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Electrical conductivity and thermal expansion coefficient of internal phases occurring in multilayer ceramic structures

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Abstract

The electrical conductivity and thermal expansion coefficients of interfacial phases, $PdPbO_2$, $PdBi_2O_4$, Pd(Pb), and Pd_3Pb, have been studied. The interfacial reactions form low conductivity products, which result in discontinuity of the internal electrode. Besides, due to the volume change associated with the interfacial phase formation and wide variation in thermal expansions, physical defects may occur at the electrode–ceramic interfaces during processing. © 2000 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

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1. Introduction

Silver, palladium, and solid solutions or mixtures of them are an important class of thick film conductors used in thick film hybrid microelectronic systems and as internal electrodes and end terminations for multilayer ceramic capacitors, transducers, varistors, actuators, chip carriers, etc. [1]. The proximity of the Ag/Pd metallization with surrounding components increases the potential for mechanical and chemical interactions during co-firing. Mechanical interactions include expansion and contraction due to oxidation/reduction of the Ag/Pd conductors, shrinkage mismatch during firing and different coefficients of thermal expansion during cooling and operation. Whereas, in a chemical interaction, the formation of undesirable phases at the interface and interdiffusion of components of the metallization and the dielectric are the major concerns. The influence of these interactions on the electrical performance are very important and must be carefully considered during the design [2].

Bi_2O_3 and lead oxides such as PbO are the two common constituents in thick film materials, multilayer ceramic capacitors, and other electronic ceramic components. Therefore, understanding the chemical and physical interaction of Ag/Pd and Bi_2O_3 and Ag/Pd and PbO during firing is very important for manufacturing reliable, high performance electronic ceramics [3,4]. Several studies have shown that the interaction between Pd and Bi_2O_3 results in the so-called "Bismuth reaction." Wang and Huebner have proposed the phase relations of Ag/Pd$-$$Bi_2O_3$ and Ag/Pd$-$PbO systems which indicate that $PdPbO_2$, $PdBi_2O_4$, Pd(Bi), Pd(Pb), and Pd_3Pb are the reaction phases [5–7]. The Pd(Bi) alloy exhibits maximum solubility of Bi at 16 at% and the Pd(Pb) exhibits maximum solubility of Pb at 14 at%. The formations of these phases indicate that not only will the electrical performance be changed, but it will also alter the physical and the mechanical integrity of the whole component. In the present study, the electrical and the thermal properties of these phases are determined. The data obtained are compared with those of internal electrodes (Pd and Ag) and dielectrics. The influence of the formation of these phases on the electrical, physical and mechanical integrity of the multilayer structure are discussed.

2. Experiment procedure

2.1. Sample preparation

For the preparation of $PdBi_2O_4$ and $PdPbO_2$, equal molar ratio of PdO and Bi_2O_3, and PdO and PbO, respectively, were mixed thoroughly in mortar and pestle.

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They were then calcined at 575°C for 48 h. Completion of the reactions was confirmed using XRD. The resulting $PdBi_2O_4$ and $PdPbO_2$ powders were mixed with 3 wt% PVA (10%) and then pelletized using uniaxial press. Since these phases are not stable at temperatures above 835°C, the pellets were densified using HIPing at 775°C under a flowing O_2. For the preparation of Pd_3Pb, Pd and Pb powders with molar ratio of three to one were mixed thoroughly in mortar and pestle. The mixture was pelletized using uniaxial press and then followed by heating at 1100°C for 2 h. The resulting pellet was confirmed as an intermetallic compound, Pd_3Pb, using XRD.

The Pd (14 at%Pb) solid solution was prepared from Pd and PbO powders. They were mixed together using mortar and pestle. The mixture was pelletized using uniaxial press and then followed by heating at 950°C for 24 h, in the presence of sacrificed phase (PbO). After polishing both the surfaces, the pellet was phase-checked using XRD.

2.2. Characterization

The conductivity measurement was performed using the four points probe method. All the samples have dimension $\phi \approx 10$ mm and $t \approx 3$ mm. Both the surfaces of the samples were polished and coated with silver paste as termination. While measurement was performed using Nano Volt/ Micro OHM Meter (HP 34420A) at 25°C.

The dimensional change of the samples with temperature was measured at a heating rate of 10°C/min from 25 to 800°C in flowing air with a computer-controlled Perkin–Elmer dilatometric analyzer. According to the data, thermal expansion of the samples were calculated.

3. Results and discussion

The electrical resistivity of $PdPbO_2$, $PdBi_2O_4$, Pd(Pb), and Pd_3Pb, obtained from the present study, compared with those of Ag, Pd and Pb, from the open literature [8], are listed in Table 1. From the table, it is seen that Pd(Pb) and Pd_3Pb have resistivity of 2.68×10^{-3} and 9.93×10^{-4} Ω-cm, respectively. $PdPbO_2$ and $PdBi_2O_4$ are semiconductors with electrical resistivity of 38 and 60 Ω-cm, respectively. The formation of these interfacial phases during firing could have dramatic impact on the electrical properties of MLCCs. These interfacial reactions not only result in discontinuity of internal electrode but also form low conductivity products. Both the factors increase the series resistance of the MLCCs and thus increase the dissipation factor (DF). Since DF value is reported to be an important factor which limits the active thickness reduction and thus the volume efficiency of MLCCs, it is necessary to avoid or reduce the interfacial reaction for the purpose of miniaturization of MLCCs. The formation of these interfacial phases indicates that not only the conductivity and melting temperature of the electrode shall be decreased ($T_m \approx 1197$°C for Pd(Pb) and $T_m \approx 2220$°C for Pd_3Pb) but, more importantly, the stoichiometry of the ceramic will be altered. The change in stoichiometry at the electrode-dielectric interface can significantly reduce the effective dielectric constant in capacitor and actuator applications.

The lattice parameters and thermal expansions of the $PdPbO_2$, $PdBi_2O_4$, Pd(Pb), and Pd_3Pb, obtained from the present study, compared with those of Ag, Pd and Pb, from the open literature [9], are indicated in Table 2. Based on the lattice parameters, it indicates that there is a swelling due to the volume change (density change) associated with the interfacial phases formation. This swelling will result in shrinkage mismatch during co-firing. Besides, due to wide variation in thermal expansion of electrode, ceramic and interfacial phases, inhomogeneous thermal stress may occur at the electrode–ceramic interfaces during co-firing and the subsequent heat cycling (such as term-fire and soldering). It will develop physical defects (such as microcrack and delamination) at the electrode–metal interfaces and thus reduce the adhesion between metal and ceramic.

Table 1
Electrical conductivity of materials

Metal	Melting temperature Decompose temperature (°C)	Electrical conductivity (Ω-cm, 298 K)
Ag	961	1.59×10^{-6a}
Pd	1825	10.8×10^{-6a}
Pb	327	20.65×10^{-6a}
Pd(Pb)	1197	2.68×10^{-3}
Pd_3Pb	1220	9.93×10^{-4}
$PdBi_2O_4$	835	38
$PdPbO_2$	835	60

[a] Data obtained from Refs. 8 and 9.

Table 2
Lattice parameters and thermal expansions of materials

Metal	Lattice parameter (Å)	Thermal expansion coefficient (1/K)
Ag	4.0857 (cubic)	19.2×10^{-6a}
Pd	3.8839 (cubic)	11.2×10^{-6a}
Pd(Pb)	3.963 (cubic)	12.8×10^{-6}
Pd_3Pb	4.024 (cubic)	13.9×10^{-6}
$PdBi_2O_4$	$a=8.62$ $c=5.89$(Tetragonal)	2.5×10^{-6}
$PdPbO_2$	$a=10.90$ $c=4.65$(Hexagonal)	3.4×10^{-6}

[a] Data obtained from Refs. 8 and 9.

4. Summary

The electrical and thermal properties of interfacial phases, $PdPbO_2$, $PdBi_2O_4$, Pd(Pb), and Pd_3Pb, were determined. The interfacial reactions result in discontinuity of internal electrode and form low conductivity products. They increase the series resistance of the MLCCs and also raise the dissipation factor (DF). Besides, due to the volume change associated with the interfacial phase formation and wide variation in thermal expansion of electrode, ceramic and interfacial phases, physical defects (such as microcrack and delamination) may occur at the electrode–ceramic interfaces during co-firing and the subsequent heat cycling).

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