The Metallization of PTC Ceramic by Magnetron Sputtering

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Abstract

DC magnetron sputtering was applied in the deposition of the electrodes of the BaTiO₃-based PTC ceramics. Multi-layered films of Ti/Ni-Cu/Ag and Al/Ni-Cu/Ag were prepared as the electrodes of PTCR ceramics. Experimental results indicated that there could form good ohmic contacts between BaTiO₃-based PTC ceramics and the electrode materials. Also, the electrodes had good adhesion to the substrates and high-temperature welding characteristics. The proposed method has such advantages as economic consumption of production cost and controllable process, thus is suitable for large-scale industrial production.

Keywords: DC magnetron sputtering; PTC; Electrode

1. Introduction

BaTiCO₃-based PTC (positive temperature coefficient) ceramic is a kind of ferro-electronic material with many fine electronic properties such as resistance-temperature characteristics, current-time characteristics, voltage-current characteristics, therefore it is widely used in electronic products such as temperature sensors, heaters, motor components, de gauss etc. In the technique of manufacturing PTC, manufacturing electrode is a process of vital importance. The properties of electrodes would influence other properties of the PTC, such as ohmic contact, aging characteristics, welding performance, etc.

PTC ceramics are not identical with other dielectric ceramics since middle contact resist would be yielded between the metal electrodes and PTC ceramics. Traditional methods applied in manufacturing PTC electrodes included the electroless nickel-plating, fired alloy method and screen printing. The electroless nickel plating was quite complex in the process and brought in poisonous Cl⁻ in manufacturing. The process of fired alloy method was simple, but its products had low impact current and poor aging characteristics. Screen printing brought in serious pollution in the manufacturing process and its metal coating contained lead, hexavalent chromium and other harmful elements. Besides, the products of this method could not withstand the melting and corrosion of high-temperature lead-free
soldering\textsuperscript{[1]}. Since better performance of electronic products as well as environment-friendly standards are called for currently, the above methods are not suitable in the production of PTC electrodes any more. Instead, magnetron, the green technology began to take their places in manufacturing process of PTC electrodes. Murata in Japan was the first company that began to study magnetron sputtering in PTC electrodes production. Their research findings indicated that sputtering had many advantages: its products had low resistance and good adhesion, slow aging process and were able to withstand high power impulse\textsuperscript{[2]}. B. Heinen in Germany studied the influence of the area and thickness of NiCr/Ag electrodes on the properties of BaTiO\textsubscript{3}-ceramic based PTCR, also pointed out that this kind of electrodes was widely used in international industries\textsuperscript{[3]}. Yongde Hao sputtered Ni on the PTCR through magnetron sputtering instrument imported from America, and the electrodes demonstrated better properties than those made from fired-Al\textsuperscript{[4]}.

2. Experiments
Experiments were carried out in the magnetron sputtering system designed by Film & RF Laboratory of Zhejiang University. The substrates used in the experiments were PTC ceramics with a size of $\varnothing$2cm*0.4cm provided by Linzhi Electronics Co.ltd, which were used as heater components in the car. Before the experiments, the substrates were placed in deionized water and acetone solution for ultrasonic cleaning 4-5 times, each time lasting for 15-20 min to get rid of the surface grease and impurities. Then the substrates were taken to the oven. After the substrates were completely dried, multi-layered films were deposited on them. Specific sputtering parameters were as follows:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>Ar Purity</td>
<td>99.999%</td>
</tr>
<tr>
<td>Target Purity (alloy target exclusion)</td>
<td>99.9%</td>
</tr>
<tr>
<td>Base Pressure</td>
<td>5×10^{-3} Pa</td>
</tr>
<tr>
<td>Sputtering Pressure</td>
<td>0.4-0.5 Pa</td>
</tr>
<tr>
<td>Sputtering power</td>
<td>10-25 W/cm\textsuperscript{2}</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>normal temperature</td>
</tr>
<tr>
<td>Target-substrate distance</td>
<td>10 cm</td>
</tr>
</tbody>
</table>

Three kinds of films were prepared in the experiments, namely, Ti/Ni-Cu/Ag, Al/Ni-Cu/Ag and Ni-Cr/Ag. For the Ti/Ni-Cu/Ag film, first the Ti was sputtered, then Ni-Cu alloy, last Ag. The other two films were prepared in similar methods (the Ni-Cu alloy used in the experiment was Ni80\%Cu20\% and Ni-Cr alloy was Ni80\%Cr20\%). In the preparation process, first one side was sputtered, then the other. After sputtering, the outer circle of the PTC ceramics was grinded in order to measure the resistance of the PTCR.

3. Results and discussion
3.1 Ohmic contact
As shown in Fig.1, the average resistance of three diverse films in normal temperature ranged between 5.5Ω to 6.5Ω, illustrating that good ohmic contacts were formed without heat treatment. Sauer\textsuperscript{[5]} thought that there were two factors that influenced the shaping of good ohmic contacts between semiconducting ceramic and metal: (i) $\Phi_s$ (work function of semiconducting ceramic) $>\Phi_m$ (work function of metal); (ii) the surface states of semiconducting ceramic. NiCr/Ag has been proved to yield good ohmic contacts with PTCR\textsuperscript{[3]}. Ti and Al had low work function
(Al:4.28eV; Ti:4.33eV) and strong reducing property, enabling them to absorb the oxygen in the interface of the ceramic. In magnetron sputtering, the bombardment of the atoms with high energy could destroy the layer of oxygen in the surface of the ceramics, which yielded a high concentration of oxygen vacancies, thus good ohmic contacts were formed. Ti, in particular, could generate TiO₂ with oxygen on the surface of the ceramic. Since PTC itself contains TiO₂, it could be a good transition layer.

3.2 Adhesion
In this experiment, adhesion was manifested by the term of tensile strength. The force gauge (K-50H, Fuzhou, China) was first tied to the film vertically, then the film was pulled at certain rate until it broke away from the substrate, the reading of the force gauge at that time referred to the tensile strength I. After sputtering, the electrodes were first soaked in water for 24 h then taken to the oven to dry. Again, the same steps of measuring tensile strength I were taken to gain the tensile strength II. Since the experimental data had great dispersion, sufficient times of measurement should be conducted then the mean of the experiment results was calculated.

As shown in Fig.2, the three-layered-films of Ti/Ni-Cu/Ag and Al/Ni-Cu/Ag had better adhesion to the substrates than the two-layered-film of Ni-Cr/Ag. Besides, the tensile stress changed little after the treatment of soaking in water and drying, indicating the electrodes had stable performance.
Table 2. Linear expansion coefficient of different materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Linear expansion coefficient (10^-6/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTC ceramic</td>
<td>8.5</td>
</tr>
<tr>
<td>Ti</td>
<td>8.4</td>
</tr>
<tr>
<td>Al</td>
<td>23.22</td>
</tr>
<tr>
<td>Ni-Cr alloy (Ni80%Cr20%)</td>
<td>14</td>
</tr>
</tbody>
</table>

As shown in Table 2, except Al, the metals used as the bottom electrodes in the experiments had similar linear expansion coefficient as PTC ceramic, among which the linear expansion coefficient of Ti was the most closed to that of PTC ceramic, thus the smallest stress was yielded. Ti, Al rapidly formed a metal oxide film on the interface of the ceramic to prevent the metal from further oxidation, which was beneficial to the aging properties of the products. Another reason of good adhesion was that, the generated oxide metal films on the interface of the bottom electrodes and the PTC had strong bond strength and adhesion with both the metal as well as the ceramic.

3.3 Welding performance

In our experiments, sputtered films were tested with high-temperature welding experiments: the electrodes were placed in the 450°C lead-free soldering dip tank for 5 s and the process was repeated for 5 times, finally the weld was checked to see whether it was loose or broken, if not, then the electrodes were considered to pass this test. Experiment results indicated that both the films of Ti/Ni-Cu/Ag and Al/Ni-Cu/Ag passed 100% of the test, while NiCr/Ag passed only 40% of the test. Both films of Ti/Ni-Cu/Ag and Al/Ni-Cu/Ag were consisted of three layers. First, the bottom electrode of Ti, Al could form good adhesion to the ceramic, playing the role of transition layer. Second, the Ni-Cu alloy has low expansion coefficient and stable performance in high temperature, and it could resist the melting and corrosion of high-temperature welding metal. The last layer is Ag, which has good weldability, good oxidation resistance and it is miscible with solder, making it suitable for welding layer. That's why the three-layered-film had better welding performance than the two-layered-film.

3.4 Film properties under optimum conditions

Sputtering power, substrate-target distance and sputtering pressure have great influence on the properties of the deposited films. The optimum sputtering parameters in our experiment were as follows: the sputtering power was 20W cm^-2, substrate-target distance was 10cm, the Ar pressure was 0.5pa and the base pressure was 5 × 10^-3Pa.

Under the above conditions, the properties of Ti/Ni-Cu/Ag and Al/Ni-Cu/Ag were the best. The thickness and area of the electrodes also influence the properties of the electrodes, especially the bottom electrode must be thick enough to cover the roughness of the ceramic. Under the optimum sputtering parameters, when the thickness of the films are Ti (100nm) /Ni-Cu( 650nm ) /Ag( 200nm), Al (200nm) /Ni-Cu( 650nm ) /Ag ( 200nm ) respectively, good ohmic contacts were formed between PTC ceramics and electrodes, besides, the electrodes had good adhesion and welding performance.

Conclusion

Electrodes on BaCO₃-based PTC ceramic were prepared using DC magnetron sputtering, the following multilayered films demonstrate good performance: Ti /Ni-Cu/Ag, Al /Ni-Cu /Ag. Good ohmic contacts and strong adhesion could be formed between the metal films and PTC ceramics without heat treatment. Besides, the electrodes had good welding performance, able to withstand the high-temperature melting and corrosion of the soldering. In practical manufacturing, the cost of the targets of Al, Ti and NiCu is much cheaper than NiCr, which enables both kinds of electrodes more applicable in large scale production.

Reference:
[6] Xiong Xuan. The research of PTCR magnetron sputtering electrode and properties [MA]. Huazhong University of Science & Technology. 2006, 5: 24-26