Preparation and Properties of Active Devices from Oxide Compounds

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Abstract

Many kinds of oxide compounds, consisting of various chemical elements in different composition ratios, have been created and their physical and electrical properties have been studied. The results of the present study indicate that oxide based systems such as tin, vanadium, and niobium oxide based systems exhibit switching, oscillating, and gas detecting phenomena, which are of special interest to us. Especially, tin oxide based systems exhibit gas detecting and switching effects, vanadium oxide based systems exhibit switching and oscillating effects and niobium oxide based systems exhibit non-volatile memorizing, oscillating, and switching effects.

Key Words: Functional Device, Oxide Compounds, Switching Device, Oscillating Device, Memorizing Device, Gas Sensing Device

1. Introduction

Oxide materials exhibiting high dielectric properties have found applications in electric activators and generators, capacitors, and sensors. Meanwhile, oxide materials exhibiting low dielectric properties have also found wide applications in, for example, bypass capacitors and ceramic substrates. Physical and electrical properties of oxides other than dielectrics have led to few applications of oxides in electronic devices. However, physical phenomena such as phase transition of oxide materials show promise in enabling application of oxides to fabrication of interesting active and passive devices.

We have found that oxide compound systems consisting of several additives added to tin, vanadium and/or niobium oxides can be applied to electric devices. In the present paper we present such systems exhibiting unique characteristics such as switching, oscillation, non-volatile memorizing, and gas detecting effects.

2. Specimens

Oxides of the materials shown in Table 1 were used in this experiment. We also used various additives except for the elements listed in Table 1, however, the results with the interest were not obtained. These materials were mixed in amounts of 5-20 in wt.% with a main component, which was an oxide of tin vanadium, or niobium such as SnO₂, VO₂ and Nb₂O₅. The resultant mixtures were presintered in air for three hours at 700°C and pulverized to minute particles. The resultant powders were formed

<p>| Table 1. List of additives. Oxides of these elements were mixed with the main component |
|-----------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|</p>
<table>
<thead>
<tr>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
<th>VII</th>
<th>VIII</th>
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<tr>
<td>Cu</td>
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<td>Mn</td>
<td>Ag</td>
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<td>Co</td>
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<td>Ni</td>
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into disks by application of a pressure of $3 \times 10^6$ Pa. The dimensions of the disks were approximately 8 mm in diameter, and 0.5mm to 1.2mm in thickness. Next, these disks were sintered in air at 1000°C to 1200°C for 3 hours. After sintering, each disk was polished and etched, and then thin film electrodes of Au, Pt, or Cd were formed on both sides of the disk by vacuum evaporation. Some samples were manufactured by thick-film technology using the above-described fine particles and sintering at high temperature. Pt conductor was used for the thick-film type specimen.

3. Results and Discussion

The physical and electrical properties of oxide compounds such as Sn-Nb-V, Zn-Sn-Co, V-Ti-Ni oxides were examined. Figs.1 and 2 show the oscillation and V-I characteristics observed in some of these specimens.

Fig.1 expresses the composition dependence of electrical properties of the SnO$_2$-VO$_2$-Nb$_2$O$_5$ system. Fig.1 (a) shows the relationship between composition ratio and the oscillation phenomenon, and Fig.1 (b) shows waveforms of the oscillation. The amplitude of the oscillation is high, the frequency is low, and the waveform differs considerably with composition. Fig.1 (c) shows the V-I characteristics, and indicates that threshold voltages are relatively high. Fig.2 illustrates the relationships between composition ratio and oscillation characteristics of the ZnO-VO$_2$-TiO$_2$ system. A certain kind of composition is shown to have relatively high oscillating frequency. With regard to both of the above systems, reproducibility of those characteristics is not very good with present techniques.

Fig.3 shows V-I characteristics of the Nb oxide based system. At the high resistance state in Fig.3 (a), the resistance changes to ohmic, resistance is approximately 3 MΩ, and the voltage at the threshold point A is about 160 V/cm. Next, region AB represents the switching state (forward switching), wherein the ratio of the high resistance value to the low resistance value is $10^3$-$10^4$ and the speed of the transition is 10μsec. The last stage, represented by region CD, is the low resistance state. After this forward switching, the resistance does not return to the high value, but retains the low value. When the applied voltage is increased after the switching, the current increases along curve BC shown in Fig.3 (b). Moving from the low resistance state to the high resistance state requires application of ac-voltage to the specimen, upon which the specimen immediately returns to the high resistance state. Therefore, the specimen has a non-volatile memorizing effect.

Fig.4 illustrates the result of applying ac-voltage to the specimen in order to return to the high resistance state from the low resistance state. When the ac-voltage (sine wave : 50Hz) applied to the specimen retaining the low resistance state is increased, the current also increases. After passing through point A, an abrupt switching action (backward switching) occurs in the interval AB and the current decreases rapidly. When the current reaches 9 mA (applied voltage : ac 3.5V), backward switching occurs and the current drops to 7μA (applied voltage : ac 14V). The speed of backward switching is roughly 100 msec to
Fig. 2 Composition dependence of electrical properties of the ZnO-VO2-TiO2 system

Fig. 3 V-I characteristics of the Nb oxide based system. Horizontal scale is 10V/div., and vertical scale is 5mA/div.

Fig. 4 V-I characteristics of the Nb oxide based system under application of ac-voltage.

Fig. 5 Temperature dependence of oscillation characteristics in Nb oxide based system. Horizontal scale is 50V/div., and vertical scale is 5μsec/div.

Fig. 6 Temperature dependence of oscillation characteristics

200 msec. The resistance changes from 200Ω at the low resistance state to 20MΩ at the high resistance state.

Fig. 5 shows the oscillation characteristics of the Nb oxide based system. Oscillation amplitude varies between 30 and 70V, and frequency varies between 200kHz and 2MHz. The oscillation waveform is blocking-like, and this remarkable oscillation is self-oscillation of the Nb based specimen. As indicated in Fig. 6, the amplitude and frequency of this oscillation depend strongly on temperature. Oscillation is observed within the temperature range of −50°C to 80°C. Oscillation frequency increases gradually with ambient temperature, whereas amplitude decreases from 110V to 60V as ambient temperature increases from −50°C to 80°C. Fig. 7 shows the temperature dependence of resistance. For example, under application of 10V, when ambient temperature increases from 80°C to 100°C, the resistance quickly increases by a factor of 10^3.

In the view of the X-ray diffraction analysis the structure of the specimen consists of (Nb, V)₂O₅, NbVO₃, α-Nb₂O₅, and Nb₂O₅ crystallites. In the case of oxide materials having the switching effect, thermal filaments of channels are usu-
ally formed. However, these thermal phenomena have not been observed in our specimen yet. A delay time of the switching or oscillation action with input signal is found, and the temperature at which these phenomena can be observed is lower than the temperature at which Nb₂O₅ shows the sharp change in the electrical resistance. This seems that the filament or channel is the most probable affecting factor for these phenomena and thermal energy probably has direct effect upon the oscillation and memory phenomena⁷,⁸.

Fig.8 shows the V-I characteristics of the vanadium oxide based system at room temperature. Stable oscillation can be found in region AC, switching action can be seen in region CD, and after the switching, unstable oscillation is often observed around region DE. Fig.9 shows the rectangular pulse-like waveform observed in region BC. The oscillation voltage is 12V, the frequency 1.1kHz, average pulse width 0.6msec, the rise time < 0.1μsec, and the fall time<0.1μsec. Figs.10 (a) and (b) show the relations between the ambient temperature and oscillation characteristics as observed before phase transition of VO₂. In both these figures, the solid lines and dotted lines represent oscillation at points B and C, respectively, in the V-I curve of Fig.8. The transition of the vanadium oxide is the affecting factor for stable oscillation and the switching.

Lastly, Fig.11 shows the characteristics of a gas detection element utilizing the tin oxide based system. Figs.11 (a) and (b), show that the tin based gas sensor heated at around 300 - 350°C exhibits high sensitivity for specific gas propane. A noteworthy finding is gas detection is effected by change in capacitance change of the specimen, rather than by the widely-used change in resistance⁹.
4. Conclusion

Table 2 summarizes our experimental results. Especially, tin oxide based systems exhibit gas detecting and switching effects, vanadium oxide based systems exhibit switching and oscillating effects and niobium oxide based systems exhibit non-volatile memorizing, oscillating, and switching effects. Of special note is that the oxide material systems described above are almost practicable at present.

(2001.4.10-Žó— 2001.7.2-ÄŽó—)

References

5) A.Kaneuchi, N.Fujikawa and S.Kawaguchi:“CaZrO3-Based Dielectric Substrate with Cu Thick Film”, Proc. IMC, pp.595-599, 1992

Table 2. Summary of our experimental results

<table>
<thead>
<tr>
<th>Composition</th>
<th>Mixing ratio (mol%)</th>
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<tbody>
<tr>
<td>ZnO</td>
<td>SnO₂</td>
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<tr>
<td>60 : 20 : 20</td>
<td>20 : 60 : 20</td>
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<tr>
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<td>Osc*</td>
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<tr>
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<td>NR</td>
</tr>
<tr>
<td>Sw, Osc</td>
<td>Sw, Osc, NR</td>
</tr>
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</table>

Sw (Switching) | S (Sensor) |
NR (Negative Resistance) | city : city gas |
Osc (Oscillation) | temp : temperature |
*thick-film type | rg : reducing gas |