PRETREATMENT FOR METALLIZATION OF PZT CERAMIC SURFACES[1]

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ABSTRACT

This paper describes the pretreatment process for metallization of PZT ceramics surfaces by electrolytic Ni plating which includes cleaning, roughening, sensitization and activation. The experimental procedure, results and influencing factors for these processes are investigated and discussed.

Key words: PZT nickel cleaning roughening sensitization activation

1 INTRODUCTION

It is necessary to make electrodes on the surfaces of PZT ceramics used as piezoelectric components, which is a process of metallization. In this paper, nickel and its alloys were applied to replace the usual silver or other noble metals as the electrode. Since the "fired-on" method, which widely used in Ag plating, is not fit for preparing Ni electrodes, chemical plating was used. In the process of chemical plating of Ni (electrolytic Ni plating), the key point is to form catalytic active centers of proper density on the surface of the ceramic substrate before plating. To form the centers, three pretreatment steps,including roughening, sensitizing and activating are necessary. The experimental procedure, results and the influence of activation time are investigated and discussed in the paper.

2 EXPERIMENTAL

The PZT ceramices used were offered by Shuzhou Chequers Electronic Company Ltd. All chemicals used were analytical reagents. PZT ceramic substrates were immersed in a de-oiling bath, which was mainly composed of Na_2CO_3 and NaOH, at 80℃ for 1 h and then rinsed by distilled water. Cleaned ceramic substrates were etched in etchant at 80℃ for 10~15 min, rinsed by distilled water, boiled in boiling water for 15 min, then ultrasonically cleaned and baked. The etchant contained $K_2Cr_2O_7$, H_2SO_4 and HF. The roughened ceramics were sensitized in $SnCl_2$ solution for 10 min and dried in air. The sensitized ceramics were put into aquerous $PdCl_2$ for 10min and then dry. The pretreatment was finished. The catalytic active center—Pd particles had formed on the ceramic surfaces at proper density, and electrolytic plating of Ni could proceed.

3 RESULT AND DISCUSSION

The aim of de-oiling and washing is to remove oil stains and dirty spots on the ceramic surface and offer a clear and well immersed surface. If the surface is dirty, in the following steps, the chemicals can not penetrate oil stains and dirty spots producing unplated spots on the surface, or even no coating. The essence of the etching process is that the etchant attacks the ceramic surface leaving behind μm-sized holes on the surface, where Sn^{2+} from the sensitizing agent and Pb^{2+} from activiting agent

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can be adsorbed, forming the active centers to enable chemical plating to proceed successfully. So etching results directly influence electrolytic plating. Insufficient roughening results in bad sensitization and bad activation. The resulting active centers will be too few to proceed with eletrolytic Ni plating. Over-roughening, on the other hand, causes to formation of overly dense and overly deep etching holes which can not be filled with Ni in plating, thereby producing pinholes and unplated spots and resulting in poor smoothness surface. "Over-etching" ceramic surface produces a layer of porous ceramic under Ni film which will decreases adhesion between electrolytically plated Ni and the PZT substrate.

Banmgartner[1]reported an etchant preferentially attacks grain-boundary areas leaving behind crevies. While PZT grains are only modestly attacked. If following this step, the ceramics is properly catalyzed and electrolytically plated, Ni will desposit in these crevices to form mechanical anchors, thereby significantly increasing the adhesion of electrolytic Ni coating to PZT. The adhesion increases with increasing etching level. A similar effect was reported by Homma and Kanemitsu for Ni deposited on alumina substrate following an NH_4F etchant[2]. Our experimental results are not quite in agreement with their results. Fig.1 ~ Fig.3 are X−ray electronic probe monographs of PZT ceramic surface before and after roughening. A fine and close surface composed of tiny spherical PZT particles can be seen in Fig. 1 where the ceramic was cleaned and dried.

By comparison of Fig. 1 , Fig. 2 and Fig. 3, we can see that a great deal of tiny spherical particles disappear in Fig. 2 and Fig. 3. Many holes with diameters of about several μm appear instead. This demonstrates that in our experiment the etchant did not mainly attack grain−boundary areas but it attacked ceramic grains themselves to form evenly distributed etching holes and hollows instead of crevices. The difference may resultfrom different ingredients in the two kinds of ceramics and etchants. Because of this , the anchor effect is not as remarkable in our experiment as in reference. The adhesion does not simply increase with increasing roughening. On the contrary, over-etching leads to formation of a porous and loose layer between the deposited Ni and ceramic substrate and decrease adhesion,which can be seen in Fig. 4, where the porous layer was not entirely filled with Ni. Though a few anchors can be found, the anchor effect is not strong because anchors were in the porous layer. On the other hand, since a lot of etching holes existed, this kind of PZT ceramic component has higher dielectric loss and a lower dieletric constant. This is why over-etching is not good for Ni plating. Therefore a proper etching is very important. Etching must match the properties of the ceramic and thickness of the coating.

Fig. 1 Monograph of PZT surface before etching

The colour of the etched ceramic surface indicates the etching result. An even gray-green colour means good, black indicates a luck of etching while a muddy yellow surface indicates over-etching. Ni cannot be deposited on the last two kinds of ceramics. Etching time influences roughening leve land the plating result which can clearly be seen in Table 1. Under our experimental condition 10～15 min etching is proper.

Fig. 2 Monograph of PZT surface after etching and general wash

Fig. 3 Monograph of PZT surface after etching and ultrasonic wash

Refering to Fig. 4, the best etching time is about 10 min. Different etchants or ceramics need different etching time. When we used HBF_4 adding HNO_3 instead of HF as the etchant, controlling the etching time from 1 s to 30 min, all surfaces of the sample were muddy yellow and all failed in chemical plating, which indicated the etchant was so severe for our PZT ceramic that the structure of the ceramics surface was distorted and chemical plating could not proceed. Following proper etching, 4 or 5 min ultrasonic cleaning was needed to thoroughly remove ceramic particles which loosely combined with the surface or those which fell off in etching and still remained in crevices.

Fig. 4 Monograph of section of Ni plated PZT ceramic

a—Ni coating; b—PZT surface with a lot of etching holes; c—PZT ceramic substrate

Table 1 Etching influences on Chemical plating *

Etching time / min	2	5	10	15	25	30
Colour of the ceramics	black		gray—yellow		muddy—yellow	
Surface after etching plating results	no coating		even coating		no coating	

* Under the same experimental condition except etching time

By comparison with Fig. 2 and Fig. 3, it can be seen that ultrasonically cleaned surface (see Fig. 3) is clearer than the unultrasonicated surface (see Fig. 2). Ultrasonic cleaning is necessary for pretreatment. If it is not, the performed particles from etching or the following steps will be encapsulated by Ni in the plating film, causing a decrease in the adhesion and dielectric constant of the PZT component and an increase in the resistance and dielectric losses of the component.

Fig. 5 Monograph of PZT surface after sensitizing

The surface of the etched ceramic adsorbs a layer of Sn^{2+} in the sensitizing process which will reduce Pd^{2-} to Pd in the activating process to form catalytic centers. The sensitizing agent used is $SnCl_2$ solution. In this process, gray-green ceramics gradually become black. The sensitization was finished when the surface appeared evenly black. The monograph of a sensitized PZT surface (see Fig. 5) shows the etching holes were covered with polyhedral particles as compared with Fig. 3 and some big holes did not fill with Sn^{2-} which illustrates over–etching is not beneficial for chemical plating. The picture of X–ray (SnLα) area analysis of the sensitized ceramic surface (Fig. 5) combined with the image of back scattered electrons yields (Fig. 6), which shows the sensitized ceramic surface evenly adsorbed a layer of Sn^{2+} ions, and the holes on the surface (black), especially bigger and deeper holes adsorbed fewer Sn^{2+} ions (shining points) than other parts, which is coincident with the result from the monograph.

The experimental results show prolonging the sensitiazing time did not apparently change the concentration of Sn^{2+} ions on the surface, because the surface had been saturated with Sn^{2+} ions in begining several minutes. Same chemical plating conditions bring about approximate thickness of Ni film, which can be seen clearly in Table 2. under our experimental condition, 10~ 15 min is the best sensitizing time.

Fig. 6 Monograph of sensitized PZT surface combined with the image of SnLα ray area analysis

black represents etching holes;

white shining points represent Sn^{2-} ions

Table 2 Influence of sensitizing time on plating

Sensitizing time min	2	5	10	15	20	25
plating results	no coating	part coating	even coating		even and shiny coating	
thickness μm			1.84	1.83	1.84	1.84
adhesion kg · mm^{-2}			> 1	> 1	> 1	> 1

Activation is a key process in pretreatment. Roughening and sensitization are preparations for activation. In this process, Sn^{2+} ions on ceramic surfaces reduce Pd^{2+} to Pd deposite on the surface as where they will serve catalytic centers for reducing Ni. It can be seen by comparing Fig. 7 with Fig. 5, that $SnCl_2$ particles on the surface are covered with bigger Pd particles and the density of Pd particles is less than that of $SnCl_2$ particles, while uncovered $SnCl_2$ particles still can be found in deeper layers. The same results can be found in Fig. 8, where white shining points represent Pd particles.

Fig. 7 Monograph of PZT after activating

Fig. 8 Monograph of activated PZT surface combineed with image of PdLα ray area analysis

black parts represent etching holes;

white shining points represent Pd

The density of catalytic centers directly influences the initial rate and violence level of electrollytic plating reaction. Insufficient activation brings about a slow rate. This leads to formation of a spotty plating layer or even no plating layer due to the lack of active centers. Menawhile over–activation causes a decline in the density of deposited Ni, producing foam on the plating layer and encapsulating impurities in the plating layer. Whether the activation good or not, depends mainly on result sensitizationion , the concentration of activating agent, activation time and technological control of the process. Table 3 shows the electrolytic plating on activation dependence time under the same experimental conditions. It indicates 10~ 15 min is the proper. If ceramics are rinsed with distilled water following activation as in the reference, the activation time must exceed 1h to yield the same result. If the concentration of Pd^{2+} in activation bath decreases, the plating layer will not form under the same condition.

Table 3 Dependence of electrolytic plating results on activation time

Activation time min	10	15	20 ~ 30
plating results	even coating	even coating	repeatedly rinsing when preplating to get even coating

By using the selected conditions and methods described above to clean, roughen, sensitize and activate PZT ceramic surfaces, the pretreatment process can finish, forming catalytic centers of appropriate density on the ceramic surface. Electrolytic Ni plating can proceed successfully on activated surfaces, forming Ni electrodes. These Ni electrodes can be made into piezoelectric PZT components.

REFERENCES

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