



Structural Model of Ni/Graphite/BaTiO₃ Composites

JUAN DU*

Freescale Semiconductor (China), No. 15, Xing hua Ave, Xiqing Economic Development Area, Tianjin, China

YUANFANG QU & WEIBING MA

Key Laboratory for Advanced Ceramics and Machining Technology of Ministry of Education, Tianjin University, 300072

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Abstract. Ni/graphite/BaTiO₃ composites are fabricated by adding Ni and graphite powders into BaTiO₃ calcined powder to achieve low room-temperature resistivity and better PTC effect. The resistivity of the composites reduced greatly with the increase of Ni, but the PTC effect deteriorates accordingly. The resistivity reduced slightly with the increase of graphite as it was less than 0.5 wt%, however it rose greatly after the graphite content exceeded 0.5 wt%, the graphite content had an optimum in this experiment. From the experimental results and regularities obtained, a structural model of the composites is proposed in this article. By employing this model the electrical properties and PTC effect of the composites can be explained properly.

Keywords: composites, PTC (positive temperature coefficient), structural model, Ni (nickel), graphite

1. Introduction

Donor-doped BaTiO₃ ceramics with a positive temperature coefficient resistance (PTCR) effect have been used widely in electronic industry since the PTC effect was discovered in 1951, such as starters for motors and compressors, over-current protectors, over-temperature sensors and self-regulating heaters. However with the rapid development in electronic technology, the relatively high room-temperature resistance of this material has become one of the obstacles for the applications at low voltage [1–4]. Therefore, reducing the room-temperature resistance of BaTiO₃ PTCR ceramics is becoming more and more crucial recently. Traditional methods of reducing the resistance of BaTiO₃ ceramics include optimizing the prescriptions, adopting high-purity raw materials, modulating the processing conditions and so on. But now it faces a choke point to employ these methods. More and more researchers begin to look for new approaches to lower the resistance. So organic PTCR materials and metallic oxide PTCR materials are fabricated and they perform

good properties, but the stability and reproducibility of these materials are not as good as that of the BaTiO₃-based ceramics [5].

In our experiments, by adding Ni and graphite powders into BaTiO₃ ceramics, Ni/graphite/BaTiO₃ composites are manufactured in local reductive atmosphere. The composites have low room-temperature resistivity and the PTC effect suffices for use. Electrical properties of the composites are discussed in this article. On the basis of experimental results and regularities obtained, a structural model of the composites is proposed. Both the electrical and PTC properties of the composites can be explained by this structural model.

2. Experimental Details

The *n*-typed semiconducting BaTiO₃ PTCR ceramics were fabricated by traditional technology. BaCO₃, SrTiO₃ and TiO₂ acted as starting materials, Sb₂O₃ and Nb₂O₅ as donors. The starting materials were calcined at 1050°C for 2 h, followed by mixing with AST (1/3Al₂O₃:3/4SiO₂:1/4TiO₂), MnO₂ (to achieve higher resistance change) homogeneously in agate planetary ball mills for 6 h and drying.

*To whom all correspondence should be addressed.

Ni/graphite/BaTiO₃ composites were prepared by adding Ni and graphite powders into dried BaTiO₃ matrix obtained above. Disk-shaped samples of the dimensions $\Phi = 12$ mm $h = 2$ mm were pressed under 300 MPa and sintered in local reductive atmosphere. (Samples were placed in an Al₂O₃ crucible by adding enough graphite powder in it, and the device was sintered in the air at 1230°C for 20 minutes. As the oxidation of graphite consumed the oxygen in the stove during the sintering process, the local reductive atmosphere was thus produced.) Resistances of the samples were measured by WQJ-1 multimeter. Microstructures of the composites were observed in Philips XL-30 scanning electron microscope (SEM), and some samples were examined by energy dispersion spectroscopy (EDS) and X-ray diffraction (XRD).

3. Results and Discussion

3.1. Experimental Results

In our experiments, Ni content ranges from 5 to 40 wt% and graphite content ranges from 0.1 to 3.0 wt%. Table 1 shows the room-temperature resistivity (ρ_{25}), the maximum resistivity (ρ_{\max}) and PTC effect (ρ_{\max}/ρ_{25}) of as-sintered samples with different Ni and graphite content. The room-temperature resistivity decreases sharply with the increase of Ni, but the graphite content has an optimal value at 0.5 wt% when the resistivity of sample is lowest.

PTC effect deteriorates when more Ni is added into BaTiO₃ matrix as is shown in Table 1. The composites have a slight resistance jump after Curie temperature when the Ni content exceeds 30 wt%.

Table 1. Electrical properties of as-sintered samples.

Sample	Nickel content/ wt%	Graphite content/ wt%	$\rho_{25}/$ $\Omega\cdot\text{cm}$	$\rho_{\max}/$ $\Omega\cdot\text{cm}$	ρ_{\max}/ρ_{25}
1	0	0	349	1.73×10^7	4.97×10^4
2	10	0.5	12.9	8.14×10^3	6.31×10^2
3	20	0.5	6.57	1.19×10^3	1.81×10^2
4	30	0.5	2.76	36.9	1.34×10
5	40	0.5	0.26	0.3	—
6	15	0.1	29.3	1.46×10^4	4.98×10^2
7	15	0.3	19.3	1.05×10^4	5.42×10^2
8	15	0.5	8.25	3.23×10^3	3.91×10^2
9	15	0.7	10.5	4.18×10^3	3.96×10^2
9	15	1.0	14.8	4.62×10^3	3.11×10^2
10	15	2.0	55.7	2.79×10^4	5.01×10^2
11	15	3.0	106	3.02×10^4	2.85×10^2

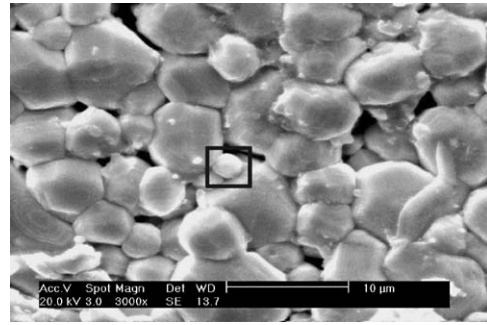


Fig. 1. SEM image of sample 2.

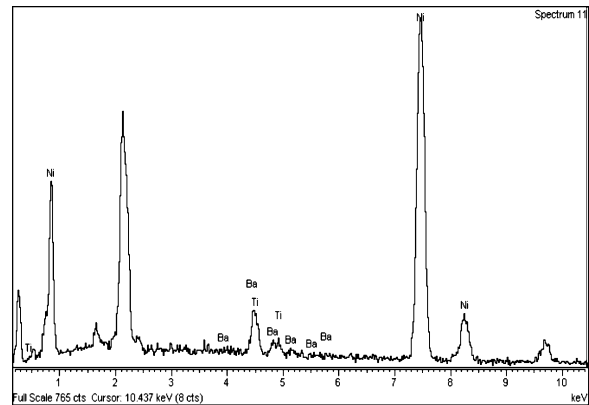


Fig. 2. EDS spectrum of the particle in the black square.

Figure 1 shows the SEM image of sample 2. The particle in the black square is Ni which is located on the grain-boundaries of BaTiO₃ ceramics. EDS analysis of the particle is given in Fig. 2. It indicates that the main ingredient of the particle is Ni instead of NiO.

3.2. Structural Model

The bulk resistivity of BaTiO₃ ceramics is composed of resistivities of grain and grain-boundary. The bulk resistivity is determined by that of the grain-boundary because the resistivity of grain is low. After adding Ni, the co-function of Ni and BaTiO₃ ceramics should be considered. Ni is metallic crystal and the resistivity is extremely low which can be neglected, but the BaTiO₃ ceramics is polycrystal. Ni powder stays on the grain-boundaries and will form electronic channels on these grain-boundaries. The baffle force to prevent electrons from moving freely decreases and mobility (μ) of electrons in the bulk increases accordingly. In addition, the contact between Ni and ceramics is ohmic contact [6];

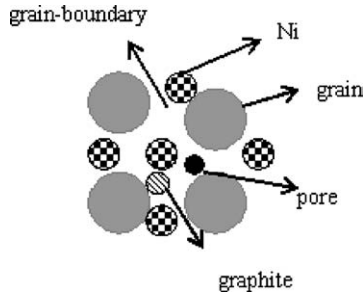


Fig. 3. Structural model of Ni/graphite/BaTiO₃ composites.

the total electron density (n) in the bulk also augments because electrons flow from Ni particles to BaTiO₃ ceramics through the interface. Thus conductivity of the composites increases according to Eq. (1); it is to say that resistivity of the composites decreases. The more Ni is added, the more electronic channels are formed and the higher the electron density is, thereby the resistivity reduces greatly with the increase of Ni content.

$$\sigma = ne\mu \tag{1}$$

The structural model of the composite is shown in Fig. 3. The grain is n -type semiconducting grain, and Ni is located on the grain-boundary. There is an acceptor state caused by the oxygen atoms adsorbed on the

grain-boundary. The pore is caused by the oxidation of graphite which is discussed subsequently in this article.

As far as we know, PTC effect is related to both the ferroelectric-paraelectric phase transition and the potential barrier of grain-boundary [7–8]. Below the Curie temperature the potential barrier is low because the acceptor state is compensated by spontaneous polarization; it will rise greatly as the spontaneous polarization disappears after the measuring temperature exceeds the Curie temperature. The resistivity undergoes a great change as a result of the heightening of the barrier.

In addition, according to the classical theory of semiconductor, the acceptor state caused by oxygen atoms on the grain-boundaries absorbs electrons from the ceramics by polarizing them. As electrons are bounded up around oxygen atoms, the carriers on the ceramic surface reduce and the space-charge region is formed which cause a high potential barrier on the grain-boundaries. After Ni is added, electrons flow from Ni particles to the grain-boundaries because of the ohmic contact between Ni and ceramics and recombine with the space-charge. This recombination process is described in Fig. 4. In the end the electron recombination between ceramics and Ni arrives at a dynamic equilibrium and the acceptor state density falls due to the compensation of the electrons; subsequently the potential barrier declines. This is described in Fig. 5. ϕ is the barrier height of BaTiO₃ ceramics.

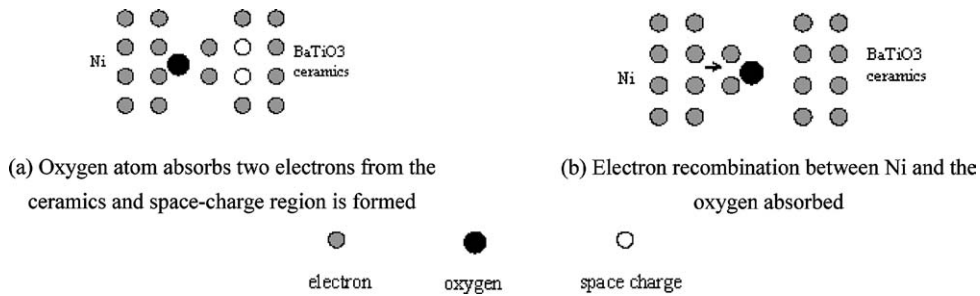


Fig. 4. Electron recombination between Ni and the grain-boundary of the ceramics.

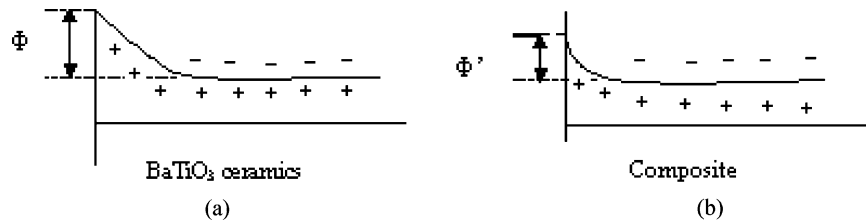


Fig. 5. Potential height on the grain-boundary of the BaTiO₃ ceramics (a) and composite (b).

ϕ' is the barrier height after the acceptor state is compensated by electron combination; the electron combination has such a great effect on the potential barrier that ϕ' is lower than ϕ . Spontaneous polarization will disappear above the Curie temperature but the electron combination remains, thus the potential barrier can not recover to the height equivalent to that of BaTiO₃ ceramics caused solely by the acceptor state. Therefore the maximum resistivity (ρ_{\max}) of the composites is much lower than that of BaTiO₃ ceramics; it is resulted in a reduction of the rate of ρ_{\max}/ρ_{25} . In a word, the co-function of Ni and BaTiO₃ ceramics is ascribed to the deterioration of PTC effect.

Graphite particles can also form electronic channels, but the conductive capacity is not as good as that of Ni. It plays another more important role to protect Ni particles from being oxidized during the sintering process.

In the bulk of the samples, Ni particles have chance to touch graphite particles as is shown in the structural model of Fig. 3. When Ni is oxidized to NiO, the reaction below will take place,



thus Ni particles with better conductive capacity are protected by consuming graphite. Figure 6 shows the XRD patterns of sample 6 (no graphite added) and sample 8 (0.5 wt% graphite added). There is a NiO peak observed in XRD pattern of sample 6, but the NiO peak is invisible in XRD patterns of sample 8. It shows that Ni is prevented from being oxidized in samples with proper content of graphite.

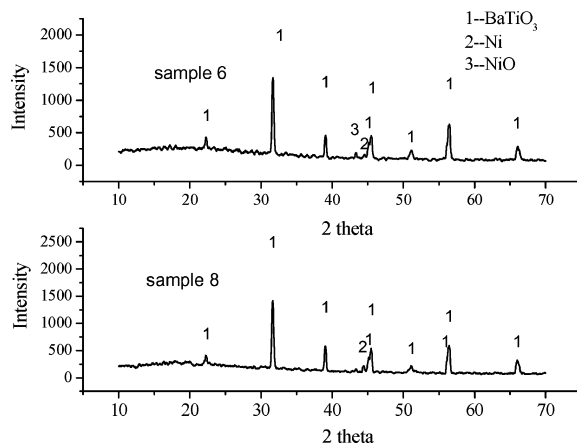


Fig. 6. XRD patterns of samples 6 and 8.

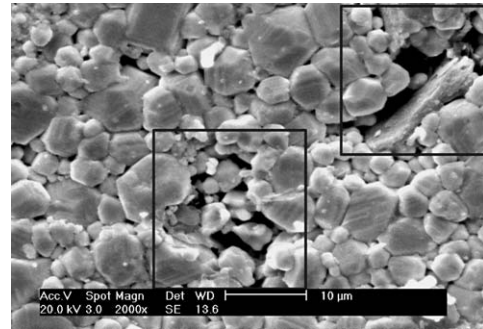


Fig. 7. SEM image of sample 11.

But the resistivity will rise evidently if overdose of graphite is added into the composites, as is attributed to the high resistivity of the pores formed by the oxidation of graphite at high temperature [9]. The pores are described in Fig. 3. Graphite will react with oxygen directly if the graphite content is high. Because the heating rate is rather high in the sintering process, CO₂ gas generated can not spill over the samples rapidly. Therefore a lot of pores will be left in the bulk or on the surface. The resistivity of pore is much higher than that of the grain-boundaries, thus the total resistivity of sample rises. Figure 7 is a SEM image of the pores on the surface of sample 11. The regions in the black square are pores.

4. Conclusions

Ni/graphite/BaTiO₃ composites are fabricated by adding Ni and graphite powders into BaTiO₃ ceramics. The room-temperature resistivity of the composites is much lower than the prototype ceramics and PTC effect is suitable for use. Electronic channels will be formed to reduce the baffle force of electron movement, and the ohmic contact between Ni and ceramics will reduce the resistivity of the grain-boundaries, so the bulk resistivity at the room temperature decreases with the increase of Ni. However, the potential barrier also decreases as the electrons compensate the acceptor state caused by the oxygen atoms on the grain-boundaries; the maximum resistivity (ρ_{\max}) above the Curie temperature reduces accordingly. Therefore the magnitude of resistivity changes diminishes to some extent. Graphite added will prevent the oxidation of Ni, but a lot of pores will be produced in the bulk with overdose of graphite so that the resistivity of the composites increases subsequently.

So the graphite content has an optimal value in our experiments. The structural model proposed in this paper can be applied to explain the electrical properties and PTC effect of the composites.

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