Metallization of Piezoelectric Ceramic Surfaces

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This paper reports metallization of PZT (lead zirconate titanate) piezoelectric ceramic surfaces accomplished by an electroless plating process with proper after-treatment. With this method, nickel electrodes can be formed on PZT piezoelectric ceramic components used in piezoelectric ceramic wave filters. The main mechanical and electric properties of the piezoelectric ceramic components with this type of plated Ni electrode are as good as, or even better than, those with "fired-on" Ag electrodes. This paper introduces the detailed process of pretreatment, electroless plating and after-treatment, and discusses the principles, results and various effective factors in each process, and indicates preferred operating conditions and control methods feasible in practical production.

Piezoelectric ceramics, as one kind of important electric ceramics used to manufacture various piezoelectric cells, are now widely applied in scientific research, national defense and everyday life. As used in piezoelectric ceramic wave filters or other devices, it is necessary to form proper metallic electrodes on the surface of the ceramic substrate. The commonly used electrode material is silver, which can form the so-called "fired-on" silver electrodes. We considered utilizing nickel to replace silver as electrode material that accords with application demands. That would save noble metal resources and cut costs greatly. Moreover, because of the lower mobility of nickel in ceramic substrates, compared to silver, the use of nickel electrodes may prolong service life and improve the stability and reliability of the components and integrated devices. The "fired-on" method, now commonly used, is not suitable for making nickel electrodes, however, because if heated in air, nickel oxidizes easily and loses its conductivity. When heated in a reduced atmosphere, ceramic substrates tend to be partially reduced and lose their dielectric characteristics. Therefore, the electroless nickel plating method was chosen to accomplish metallization of the PZT ceramic surface. By this method, including proper pretreatment, electroless plating and proper after-treatment, satisfactory nickel electrodes, capable of replacing the commonly used silver electrodes, can be formed on the surface of piezoelectric ceramic substrates. In this paper, the processes of pretreatment, electroless plating and after-treatment are reported, various influencing factors of each process are pointed out and discussed, as well as the proper process conditions and controlling indexes.

Experimental Procedure

Pretreatment

Degreasing

Sintered PZT ceramic substrates were soaked in de-oiling solution at 85 °C for 1 hr, then rinsed with distilled water. The composition of the degreasing solution was: 50 g/L Na₂CO₃, 30 g/L NaOH, 30 g/L Na₃PO₄, and 10 g/L NaSiO₃.

Roughening

De-oiled, clean ceramic substrates were roughened in an etchant at 80 °C hr for 2-30 min, then rinsed with distilled water, boiled in water for 15 min, then ultrasonically cleaned

Sensitization

The roughened substrates were sensitized in $SnCl_2$ solution (typically prepared by adding 2.26 g $SnCl_2$ in 8.4 mL 12 M HCl solution, then diluted to 200 mL) for 10 min, then baked dry.

Activation

The sensitized substrates were soaked in $PdCl_2$ solution (typically prepared by adding 0.2 g $PdCl_2$ in 2 mL 37 wt percent HCl solution, then diluted to 80 mL) for 10 min to activate their surfaces, then baked dry.

Electroless Plating

Following the pretreatment process described above, the ceramic substrates were pre-plated by dipping in a preplating solution of 60 g/L NaH₂PO₂ solution at 75 °C and drawing out immediately. This was repeated three or four times, then the substrates were plated in an aqueous solution containing 40 g/L NiCl₂·6H₂O, 40 g/L NaH₂PO₂·H₂O, 30 g/L Na₃C₆H₅O₇·2H₂O and 30 g/L NH₄Cl and operated in batch mode under thermostatic control.

The results of plating under various conditions were compared to optimize plating conditions. The acidity and composition of the plating bath were continually recorded while the electroless plating was carried on under optimal conditions so as to determine the controllable process indexes for practical production.

Evaluation of Electroless Plating Quality

The appearance of the coating was checked by direct observation to determine whether it was fully covered and smooth, and whether there were any apparent defects, such as unplated areas, pores, pinholes and curved edges, etc. In addition, the surface resistance, Rs, of the coating was chosen as an index to evaluate the quality of the coating. Raw resistance values were measured between two points at a distance of one cm on the surface tested; Rs is the average of the raw resistance values obtained from 4-5 different areas. The value of Rs is closely related to the density of the coating; it can be used to indicate coating quality.

The adhesion of coating to substrate is an important index of coating quality. It is measured by soldering a copper wire vertically on the coating, with the area of soldering controlled to 5×5 mm. With the substrate firmly fixed, the copper wire is pulled vertically, while the pulling force is measured with a spring meter. The pulling force value measured as the coating is pulled apart from the substrate is the adhesion between coating and substrate.

Coating thickness is also one of the important indexes related to coating quality. Three methods were used to measure coating thickness:

(1) Weight loss. A nickel-plated substrate is weighed, then its nickel coating is stripped off and the substrate is weighed again. The difference in weight gives the mass of the nickel coating, from which, with the density of nickel and the area of the coating, the coating thickness can be calculated .

- (2) Coulometric analysis. Under constant potential (or constant current), a small square (*e.g.*, 1 cm²) of nickel coating as the anode and a nickel flake as the cathode. Electrolysis will cease when the nickel coating square, used as the anode, is dissolved completely because the remaining ceramic substrate does not conduct. Measurement of the mass of this nickel coating square can provide the coating thickness.
- (3) SEM. The coating thickness can be measured approximately from SEM photos of the sections of nickel plated substrates. The average of several values obtained from different parts of the substrate were used because of inhomogeneity of thickness.

The results obtained by the three methods agreed closely with each other. Thickness data used here are mostly obtained by the first method.

Measurement of concentrations of main components in plating bath

The acidity of the plating bath was determined by pH meter.^a The concentration of Ni⁺² in the plating bath was determined by spectrophotometry. The absorbances were measured by a spectrophotometer,^b operating at a wavelength of 500 nm, using butanedione dioxime as developer.

After-treatment

Electroplating

After electroless plating, washing in order with dilute acid and base, and ultrasonically washed with distilled water, the substrates were then electroplated. The electroplating bath was prepared as follows: 300 g NiSO_4 .7H₂O, 15 g NaCl, 40 g H₃BO₃ and 0.5 mL nickel brightener were mixed and diluted to 1 L with distilled water. Electroplating parameters were temperature of 50 °C, current density of 0.1 A/cm², and time of 1 min.

Heat treatment

Washed with water and dried after electroplating, the substrates were treated at 200 °C for 8 hr, then heated in N_2 atmosphere to 400-460 °C and maintained at that temperature for 35 min.

Disposition

By the steps above, nickel electrodes were formed on PZT ceramic substrates that can be used in wave filters. These substrates were returned to Suzhou Chequers Electronic Company Ltd., then polarized, severed and mounted to devices with conventional procedures. Their performance was then measured. The electrical property data reported below were all developed by Suzhou Chequers Electronic Company Ltd.

Results and Discussion

The process of nickel plating on surfaces of piezoelectric ceramic substrates reported here is in fact a catalyzed oxidation-reduction reaction that occurs on the interface between the electroless plating solution and the ceramic surface. The essential requirement for this reaction to progress successfully is that some active centers should be formed that can catalyze the reduction of Ni⁺² by NaH₂PO₂. That is the reason that pretreatment of the ceramic substrates is necessary before plating. Pretreatment includes degreasing and rinsing, roughening, sensitization and activation.

The ceramic surface was etched chemically by an etchant in the roughening process; holes and crevices of μ m size, that can adsorb Sn⁺² from the sensitizing solution and adsorb Pd⁺² from the activating solution, were produced on the surface. During activation, palladium metal is produced:

$$Sn^{+2} + Pd^{+2} \longrightarrow Sn^{+4} + Pd$$

The newly produced Pd is the activating center capable of catalyzing the reduction of Ni^{+2} by NaH_2PO_2 , so roughening is a critical step in pretreatment, it directly influences the process of electroless plating. Insufficient roughening causes insufficient sensitization and activation, therefore no adequate activating centers will be formed, making electroless plating difficult; a satisfactory coating cannot be obtained. On the other hand, over-roughening will produce holes that are too large, too deep and too numerous on the ceramic surface, holes that cannot be completely filled by deposited Ni; therefore, defects, such as pinholes or even unplated spots, will appear and degrade the smoothness and density of the Ni coating.

Other investigators have reported that the roughening process occurs mainly on the grain boundaries of the surface of a ceramic body, and that grains themselves are only modestly etched.^{1,2} The crevices left by etching are mostly distributed in hollows of ceramic grain boundary areas. During electroless plating, nickel will be reduced and deposited in those crevices, joining with the surface plating as a

ening. Our



Fig. 1—Morphology of degreased, dry, clean surface of PZT ceramic substrate before roughening.

electron probe microanalyzer model EPM-810Q.

Figure 1 is a photograph of a de-oiled, dry, clean surface of PZT ceramic substrate before roughening. It shows clearly a fine and closely packed surface composed of tiny spherical PZT ceramic particles. In Fig. 2, a photograph of a dry, clean surface of a roughened substrate having many holes with diameters of about several μ m, instead of the tiny spherical particles shown in Fig. 1. That indicates that in our experiments,

<u>ΜΗ 8</u>

whole and exhibiting an "an-

chor effect" that can greatly in-

crease adhesion of the Ni coat-

ing to the ceramic body. Ac-

cordingly, adhesion will in-

crease with increasing rough-

experimental results are not in

agreement with those reported

by references, however. It was

necessary to observe the morphology of the surfaces and sec-

tions of PZT piezoelectric ce-

ramic substrates after different

pretreatment steps and electro-

less plating with a Shimadzu

Fig. 2—Morphology of dry, clean surface of roughened PZT ceramic substrate.



Fig. 3—Section of electroless-nickel-plated PZT ceramic substrate: (a) nickel coating; (b) loose ceramic layer with copious etching holes; (c) PZT ceramic body.

reported in the references. Also, adhesion of the coating to the substrate does not simply increase with increasing roughening. This difference between our results and that of the references probably results from the different ceramic substrates and different compositions of roughening solution used.

the etching during

roughening occurred,

not only on grain

boundary areas, but also on the grains

themselves. The holes

and hollows were

evenly distributed on

the whole ceramic sur-

face rather than being

mainly concentrated

in hollows of the grain

boundary area. So, the

"anchoring effect" is

not as remarkable as

Fig. 4-Morphology of sensitized

surface of PZT ceramic substrate.

down from the nickel layer,

their anchoring effect is not

very strong because they

penetrate a very loose layer

of the substrate surface with

plenty of etching holes, just

as though the anchors were

in a porous, sandy soil. The

presence of this porous, loose

layer also increases the con-

tact resistance between elec-

trode and substrate, and

Figure 3 shows the section morphology of electrolessnickel-plated PZT ceramic substrates. It can be observed clearly that there is a loose layer retaining plenty of etching holes between the deposited Ni and the substrate, because the roughening holes were not completely filled with deposited nickel. Although some "rivets" are found stretched



Fig. 5—Morphology of activated surface of PZT ceramic substrate.

makes the electrical properties of devices worse.

Control of roughening conditions and the after-treatment is needed to improve the properties of components. The composition of the roughening solution and the roughening time should be carefully chosen through experiments, according to the composition, properties and thickness of the ceramic substrate, and so on, because they directly influence the roughening level and results. The color of roughened substrates after being boiled in water indicates the level of roughening and can be used as a general criterion to control the roughening, and electroless nickel plating can proceed. An original black without noticeable changes indicates insufficient roughening; nickel cannot be deposited on the ceramic surface. A muddy yellow indicates over-etching and electroless plating is also impossible. Experimental results show that 8-9 min of roughening is satisfactory for the PZT ceramic substrates used.

HBF₄ and HNO₃ were used instead of HF and H₂SO₄ to prepare the roughening solution, controlling roughening time from 0.5 to 30 min. The results showed that this etchant is too severe for our PZT ceramic; the surface structure was damaged seriously, making plating difficult. This severe etchant may be used for PZT ceramic substrates with thickness more than 1.20 mm if roughening time is controlled precisely. It is not applicable for substrates less than 1.00 mm thick. Following proper roughening, 4-5 min ultrasonic cleaning were needed to remove ceramic particles loosely connected to the surface and those that had fallen off in roughening, but still remained in crevices of the ceramic body. Otherwise, those particles would be sandwiched between the nickel coating and the substrate, thereby decreasing the adhesion of the electrode layer and increasing the contact resistance and dielectric loss.

The aim of sensitization is to have the surface of roughened substrates adsorb a layer of Sn^{+2} that will reduce Pd^{+2} to Pd in the succeeding activation process to form catalytic centers. During sensitizing, the gray-green ceramic substrate gradually turned black. Sensitization was finished when an even black surface was obtained. Figure 4 shows the morphology of the sensitized surface of a PZT ceramic. Compared with Fig. 2, it can be observed that etching holes had been covered with polyhedral $SnCl_2$ particles, but that a few large etching holes had not been covered entirely. This is another indication that over-roughening is not good for plating.

The sensitizing time is the main factor affecting sensitizing outcome. Experimental results show that the concentration of adsorbed Sn^{+2} ions on the ceramic surface was saturated in the first several minutes and that prolonging sensitizing time thereafter would not change the apparent concentration of Sn^{+2} ions on the surface. The same kind of PZT ceramic substrates were sensitized, using various sensitizing times, from 2-30 min. They were then activated and plated in an electroless solution under identical conditions. Coating thickness and adhesion of coating to substrate were then measured. The results show that 10-15 min is the proper sensitizing time under our experimental conditions. A shorter time causes plating failure; a longer time brings no improvement.

Activation is the key step in the entire pretreatment. Prior steps, such as rinsing, roughening and sensitizing are only the preparations for it. Figure 5 is a photo of the surface morphology of a PZT ceramic substrate after activation. Compared with Fig. 4, it can be seen that the SnCl₂ particles adsorbed during sensitization are covered with a layer of larger polyhedral particles that are the Pd grains, (*i.e.*, the active centers), that were reduced and deposited there during activation. The distributive density of Pd grains on the substrate surface is obviously less than that of SnCl₂ particles—the uncovered SnCl₂ particles and unfilled etching holes can still be observed in deeper surface layers. The whole number and density of active centers directly influence the initial rate and level of hydrogen evolution in electroless plating. Insufficient activation brings about a low rate; moreover, because of lack of active centers in some areas, it may lead to formation of unplated patterns or even no plating at all. Over-activation will lead to a plating reaction too violent, with too high a rate, that will cause a decline in the density of deposited Ni, a tendency to bubble, and the encapsulation of impurities. Whether activation is good or not is influenced by the results



Fig. 8—Relation of coating thickness to plat-

Fig. 7—Relation of coating thickness to plating temperature.

of sensitization, the concentration of the activating agent, activation time and activating procedure, etc. After proper sensitization, with certain concentrations of activating agent, the results of activation depend mainly on the latter two factors. Experimental results indicate that under our conditions, 10-15 min is the proper activation time. Activation time should be prolonged to 30 min if the substrates are first rinsed with distilled water after being pulled from the activating solution. Electroless plating can then proceed, following the referenced method.

Factors in Control of Electroless Plating

In terms of use of the platings as electrodes, the density of the electroless nickel coating and the contact state and adhesion between plating and substrate are important indexes in investigating and evaluating the quality of the nickel plating. The surface resistance, R_s , of the coating was selected as an indicator of density of the coating and it was discovered that when $Rs \leq 8\Omega$ (most are about 3Ω), the density of plating matches application demands; because with only a slight fining in after-treatment, the R_s of these coatings will decrease to less than 1Ω , equivalent to the surface resistance of pure nickel flakes. When $Rs > 10\Omega$, it indicates that the density of the coating is not up to standard and that the plating is not suitable for application, even after a fining.

When used as electrodes of piezoelectric components, the nickel plating should adhere to the ceramic substrates firmly and not peel off, even after repeated mechanical and electromagnetic driving and long-term vibration at high frequency. Adhesion of plating to substrate, therefore, becomes an important index in evaluating plating quality. It is commonly required that adhesion be more than 0.5 MPa/cm², but the measurement of adhesion is a destructive test; only spot checks can be made during production, and the test results are no help in preventing defective products in the plating process. Another indicator was needed to quantify adhesion.

Other investigators pointed out that the adhesion between coating and substrate is closely related to the thickness of coating.¹ If the coating is too thick, its adhesion will decrease greatly, because its internal stress becomes greater than the adhesive force. The same conclusion was reached in our study. It was demonstrated that test results of adhesion always matched application demands when the thickness of the coating remained at the level of several μ m.

Further increase in coating thickness caused remarkable decrease in adhesion. When coating thickness is more than 20 μ m, the coating frequently has curved edges and peels off easily. The adhesion of the coating can be controlled, therefore, by regulating the thickness of the coating; it is unnecessary to test the adhesion of each item.

Platingtime

With other conditions unchanged, the longer the plating time, the thicker the electroless nickel layer, but the rate of deposition of Ni onto the ceramic surface decreases as plating proceeds. Accordingly, a curve can show the relationship between plating time and coating thickness. Figure 6 shows the relation of coating thickness to plating time when using the same plating bath with pH 5.2 and temperature of 75 °C. It can be seen from Fig. 6 that under these conditions a nickel coating about 2 μ m thick will be obtained after 30 min. The thickness should be controlled to about 1 μ m so as to leave some room for fining in after-treatment; therefore, the preferred plating time is 10-15 min.

ing bath pH.

Plating temperature

Figure 7 shows the relation between coating thickness and plating temperature obtained using the same plating bath: pH 5.2, plating time 20 min. It shows that with other conditions remaining unchanged, a higher plating temperature results in a thicker plated layer. If the temperature is below 65 °C, the deposition rate of Ni is so slow that deposition hardly occurs in a practical process. The deposition rate of Ni and the thickness of the plated layer are both appropriate when the plating temperature ranges from 70-80 °C, with 75 °C selected as the preferred temperature.

pH of plating bath

The curve in Fig. 8 shows the relation of the thickness of the plated layer to the pH of the plating bath (adjusted with dilute hydrochloric acid or aqueous ammonia, and measured with a pH meter), with temperature 75 °C and plating time 15 min. It can be seen from Fig. 8 that under the same conditions as before, coating thickness increases with increased pH, indicating that the deposition rate of Ni also increases with increasing pH. If the deposition rate is too high, the plated layer will be less dense and impurities in the bath will contaminate the Ni plating because of codeposition or adsorbtion, so that the quality of the plating will be degraded. On the other hand, basicity will lower the stability of the bath, because in addition to low solubility of orthophosphite, the reaction of oxidizing H₂PO₂⁻ to HPO₃⁻² becomes spontaneous rather than a catalyzed reaction under basic conditions. So, bath pH cannot be too high or too low. During the electroless plating process, the pH of the bath continuously decreases because of the production of H⁺ ions. That makes the deposition rate of Ni lower and lower, with more and more noplating spots. When the pH bath reaches about 4.0, the quality of plating is already quite poor; when pH goes down to about 3.8, the plating process has practically ceased. We preferred to control pH in the range of 5.2-5.8. Obviously, the pH of the bath should be monitored and regulated constantly during plating.

Influence of After-treatment on Electrical						
Properties of PZT Ceramic Substrates						
Exper. group	Substrate thickness d/mm	A B C	$egin{array}{c} { m R}_{_0} \ \Omega \end{array}$	Q _m		
1	1.20		7.44	1340		
2	1.20	- + -	9.19	1092		
3	1.20	+	7.00	1424		
4	1.20	- + +	7.66	1369		
5	1.20	+ + +	5.98	1720		
6	0.85		7.22	839		
7	0.85	- + -	7.66	814		
8	0.85	+	6.73	945		
9	0.85	+	6.10	1089		
10	0.85	+ + +	4.25	1575		

Table 1

A: Electroplated; B: Low-temp heat treatment; C: High-temp heat treatment; -: Not performed; +: Performed

Table 2 Comparison of Electrical Properties of PZT Ceramic Substrates With Different Electrodes

Type* of Electrode	Substrate thickness d/mm	$egin{array}{c} {\sf R}_0 \ \Omega \end{array}$	Q _m
А	1.20	5.98	1720
А	0.85	4.48	1537
В	1.00	4.71	1567

* A: Plated nickel; B: Fired-on silver

After-treatment

After all the previously described procedures, an even coating of silver-gray nickel, with a smooth, dense surface and a thickness of about one μ m, can be obtained on the surface of the PZT ceramic substrate. This kind of coating has good corrosion resistance, mechanical strength, solderability and adhesion to the substrate. Its surface resistance, R_s, is generally several ohms, but the contact resistance between coating and substrate is relatively high, as are the resonant resistance, R₀, and dielectric loss. A piezoelectric component with this kind of coating has too low a mechanical quality factor, Q_m. For applications in wave filters, transducers, etc., however, low dielectric loss and high Q_m are necessary. Accordingly, the after-treatment must be performed for the electrodes formed by electroless plating to improve their electric properties further to meet application demands.

Here the high dielectric loss and low mechanical quality

factor are the key problems. It was thought that the main cause of high dielectric loss was that the etching holes formed in roughening were not being completely filled with deposited Ni during plating, so that there was a porous and loose layer between the electrode layer and the substrate that caused high contact resistance and, consequently, high dielectric loss. Additionally, the slightly high R_s of nickel plating indicates that the density of the plating is not great enough, which slightly elevates the dielectric loss. The lower mechanical quality factor is mainly related to the higher resonant resistance, R_a .

Influence of plating on electrical properties

Generally, Q_m has an inverse correlation with R_0 , and R_0 is mainly related to the resistivities of ceramic and electrode materials. Because we are comparing different metallic electrodes on the same ceramic material substrates, the significant factor is the different influence of the resistivities of different metals on R_0 . Usually, the smaller the resistivity of the electrode material, the smaller the corresponding R_0 . Although the Q_m of piezoelectric ceramic components with nickel electrodes is often not as good as those with silver electrodes, because of the better conductivity of silver, nickel is still expected to replace silver electrodes because of its advantages in cost and service life. Accordingly, the aim of this work is to reduce R_0 of piezoelectric ceramic components with nickel electrodes as much as possible to improve Q_m .

During electroless plating, because of dismutation or reduction by newly released atomic hydrogen, part of the reducing agent, sodium hypophosphite, will be reduced to phosphorus atoms that co-deposit with nickel; consequently, the so-called "nickel coating" obtained by electroless plating is in fact a nickel-phosphorus alloy. Analytical results show that the electroless nickel coatings obtained in our experiments contain 9-10 wt percent phosphorus. The resistivity of this alloy is greater than that of pure nickel by nearly 10 times. Accordingly, a layer of nickel was plated over the electroless nickel coating to reduce its resistivity, with the expectation of reducing the R₀ of the components and improving their Qm (in this case, electroplating cannot be carried on without electroless plating, so it cannot replace the electroless plating process). Moreover, electroplating has a fining function also for the electroless coating, repairing possible defects on the surface, such as pinholes, and making the coating more dense. That also assists in reducing R_s and R_0 of the coating. Experiments demonstrate that surface resistance R₂ of a fine electroless coating is generally about 3 Ω before electroplating, and is reduced to 10^{-1} to $10^{-2} \Omega$ after electroplating, equivalent to that of pure bulk nickel. In particular, for the piezoelectric ceramic substrates with electrodes made of electroless nickel and fined by electroplating, their resonant resistance is apparently lower, and their mechanical quality factor has been improved (see Table 1). The PZT ceramic substrates used in experimental groups 1-5, listed in Table 1, were identical, having the same shape, size and composition, and pretreated and plated with electroless nickel, then polarized under the same conditions; the only differences being subjected to different after-treatment. The difference in their electrical properties should then be attributed to the different after-treatments they experienced. Experimental results of groups 6-10 in Table 1 also indicate the influence of aftertreatment on electrical properties of piezoelectric ceramic components. Comparing data in Table 1, it can be seen clearly that the R_0 of the substrates was significantly reduced by



electroplating, with Q_m improved as well. That verified our former analysis and conclusions, and demonstrated the necessity and importance of after-treatment.

Fig. 9—Section of PZT ceramic substrate after lowtemperature heat treatment: (a) nickel coating; (b) loose ceramic layer with copious etching holes; (c) PZT ceramic body.

Effects of heat treatment Comparing results of experi-

ment group 1 with those of experiment groups 4 and 5, listed in Table 1, or comparing results of groups 6 and 9 with those of group 10 in Table 1, it can be seen that heat treatment will improve Q_m of piezoelectric components and is an indispensable step. The effect of heat treatment on improvement of Q_m is much less than that of electroplating. Results in Table 1 also show that heat treatment is of no benefit in reducing R_0 of substrates—it probably increases R_0 somewhat occasionally.

Accordingly, the improvement effect of heat treatment on Q_m is not the method of reducing R_0 . It was thought that during heat treatment, the nickel atoms (including the electroless and electroplated coatings) might penetrate the ceramic surface by thermal diffusion, filling the loose layer formed in roughening. Also that ohmic contact would be formed be-



would be formed be- *Fig. 10—Section of PZT ceramic substrate* tween metal coating and *after low- and high-temperature heat treat*-ceramic substrate, and *ment.*

reduce the contact resistance and improve the Q_m.

Heat treatment includes two steps. Experiments indicated that heat treatment at 200 °C has no noticeable effect on improvement of the electrical properties of PZT ceramic components. The purpose of this step is to remove the water and air trapped inside coatings and substrates, that may not be able to escape sufficiently in a direct high-temperature heat treatment and would oxidize nickel at high temperature. A direct high-temperature heat treatment may also cause thermal stress and reduce the mechanical strength of the ceramic base. It is the high-temperature heat treatment that has an apparent effect on improving electrical properties of PZT ceramic components. Experiments indicated that heat treatment at 200-500 °C will reduce resistivity and improve electrical properties of PZT ceramic components (see Table 1). Temperature higher than 500 °C, however, is not productive for heat treatment because it has no better effect, and nickel will be oxidized more easily. We investigated the

^aModel PHS-4, Shanghai Leici Instrument Factory.

^bModel UV/VIS-731, Shanghai No. 3 Analytical Instrument Factory.

variation of contact quality between the nickel coating and the ceramic substrate through heat treatment, by means of an electron probe microanalyzer. The results of our investigation confirms our analysis (see Figs. 3, 9 and 10).

The effects of low- and high-temperature heat treatment can be seen by comparing Figs. 9 and 10 with Fig. 3. There is no significant difference between Figs. 3 and 9; a loose layer having plenty of etching holes is still there between nickel and ceramic in Fig. 9. While in Fig. 10, that loose layer can hardly be seen, most etching holes have been filled by nickel. There is no obvious dividing line between nickel coating and ceramic base. That indicates that ohmic contact has been formed between coating and base.

Summary

After electroplating and low- and high-temperature heat treatments, application performances of electroless nickel electrodes have improved. Electrical properties of PZT piezoelectric ceramic substrates with these nickel electrodes are as good as, or better than, those with "fired-on" silver lectrodes (see Table 2).

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