Experimental Evaluation of a Phenomenological Model for the Positive Temperature Coefficient Resistance in BaTiO$_3$-type Ceramics

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1. Introduction

Although the positive temperature coefficient resistance (PTCR) effect in BaTiO$_3$ is discovered in the fifties, the relation between the processing and the PTCR properties is still not yet well understood. To clarify this relation a phenomenological model is proposed. The model is based on the assumption that the PTCR-behavior is mainly governed by the acceptor state density, $N_s$, at the grain boundaries and the energy difference, $E_s$, between the conduction band and the energy level of the acceptor trap. This is also assumed in the well accepted Heywang-model. The difference between this new model and the Heywang model lies in the fact that the Heywang model explains the relation between the resistivity behavior and the parameters $N_s$ and $E_s$, while the new model clarifies the relation between the production procedure and the above mentioned parameters. Also experimental evidence for this model will be explained and it will be shown that smaller acceptor additions and longer oxidation time lead to improved PTCR-properties.

2. The Proposed Phenomenological Model

The proposed phenomenological model for acceptor doped PTCR ceramics, is based on a model proposed by Ueoka [1]. He assumed that there is an acceptor enriched region at the grain boundaries. The acceptors, usually Mn, which are in the 2+ oxidation state during sintering, oxidize during cooling to Mn$^{3+}$ or Mn$^{4+}$. The oxidation is caused by the diffusion of double charged oxygen vacancies towards the grain boundary. As Mn$^{2+}$ does not cause an electron trap no PTCR is observed after quenching from the sintering temperature. Ueoka did not specify whether the Mn was in the 3+ or the 4+ oxidation state. Recently the present authors have found that $E_s$ increased after oxidation at high P$_{O_2}$ or after long annealing [2]. The rise in $E_s$ was attributed to the oxidation of Mn to its 4+ oxidation state. Based on this finding the authors proposed the following schematic PTCR-chart, see figure 1. Figure 1a shows a PTCR-chart for a small concentration of acceptor dopant, [M$_A$]. It can be seen that the acceptor state density, $N_s$, increases with increasing oxidation time. The bottom half of the figure shows the relation between the acceptor state
density, \( N_s \), and the maximum resistivity, \( \rho_{\text{max}} \), and the minimum resistivity, \( \rho_{\text{min}} \). The relation between \( \rho_{\text{min}} \) and \( N_s \), which is discussed in detail in reference 3, will not be explained here. It can be shown by using the equations proposed by Heywang [4,5] that in the graph \( N_s \) vs \( \rho_{\text{max}} \), the lines for higher \( E_s \) lie above the lines for lower \( E_s \). Therefore the line for \( M^{4+} \) lies above the line \( M^{3+} \). During oxidation the points \( (N_s,\rho_{\text{max}}) \) lie on the \( 3+ \) line but when all \( M^{2+} \) is oxidized to \( M^{3+} \), \( M^{3+} \) is further oxidized to \( M^{4+} \) and the points \( (N_s,\rho_{\text{max}}) \), lie on the \( 4+ \) line. Figure 1b shows the PTCR chart for a higher acceptor concentration. One can see that the jump from \( 3+ \) to \( 4+ \) is shifted to higher \( N_s \). Figure 1c shows the PTCR chart for an even higher acceptor concentration. It can be seen that the \( 4+ \) line is not reached, because of the high concentration of \( M^{2+} \). By comparing the figure 1a, b, and c it is clear that the oxidation rate increases with increasing acceptor concentration. This is due to the fact that the oxygen vacancy concentration increases with increasing acceptor concentration.

3. Experimental

BaTiO\(_3\) powder (UBE) was ball milled for 16 h with 0.15 mol\% Sb\(_2\)O\(_3\), 1 mol\% Al\(_2\)O\(_3\), 1 mol\% TiO\(_2\), and 1.5 mol\% Si\(_2\) using Al\(_2\)O\(_3\) balls and deionized water. After drying the powder was mixed with the appropriate amount of Mn(NO\(_3\))\(_6\)\(\cdot\)H\(_2\)O solution in order to obtain 0.02 mol\% Mn. The mixing was done using a magnetic stirrer. After drying, the powder was calcined at 750°C for 4 h. The calcined powder was sieved and subsequently uniaxially pressed (47 MPa) in 2 gram pellets with a diameter of 20 mm. The samples were placed on a bed of powder presintered at 1360°C for 1 h. Sintering and annealing took place in a tube furnace. The samples were heated at 20°C/min up to 1330°C. Sintering time was 1 h. After sintering the samples were cooled to 1183°C, and annealed for 0 to 64 h.

After annealing the samples were furnace cooled to room temperature. The resistance temperature characteristics were measured after In-Ga electroding using a computer controlled 2 probe technique. The complex impedance was measured using a Hewlett-Packard 4192A-LF Impedance Analyzer in the range 5 Hz-13 MHz.

4. Results and Discussion

The intragrain resistivity, \( \rho_g \), obtained from complex impedance measurements, was about 9 \( \Omega \)cm for all the samples. The charge carrier density, \( N_d \), was obtained using the following equation:

\[
N_d = \frac{1}{\rho g \mu e}
\]  

(4)

where \( \mu \) is the mobility of the electrons (0.5 cm\(^2\)V\(^{-1}\)s\(^{-1}\) [5,6]), and \( e \) is the electron charge. Using equation 4, \( N_d \) was 1.39x10\(^{24}\) m\(^{-3}\). Using \( C=1.5x10^5 \) K and \( \theta=383 \) K, \( N_s \) is obtained from \( S_{\text{arth}} \), minus the slope in the reciprocal temperature plot log \( \rho \) vs 1/T in the region from low \( \rho \) to high \( \rho \). Until trapped electrons start to jump to the conduction band this slope is constant and can be expressed by the following
Figure 1. Proposed PTCR-charts for 3 different acceptor concentrations, $M_A$, $M_B$, and $M_C$ ($M_A < M_B < M_C$) Remark that the oxidation rate increases with increasing acceptor concentration and that the jump from the 3+ to the 4+ line shifts to higher $N_s$. From this figure it is clear that not only the acceptor state concentration should be optimized but also the oxidation time.
Calculation of $N_s$ for samples annealed for 0, 1 and 3 h was not possible due to the broad peak and consequently small linear region. The exact reason why there is no distinct linear region is still unclear, but it might be caused by shallow electron traps (i.e. traps with a small $E_s$).

Figure 2 shows the PTCR-chart for these materials. It is clear that at first $N_s$ increase quickly with time, but it then reaches a plateau at about $N_s=7\times10^{17}$ m$^{-2}$. After this plateau $N_s$ increases once again with time. $\rho_{\text{max}}$ increases with increasing $N_s$. $\rho_{50}$ is constant until about $6\times10^{17}$ m$^{-2}$ and starts to rise above this value. It is clear that for higher $N_s$ the increase in $\rho_{50}$ is faster than the increase in $\rho_{\text{max}}$, thereby decreasing the height of the resistivity jump.

The data shown in figure 3 are in agreement with this model. It is not very clear if there is an increase in $E_s$, although it seems there is an increase at about $7\times10^{17}$ m$^{-2}$. To obtain exclusion about this, calculations using the Heywang model are necessary. At this stage these calculations are not yet available, therefore the increase in $N_s$ is not very clear.

5. References