
Paper

Electrical Properties of ZnO/PrCoOxide Multilayered Composites

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ZnO/PrCoOxide 積層複合体の電気的特性
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Multilayered composites having the structure of Ni/ZnO/PrCoOxide/Au were fabricated by the sputtering technique and their electrical properties were examined. It was found that a multilayered composite is an excellent low voltage varistor (a=30, breakdown voltage=6.5 V). The results of the voltage-current (V-I) and the capacitance-voltage (C-V) measurements revealed that a depletion region was formed in the ZnO thin film close to the ZnO/PrCoOxide interface. The potential barrier in the ZnO/PrCoOxide multilayered composite was discussed in comparison with a single grain boundary model in ZnO ceramic varistors.

Key-words: Varistor, Composite, Thin film, ZnO, Junction

1. Introduction

Recently, transient surge suppression in low voltage electronic circuits has attracted attention because of advances of semiconductor processes such as VLSI and various packages. On the other hand, many kind of liquid crystal display (LCD) panels have been developed. In order to achieve low cost and high reliability, two terminal devices for LCD driving circuits are important. For these purpose, devices with highly nonlinear voltage-current (V-I) characteristics at below 10 V are necessary.

ZnO varistors are ceramic devices produced by sintering ZnO powder with additives such as Bi, Pr, Co, etc. These devices exhibit nonlinear V-I characteristics as expressed by the relation \( I=KV^{\alpha} \), where \( K \) is a constant and \( \alpha \) is a nonlinearity coefficient. The exponent \( \alpha \) depends on the microstructure of ceramics and the electrical structure of ZnO. The voltage \( V \) can be written as \( V=NV_g \), where \( N \) is the number of grains in series within a sample and \( V_g \) is the voltage per grain which is estimated to be 3–4 V. The number of grains \( N \) is related to the thickness of ZnO sample \( D \) by relating \( N=D/d \), where \( d \) is the grain size (10–20 \( \mu \)m in a typical commercial varistor). For low voltage applications (e.g. 3–10 V) at a given current, the thickness of the device becomes very small (10–100 \( \mu \)m) as seen from the above relations. This low voltage varistor is difficult to fabricate by the conventional ceramic technique. Hence, several methods have been proposed to make low voltage varistors. One method is the use of a huge grain size. The thickness of the device is as same as conventional varistors. Another method is the use of multilayer ceramics. The multilayer varistors are manufactured by applying a ceramic green sheet lamination technology to a varistor material composition. The green sheet thickness is 20–100 \( \mu \)m. The \( \alpha \) of both low voltage varistors are about 15. The value is lower compared with conventional varistors (\( \alpha=30–100 \)). It seems that technical difficulty is remained in these two method.

In this paper, we report the third method for making low voltage varistors. The highly nonlinear V-I characteristics originate in a grain boundary (i.e. interface). The concept of this method is the use of a ZnO/PrCoOxide interface. We fabricated multilayered composites having the structure of Ni/ZnO/PrCoOxide/Au by the sputtering technique, and then examined the electrical properties of the junctions. Interface phenomena in ZnO/PrCoOxide multilayered composites are compared with ceramic varistors as a model of a single grain boundary.

2. Experimental

The structure of the multilayered composite sample is schematically shown in Fig. 1. After Ni electrode had been evaporated on a glass substrate (Corning 7059), the ZnO film was prepared by the RF magnetron sputtering system (Nichiden Anelva SPF-430H) with the ZnO target. Ar gas was used as the sputtering gas (gas pressure 4 Pa; input power 120 W; substrate temp. 250°C). The PrCoOxide film was prepared by the RF magnetron sputtering system with a powder target of Pr-oxide and Co-oxide

![Fig. 1. Schematic structure of the ZnO/PrCoOxide multilayered composite.](image_url)
mixture (Pr 50 at%, Co 50 at%) in Ar gas as sputtering gas (gas pressure 8 Pa; input power 150 W; substrate temp. 250°C). Au electrode (1 mm²) was evaporated onto the PrCoOxide film.

The V–I characteristics of multilayered composites were measured at room temperature with a Hewlett-Packard Semiconductor Parameter Analyzer Model 4145B. The capacitance–voltage (C–V) measurement were carried out at room temperature with a Hewlett-Packard LF Impedance Analyzer Model 4182A. The applied AC voltage was 10 mV at 100 kHz.

3. Results and discussion

Figure 2 shows a typical cross sectional view of the multilayered composite sample obtained with a scanning electron microscope (SEM). The interface between the ZnO film and the PrCoOxide film is smooth. From the secondary ion mass spectrometry (SIMS) measurements, inter-diffusion at the interface was not found within the accuracy.

From the X-ray diffraction (XRD) and the high energy electron diffraction (RHEED) observations, the ZnO film was polycrystal which had a c-axis orientation perpendicular to the substrate and the PrCoOxide film was amorphous. The composition of the PrCoOxide film was found to be Co/Pr=0.951 by the electron probe X-ray microanalysis (EPMA).

3.1 V–I characteristics

Figure 3 shows a typical V–I characteristic for the multilayered composite having the structure of Ni/ZnO(200 nm)/PrCoOxide(200 nm)/Au. The non-ohmic V–I characteristic was observed. It should be noted that the magnitude of the current when the Ni electrode was negatively biased (forward bias) was greater than that when it was positively biased (reverse bias). From the separate measurements on junction systems of Ni/ZnO/Au and Ni/PrCoOxide/Au, the nonlinearity was not observed and the resistivity of these junctions was 0.1 Ω and 1 Ω, respectively. Therefore, the junction of the Ni/ZnO/PrCoOxide/Au will be designated simply as the ZnO/PrCoOxide.

As we can see in the figure, there is a varistor characteristic for the reverse bias. The α value and the breakdown voltage were 30 and 6.5 V respectively. The varistor voltage did not depend on the thickness of the PrCoOxide films. The breakdown mechanism is now being investigated.

The forward characteristic is roughly exponential. The standard diode equation is expressed by the form

$$J_f = J_0 \exp\left(qV/nkT\right)$$

(1)

where $J_f$ is the forward current density, $q$ is the electronic charge, $V$ is the applied voltage, $n$ is the diode factor, $k$ is the Boltzmann's constant, $T$ is the temperature, and

$$J_0 = A^*T^4\exp\left(-\phi_b/kT\right)$$

(2)

where $\phi_b$ is the barrier height and $A^*$ is the Richardson constant. The experimental result shown in Fig.3 (dashed line) satisfies the Eq. (1). Series resistance effect gives rise to deviation from the exponential behavior at higher voltages. We obtained the $\phi_b=0.73$ eV by fitting the experimental data to the Eqs. (1) and (2).

It turns out from these results that a depletion region is formed dominantly in the ZnO film near the interface between the ZnO film and the PrCoOxide film. We believe that the reason why the ZnO film is depleted is caused by the existence of the positive excess charges trapped at the interface such as ceramics varistors (DSB-defect model). However, more experimental research is required for a better understanding of the junction.

3.2 C–V characteristics

A typical C–V characteristic for the multilayered composite having the structure of Ni/ZnO(200 nm)/PrCoOxide(200 nm)/Au is shown in Fig. 4. The decrease of the capacitance is observed when the
ZnO film is positively biased. This result suggests that a depletion region is formed in the ZnO film. For an ideal Schottky diode with a uniform concentration of donor, the plot of $C^{-2}$ against $V$ is linear with a slope equal to $2/\varepsilon q N_d$, where $\varepsilon$ is the permittivity and $N_d$ is the donor density. The flat-band barrier height can be deduced from the plot. However, the plot of $C^{-2}$ against $V$ obtained from Fig. 4 was not linear. This indicates that the junction of ZnO/PrCoOxide is not an ideal Schottky diode with a uniform concentration of donors.

If $C^{-2}$ is plotted as a function of $V$, the slope of the curve will be

$$\frac{\partial C^{-2}}{\partial V} = \frac{2}{\varepsilon q N_d(x)}$$

where $x$ is the width of the depletion region and $N_d(x)$ is the donor density at the edge of the depletion region.\(^7\) The Eq. (3) shows that, if the $N_d$ is non-uniform, the plot of $C^{-2}$ against $V$ is not linear but its slope at any particular bias voltage is inversely proportional to the $N_d$ at the edge of the depletion region. Equation (3) consequently gives

$$N_d(x) = \frac{2}{\varepsilon q} \left( \frac{\partial C^{-2}}{\partial V} \right)^{-1}$$

and the capacitance of the depletion region is equal to that of a parallel-plate capacitor of thickness $x$ and permittivity $\varepsilon$, so that

$$x = \varepsilon/C$$

Equations (4) and (5) show that, from $C$ and $V$, it is possible to determine $x$ and $N_d(x)$. The value of $x$ is equal to the distance from the interface. Therefore, we can measure the depth profile of the $N_d$ in ZnO films. Figure 5 shows the depth profile of $N_d$ obtained from Fig. 4. It is clear from the figure that $N_d$ decreases with decrease of $x$. At $x < 90$ nm, there is a parabolic relationship between $N_d(x)$ and $x$. $N_d$ at $x > 90$ nm is $7 \times 10^{17}$ cm$^{-3}$.

If the donor distribution is expressed in the form $N_d(x) = a_1 x^2$ where $a_1$ is a constant, the electric field $V(x)$ in the depletion region is given by Poisson's equation:

$$\frac{d^2}{dx^2} V(x) = \frac{q N_d}{\varepsilon} = \frac{q}{\varepsilon} a_1 x^2$$

By solving Eq. (6), it becomes

$$C^{-4} = A (V_d - V)$$

where $A$ is a constant and $V_d$ is the diffusion voltage. Figure 6 shows a plot of $C^{-4}$ against $V$, where a linear relation was observed. From an intercept $V_d$ on the horizontal axis in the figure, we obtained the flat-band barrier height of 0.78 eV by using Eq. (7). This agrees with the value obtained from the $V-I$ measurement.

On the basis of Figs. 4, 5 and 6, it can be regarded that the junction of ZnO/PrCoOxide is a Schottky junction with a non-uniform concentration of donors.
ZnO is an N-type defect semiconductor in which deviations from stoichiometry are electrically active. The excess Zn, acting as donors, can be ascribed to Zn interstitials. In case of ZnO/PrCoO$_x$ide junctions, the decrease of the $N_d$ in ZnO is caused by the decrease of the excess Zn. The decrease of the excess Zn is due to the transport of oxygen from the surface (interface) to the interior of ZnO films. It seems that oxygen in PrCoO$_x$ide films is diffused into ZnO films. The diffusion is estimated to be 100 nm or less.

### 3.3 Comparison of ZnO/PrCoO$_x$ide multilayered composites, ceramic varistors and Zener diodes

Table 1 shows a comparison of the basic varistor characteristics of ZnO/PrCoO$_x$ide multilayered composites, low voltage ceramic varistors and Zener diodes. Note that the electrodes of ceramic varistors are larger than those of the other devices. In order to permit comparison between same-size devices, additional columns are included which show calculated data for multilayered composites and Zener diodes based on a 7 mm$^2$ electrode area. This data shows that the multilayered composite exhibits lower varistor voltage and higher peak current than the ceramic varistor having the same-size device. This is presumably because one barrier is homogeneously formed in the ZnO/PrCoO$_x$ide multilayered composite. When the ZnO multilayered composite is compared with the Zener diode, the latter shows higher peak current. This is not surprising because Zener diodes are made from Si single crystals and barriers formed at junctions in those crystals are known to be perfect.

<table>
<thead>
<tr>
<th>Electrode (mm$^2$)</th>
<th>Ceramic Varistor</th>
<th>ZnO/PrCoO$_x$ide Composite</th>
<th>Calculated from Composite</th>
<th>Zener Diode</th>
<th>Calculated from Diode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area</td>
<td>7.1</td>
<td>1.0</td>
<td>7.1</td>
<td>1.8</td>
<td>7.1</td>
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<tr>
<td>Varistor Voltage $V_{0.1mA}$ (V)</td>
<td>10.0</td>
<td>6.5</td>
<td>6.5</td>
<td>8.0</td>
<td>8.0</td>
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<tr>
<td>Leakage Current $I_{2.5V}$ (A)</td>
<td>$1.5 \times 10^{-7}$</td>
<td>$1.2 \times 10^{-6}$</td>
<td>$8.5 \times 10^{-6}$</td>
<td>$4.0 \times 10^{-7}$</td>
<td>$1.6 \times 10^{-6}$</td>
</tr>
<tr>
<td>Maximum Clamping Voltage $V_{1A}$ (V)</td>
<td>22</td>
<td>12</td>
<td>12</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>Maximum Peak Current $I_p$ (A)</td>
<td>35</td>
<td>9</td>
<td>64</td>
<td>above</td>
<td>above</td>
</tr>
</tbody>
</table>

### 4. Conclusions

In the present study, we fabricated composites having the structure of Ni/ZnO/PrCoO$_x$ide/Au by the sputtering technique, and then examined the electrical properties of the composite. It was found that multilayered composites work as a good low voltage varistor ($\alpha=30$, breakdown voltage = 6.5 V).

From the $V$–$I$ and $C$–$V$ measurements, it was found that a depletion region is formed in the ZnO film close to the ZnO/PrCoO$_x$ide interface. It can be regarded that a ZnO/PrCoO$_x$ide multilayered composite is a one-sided single Schottky junction in the DSB-defect model.

The ZnO/PrCoO$_x$ide multilayered composite is important as a model of a single grain boundary in a ceramic varistor to study their conduction mechanisms, interface states and effects of additives.

### References