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Electronic interface states at grain boundaries in ZnO:Pr varistors by single grain boundary measurements

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Abstract

Electronic interface states at grain boundaries in ZnO:Pr varistors were directly observed by single grain boundary measurement. Photo-capacitance spectroscopy and photo-isothermal capacitance transient spectroscopy(photo-ICTS) were applied to these experiments. Photo-capacitance spectrum in the near infrared region showed a peak at 1380 nm, i.e. 0.9 eV. Since this peak is originated by electron excitation from the interface states at the grain boundary, the energy for this peak indicates that the electronic states at the grain boundaries are located at 0.9 eV below the top of the double Schottky barrier. This result is the direct evidence which shows the value of the energy level of the interface states in ZnO varistors. Moreover the ICTS peak shifted to shorter range by the irradiation of 1380 nm light. The photo-intensity change of ICTS peaks revealed the linear relation between emission rate of the interface states and the light intensity.

Keywords: Electrical properties; Varistors; ZnO

1. Introduction

Electrical properties of ceramic semiconductors are strongly dependent on the double Schottky barriers (DSBs) formed at grain boundaries in the ceramic semiconductors.[1] Since a DSB is built by electrons trapped by the interface states at the grain boundary, it is important to characterize the electronic states in order to investigate their electrical properties. Isothermal capacitance transient spectroscopy (ICTS) has been reported to clarify the electronic characteristics of grain boundaries in zinc oxide varistors.[2–4] In this paper, the direct photo-capacitance and photo-ICTS measurements of single grain boundaries using micro-electrodes will be reported and the quantitative relation between the light intensity and the emission rate will be discussed.

2. Experiment

Samples were prepared by ordinary ceramic processes. For measurements of single grain boundaries, micro-electrodes were provided using photolithography technique. There were 72 pairs of electrodes on this pattern. The tips of the electrodes were 5 μm wide. The distance between a pair of electrodes was 10 μm. The grain boundaries which ran between a pair of micro-electrodes were confirmed by using an optical microscope. An SEM photograph of a single grain junction and micro-electrodes is shown in Fig. 1. For photo-capacitance and photo-ICTS measurements, an apparatus shown in Fig. 2 was used. The detailed description of the apparatus and the theory of ICTS measurement were reported in a previous paper.[5] Photo-capacitance or photo-ICTS measurements were carried out under irradiation of monochromated light on the surface of the sample.

3. Results and discussions

3.1. Photo-capacitance measurement

In a previous paper,[5] two peaks at 700 nm (1.8 eV) and 500 nm (2.5 eV) were found in photo-capacitance spectrum of a single grain boundary as shown in Fig. 3. When the light was irradiated on the sample, junction capacitance changed by emission or capture of

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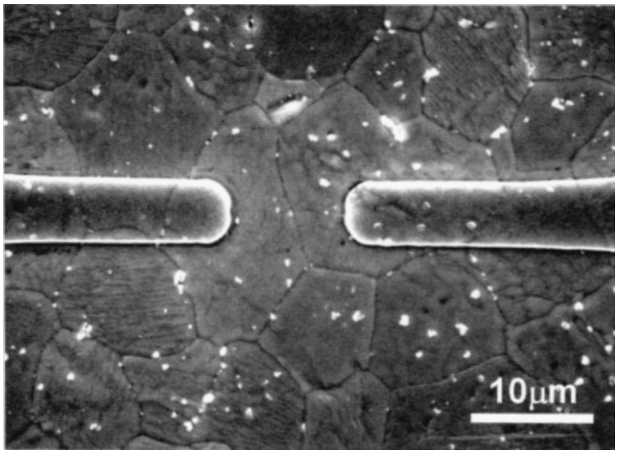

Fig. 1. SEM photograph of micro electrodes.

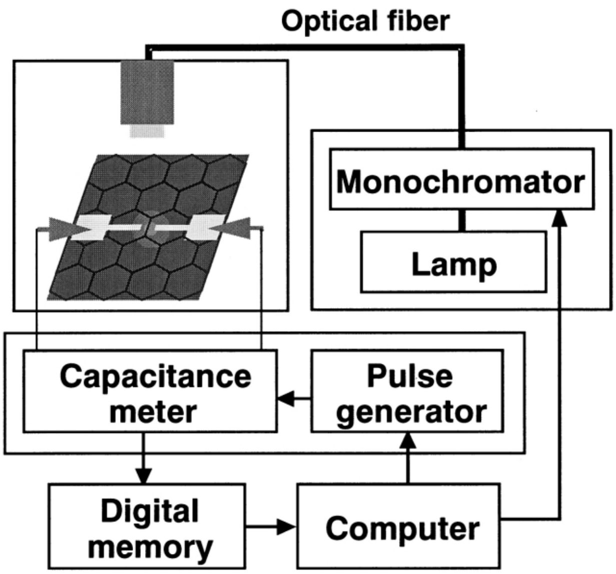

Fig. 2. Block diagram of photo-ICTS measurement.

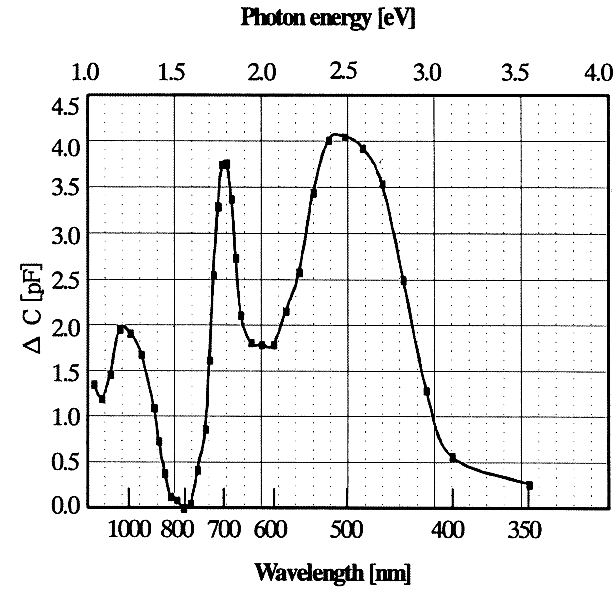

Fig. 3. Photo-capacitance spectrum for single grain boundary by visible light.

electrons. Junction capacitance increased when the electrons captured at electronic states were emitted to conduction band. Therefore, the capacitance increase in Fig. 3 implies that certain trap levels exist at energies below the conduction band edge. These two levels were supposed to be the intrinsic defect level of zinc oxide or the cobalt impurity level. For example, oxygen defect levels were reported to be located at 1.8 eV[6] and cobalt impurity levels were reported to be located at 2 eV[7] below the conduction band. Although there seemed to be a weak peak below 800 nm in Fig. 3, the reliability of this peak was very low because of the low intensity of the irradiated light and the poor accuracy of the wavelength in this area. Therefore, in the present work, the behavior in the near infrared region between 730 nm (1.7 eV) and 1770 nm (0.7 eV) was examined using a near infrared source. This area is important for ZnO varistors since the energy at these wavelengths corresponds to that of the interface states at the grain boundaries. In the photo-capacitance spectrum for a single grain boundary in a ZnO–Pr–Co varistor only a slight increase in capacitance was found. However, this result should be corrected considering the light absorption of the source by the optical guide. The correction was carried out by normalizing the relative capacitance increase by the light intensity. The normalized result revealed a sharp peak at 1380 nm (0.9 eV) as shown in Fig. 4. This peak should be attributed to the electron emission from the interface states at grain boundaries. The peak position at 0.9 eV should be regarded as the direct evidence that the interface states is located at 0.9 eV below the top of the DSB.

3.2. Photo-ICTS measurement

In addition to the photo-capacitance measurement, photo-ICTS spectra were also obtained under irradiation of 1380 nm light. Fig. 5 is the dark-ICTS spectra over the temperature range 60–100°C. The peak shifted to shorter time with increasing temperature because of the thermal relaxation of the captured electrons at the interface states. The emission rate of the electrons from the interface states were obtained by the peak position of Fig. 5. From the obtained values of the emission rate, Fig. 6 was obtained as the Arrhenius plot of $\left(e_n/T^2\right)$. The slope of the line in Fig. 6 gave 0.9 eV which corresponded the location of the interface states below the top of the DSB.

Fig. 7 shows the observed photo-ICTS spectra under irradiation of 1380nm. The intensity of irradiated light was changed by optical filter. Peaks in Fig. 7 shifted to shorter time with increasing light intensity. This phenomenon is interpreted as the electron emission from the interface states being accelerated by the absorption of 1380nm light. The relation between the emission rate and the intensity of the light can be expressed by the following equation.

$$e_n = e_{\text{opt}} + e_{\text{therm}} = \frac{\sigma_n^o}{h\nu}\Phi + e_{\text{therm}} \tag{1}$$

where e_{opt} and e_{therm} are the emission rates of the optical and thermal relaxation processes respectively, σ_n^o is the optical cross section of the interface states and h is Plank's constant, ν is the frequency of the light, and Φ is the intensity of the light. When we plot the emission rate obtained from Fig. 7 as a function of light intensity, Fig. 8 was obtained. A linear relation was found in accordance with Eq. (1). The optical cross section was also obtained as 2.3×10^{-14} cm^2. Values of σ_n^o for three trap levels are listed in Table 1. Since the value of σ_n^o for the level at 0.9 eV is 1–2 orders of magnitude higher than those for the other two levels, the origin of the interface states at 0.9 eV should be different from the other two levels. This result suggests the interface states are originated from chemisorbed oxygen ion.

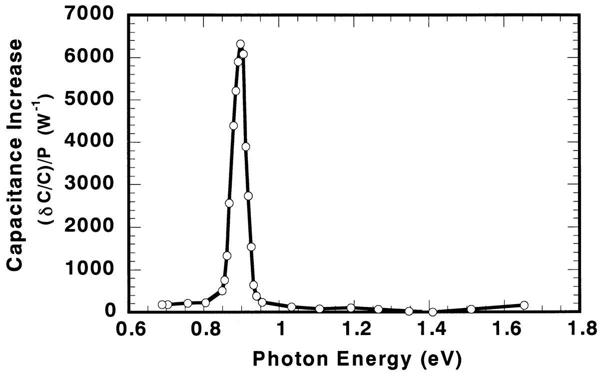

Fig. 4. Photo-capacitance spectrum of single grain boundary in near infrared region.

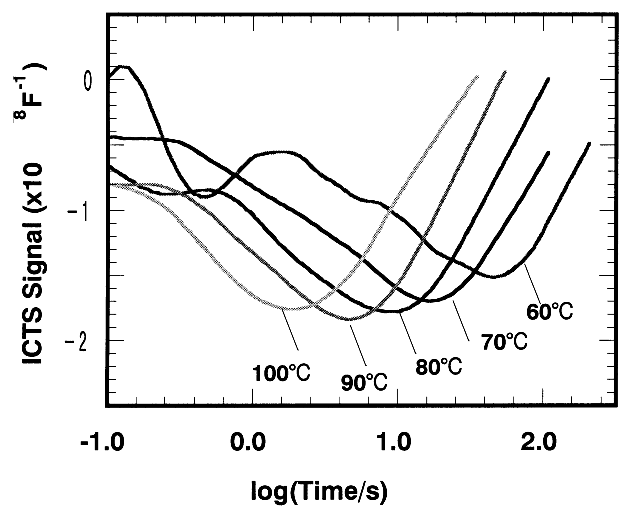

Fig. 5. Temperature dependence of dark ICTS spectra.

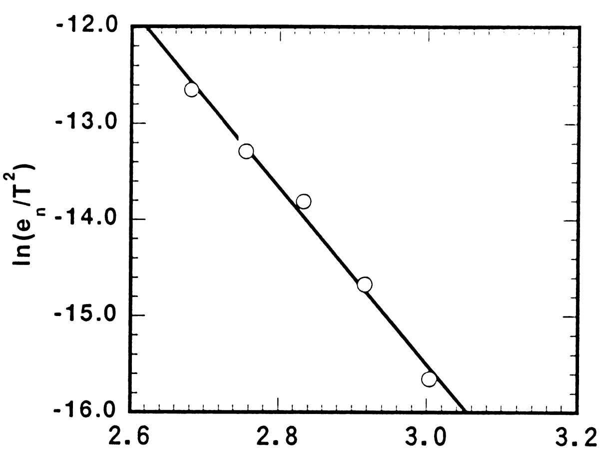

Fig. 6. Arrhenius plot of (e_n/T^2) for single grain boundary.

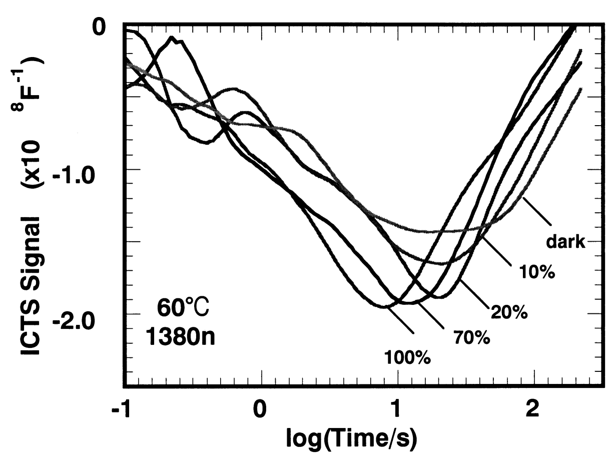

Fig. 7. Photo-ICTS spectra under irradiation of 1380 nm.

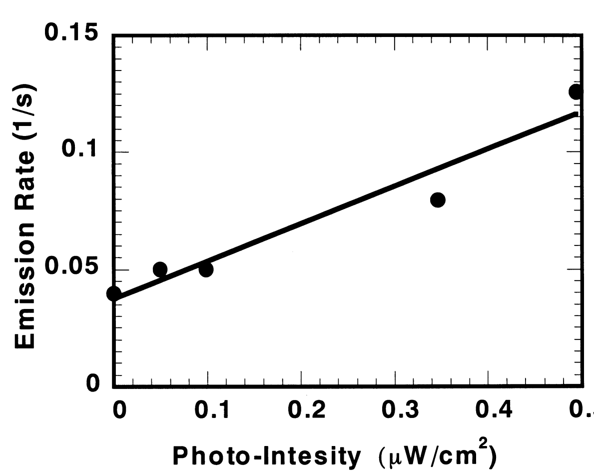

Fig. 8. Relation between emission rate and photo-intensity.

Table 1
Optical cross-section of trap levels

Wave length (nm)	Energy level (eV)	Optical cross-section (10^{-16} cm^2)
1380	0.9	230
700	1.8	8.7
500	2.5	23

4. Conclusions

Direct measurement of photo-capacitance and photo-ICTS of single grain boundaries in ZnO:Pr varistors were carried out using micro-electrodes and near infra-red light. Photo-capacitance measurement showed a sharp peak at 0.9 eV which is the direct evidence of the depth of the interface states at grain boundaries in ZnO varistors. Peaks in photo-ICTS spectra shifted to shorter range compared with the dark-ICTS spectrum when the wavelength of the irradiated light were the same as those at peaks in photo-capacitance spectra. In addition, a linear relation between emission rate of the interface states and light intensity was obtained which agreed with theory. The calculated optical cross section suggested the interface level is originated from chemi-sorbed oxygen ion.

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