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Electrical contact properties at the interface between PTCR (positive temperature coefficient of resistance) ceramics and various electrodes suitable for a co-firing process

Jun-Kwang Song[a], Hyun-Gyoo Shin[a], Yong-Nam Kim[a], Min-Seok Jeon[a], Jin-Sook Lee[b] and Hee-Soo Lee[c,]*

[a]*Material Testing Team, Korea Testing Laboratory, Seoul 152-848, Korea*
[b]*Department of Chemistry, Yonsei University, Seoul 120-749, Korea*
[c]*School of Materials Science & Engineering, Pusan National University, Busan 609-735, Korea*

The electrical contact behavior between various electrodes(Ag, Ni, Au-Ti alloy) and PTCR ceramics was evaluated by a complex impedance analysis and an equivalent circuit conception. PTCR ceramics with ohmic-Ag and Ni electrodes exhibited a very low resistance in normal conditions. Ohmic-Ag and Ni were inappropriate for internal electrodes because ohmic-Ag vaporized above 1,000 °C and Ni oxidized above 400 °C. Au-Ti electrodes were deposited on the surface of PTCR ceramics by a sputtering method and the Au containing 3.00 wt% and 19.56 wt% of Ti showed non-ohmic contact behavior, while the Au containing 5.73 wt%, 10.84 wt% and 13.95 wt% of Ti showed ohmic contact and these Au-Ti electrodes exhibited good thermal stability up to 1300 °C.

Key words: PTCR ceramics, Inner electrode, Ohmic contact, Co-firing.

Introduction

Ceramics with a positive temperature coefficient of resistance (PTCR) based on barium titanate ($BaTiO_3$) are important functional materials that have found various applications such as degaussing components in color TVs, starters for motors and compressors, overload protectors, thermal sensors and self-regulating heaters [1-3]. Their use in overload protection has attracted more attention than other applications as they help to enhance the safety and reliability of electrical and electronic products [4-6]. Hence, the demand for PTCR materials has increased markedly in recent years. With the rapid development of computer, mobile telecommunication and automobile technologies, PTCR ceramics are facing challenges of lower the room temperature resistivity and smaller size for their applications at low voltages [6, 7].

In most cases of multilayered ceramic devices, noble metals such as Au, Pt and Pd have been used as internal electrodes. These noble metals cannot be used as an internal electrode for PTCR ceramics due to the non-ohmic contact between electrodes and PTCR ceramics [8]. Seiter et al. [9], reported that the contact resistance was closely related to the oxidation of the metallic electrode. Many research activities on electrodes forming ohmic contact electrodes with $BaTiO_3$-based PTCR ceramics have been carried out and the general trend indicated that metals with a large affinity for oxygen tended to yield ohmic contacts (e.g., Zn, Fe, Sn, Ni and Cd). However, these metal electrodes are not suitable for internal electrodes for multilayered PTCR ceramics because of low melting temperature or high oxidizing properties [9-12].

In this study, PTCR ceramics were prepared using several electrodes which have a possibility of being internal electrodes (Ni, Ag, Au-Ti alloy). The electrical and contact properties of the PTCR specimens were examined by a complex impedance analysis and as equivalent circuit concept. Then, the relative importance between the candidate metals was evaluated especially in view of their application possibilities as internal electrode for a co-firing process.

*Corresponding author:
Tel : +82-51-510-2388
Fax: +82-51-512-0528
E-mail: heesoo@pusan.ac.kr

Experimental Procedure

$BaTiO_3$-based PTCR ceramics were prepared by solid state reactions of powder mixtures. The $BaTiO_3$ powder was admixed with contents of 3.5 mol% Sb_2O_3, 0.02 mol% MnO_2 and 1.5 mol% SiO_2. The powder was prepared by wet ball milling for 24 h and calcining at 1100 °C for 2 h. The calcined powders were ground and admixed with a 5 wt% PVA binder, and pressed at 100 MPa. The green bodies were sintered at 1230 °C for 1 h in an ambient atmosphere after burning out the binder at 400 °C for 2 h. The resistance at room temperature and the PTCR effect ($\log(R_{max}/R_{min})$) of PTCR ceramics were 11.6 Ω and 3.95, respectively.

Metal electrodes were formed by a sputtering method to identify contact properties and co-fireability of electrode candidates such as Ni, Ag and Au-Ti alloys. According to the phase diagram [13], Au-Ti alloy compositions were designed to be different Ti contents with 3 wt%, 5.73 wt%, 10.84 wt%, 13.94 wt% and 19.56 wt% and were deposited on one side of the PTCR ceramics using a DC sputtering system. The as-deposited samples were heated at 1230 °C for 1 h in an ambient atmosphere and In-Ga electrodes were treated as a standard electrode on the other side.

The thermal stability of the electrode was measured using TG-DTA up to 1300 °C. The temperature dependence of the resistance was measured in the temperature range from 20 to 150 °C with a rate of 1.5 $Kmin^{-1}$. Current-voltage (I-V) characteristics were measured using a source-measure unit (Keithely 237). Complex impedance was measured by an impedance analyzer (HP4194A) in the frequency range from 100 Hz to 40 MHz under an oscillating voltage of 10 mV.

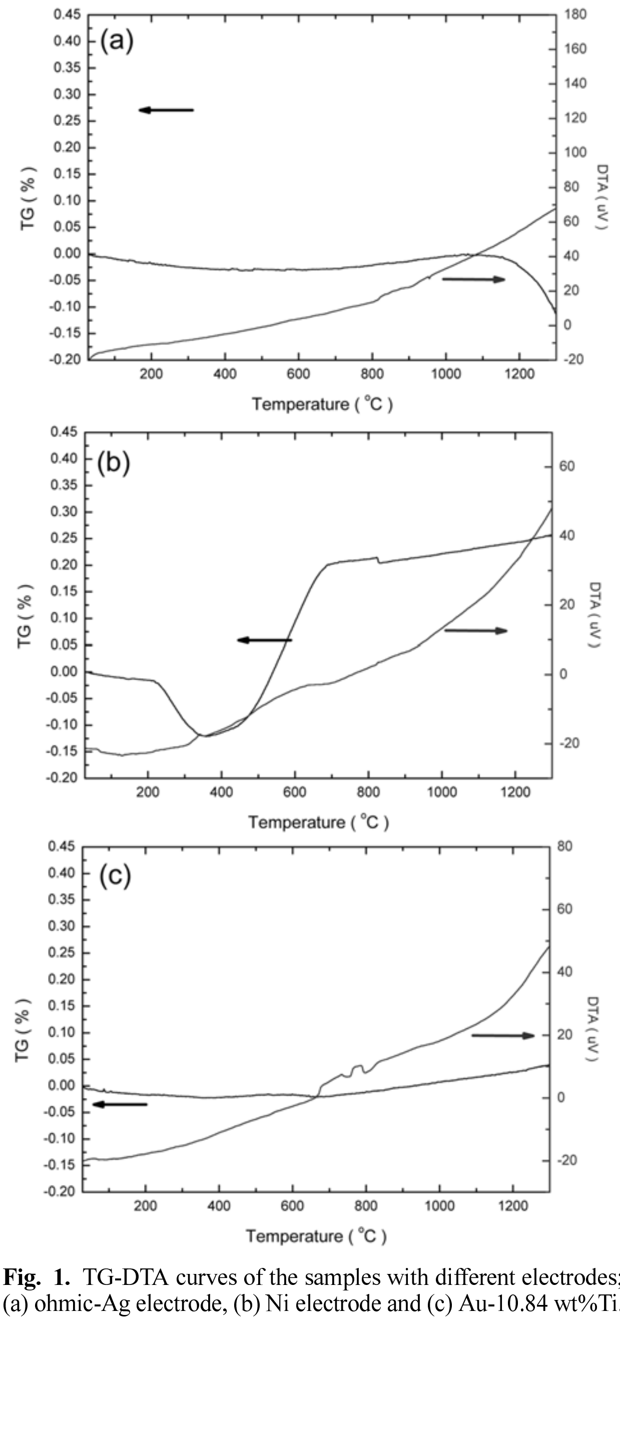

Fig. 1. TG-DTA curves of the samples with different electrodes; (a) ohmic-Ag electrode, (b) Ni electrode and (c) Au-10.84 wt%Ti.

Results and Discussion

It is known that metal for inner electrodes of multi-layered components should not be melted, oxidized and volatilized during firing [14]. To estimate the thermal behavior during co-firing with the PTCR ceramics, three types of electrodes (ohmic-Ag, Ni, Au-Ti) which have the possibility of good contact resistance were analyzed by TG-DTA Fig. 1. Ohmic-Ag represented mass reduction owing to volatilization after heating at 1100 °C, and Ni electrodes showed mass increase due to oxidation after heating at 400 °C. As a result, Ni electrode as an inner electrode should in particular be fired in a reducing atmosphere. Therefore, the Ni electrodes are not suitable as inner electrodes because the reducing atmosphere lowers the potential barrier of grain boundaries and the PTCR effect [5, 14]. As opposed to this case, Au-Ti electrodes were stable up to the sintering temperature of 1230 °C. Considering its stability at high temperature, the Au-Ti electrode was suggested to be applicable as a promising inner electrode.

Au-Ti electrodes were fabricated by a sputtering method containing different Ti contents of 3.00, 5.73, 10.84, 13.95 and 19.56 wt%. These were deposited on the PTCR ceramics and heated at 1230 °C. From the results of the XRD patterns, it was found that Au-Ti electrodes were all Au-Ti alloys without metal oxides such as titanium dioxide. Thus these electrodes are suitable as inner electrodes considering the co-firing with PTCR ceramics.

Figure 2 shows the resistance-versus-temperature curves

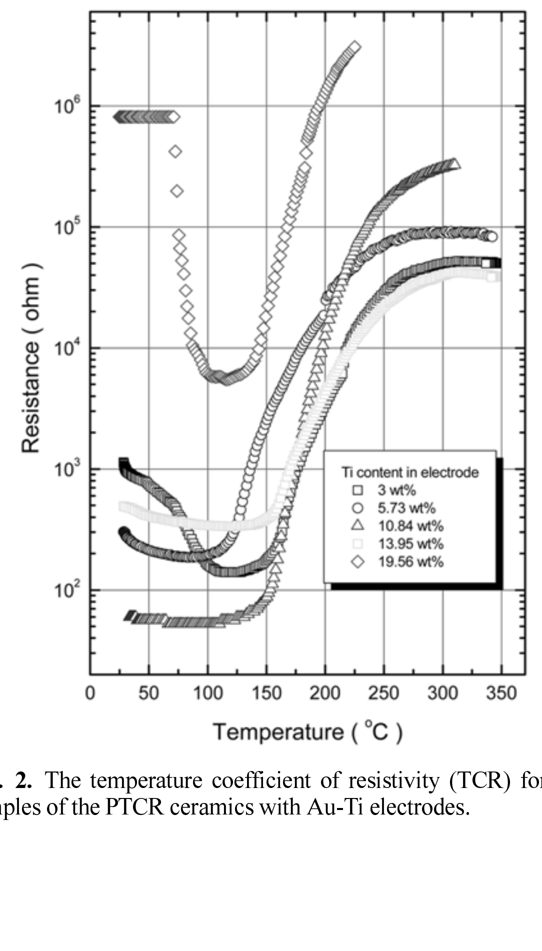

Fig. 2. The temperature coefficient of resistivity (TCR) for the samples of the PTCR ceramics with Au-Ti electrodes.

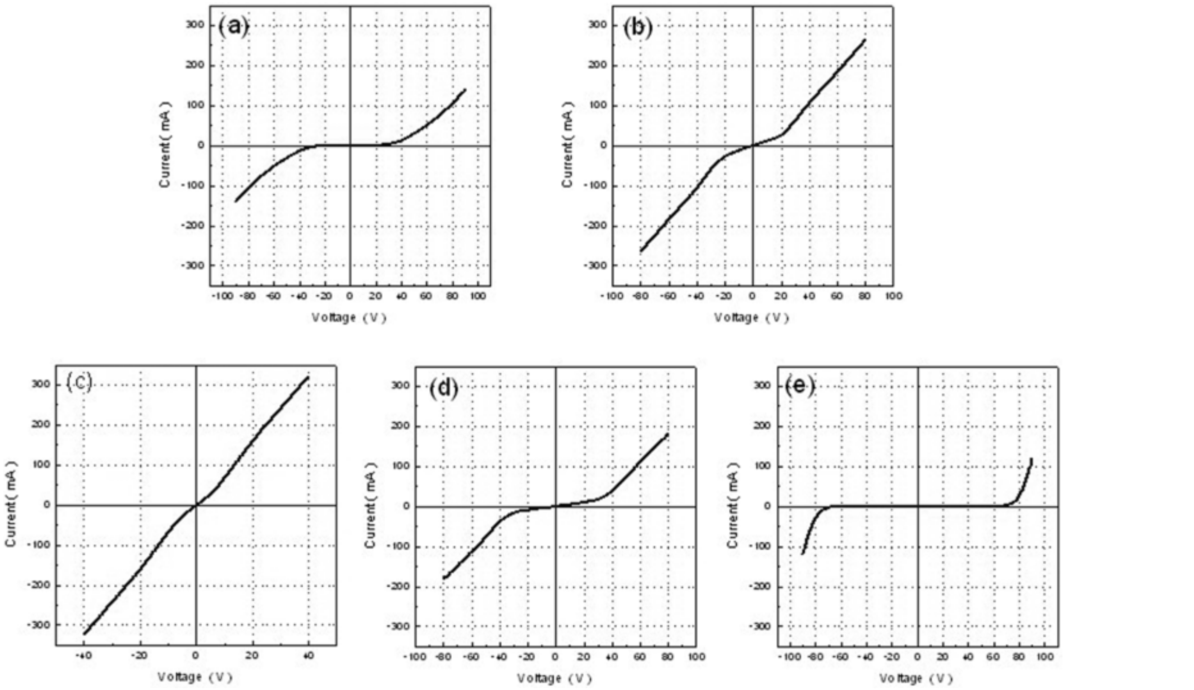

Fig. 3. I-V characteristics of the PTCR ceramics with Au-Ti electrodes; (a) 3.00 wt%Ti, (b) 5.73 wt%Ti, (c) 10.84 wt%Ti, (d) 13.95 wt%Ti and (e) 19.56 wt%Ti.

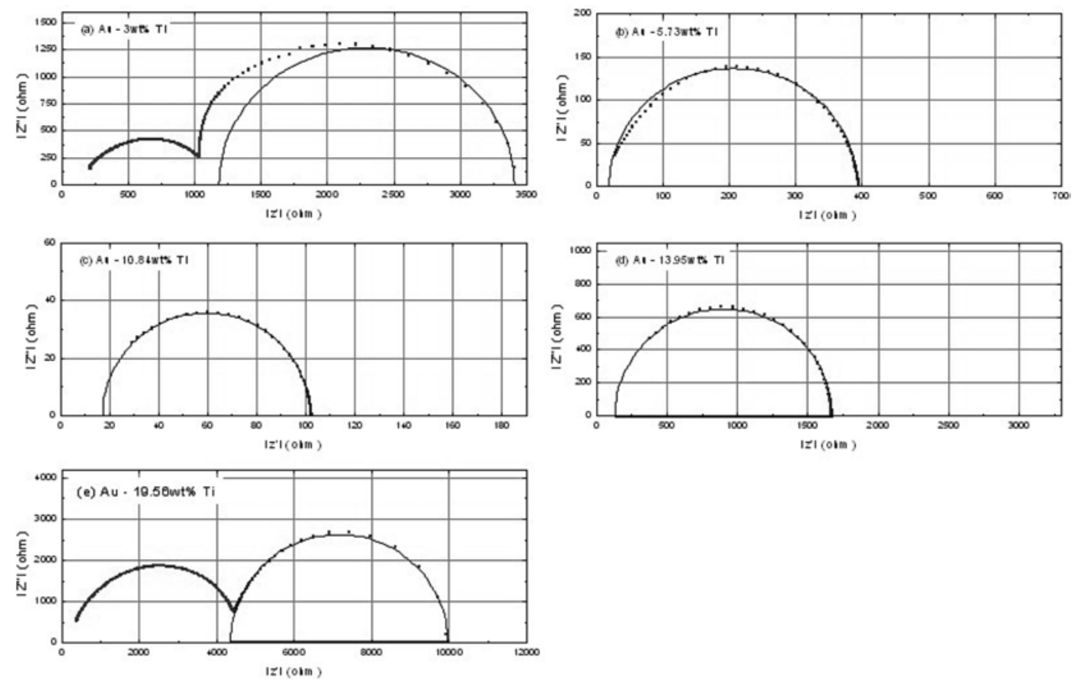

Fig. 4. Complex impedance spectra of the PTCR ceramics with different Au-Ti electrodes; (a) Au-3.00 wt%Ti, (b) Au-5.73 wt%Ti, (c) Au-10.84 wt%Ti, (d) Au-13.95 wt%Ti and (e) Au-19.56 wt%Ti.

of the PTCR ceramics with Au-Ti electrodes. All samples showed that the resistance increased above 120 °C. The PTCR effect of Au-10.84 wt%Ti exhibited the highest value of 3.77 and this value was slightly lower than that of the reference sample. Up to 120 °C the resistances of all samples decreased with a temperature increase. It could be considered that the decrease of gap work-function caused the contact resistance of the electrode. A rapid increase of resistance was observed above this temperature, where it was considered that the self-resistance of the PTCR ceramics was higher than the contact resistance.

The electrodes of 3.00 and 19.56 wt% Ti-content were found to be non-ohmic as evidenced by both current-voltage plots Fig. 3(a) and (e) and complex impedance spectra

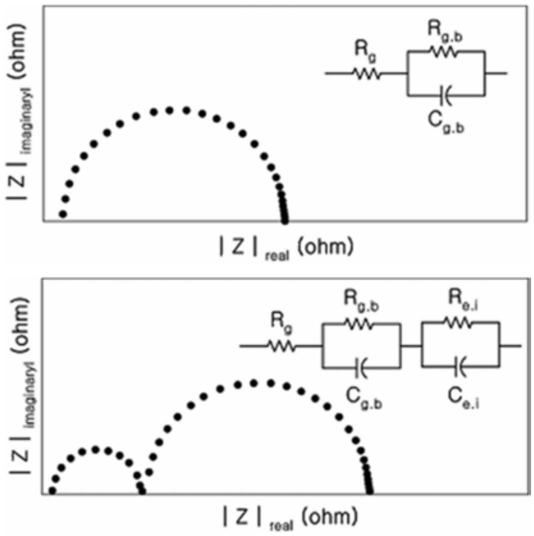

Fig. 5. Equivalent electrical circuit models and impedance spectra of the $BaTiO_3$-based PTCR ceramics; (a) ohmic contact and (b) non-ohmic contact.

Fig. 4 (a) and (e). In the current-voltage plots, rapid increases of current (the varistor characteristics) were observed above the threshold voltage. In the impedance measurements, the data exhibited a double semicircular shape characteristic of the circuit pictured in Fig. 5(b). In the equivalent circuit [15], the resistance R_g is the intrinsic resistance of the grain interiors, the elements $R_{g,b}$ and $C_{g,b}$ are the intrinsic values associated with the grain boundary resistance and capacitance, and the elements $R_{e,i}$ and $C_{e,i}$ are representative of the contact resistance and capacitance indicative of a Schottky barrier present at the electrode-semiconductor interface. The In-Ga electrode was found to show ohmic contact with only one semicircle appearing in the impedance plots [16]. The impedance data for 5.73, 10.84 and 19.56 wt% Ti-contents are shown in Fig. 4(b), (c) and (d). These data exhibited only one semicircle, indicating that the equivalent circuit for ohmic contact is applicable Fig. 5(a). Further evidence of ohmic contact was observed in the current-voltage measurements shown in Fig. 3 (b), (c) and (d).

Conclusions

The behaviors of the PTCR ceramics containing various electrodes such as ohmic-Ag, Ni and Au-Ti systems were investigated to observe the contact properties and co-fireability with the PTCR ceramics. Ohmic-Ag and Ni turned out to be not suitable for an inner electrode for the $BaTiO_3$-based PTCR ceramics sintered at 1230 °C because ohmic-Ag was volatilized above 1000 °C and Ni electrodes were oxidized above 400 °C. In accordance with these results, newly-designed electrodes were suggested as an alternative to ohmic-Ag and Ni electrodes. The electrical contact properties of Au-Ti electrodes were evaluated using complex impedance analysis and the equivalent circuit concept. These electrodes were stable until the sintering temperature of the $BaTiO_3$-based PTCR ceramics, and some showed ohmic contact behavior. As an optimized composition from the Au-Ti system electrodes, the PTCR effect and room temperature resistance of Au-10.84 wt%Ti electrode represented excellent values of 3.77 and 124 Ω, respectively.

Acknowledgments

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