MICROSTRUCTURAL STUDIES OF Ni-P THICK FILM RESISTOR TEMPERATURE SENSORS

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Thick Ni-P films have been widely investigated at our Institute. This article tends to visualize by use of various microscopic methods how the growth and sintering of individual conducting grains, results in the formation of nickel dendrites responsible for the metallic character of electrical conduction.

1. INTRODUCTION

Thick film resistors based on nickel-phosphor have been investigated for some years. The technology, electrical properties and structural constituents of these resistors were described in previous papers^{1,2,3,4,5}. In this paper we present the results of microstructural studies including elemental mapping. It was observed that the examined resistors had specific microstructures due to the more or less advanced sintered state of the conducting particles. Microscopic investigations combined with other published results allowed us to elucidate this temperature activated process during the firing.

2. EXPERIMENTAL METHODS

2.1. Characterization of samples

Samples investigated in this paper were produced from two ink compositions: 55 wt % Ni-P + 35 wt% glass + 10 wt% B₂O₃ and 40 wt% Ni-P + 50 wt% glass + 10 wt% B₂O₃. The pastes were printed on 96 % alumina substrates through 200 mesh stainless screens and fired in an air atmosphere, under typical conditions with peak firing temperatures of 650° and 800°C lasting for 10 minutes. These compositions and their firing temperatures were chosen after previous measurements^{1,3,5}. After firing at 650°C the films showed different sheet resistances. The samples containing 55 wt % Ni-P, identified later in the paper as 55-650, exhibited a sheet resistance equal to 5Ω/□ and a TCR equal to +3600 ppm/°C. The sample containing 40 wt % Ni-P, marked as 40-650, showed very high sheet resistance, greater than 30 MΩ/□. After firing at 800°C, both compositions, marked respectively as 40-800 and 55-800, had very low sheet resistances, about 0.2 Ω/□ and a very high TCR, +5700 ppm/°C. Since these films exhibited particular electrical properties they seemed interesting for microstructural investigations.

2.2. Microscopic methods

Using an optical microscope, a scanning electron microscope and an electron microprobe, natural, polished and chemically etched resistor surfaces were examined

FIGURE 1 Ion beam cutting method, a) cut parallel to the substrate surface, b) cut perpendicular to the substrate surface: IB – ion beam, E – screen edge, L – thick film layer, S – substrate, A – cut area, R – bombed region.

and observed. To investigate the inner structure, the sections of the thick film were prepared parallel and perpendicular to the substrate surface by mechanical methods, breaking, grinding, polishing, deep lapping; and by special ion beam cutting. The latter⁶ was employed to get parallel (a) or perpendicular (b) cuts through the layer-substrate-system (see Figure 1). An ion beam with high parallelity removed the material up to a border line projected by a very smooth edge of a screen. This section was observed by SEM with secondary and backscattered electrons. Elemental maps of Ni, P, Pb and Si for mechanically polished surfaces were made by electron microprobe.

3. EXPERIMENTAL RESULTS

Microscopic results are presented in the growing depth sequence of the structure revealed by various preparation methods. We start with a natural (or as-fired) surface, then we show a near surface region exposed by mechanical polishing or fine chemical etching. Finally we examine the inner structure after mechanical breaking, ion beam cutting or deep chemical etching.

3.1 *As-fired Surface of Resistors*

SEM photographs of as-fired surfaces allowed us to distinguish glass areas and conducting grains. Their distribution depends on the ink composition and its firing temperature. The 40–650 sample showed an electrical charging effect caused by the low concentration of the conducting particles forming clusters (Figure 2). In a low concentration region the clusters are less packed than in the region of the higher

FIGURE 2 40-650, natural surface, a) light charging regions on the dark no-charging background, b) charging region, c) no-charging region.

concentration. At the surfaces of the 55–650 and 40–800 samples (Figure 3a, b) are seen bright, tightly packed grains in the inner structure of which cluster forms are not observed. These bright grains seem to be more elongated after being fired at higher temperature. A very significant change was observed in the 55–800 sample (Figure 3c),

FIGURE 3 Natural surfaces, a) 55–650, b) 40–800, c) 55–800.

FIGURE 4 Polished surfaces, a) 55-650, b) 40-800, c) 55-800.

FIGURE 5 Optical pictures (reflection and transmission modes): a, b) 40-800; c, d) 55-800.

where, under higher concentration and higher firing temperature conditions, the individual grains were transformed into wide and large dendrites protruding from the surface.

3.2 Internal Structure of the Surface Region Revealed by Mechanical Polishing or Chemical Etching

Additional details have been revealed by mechanical polishing. If in the 55-650 sample (Figure 4a) only the initial arrangement of grains can be seen then the sintered grains tending to form bulk dendrites are observed in the 40-800 sample (Figure 4b). White charging spots in the regions devoid of the grains prove once more their conducting character. Bright polished dendrites of the 55-800 sample (Figure 4c) seem to contain different components.

Optical microscope pictures of the 40-800 (Figure 5a and 5b) and 55-800 (Figure 5c and 5d) samples confirmed the SEM results presented in Figure 4b and 4c. High reflectivity or deep absorption of the pure metal yields a strong contrast for conducting chains. In the case of 55-800 the chains reached a width of 10-20 μm . The formation of intergranular connections could be revealed if the glass phase was removed by chemical etching. The separate approximately 2 μm in diameter globular grains in the 40-650 sample (Figure 6a) form chains in the 40-800 sample (Figure 6b) due to sintering at a higher firing temperature.

3.3 Cross-sections by Mechanical Breaking, Ion Beam Cutting or Chemical Etching

Cross-sections made for 40-650, 55-650 and 40-800 samples show at the surface compact sheets of grains. Significant variations were observed solely in the volume

FIGURE 6 Chemically etched surfaces, a) 40-650, b) 40-800.

concentration of the grains. In the 40-650 sample (Figure 7a) the grains are uniformly dispersed throughout the volume. In the 55-650 sample (Figure 7b) distinct grains are present on the hole border whereas only a small volume concentration of grains can be seen in the 40-800 sample (Figure 7c and 7d).

3.4 Elemental Mapping

Large grains in the 55-800 sample enabled us to carry out an elemental mapping by

FIGURE 7 Cross-sections: a) 40-650, mechanical breaking and polishing; b) 55-650, ion beam cutting; c) 40-800, ion beam cutting; d) 40-800, chemical etching

FIGURE 8 55–800, a) polished surface analyzed by X-ray microprobe b) distribution of Ni, P, Pb and S after X-ray mapping

electron microprobe. The central region shown in Figure 5c was selected for investigation of the polished resistor surface. The SEM picture of this region is presented in Figure 8a. The distribution of Ni, P, Pb and Si based on the elemental maps is shown in Figure 8b. Pure Ni dendrites, which give a very sharp contrast in the optical microscope (Figure 5c), are connected with grains containing other investigated elements. Four different compositions are distinguished and described by arbitrary units giving 0, 1 and 2 concentration levels. Therefore in Figure 8b there are marked such areas as Ni2, P2Ni1Pb1, Pb2P1Si1 and Si2P1. These compositions are not complete because boron cannot be analysed by the electron microprobe. Figure 8b corresponds to the SEM picture shown in Figure 8a.

4. DISCUSSION

In the sample fired at 650°C one can distinguish globular grains of diameter 1–2 μm dispersed throughout the whole resistor volume and tightly packed at the surface (see Figures 3a, 6a, 7a). Their conducting properties (Figure 2) are due to the content of Ni and Ni₃P detected by X-ray diffraction.¹ X-ray patterns proved the increase of the intensity of the nickel line with increasing temperature of firing, ranging from 300 to 800°C, and the vanishing of the Ni₃P line at 700°C. The electrical properties of all investigated resistors depended on the stage of the conducting network development. Grains arrangements forming conducting paths or neck growth effects were not observed in the sample 50–650 (Figures 2 and 6a). Probably that was the reason why the sheet resistance exhibited by this sample was higher than 30 MΩ/□.

It has been stated that at a higher concentration of conducting particles in 55–650 sample, the sintering level at the same temperature was more advanced (Figure 3a, 4a).

Therefore, the sheet resistance of this sample being equal to 5Ω/□ it is much lower than that of the 40–650 sample. The former sample exhibits moreover the metallic conductivity (TCR equal to +3600 ppm/°C) while the 40–650 sample shows the hopping conductivity.³ The higher firing temperature of the 40–800 sample, even at a lower conducting medium concentration, leads to the necks growth comparable in

diameter to the grain dimension (Figure 4b, 5a, b; 6b). The higher concentration of the conducting medium and the higher firing temperature of the 55-800 sample result in growth of nickel dendrites width ranging within 10-20 μm . The dendrites which form the conducting network, are surrounded by other grains distinguished in the SEM photographs (Figure 4c). Compositions of these grains, estimated from elemental maps (see chapter 3.4) suggest dissolution of B_2O_3 and products of Ni and Ni_3P oxidation in the glass. The samples 40-800 and 55-800 have very low sheet resistances and the TCR is very similar to that of pure nickel. Such a pure metallic conductivity⁵ appears, probably, to be due to the advanced level of the sintering process and to the transfer of conducting grains from the resistor volume to its surface. This transfer direction, which may be caused by the surface tension, is proved by the various examination methods. Pictures taken in the transmission or reflection mode of an optical microscope correspond very well to each other (Figure 5a, b, c, d). X-ray diffraction patterns indicate the maximum intensity of the Ni line after firing at 800°C. Other evidence is given by the fact that the ohmic contact exists only when the conducting path is deposited on the resistor film.

5. CONCLUSIONS

Nickel phosphorous films prepared by using thick film technology have been examined by various microscopic methods, including optical microscopy, scanning electronic microscopy and electron microprobe analysis. It has been found that the preparation methods, including the sintering, results in the formation of nickel dendrites which are responsible for the metallic nature, including high positive temperature coefficient of resistance of the films.

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