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"Two Step" Varistor Action observed at the ZnO(Co)-ZnO(Co) Homojunction

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Zinc oxide (ZnO) single crystals heavily doped with CoO are prepared by the vapor reaction method using the reaction of vaporized $ZnCl_2$ and $CoCl_2$ with water vapor at 1150°C. In some cases, a CoO doped ZnO crystal (ZnO(Co) crystal) is non-epitaxially grown on the surface of another ZnO(Co) crystal and the ZnO(Co)-ZnO(Co) homojunction is formed between two crystals. Such a type of the homojunction shows pronounced nonlinearity with negative resistance in its current-voltage (I-V) characteristics. Moreover, it has a novel function, so called "two-step" varistor action. It is suggested that the first step varistor action is thought to be the "real" breakdown, which is occurred due to the fusion of the potential barrier at the boundary region. The second step varistor action is suggested to be due to the change in the bulk resistance of the ZnO(Co) crystals as a function of the enhanced surface temperature by self-heating under the current stress. The mutual interaction between the bulk and boundary properties is the origin of such the novel function, "two-step" varistor action observed at the ZnO(Co)-ZnO(Co) homojunction.

Key words: Zinc oxide, Cobalt oxide, Varistor action, Self-heating, PTC

1. INTRODUCTION

A lot of kind of functional ceramics or electroceramics, including varistors, PTC theirmistors, superconductors, sensors, or others, have been ruled out and some of them had already been commercially available. Most of the functional ceramics are made by polycrystalline solids and in some cases, grain boundaries play an important role for their novel functions. Zinc oxide (ZnO) varistors have been regarded as prototype of the functional ceramics and they are still an interesting objective for research and development. Research works on the characterization of the non-ohmic grain boundary are still in progress and some important results on the grain boundary electronic structure have been obtained[1-3].

For the evaluation of the grain boundary phenomena such as varistor action, fabrication and its electrical characterization of a simple model of grain boundaries are thought to be attractive methods. Several kinds of model interfaces of ZnO varistors are fabricated and their electrical properties are characterized[4,5]. The authors had been trying to fabricate a simple model of the grain boundary of ZnO polycrystalline (ZnO-ZnO homojunction) by the traditional vapor reaction method and its electrical properties were evaluated[6,7]. Without varistor forming constituents, some model interfaces show pronounced nonlinear I-V characteristics. In addition, some model interface shows novel properties which can never been observed at polycrystalline ZnO or ZnO varistors. For example, the temperature coefficient of the apparent resistivity of the ZnO-ZnO homojunction is dramatically changed as a function of applied current or voltage and its application to thermistor type IR detectors is suggested[8]. In the present study, a model interface of the grain boundary of ZnO polycrystalline (ZnO-ZnO homojunction) is prepared by the vapor reaction method and the effect of CoO doping on its I-V characteristics is discussed. Novel varistor action, i.e. two-step varistor action, is observed at the ZnO-ZnO homojunction by heavy doping of CoO to ZnO crystals.

2. EXPERIMENTAL PROCEDURE

Zinc oxide single crystals are obtained through the pyrolysis of zinc chloride ($ZnCl_2$) and cobalt chloride ($CoCl_2$) in the mixture of steam and oxygen at 1150°C. Apparatus for the crystal growth is similar to that designed by Takahashi et.al.[9] and we added a vessel for Co source in the reactor. The experimental setup for the preparation of the ZnO single crystals doped with Co is shown in Figure 1. The weight ratio of Zn source ($ZnCl_2$) and Co source ($CoCl_2$) is fixed at 900 : 1 and the vessel for Zn and Co source is heated at 560°C and 700°C, respectively. After the 12hrs reaction, ZnO single crystals are produced on the top of the inner tube of the reactor and the obtained crystals are colored green due to CoO doping. Zinc oxide crystals tend to grow to c⊥ direction rather than c// in this experimental condition and the cross sectional areas of the plates are indexed as polar surface of ZnO. Cobalt oxide (CoO) doped zinc oxide crystals with single boundary (ZnO(Co)-ZnO(Co) homojunction) are fractionated from the inadvertently aggregated CoO doped ZnO crystals, which are grown on the top of the inner tube of the reactor. The fractionated ZnO(Co)-ZnO(Co) homojunctions are annealed at 800°C for 2 hours in air for the oxidation of the boundary region. Figure 2a shows schematic illustrations of the prepared ZnO(Co)-ZnO(Co) homojunctions in the present study. Three types of homojunctions are prepared and a type c specimen is used for the electrical characterization. A photograph of a typical example of type c specimens is also shown in Figure2b. Current-scan four probe method is conducted for the measurement of the current-voltage (I-V) characteristics of the specimen.

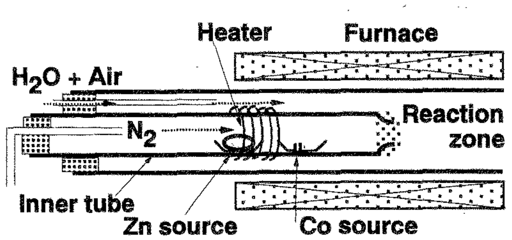

Figure 1 Experimental apparatus for the preparation of the ZnO(Co)-ZnO(Co) homojunctions.

For the electroding, platinum wires are attached to the ZnO(Co) crystals by indium powder dispersed silver conducting pasts (Degussa Co., No. 61900781) and the current and potential probes are attached on each side of the boundary. The I-V characteristics of each specimen is measured by stepping up the current at the range of 0- ±120mA by using a programmable dc standard (HIOKI, Model 7005-01) and potential drop at the boundary region is monitored by a digital multimeter(ADVANTEST, Model TR2114 H).

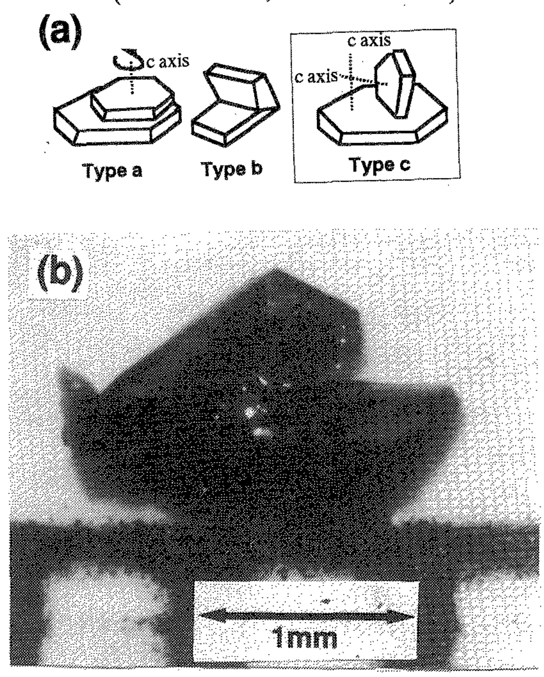

Figure 2 (a)Schematic illustrations of the prepared Zn(Co)-ZnO(Co) homojunctions. (b) The photograph of the CoO doped ZnO bicrystal, which is classified to the Type c specimen.

3. RESULTS AND DISCUSSIONS

Obtained ZnO single crystals are colored green due to the cobalt ion doping. Similar to the case with the non-doped ZnO crystals, they well grow to the c⊥ direction [9] and marked suppression or acceleration on the growth rate is not performed by CoO doping. Different from the case with non-doped ZnO-ZnO homojunctions [6,7], most of the ZnO(Co)-ZnO(Co) homojunction specimens show nonlinear I-V characteristics because added CoO works as a varistor forming constituent. A variety of the I-V characteristics are experimentally obtained, however their nonlinearity in I-V characteristics hardly depend on their macroscopic boundary structures. Therefore, some specimens, whose macroscopic boundary structure is in Figure 2b show pronounced nonlinear I-V characteristics with negative resistance. In the case of non-doped ZnO-ZnO homojunctions, the specimens whose macroscopic boundary structure is similar to the specimen in Figure2b, also tend to show pronounce nonlinear I-V characteristics with large α value. In such specimens, non-polar plane of a ZnO crystal is joined to the polar of another ZnO crystal with an angle of 45 –90° and forms a "polar-nonpolar" boundary.

Figure 3 shows the I-V characteristics of the ZnO(Co)-ZnO(Co) homojunction, whose macroscopic boundary structure is similar to that shown in Figure 2b. It shows two step varistor action, whose breakdown voltages are 4 - 4.5V (step 1) and 5V over (step 2). Moreover, at around the applied current of ±60mA, negative resistance is observed and the hysteresis in I-V characteristics is also observed. Different from ZnO varistors (Polycrystalline ZnO doped with Bi_2O_3,CoO, Mn_2O_3 or others additives), the increase in the surface temperature due to the self-heating of the boundary and near boundary region play an important role for the generation of the nonlinear properties in its I-V characteristics[7]. The relation between the applied current and the surface temperature of the near boundary region of the ZnO(Co)/ZnO(Co) homojunction is shown in Figure 4.

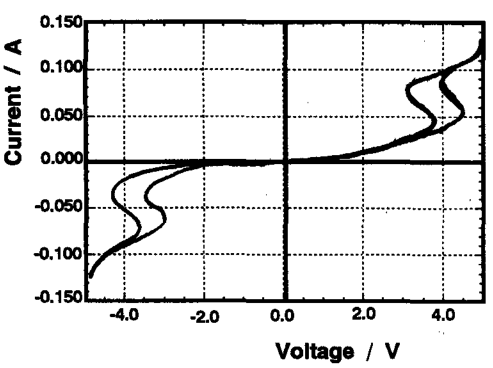

Figure 3 The I-V curve of the ZnO(Co)-ZnO(Co) homojunction (Type c) measured at room temperature.

Surface temperature of the specimen gradually increases with an increase in the applied current and when the applied current is set at over 100mA, the surface temperature becomes over 300°C. In the case of the non-doped ZnO/ZnO homojunctions, rapid enhance in the surface temperature is thought to be the origin of the pronounced nonlinear I-V characteristics with negative resistance[7] and similar effect is expected in the ZnO(Co)-ZnO(Co) homojunctions. Such the characteristic "step" like I-V response, which had never been observed at the non-doped ZnO-ZnO homojunctions or ZnO varistors, is observed at the ZnO(Co)-ZnO(Co) homojunctions and more discussion will be needed for explaining such the novel I-V response shown in Figure 3.

Figure 5 shows the temperature dependence of (a)the resistance (c⊥ direction) of a CoO doped ZnO single crystals (ZnO(Co)) and (b)the apparent resistance of the ZnO(Co)-ZnO(Co) heterocontact measured at the applied current of 0.1mA. Measured at sufficiently low applied current, the enhancement of the surface temperature by self-heating need not to be considered as is shown in Figure 4. The resistance of a CoO doped ZnO single crystal shows positive temperature coefficient (PTC) characteristics and it gradually increases with an increase in the ambient temperature, while the apparent resistance of the homojunction specimen shows weak negative temperature coefficient (NTC) characteristics (Figure 5b). From these results, the junction properties of the ZnO(Co)-ZnO(Co) homojunction shows NTC characteristics, while that of ZnO(Co) bulk shows PTC characteristics. After the first step breakdown at around 4.5 – 5 V, the larger current flows due to the fusion of the potential barrier at the boundary region. By the applying larger current to the boundary, the surface temperature is enhanced more and more by self-heating, then the resistance of ZnO(Co) bulk increases. Increase in the resistance of ZnO(Co) bulk would inhibit the current flow through the boundary, then the decline of the I-V curve gradually decreases after the first breakdown is occurred. The "step" like I-V characteristics observed at the ZnO(Co)-ZnO(Co) homojunction is thought to be due to the self-control of the resistivity by PTC characteristics of the ZnO(Co) bulk. When the over 100mA of current is applied to the junction, the second step "breakdown" is occurred and the decline of the I-V curve increases gradually again. The origin of the second step "breakdown-like" characteristics has not fully understood yet. However, the possible reason which causes the enhancement of the apparent electric conductivity at higher current region may be attributed to the increase in the carriers activated from extrinsic donor states introduced by CoO doping. The electric conduction mechanisms of CoO doped ZnO are discussed previously and creation of a narrow band as the electronic states of the dopant overlap are suggested. This would be the origin of the enhancement of the high temperature electric conduction of CoO doped ZnO ceramics.[10] As shown in Figure 5b, temperature coefficient of the resistivity is close to be 1 at over 250°C and that would be due to the contribution of thermally activated carriers from the extrinsic narrow band to the total electric conduction of CoO doped ZnO bulk. Two-step varistor action is only observed at the boundary between polar and nonpolar plane in CoO doped ZnO crystals. From the result of Figure 3, the varistor action of the ZnO(Co)-ZnO(Co) homojunction is apparently two step process. It is suggested that first step varistor action is thought to be due to the "real" breakdown at the boundary region and that of second step is suggested to be due to the decrease in the bulk resistance of the CoO heavily doped ZnO crystal.

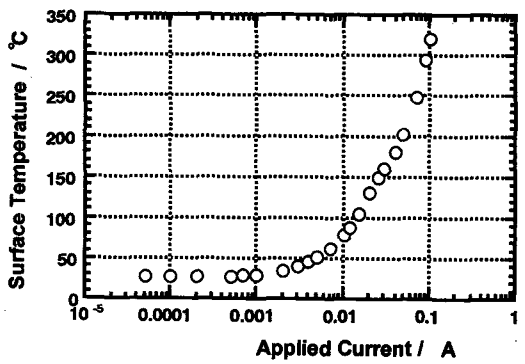

Figure 4 Surface temperature of the near boundary region of the ZnO(Co)-ZnO(Co) homojunction (Type c) as a function of applied current.

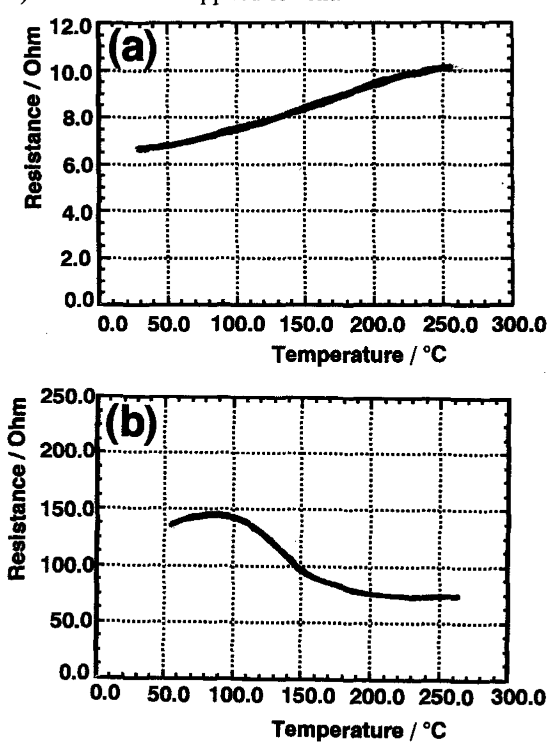

Figure 5 Temperature dependence of (a) the resistance of the CoO doped ZnO single crystal ZnO(Co) and (b) the apparent resistance of the ZnO(Co)-ZnO(Co) homojunction (Type c). The applied current is fixed at 0.1mA.

4. CONCLUSIONS

A novel function, "two step" varistor action is observed at the ZnO(Co)-ZnO(Co) homojunction which is made by the vapor reaction method. First step breakdown is suggested to be "real" breakdown and it would be due to the fusion of the potential barrier at the boundary region accompanied by the rapid increase in the surface temperature by self-heating. The second step is suggested to not to be due to the decrease in the apparent resistivity of the boundary but decrease in the resistivity of ZnO(Co) bulk. The ZnO(Co)-ZnO(Co) homojunction shows NTC characteristics, while that of ZnO(Co) bulk shows PTC characteristics. The mutual interaction between the bulk and boundary properties is the origin of such the novel function, "two-step" varistor action observer at the ZnO(Co)-ZnO(Co) homojunction.

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