using Ar gas with 99.999% purity. The subsequent sample implantation was performed using nitrogen gas with 99.996% purity. The treated sample characterization included surface diagnostic such as energy-dispersive x-ray spectroscopy (EDS) and thermal shock test (soldering process). For the EDS analysis, a scanning electron microscope from Jeol, model JSM-S310, was used.

As an alternative to the PIII treatment, an annealing treatment was also used. In this case, pristine commercial PZT samples were also heated during 80-90 min using a Marshall furnace, model 1027, with controlled constant temperature of about 150 °C for thermal stress relief at the ceramic-metal interface.

IV. RESULTS AND DISCUSSION

First, the experiments were started with the scratch test of pristine samples to check the film anchoring on substrate surface. Fig. 3 shows the scratch test of a non-treated PZT sample using a UMT-CETR tribometer with acoustic sensor. As seen in Fig. 3, no failures or debris are observed on the scratch track image as well as no noticeable peaks detected on the testing waveforms of the normal force, coefficient friction and acoustic sensor. These results confirm that wear occurs only on the scratch area, having good film adhesion on non-treated substrate at ambient temperature as surface cracks and debris are not observed.

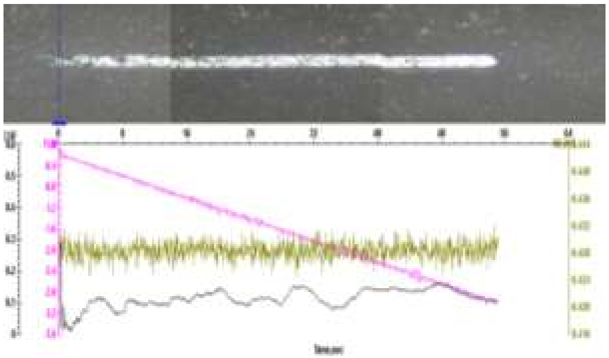

Figure 3. Above the surface scratch image and below the scratch test results showing the normal force in N (magenta), non-dimensional friction coefficient μ (black) and acoustic sensor output in V (brown).

However, when the non-treated sample is submitted to thermal stress during soldering process film release occurs with subsequent crack of the film/ceramic junction as shown in Fig. 4.

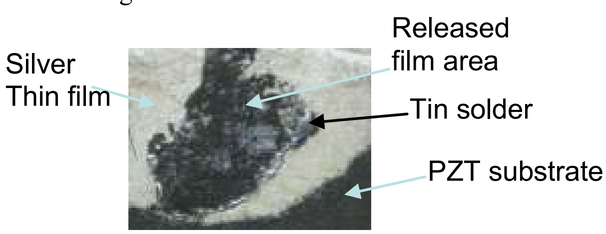

Figure 4. Film release occurred during soldering process.

Then to overcome this problem PZT samples were treated by PIII process with pulse amplitudes of 50 kV and 1 μs duration at repetition rates of about 100 Hz. This treatment with high-energy ions pushes the metallic film atoms towards the PZT crystalline structure of the ceramic bulk by recoil as described in Fig. 5, increasing the adherence between the film and the substrate surfaces [8]. The implantation of nitrogen ions into the silver electrode surface is confirmed by the analysis of the EDS spectrum as shown in Fig. 6 by the N peak. The corresponding chemical composition of the EDS spectrum is shown in Table I. In this table one can observe that film is basically composed by silver (Ag) with a surface oxide layer, being Al a contaminant element originated from the vacuum chamber walls and N the implanted element. The implantation of nitrogen ions in the lattice structure of the film prevents the free movement among atoms, modifying the properties of the material surface. The most common effect on the material surface is the hardness and tensile strength increasing, which in turn reduces the thermal stress by surface dilatation and, thus the likelihood of silver film release during soldering process. To check that Fig. 7 shows the image of a PZT sample surface treated by PIII process with the metallic film electrode firmly soldered to a terminal without the presence of cracks or film release at the metal/ceramic interface.

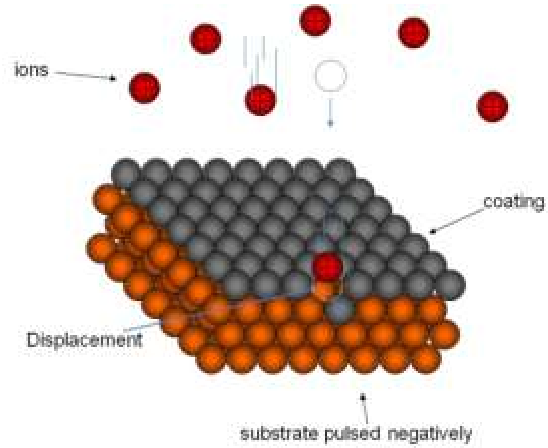

Figure 5. Illustration of recoil phenomenon by ion implantation process.

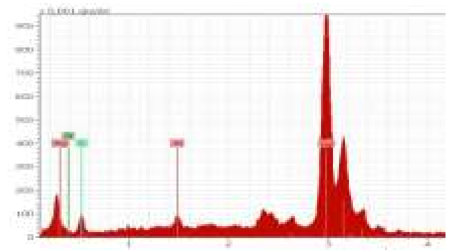

Figure 6. EDS spectrum of the silver film treated by PIII.

Table 1. Chemical composition of the EDS spectrum.

Element	A	Layer	wt.%
Ag	47	L	80,87
O	8	K	14,35
N	7	K	2,64
Al	13	K	4,13

Figure 7. Cooper terminal firmly soldered to the PZT metallic electrode with no cracks or film release.

Besides deposition, metallic film layers can also be formed by thermal evaporation or sputtering. In any case the films have discontinuities at the film/substrate interface that contributes with film release during soldering process. As alternative to the PIII technique, annealing process [9] can be used to relieve the thermal stress between two different crystalline structures. In this work, pristine samples of commercial PZT ceramics were placed in a furnace with a constant temperature of about 100ºC during 80-90 min. This process relieves thermal stress and gives mechanical conformation for the first layers of deposition, enhancing the film adhesion on ceramic substrate, in a similar way to the PIII process. The results for the soldering tests with annealed samples were good as in the previous treatment using PIII technique. In principle, no significant changes between annealed and standard surfaces are visually detected on the surface microstructure of the film because annealing temperature used is too low to produce any chemical and morphological modifications. However, using scanning electronic microscopy (SEM) with 100 times magnification, it is possible to observe a mechanical accommodation of the silver film because of the presence of the small pores and surface deformations in the annealed PZT ceramic as shown in Fig. 8. For comparison, see in Fig. 9 the SEM image of a standard sample without treatment with the same SEM magnification, which shows a more homogeneous and smoother surface with less deformations and smaller pores.

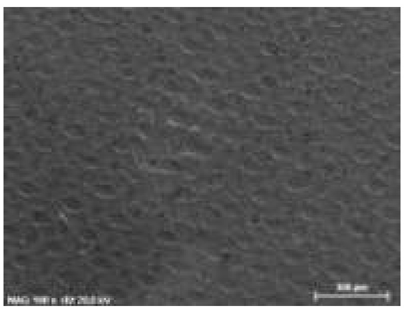

Figure 8. SEM image with 300 μm resolution of a PZT sample metallic surface annealed.

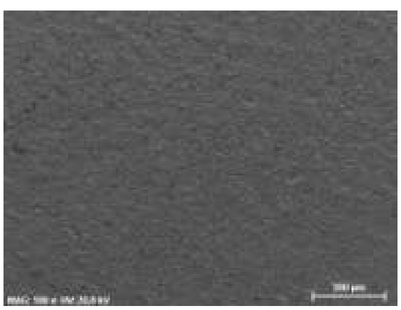

Figure 9. SEM image with same resolution obtained for a standard PZT sample metallic surface.

V. SUMMARY

In this work, it was shown that silver film adhesion on ceramic substrate during soldering process can be significantly improved treating the PZT samples by using two different techniques: nitrogen plasma implantation and process annealing. Both tested processes produced good results, considering the absence of film release or cracks on film surface when it is soldered to the terminal of a component. For the PIII technique, displacement of Ag atoms into substrate structure caused by the recoil of nitrogen ions was an important factor for increasing the film mechanical anchoring on ceramic substrate at higher temperatures. Finally, the second method, annealing process, introduces small deformations and pores on the surface structure relieving thermal stress and also increasing the film adhesion, which prevents cracks or film release during a thermal shock produced in the soldering process.

VI. REFERENCES

[1] J. G. Pepin, W. Borland, P. O. Callaghan, and R. J. S. Young, “Electrode-based causes of delaminations in multilayer ceramic,” Journal of the American Society 72 pp. 2287-2291, 1989.

[2] C. C. Lee, T. Y. Lee, and Y. J. Jen, “Ion-assisted deposition of silver thin films,” Thin Solid Films 359, pp. 95-97, 2000.

[3] P. W. Smith, Transient electronics: pulsed circuit technology. West Sussex, UK: John Wiley & Sons, 2002, pp. 245-255.

[4] Ming-Jen Pan; Randall, and Clive A., "A brief introduction to ceramic capacitors," IEEE Electrical Insulation Magazine, vol. 26, no. 3, pp. 44-50, 2010.

[5] J. O. Rossi, M. Ueda, and E. Schamiloglu, “Advances in high-voltage modulators for applications in pulsed power and plasma-based ion implantation,” IEEE Transactions on Plasma Science*,* v. 39, pp. 3033-3044, 2011.

[6] M. Ueda, A. R. Silva, C. B. Mello, G. Silva, H. Reuther, and V. S. Oliveira, “Influence of the residual oxygen in the plasma immersion ion implantation (PI3) processing of materials,” Nuclear Instruments & Methods in Physics Research B, v. 269, p. 3246-3250, 2011.

[7] M. Ueda, L. A. Berni, G. F. Gomes, A. F. Beloto, E. Abramof, and H. Reuther, “Application of a dc glow discharge source with controlled plasma potential in plasma immersion ion implantation,” J. Appl. Phys. 86, p. 4821, 1999.

[8] G.F. Gomes, M. Ueda, H. Reuther, E. Richter, and A.F. Beloto, “Nitrogen recoil chromium implantation into SAE 1020 steel by means of ion beam or plasma immersion ion implantation,” Surface and Coatings Technology, Vol. 196, pp. 275-278, 2005.

[9] J.C.N. Reis, A.F. Beloto, and M. Ueda, “Annealing effects in samples of silicon implanted with helium by plasma immersion ion implantation,” Nuclear Inst. Met. Phys. Research B, vol. 240, pp. 219-223, 2005.