Effect of the addition of silver compounds during the pyrolysis of manganese nitrate on tantalum anodic oxide film

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Abstract

A study of the pyrolysis of an aqueous solution of manganese nitrate in the presence of silver compounds has been carried out. Thermal analysis showed that the MnO_2 formation temperature and the transformation temperature from MnO_2 to Mn_2O_3 shifted towards a lower temperature in the presence of silver acetate. A large particle-size and high crystallinity MnO_2 was formed; this may be a useful method of making an excellent tantalum capacitor with high capacitance.

Keywords: Tantalum; Manganese dioxide; Capacitors

1. Introduction

The process for preparing a tantalum capacitor consists of five steps: (i) a macroporous anode of sintered tantalum: (ii) formation of tantalum oxide (Ta_2O_5) by the anodic oxidation of tantalum: (iii) formation of manganese dioxide layer on Ta_2O_5 by heat treatment of impregnated aqueous solution of $Mn(NO_3)_2$; (iv) a surrounding outer layer consisting of graphite, silver and solder, and (v) formation of a protective capsule of resin.

The properties of the capacitor are dependent on the condition of the impregnation and the pyrolysis process of an aqueous solution of $Mn(NO_3)_2$. In addition, the steps of impregnation and thermal decomposition should be repeated several times.

Due to the technological interest in tantalum capacitors, there are studies on the pyrolysis process of $Mn(NO_3)_2$ [1–3], on pyrolysis under an atmosphere of high relative humidity [4–6] and on the pyrolysis of a slurry-type manganese solution [3,7,8].

When pyrolysis is carried out using an aqueous solution of $Mn(NO_3)_2$ containing silver acetate, excellent physical and electrical characteristics of the resulting MnO_2 coating have been obtained as shown below. Improvement of the coating process by a MnO_2 layer could be important, since the capacitor size has been miniaturized year by year. Our aim is to investigate the MnO_2 layer obtained by pyrolysis of an aque-ous solution of $Mn(NO_3)_2$ and to improve the coverage by the MnO_2 layer.

2. Experimental

In order to form a dielectric film (Ta_2O_5) on the surface of a tantalum-sintered body, a porous sintered tantalum anode (1.4 mm×3.0 mm×3.8 mm) was anodized at a constant current to a final voltage of 15 V, and then it was held at this voltage for 2 h. The anodization electrolyte was 0.03 M solution of H_3PO_4 in water at 85 °C.

Then the anode was impregnated in an aqueous $Mn(NO_3)_2$ solution (6.4 M) with and without silver acetate, and heated at 300 °C to form a MnO_2 layer in two types of furnaces, i.e., a dry furnace (a convectional furnace) and a wet furnace (a saturated water vapor furnace). These impregnation/heating processes were repeated six times.

The conductive counter layer was formed on the MnO_2 layer to measure capacitor characteristics. The process is as follows: (i) colloidal carbons dispersed in water were pasted on the MnO_2 layer, and heated at 125 °C, and (ii) the counter electrode was finally constructed by heating the silver paste (silver is dispersed in an organic solvent) on the MnO_2–carbon layer at 125 °C.

Two capacitor characteristics, capacitance and dissipation factor (tan δ), were measured with a Hewlett-Packard 4262-A LCR meter at frequencies of 120 Hz and 1 kHz. We denoted the value of a capacitor without MnO_2 layer measured in a 3.4 M H_2SO_4 solution as a maximum capacitor. In

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the manufacturing process of a tantalum capacitor, more than ten impregnation/heating process steps using $Mn(NO_3)_2$ solutions of different concentrations and using slurry-type manganese compounds solution [3,8] sould be done to decrease the value of tan δ and to increase its capacitance. Since we used only six steps of pyrolysis, the values of tan δ are higher than those found for a commercially available capacitor. There are, however, experimentally sufficient pyrolysis processes in order to investigate the characteristics of the MnO_2 layer.

Differential scanning calorimetry (DSC) of the aqueous $Mn(NO_3)_2$ solution was carried out with a Thermal Analysis Station TAS-100 of Rigakudenki Co., Ltd. The scanning speed of the temperature in the analysis was 5 °C/min. Powder X-ray diffraction (XRD) measurements were carried out using a Rigaku diffractometer (RINT 1000).

3. Results and discussion

The effect of the addition of various metal compounds to the $Mn(NO_3)_2$ solution on the characteristics of tantalum capacitors has been investigated. High values of capacitance were obtained by pyrolysis of manganese solutions containing silver nitrate.

Characteristics of tantalum capacitors, such as capacitance and dissipation factor (tan δ), using the MnO_2 layer obtained from the pyrolysis of the $Mn(NO_3)_2$ solution containing CH_3COOAg in an atmosphere of saturated H_2O are shown in Fig. 1.

The increased capacitance and the decreased tan δ at 120 Hz were obtained from the MnO_2 layer obtained from pyrolysis of $Mn(NO_3)_2$ solution containing CH_3COOAg. To clarify the reason for the increased capacitance, typical scanning electron microscopy (SEM) photographs of the MnO_2 surface layer formed on the Ta_2O_5 obtained from the $Mn(NO_3)_2$ solution with or without CH_3COOAg are shown in Fig. 2. Fine particles of formed MnO_2 (about 10 μm in diameter) and the large size of MnO_2 particles (about 20 μm in diameter) obtained by the pyrolysis of the $Mn(NO_3)_2$ solution without or with CH_3COOAg are shown, respectively.

The MnO_2 deposition process can be considered to be two competitive processes: (i) formation of new nuclei, and (ii)

growth of the nuclei. The crystallinity of MnO_2 is increased with a decrease in number of the nuclei, probably because the rate of the nuclei formation decreases and the growth of nuclei is rather complete. Because the rate of growth of the nuclei was high, larger particle size of MnO_2 would be obtained.

The number of MnO_2 nuclei is decreased and the growth rate of MnO_2 nuclei may increase during the pyrolysis process of the $Mn(NO_3)_2$ solution in the presence of CH_3COOAg. If the particle size is large, then the coverage of Ta_2O_5 by MnO_2 would not be complete.

To improve the coverage of Ta_2O_5 by the MnO_2 layer, addition of a surface-active reagent (Triton X-405 0.01 wt.%) to the first impregnation solution ($Mn(NO_3)_2$–CH_3COOAg) was carried out.

Fig. 3 shows results when the first MnO_2 coat was carried out by the pyrolysis of an aqueous $Mn(NO_3)_2$ solution containing 1 wt.% CH_3COOAg and 0.01 wt.% surface-active reagent (Triton X-405); repeated pyrolysis was done without the surface-active reagent.

Excellent capacitor characteristics, such as the maximum capacitance (200 μF) and low tan δ value (at 120 Hz), were obtained as shown in Fig. 3.

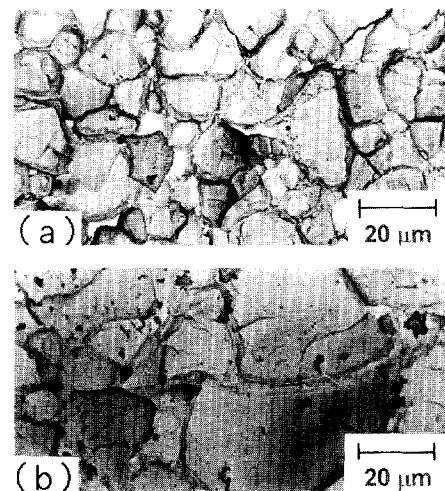
Fig. 2. SEM photograph of the obtained MnO_2 surface layer: (a) obtained from pyrolysis of $Mn(NO_3)_2$ solution at 300 °C, and (b) obtained from pyrolysis of $Mn(NO_3)_2$ solution in the presence of silver acetate at 300 °C.
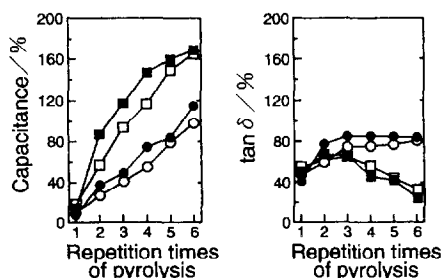

Fig. 1. Capacitance and dissipation factor (tan δ at (□,■) 120 Hz and (○,●) 1 kHz of the obtained tantalum capacitor. MnO_2 layers were obtained with (■,●) silver acetate and (□,○) without silver acetate.
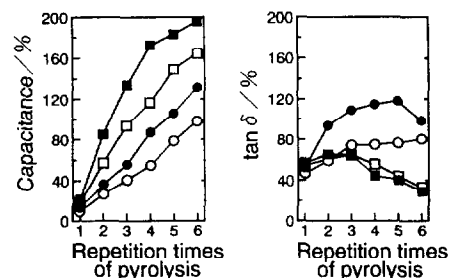
Fig. 3. Capacitance and dissipation factor (tan δ at (□,■) 120 Hz and (○,●) 1 kHz of tantalum capacitor. The first impregnation solution (■,●) contained 0.01 wt.% surface-active reagent (Triton X-405).

Fig. 4(a) shows the results of DSC and thermal gravimetry (TG) of $Mn(NO_3)_2$ (b) with and (a) without CH_3COOAg. The results of the aqueous solution of $Mn(NO_3)_2$ showed a steep endothermic band around 80 °C (dehydration), a steep endothermic band at 174.6 °C (peak B) and a small endothermic band at 186 °C (peak C). With the addition of CH_3COOAg to the $Mn(NO_3)_2$ solution, a larger endothermic band due to dehydration shifted towards a lower temperature and its intensity was increased, which may be due to the acceleration of the dehydration process. Both bands B and C shifted towards lower temperatures. The intensity of the band B was decreased, in contrast to the intensity of the band C that was increased.

Fig. 4(b) shows the thermal gravimetric data. The weight loss in wt.% based on an initial sample weight versus temperature is shown.

As can be seen in Fig. 4(b), the thermal gravimetric data of the $Mn(NO_3)_2$ solution can be divided into three parts. The weight loss at region (I) was mainly due to the released water. Region (II) shows the weight loss between 148 and 175 °C. Region (III) shows the weight loss between 175 and 350 °C. In order to explain the pyrolysis process, the sample weight at 350 °C is temporarily considered to be MnO_2, because the weight of samples between 250 and 350 °C is essentially constant in TG.

We calculated the weight gain based on the sample weight at 350 °C. The values of weight gain in regions (II) and (III) in Fig. 4(b) were 206 and 140%, respectively.

According to Albella et al. [6], the pyrolysis process can be divided into the following reactions:

$$Mn(NO_3)_2 \rightarrow MnONO_3 + NO_2 \tag{1}$$

$$MnONO_3 \rightarrow MnO_2 + NO_2 \tag{2}$$

The weight gains in regions (III) and (II) are calculated to be 141 and 205%, respectively, if regions (III) and (II) are due to the transformation of MnO_2 to $MnONO_3$ (Eq. (2)) and $MnONO_3$ to $Mn(NO_3)_2$ (Eq. (1)). These values agree well with the experimental values. These results support the decomposition process of an aqueous solution of $Mn(NO_3)_2$ as $Mn(NO_3) \cdot nH_2O \rightarrow Mn(NO_3)_2 \rightarrow MnONO_3 \rightarrow MnO_2$.

TG results lead to the following conclusion. In region II, which is represented by the DSC peak of B and C, decomposition of $Mn(NO_3)_2$ to $MnONO_3$ occurs. This process may have a more complex process because two peaks (B and C) are shown.

The decomposition process of the $Mn(NO_3)_2$ solution containing CH_3COOAg is fundamentally the same as that of the $Mn(NO_3)_2$ solution, although the peak temperature based on B and C shifted to a lower temperature as described before.

XRD patterns of MnO_2's obtained from the pyrolysis of an aqueous solution of $Mn(NO_3)_2$ in a convectional furnace (curve A), from in a saturated H_2O atmosphere (curve B) and of aqueous $Mn(NO_3)_2$ with CH_3COOAg in a saturated H_2O atmosphere (curve C) are shown in Fig. 5.

All these main products were β-MnO_2. The order of the peak intensity of (101) plane of β-MnO_2 is as follows: (curve A) < (curve B) < (curve C). The crystallinity of β-MnO_2 is increased in this order.

The existence of α-Mn_2O_3 as a by-product is shown in Fig. 5. The decomposition temperature when heat-treating MnO_2 to Mn_2O_3 was reported to be 420 °C [9]. However, the transformation temperature of MnO_2 to Mn_2O_3 was found to shift to a lower temperature. Since α-Mn_2O_3 has a higher electrical resistance than that of β-MnO_2, this may cause a higher dissipation factor of the capacitor. However, our data show the opposite results. This contradiction may be explained as follows. Electric conductivity in the particle inside would be high, however, the conductivity between
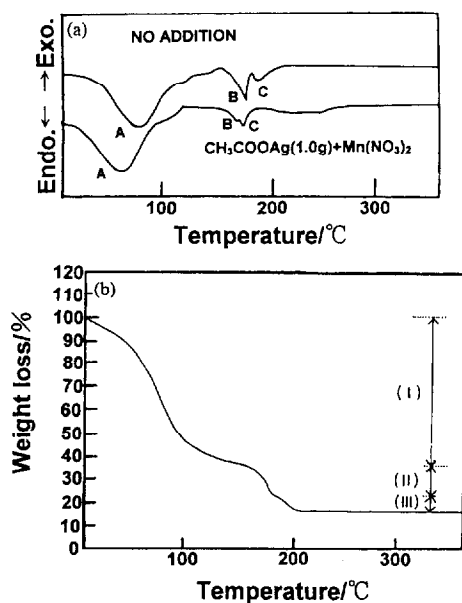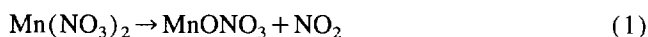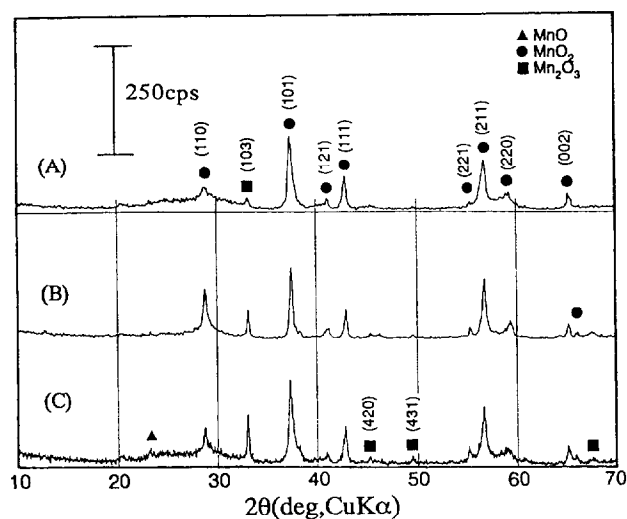

Fig. 4. (a) DSC curve of an aqueous solution of manganese nitrate (curve b) with and (curve a) without silver acetate. (b) TG of an aqueous solution of manganese nitrate.

Fig. 5. XRD patterns of the obtained MnO_2 layer. MnO_2 layers were obtained from the pyrolysis of $Mn(NO_3)_2$ solution (A) in a convectional dry furnace, (B) in a saturated H_2O atmosphere furnace, and (C) from an $Mn(NO_3)_2$ solution with silver acetate in a saturated H_2O furnace at 300 °C.

particles (at boundaries between particles) would be hindered. Factors affecting the resistance would not be existence of a by-product, but of the particle size. This is the main reason why the capacitor having large particles of MnO_2 shows excellent performance.

4. Conclusions

The capacitance of a tantalum capacitor has been increased using a MnO_2 layer obtained from pyrolysis of an aqueous solution of manganese nitrate in the presence of silver acetate in an atmosphere of saturated H_2O.

The obtained MnO_2 layer showed high crystallinity in the XRD pattern; large particles are seen in a SEM photograph.

The MnO_2 formation mechanism has been discussed based on thermal analyses.

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