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Electronic characterization of single grain boundary in ZnO:Pr varistors

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Abstract

Isothermal capacitance transient spectroscopy (ICTS) has been applied to study single grain boundaries of ZnO:Pr varistors using micro-electrodes prepared on the surface of the ZnO ceramic. A similar ICTS peak was observed as in the case of bulk measurement. This peak has directly proved the existence of the electronic interface states and formation of double Schottky barrier (DSB) at the grain boundary. The quantitative analysis of ICTS peak height revealed that the higher density of the interface states gave the higher nonlinearity of a I–V relation. Photo-ICTS spectra were also examined for the single grain boundary. The peaks shifted to shorter time compared with the dark-ICTS spectrum when the irradiated light brought about an increase of the junction capacitance. This result gave detailed information about deep electronic interface states of DSB.

Keywords: Electronic characterisation; D. ZnO:Pr; E. Varistors

1. Introduction

Electrical properties of ceramic semiconductors are strongly dependent on the double Schottky barriers (DSB's) formed at grain boundaries in the ceramic semiconductors [1]. Since DSB is built by electrons trapped by the interface states at the grain boundary, as shown in Fig. 1, it is important to characterize the electronic states to investigate their electrical properties. Isothermal capacitance transient spectroscopy (ICTS) measurement being an intensive method to characterize deep electronic states in semiconductors [2], it has been applied to characterize electronic interface states at grain boundaries in ceramic semiconductors such as zinc oxide varistors. Since ZnO varistors are electric surge absorbing devices widely used for circuit protection [3,4] and their nonlinear current-voltage characteristics are attributed to the DSB at grain boundaries [5–7], several works on ICTS about ZnO varistors have been reported [8,9]. However, these works have been limited to qualitative analysis of ICTS intensity. Since ICTS intensity corresponds to the density of interface states, a quantitative relation between the density of interface states and I–V characteristics can be understood by quantitative analysis of ICTS intensity. In the present work, direct characterization of single grain boundaries using micro-electrodes will be reported and ICTS and photo-ICTS measurements will be quantitatively discussed in order to characterize the electronic interface states of DSB and to obtain the relation between I–V nonlinearity and electronic interface states.

2. Theory

ICTS measurement is one of the capacitance transient methods by which electronic states in the forbidden band of semiconductors are characterized like DLTS measurement [10]. When we apply this method to ceramic semiconductors, we can estimate the characteristics of electronic interface states at grain boundaries. When a certain voltage is applied across a grain boundary, the capacitance will decrease because electrons are injected to the interface states as shown in Fig. 2(a) [11,12]. Then if the applied voltage is eliminated, the capacitance will increase up to the initial value because captured electrons are emitted from the interface states as shown in Fig. 2(b). The ICTS method measures this transient recovery

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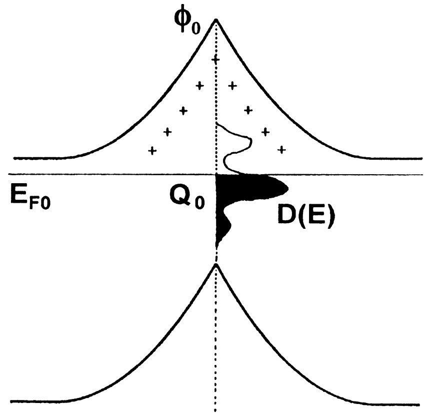

Fig. 1. Double Scottky barrier at grain boundary.

of capacitance and obtains the emission rate and other parameters of the interface states by mathematical processing described below.

ICTS signal $S(t)$ is defined by the following equation [2],

$$S(t) = t\frac{\mathrm{d}f(t)}{\mathrm{d}t} \tag{1}$$

where $f(t)$ is given by [9]

$$f(t) = \left(\frac{1}{c(t)} - \frac{1}{c(\infty)}\right) \tag{2}$$

where $C(t)$ is the capacitance of the varistor at time t after the elimination of the applied voltage, $C(\infty)$ is capacitance at the steady-state without the applied voltage. Since capacitance transient occurs by emission of electrons at the interface states, $f(t)$ is described by the following relation.

$$f(t) \propto \exp(-e_n t) \tag{3}$$

where e_n is thermal emission rate of electrons from the interface states which are given by

$$e_n = N_C \sigma_n \nu_{th} g^{-1} \exp(-E_{IS}/kT) \tag{4}$$

where N_C is the effective density of states in the conduction band, σ_n is the capture cross-section, ν_{th} is the thermal velocity, g is the degeneracy, E_{IS} is level of the interface states below the conduction band edge, k is the Boltzmann constant, and T is the absolute temperature, respectively. From Eqs. (1) and (3), one can find that $S(t)$ has a peak value S_{max} at $e_n t = 1$.

$$S_{max} = -\frac{N_{IS}}{\varepsilon_S N_D A e} \tag{5}$$

where N_{IS} is the density of interface states, ε_S is the dielectric constant of semiconductor grain, N_D is the shallow donor concentration, and A is the junction area. The interface states level E_{IS} or the capture cross section σ_n are obtained from the values of e_n measured at several temperatures. Since $\sigma_n N_C$ is proportional to T^2, the activation energy E_{IS} of the interface states is obtained from the slope of Arrhenius plot of $\ln(e_n/T^2)$ and $1000/T$. Meanwhile the interface states density is obtained by peak value of ICTS spectrum using Eq. (5).

3. Experiment

Samples were prepared by ordinary ceramic processes. For measurements of single grain boundaries, microelectrodes were provided using the photolithography technique. The surface of samples were polished and

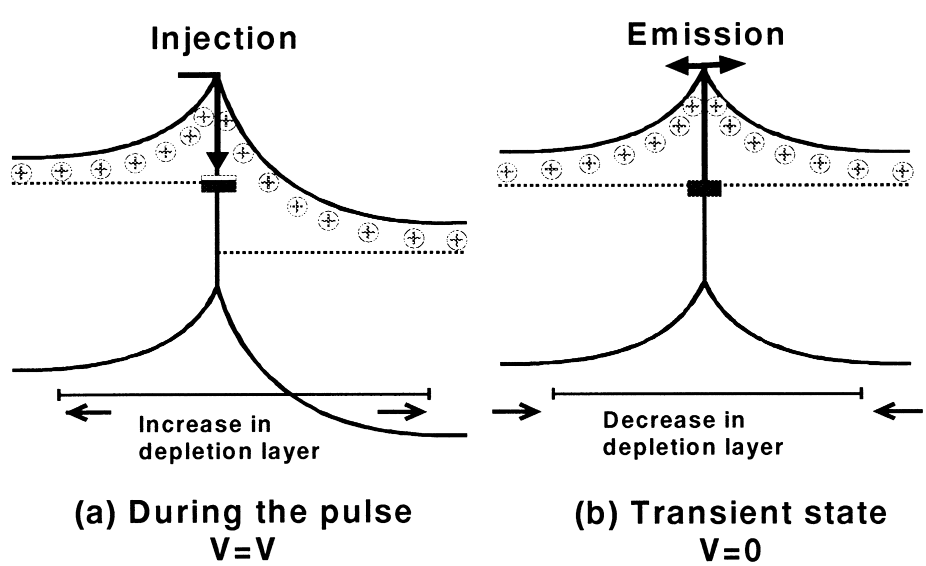

Fig. 2. Change of DSB in ICTS measurement.

thermally etched at 1050°C for 1 h to make the grain boundary visible and relax the damage to the surface by polishing. Aluminium thin film was evaporated on the surface and patterned by photolithography to form micro-electrodes. Fig. 3 shows the pattern of micro-electrodes. There are 72 pairs of electrodes in this pattern. The tips of the electrodes are 5 μm wide. The distance between a pair of electrodes is 10 μm. The grain boundaries which ran between a pair of micro-electrodes were confirmed by an optical microscope. A SEM photograph of a single grain junction and micro-electrodes is shown in Fig. 4.

For ICTS and photo-ICTS measurements, an apparatus shown in Fig. 5 was used. Transient capacitance was measured by a capacitance meter and stored in digital memory. Applied voltage was supplied by the pulse generator. Stored capacitance change was processed mathematically by the desk top computer to obtain ICTS spectrum. Samples were placed on the heater inside the sample box. Temperature was controlled by a low noise solid state regulator. Tungsten microprobes were used for electrical contacts. I–V characteristics were measured by using a curve tracer. Measurements of single grain boundary ICTS spectra were performed using the same apparatus described above connecting tungsten microprobes. The applied voltage was kept constant as 1.5 V. Photo-ICTS or photo-capacitance measurement was carried out under irradiation of monochromated light on the surface of the sample using a Xenon lamp.

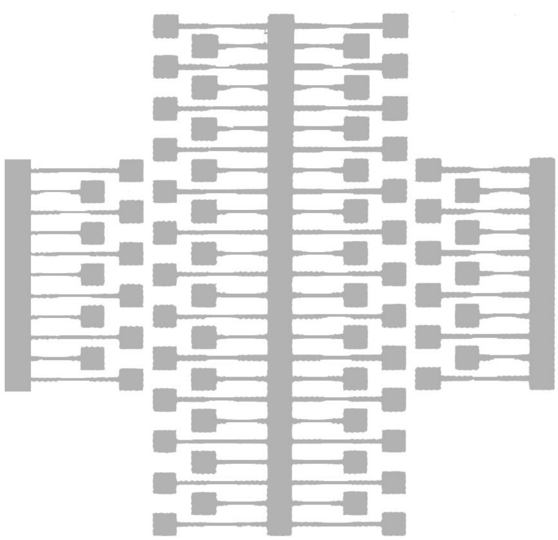

Fig. 3. Pattern of micro-electrodes.

4. Results and discussion

4.1. I–V characteristics and ICTS measurement

Fig. 6 shows I–V characteristics for several single grain boundaries on the same ceramic ZnO-Pr-Co varistor. Their I–V characteristics changed with boundaries. The threshold voltage varied from 2 to 4 V which is higher than those obtained by bulk samples because of the higher current density. The nonlinearity was also changed with boundaries and their nonlinear exponent varied from 3 to 15. Characteristics of sintered material, $\alpha = 8.6$ seems to be an averaged character of these grain boundaries.

Fig. 7 shows an example of ICTS spectra obtained for a single grain boundary in a ZnO–Pr–Co varistor. Only single peaks were observed and those peaks were shifted to shorter time with increasing temperature. These peaks can be regarded as the direct evidence of the interface states at the grain boundary. Fig. 8 shows the Arrhenius plot of peak temperatures and $\ln(e_n/T^2)$. The interface state level and the capture cross section were obtained from the slope and the intercept, respectively. Table 1 shows the interface state parameters obtained by this method. The listed values are average over 11

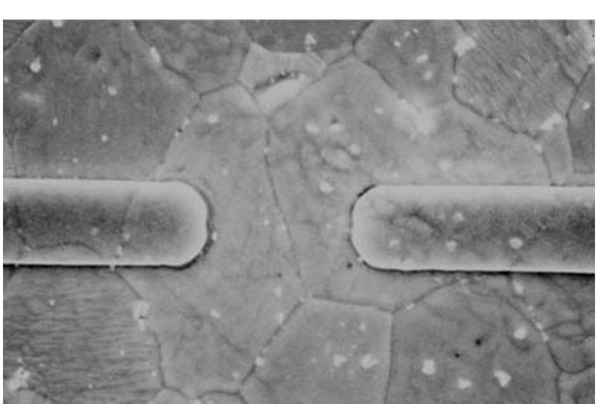

Fig. 4. SEM photograph of microelectrodes.

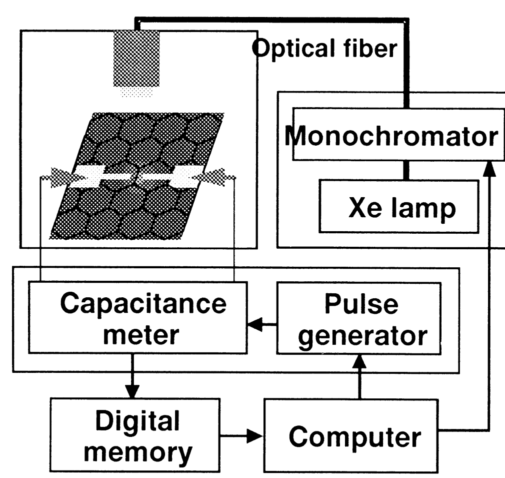

Fig. 5. Block diagram of ICTS and photo-ICTS measurement.

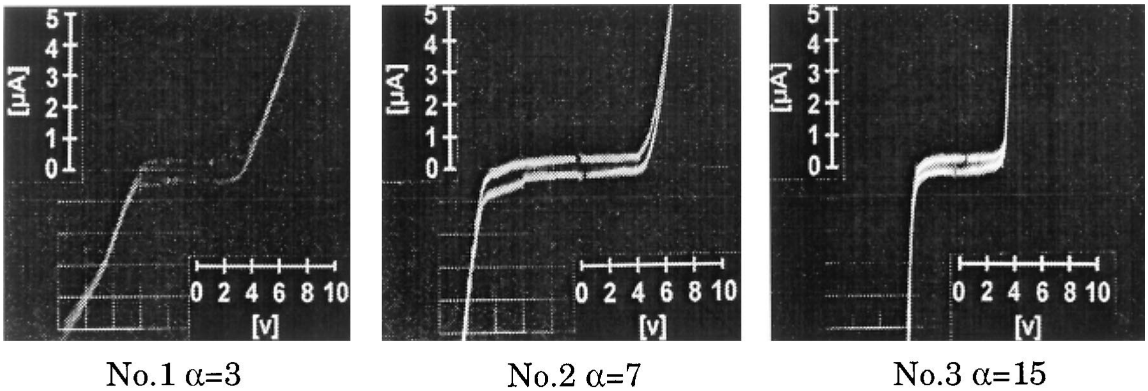

Fig. 6. I–V curves of single grain boundaries on the same Zn–Pr–Co variation.

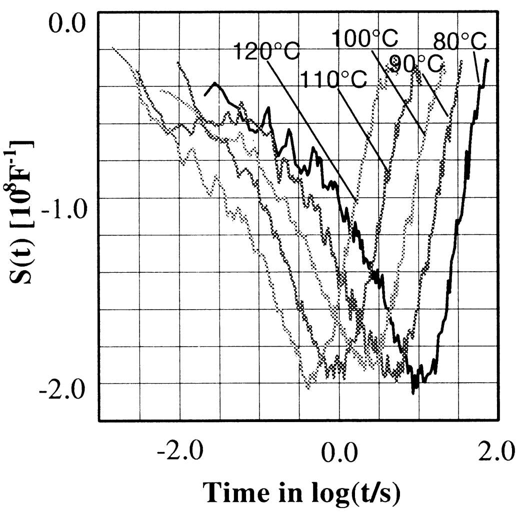

Fig. 7. ICTS spectra of single grain boundary in ZnO:Pr variation.

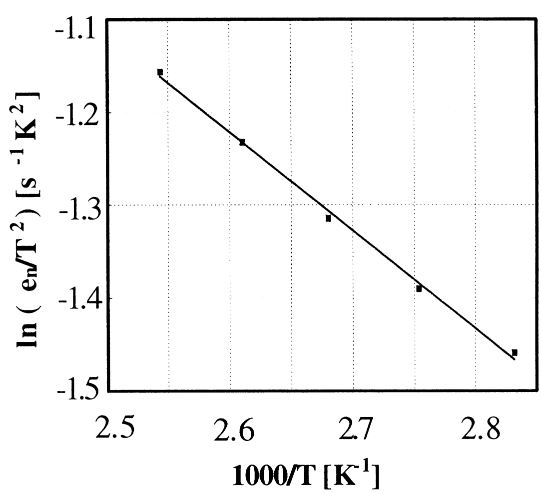

Fig. 8. Arrhenius plot of single grain boundary.

grain boundaries. The interface state levels were located at 0.9 eV below conduction band edge which are almost the same as those obtained by bulk measurement. These values were stable for every grain boundary. On the other hand, capture cross-section and the density of interface states varied with the grain boundary. Moreover the density of interface states were different from those by bulk measurement. The discrepancy might be attributed to the effect of surrounding grain boundaries since their capacitance was added to the aimed single grain boundary.

The difference of I–V characteristics between single grain boundaries shown in Fig. 6 could be explained by the change in the properties of single grain boundaries. These changes can be generated by donor concentration N_D of ZnO grain, the interface state level or the density of states. However, N_D is the same for each grain boundary because of the same ceramic disk and the interface states level is quite stable as indicated above. Therefore, the density of interface states seems to be responsible for the difference of the I–V characteristics. Each ICTS spectrum of these single grain boundaries are shown in Fig. 9. the density of interface states were

Table 1
Calculated parameters of interface states of single grain boundary

E_{IS} (eV)	s_n (cm^2)	N_{IS} (cm^{-2})
0.91	3.78×10^{-14}	3.10×10^{9}

calculated by the peak intensity using Eq. (5). therefore the relation between nonlinearity and density of interfaces states for single grain boundaries was obtained as shown in Fig. 10. In this figure, one can find that grain boundaries with higher density exhibited higher nonlinearity.

4.2. Photo-ICST measurement

Photo-ICTS or photo-capacitance measurement was carried out using wavelengths from 350 to 1200 nm. Fig. 11 shows photo-ICTS spectra for ZnO–Pr–Co sample for several wavelengths. The vertical axis is the ICTS signal intensity and the horizontal axis is the time after the electrical pulse was removed. From Fig. 11, it is clear that peaks are shifted to shorter time compared

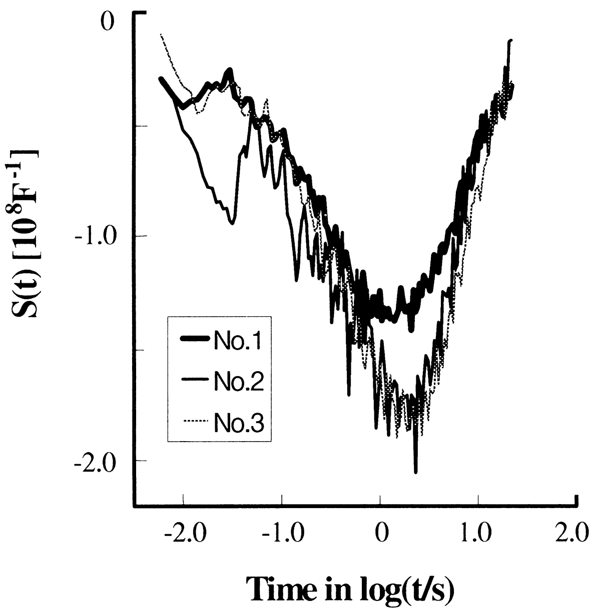

Fig. 9. Single grain boundary ICTS spectra on the same disk.

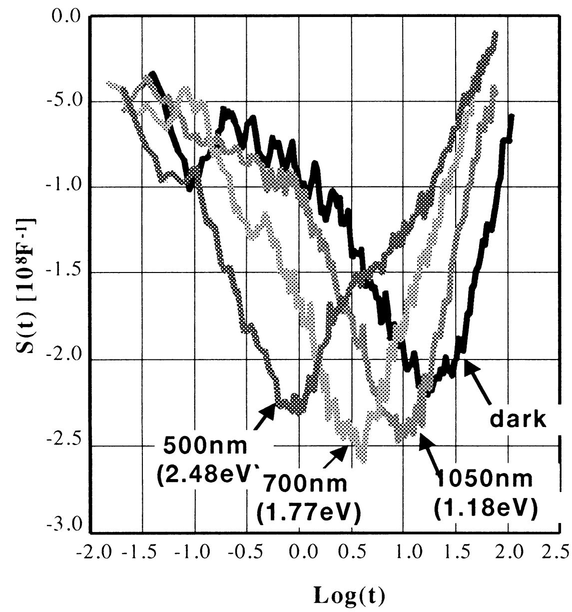

Fig. 11. Photo-ICTS for single grain boundary under irradiation of several wavelength.

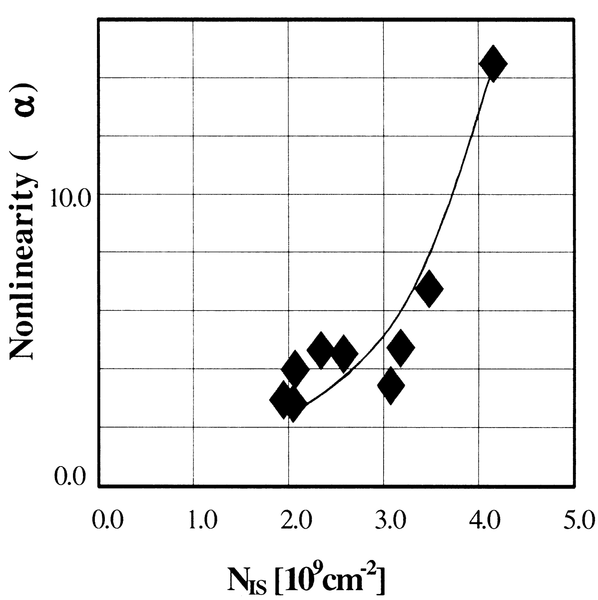

Fig. 10. Relation between nonlinearity and density of interface states.

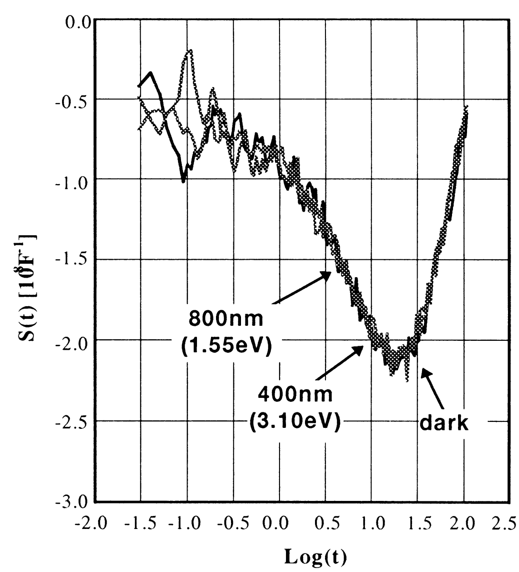

Fig. 12. Photo-ICTS spectra of the same sample under different wavelength.

with the spectrum in the dark. This is interpreted on the basis of an accelerated relaxation by light irradiation. However, at a certain wavelength of light, the ICTS spectrum is almost the same as the spectrum in the dark and no peak shift is observed as in Fig. 12. Wavelengths at which peak positions are shifted are 1050 nm (1.18 eV), 700 nm (1.77 eV), and 500 nm (2.48 eV). On the other hand, no peak shift was observed at 800 nm (1.55 eV) and 400 nm (3.10 eV).

To clarify these peak shifts, photo-capacitance measurements were carried out. Fig. 13 shows the photon energy dependence of the steady-state capacitance change for the ZnO–Pr–Co single junction. At 1.2, 1.8, and 2.5 eV the capacitance increases rapidly. When the light is irradiated on the sample, the junction capacitance will change by emission or capture of electrons. Junction capacitance increases when the electrons at the interface states are emitted to conduction band by photon energy. Therefore, the capacitance increase in Fig. 13 implies the existence of trap levels below the conduction band edge. The photon energy corresponds to the depth of the levels. The identification of these levels are not

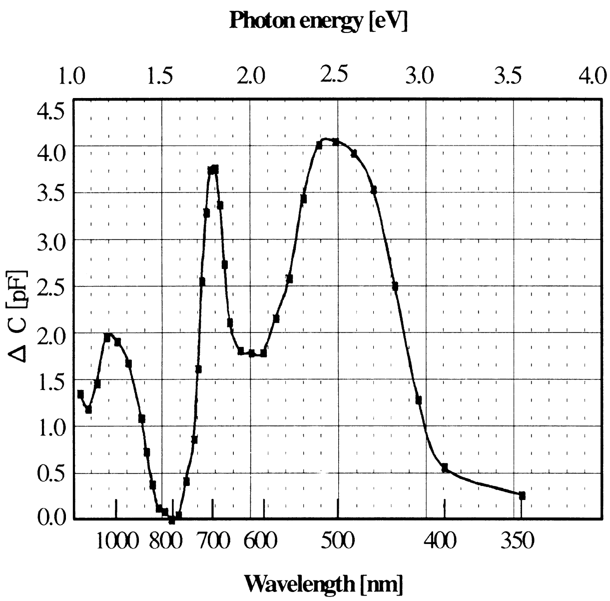

Fig. 13. Photo-capacitance spectrum for single grain boundary.

completed at yet. However, since electron emission from bulk trap levels also causes capacitance increase as in the interface states, we speculate that the peak at 1.2 eV should be assigned to interface states which are 0.9 eV below the conduction band edge obtained by dark ICTS. Though the discrepancy of the obtained values between photo-capacitance and dark-ICTS are still unsettled, the other two levels are supposed to be the intrinsic defect level of zinc oxide or the cobalt impurity level. For example, oxygen defect levels are reported to be located at 1.8 eV [13] and cobalt impurity levels are reported to be located at 1.2 eV [14] below conduction band.

5. Conclusions

Direct measurements of ICTS and I–V characteristics of single grain boundary in ZnO:Pr varistors were carried out using micro-electrodes. Single grain boundaries gave similar spectra as for bulk ceramic varistors. Observed ICTS peaks can be regarded as the direct evidence of the existence of interface states at grain boundaries. Interface state levels were found to be about 0.9 eV below the conduction band edge for every junction. Quantitative analysis of ICTS intensity revealed that higher density of interface states gave higher nonlinearity in I–V characteristics.

In photo-ICTS spectra, peaks shifted to shorter time compared with the dark-ICTS spectrum when the wavelength of irradiated light were 1000 nm (1.24 eV), 700 nm (1.77 eV), and 500 nm (2.48 eV). On the contrary, no peak shift was observed when the wavelength of light are 850 nm (1.45 eV) or 400 nm (3.10 eV). The strong peak in photo-capacitance spectra suggested that the peak shift by 1000 nm irradiation corresponds to the interface states at grain boundaries in ZnO varistors.

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