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REDOX PROCESSES AT THE GRAIN BOUNDARY IN BARIUM TITANATE BASED POLYCRYSTALLINE FERROELECTRICS-SEMICONDUCTORS

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Barium-titanate, which is characterized by positive temperature coefficient of resistance (PTCR), is widely used in practice. At the same time, it is unknown why only a small percentage of the introduced donor dopant takes part in the formation of PTCR effect, what phases appear at the grain boundary, how the introduced acceptor dopants affect the properties of grains. Elucidation of the above questions is of a considerable scientific and practical interest.
It has been shown that the phases $Ba_6Ti_{17}O_{40}$ and $Y_2Ti_2O_7$ precipitate on grains of barium titanate doped with donor dopant (yttrium). We identified paramagnetic impurities (iron, manganese, chromium) in starting reagents. These impurities can occupy titanium sites. When yttrium ions are partly substituted for barium ions, electroneutrality persists through the transitions $Mn^{4+}\rightarrow Mn^{2+}$, $Mn^{3+}\rightarrow Mn^{2+}$, $Cr^{4+}\rightarrow Cr^{3+}$, $Fe^{3+}\rightarrow Fe^{2+}$. Therefore, the part of the donor dopant that is spent on the charge exchange of acceptor dopants does not participate in the charge exchange of titanium $Ti^{4+}\rightarrow Ti^{3+}$, which is responsible for the appearance of PTCR effect in barium titanate. It has been found that extra acceptor dopant (manganese) is distributed mainly at grain boundaries and in the grain outer layer.

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GRAIN BOUNDARY PASSIVATION WITH ALUMINA IN ZnO-BASED VARISTORS

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We study the effects of Al_2O_3 on the grain boundary electronic structure of ZnO-based varistors. Alumina is known to passivate the electrical activity of grain boundaries in polycrystalline silicon, but no reason for this effect has been found up to now. We find a similar effect in ZnO-based polycrystalline materials, and we find that the passivation is really a grain boundary effect, and not related to an increase of the conductivity of the bulk material. Addition of excess alumina causes interface electronic states to disappear below the grain boundary Fermi level, hence hampering the electrical activity of the grain boundary. Charge transport through these type of electrically active interfaces is thus favoured by alumina addition due to a purely interface electronic-structure related effect.