An optical method for evaluating the degradation mechanism of a developing RuO₂ thick film resistor element for power modules

Yoshinobu NAKAMURA[†], Yuki KITANAKA, Masaru MIYAYAMA, Takeshi ITO*, Koichi URANO*, Kiyoshi TANAKA*, Tomohiko NAKAJIMA** and Tetsuo TSUCHIYA**

Department of Applied Chemistry, Graduate School of Engineering, The University of Tokyo,
7–3–1 Hongo, Bunkyo-ku, Tokyo 113–8656, Japan

*KOA Corporation, 14016 Oaza, Naka-Minowa, Minowa-machi, Kamiina-gun, Nagano 399–4697, Japan

**Advanced Coating Technology Research Center, National Institute of Advanced Industrial Science and Technology,
1–1–1 Higashi, Tsukuba, Ibaraki 305–8565, Japan

We devised a simple and noninvasive method for evaluating the spacial distribution of local electron densities of a thick-film RuO₂-based chip resistor using UV–VIS–IR reflectance microscopy. After a long-term durability test for 874 h under an elevated temperature of 623 K, RuO₂ resistors were thermally damaged, and their resistance became more than 10% higher. We identified the thermally damaged region by this new method and found that the thermal degradation is mainly due to an increase in the resistance between the Ag electrode and the RuO₂ resistor film.

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1. Introduction

Active electronic devices produced by a wide-gap semiconductor receive much attention for their application to next-generation power electronics. Recent progress in silicon carbide (SiC) wafer technologies enables us to manufacture more efficient energy supply and conversion systems for constructing a sustainable low-carbon society.¹⁾ For steady progress in R&D in power electronics, progress not only in active semiconductor devices but also in passive device technologies, e.g., resistors, capacitors, and inductor technologies, is strongly in demand. Accompanying the trend of high-output power devices, a self-heating effect from active areas will limit device performance. Accordingly, heat resistance and good thermal management are required for the design of reliable power modules.

The developing 1200 V/150 A class SiC power modules will be used for next-generation power electronics, and it is rated to an operation temperature of greater than 523 K because of the extremely high junction temperature (T_j) of SiC devices (upward of $T_j = 873$ K) under operation.²⁾ Therefore, heat resistance at least to over 523 K will be required in resistors or other passive devices for SiC power modules. Ruthenium dioxide (RuO₂) is a highly electro-conductive material with resistivity of about $4 \times 10^{-5} \Omega \text{ cm}$ and with high chemical stability,³⁾ and it is used as a basic material for metal-glaze chip resistors. Commercial chip resistors are often made by screen-printing and sintering RuO₂–PbO–SiO₂ glass composites, and they provide sufficient performance with long-term stability when the device is operated at room temperature with low power consumption.⁴⁾ However, in commercial chip resistors, the upper limit of the operating temperature is 423 K at most,⁴⁾ and they are not designed for high-temperature

and high-power use. Therefore, studies on the degradation of RuO₂ resistors had been limited to those which occurred below the maximum recommended service temperature of a commercial RuO₂ resistor.^{5)–9)} The conductive component, RuO₂ reacts with water vapor at humidity ambient and that reduce the resistance of a resistor film accompanied by forming ruthenium oxide hydride (RuO₂·xH₂O). At the elevated temperature ranging up to 443 K, dehydration of surface RuO₂·xH₂O proceeds and that causes the drift of the resistance.^{8),9)} The effect of forming gas (H₂/N₂ mixture) introduction on the stability of the resistance of an RuO₂ thin film resistor is discussed by Jelenkovic and the resistance rapidly increases, then decreases by the exposure of forming gas at over 423 K. The decrease in resistance is caused by the reduction of RuO₂ to Ru, while the increase in the resistance is due to the morphological degradation.¹⁰⁾ Not only an RuO₂ film itself but metallic Ag used for a conductive assistant and/or electrode degrades during the temperature test, because Ag is known to convert to Ag₂O by heat treatment at 423 K.⁸⁾ Therefore, Ag electrodes, which are often used as electrodes for a resistor will also degrade under the severe temperature conditions in air.

The key point is to clarify which part is most sensitive to the temperature fluctuation. For clarifying the thermally degraded area of an RuO₂ resistor, direct measurement of the electrical resistivity of local areas is applicable;¹¹⁾ however, that is not an easy process because of the technical difficulties in the micro-electrode wiring on the limited area, typically less than 100 μm square.

Here, we propose an easy but reliable method for evaluating the micro-area resistance of a resistor device by using optical reflectance data. RuO₂ is a metallic conductor, and its optical reflection is dropped off at the critical photon energy (or wavelength) due to the free and bound electron absorption.¹²⁾ When the optical absorptions by bound electrons are extremely small or negligible, this critical photon energy for a metallic conductor is roughly correlated with the plasma frequency ω_p , which is simply expressed by

[†] Corresponding author: Y. Nakamura; E-mail: tnakamu@mail.ecc.u-tokyo.ac.jp

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$$\omega_p = \sqrt{\frac{ne^2}{\epsilon\epsilon_0 m^*}} \quad (1)$$

where n , e , ϵ , ϵ_0 , and m^* are the electron concentration, elementary charge, specific dielectric constant of a material, dielectric constant of vacuum, and effective mass of electron, respectively. Since the ω_p is closely related to the electron concentration of n , and using this relation of $\omega_p \propto \sqrt{n}$, one can evaluate n as a function of ω_p .

The objective of the present study is to obtain the spacial distribution of the local electron concentrations of an RuO₂ resistor film, especially in the vicinity of the electrode-resistor film interface, by the analysis of the local reflectance spectra obtained by a microscope spectrometer. The optical method we devised in the present study is a simple and noninvasive method for evaluating a local electron concentration. The spacial resolution of our optical method is less than 20 μm and that is rather higher than that by the direct resistance measurement by using micro-electrodes. Comparing the spectrum of each local region, we can identify the damaged region of an RuO₂ resistor film and speculate the thermal degradation mechanism of each region.

2. Experimental procedure

2.1 Materials and their electrical characterization

For the high-temperature durability test, we prepared an RuO₂ film whose heat-resistance properties were almost equivalent to a conventional metal-glaze chip resistor. In the first step of the preparation of a resistor chip, Ag paste including 5 wt % of palladium and 5 wt % of glass flit was screen printed on an alumina substrate and fired at 1123 K for 45 min. The Ag electrode was almost fully dense and >0.6 wt % of impurities was not detected by the EDX analysis. For the preparation of an RuO₂ film, a conductive component (RuO₂), PbO–B₂O₃–SiO₂ glass frit, and an organic binder were mixed in the desired proportion, screen-printed over the Ag parallel electrodes on top of an alumina substrate, then, fired at 1123 K for 45 min in air. The cross-sectional view of an RuO₂ resistor was illustrated in **Fig. 1**. Two prototypes with different resistances were provided: a high-resistance type (HR_RuO₂) and a low-resistance type (LR_RuO₂). The resistance of an RuO₂ resistor was controlled by controlling the ratio of the amount of conductive component to glass flit. A high-resistance type resistor; HR_RuO₂, whose component ratio between conductive component and glass flit was 60:40 in weight, was mainly used for the durability test under an elevated temperature. For the optical reflectance measurement, the surface of an RuO₂ resistor film was finished to an optical flat (roughness $\sim 0.5 \mu\text{m}$) using polishing film sheets. The high-temperature durability test was conducted in a tube furnace at 623 K in a O₂ gas stream for 192 and 874 h. The environmental condition for the durability test was accelerated condition, which was more severe than the operation condition of a SiC power module of $\sim 523 \text{ K}$ in air. The electrical resistance of test sample HR_RuO₂ was checked using a dc 2 probe method after the predetermined period. In this measure-

Fig. 1. Cross-sectional view of an RuO₂ resistor, HR_RuO₂.

ment, the contribution of the interface resistance between the Ag electrode and the RuO₂ resistor film was included. The carrier concentration and conduction type of the resistor film were determined by Hall effect measurement under a field from -8 to $+8 \text{ T}$ using a Physical Properties Measuring System (PPMS: Quantum Design, Co., Ltd., San Diego, CA, USA).

2.2 Measurement of the microscopic reflectance spectra

Local area reflectance spectra of HR_RuO₂ or LR_RuO₂ finished-surface resistor films were measured using UV–VIS–IR microscope spectrometer (JASCO Inc., model MSV-370). The spectrum data were obtained as the relative reflectance collected by using aluminum film as a reference. The dimension of the scanning probe was $20 \times 200 \mu\text{m}$ and its position: x (distance from the Ag–RuO₂ interface) was moved by moving the sample stage of the microscope spectrometer. The reflection spectrum of each measuring point was collected at a wavelength scanning rate of 100 nm/min. The spatial resolution of the optical spectroscopy can be determined by the dimension of an optical spot of the spectrometer, which was limited by the wavelength of the light carried to the specimen. The theoretical spatial resolution of the spectroscopy at $\lambda = 2000 \text{ nm}$ was about 2.7 μm . For a better S/N ratio of spectroscopy, the minimum spot size should be 15–20 μm square. For our purpose, a higher spacial resolution to the y direction (along the Ag–RuO₂ interface) was not necessary, and then we expanded the dimension of an optical spot to $20 \times 200 \mu\text{m}$; the spacial resolution to the x direction was determined to 20 μm . Optical characterization was conducted before and after the long-term durability test at 623 K in a O₂ gas stream for 192–874 h, and the electrical resistance of the specimen was checked after the predetermined period.

The amount of Ag diffused and precipitated over the surface of the RuO₂ film was also evaluated as a function of the distance from the Ag electrode by the analysis of the reflectance spectra. The inter-band absorption of Ag¹³⁾ which was observed at $\lambda = 316 \text{ nm}$ and the amount of Ag were defined as $R_{316 \text{ nm}}/R_{500 \text{ nm}}$, where $R_{316 \text{ nm}}$ and $R_{500 \text{ nm}}$ were reflectance at 316 and 500 nm, respectively. If we reverse the direction of the vertical axis, this graph would indicate the amount of Ag over an RuO₂ surface as a function of the distance from the electrode.

2.3 Admixture of Ag and RuO2 powder as a model system of Ag–RuO2 interface

As described later, the solid-state reaction between the Ag electrode and the RuO₂ film accompanied by the transferring oxygen ions played an important role in the gradual change in resistance during the durability test. For the evaluation of oxygen transferring in the vicinity of the Ag–RuO₂ interface, we prepared an admixture of Ag and RuO₂ powder with a molar ratio of 1:4 and analyze its thermal gravity (TG). The admixture of RuO₂ and Ag powder was uni-axially pressed into a disk. The large interface area between Ag and RuO₂ particles is guaranteed. Therefore, this system was considered to be a model system of a Ag–RuO₂ interface, and the oxygen-transfer process was speculated from the TG data. The temperature profile for the TG analysis was 398 K for 3 h, 673 K for 3 h, and 1123 K for 45 min, which are the same as that in the manufacturing process of HR_RuO₂ and LR_RuO₂.

3. Results and discussion

Figure 2 shows the degradation degree of the resistance of an RuO₂ resistor: HR_RuO₂ during the long-term durability test at

Fig. 2. Time dependence of the resistance of an RuO₂ resistor, HR_RuO₂, during a durability test in a O₂ gas stream at 623 K. Temperature coefficient of resistivity (TCR) ($\times 10^{-6} \text{ K}^{-1}$) before and after the durability test, shown in brackets.

Fig. 3. Reflectance spectra of a local area ($20 \times 200 \mu\text{m}$) of the as-prepared RuO₂ resistor, HR_RuO₂, (a) near the Ag-RuO₂ interface ($x = 40 \mu\text{m}$) and (b) far from the interface ($x = 460 \mu\text{m}$). x (μm) is the distance from the electrode, which was defined in Fig. 1.

623 K. This temperature condition, 623 K was 100 K higher than the temperature assumed in a high-power module under operation. The initial resistance of HR_RuO₂ was 135Ω with a temperature coefficient of resistivity (TCR) of $309 \times 10^{-6} \text{ K}^{-1}$. In the beginning, its resistance increased gradually, then, rapidly increased in the last part of the durability test. The TCR properties also degraded to $746 \times 10^{-6} \text{ K}^{-1}$ after the durability test for 874 h. Taking a look at the microscopic view, the Ag electrode was mechanically damaged after the durability test in this condition. Accordingly, in the total change of electrical resistance, both of the changes by electrical properties of RuO₂ resistor film itself and by mechanical damage of Ag electrode are included.

3.1 Observation and analysis of the reflectance spectrum of an RuO₂ resistor film

The reflectance spectra of a local area ($20 \times 200 \mu\text{m}$) of the as-prepared HR_RuO₂ resistor (a) near the Ag-RuO₂ interface ($x = 40 \mu\text{m}$; x is the distance from the electrode) and (b) far from the interface ($x = 460 \mu\text{m}$) are shown in Fig. 3. The spectra are characterized by the rapid decreases in reflectance in the near-infrared region, which are due to the free electron absorption of RuO₂. The critical wavelength at which the reflectance spectrum dropped off is defined as λ' . The experimentally obtained reflectance spectra shown in Figs. 3(a) and 3(b) are relative reflectance spectra using an aluminum mirror for a reference, but the result contains the characteristic feature of the optical properties of RuO₂ single crystals reported by Goel, et al.¹²⁾ The fine structures assigned to inter- and intra-band adsorption such as p-d and d-d absorption, were observed in the spectrum of an RuO₂ single crystal;¹²⁾ however, no characteristic fine structure was observed in our specimens [Figs. 3(a) and 3(b)]. Similar reflectance spectra, whose fine structures were missing, were observed in poly-

Fig. 4. Reflectance spectra of a (a) high-resistance product (HR_RuO₂) and (b) low-resistance product (LR_RuO₂).

crystalline RuO₂ films.^{14)–16)} In addition, a sharp absorption peak at $\lambda = 316 \text{ nm}$ was observed in the spectrum of the near interface region [$x = 40 \mu\text{m}$ in Fig. 3(a)], which was assigned to inter-band transition of Ag,¹³⁾ and this is evidence for the diffusion of Ag from the electrode to the RuO₂ film during the manufacturing process.

From the result shown in Figs. 3(a) and 3(b), we can uniquely obtain a parameter: λ' , that is the critical wavelength at which the reflectance spectra were dropped off by the free electron absorption. Since the λ' is not exactly equal to the “real” plasma edge of $\lambda_p = 2\pi c/\omega_p$ which is derived from Eq. (1), we conducted following experiments. We checked the reflection spectra of RuO₂ resistors having a different resistance, which were named HR_RuO₂ for a high-resistance type and LR_RuO₂ for a low-resistance type (Fig. 4). These spectra were obtained from the center part of an RuO₂ film ($x = 2100$). The lower shift in the λ' of LR_RuO₂ (low-resistance product) was observed and λ' was suggested to be linked with the carrier concentration of RuO₂. Supposing the Drude model, the carrier concentrations were calculated using the Eq. (1) and $m^* = 9.11 \times 10^{-31} \text{ kg}$ (electron rest mass) and $\varepsilon = 1$. The results are $1.21 \times 10^{21} \text{ cm}^{-3}$ for HR_RuO₂ and $1.41 \times 10^{21} \text{ cm}^{-3}$ for LR_RuO₂.

We also checked the polarity and concentration of charge carriers of HR_RuO₂ and LR_RuO₂. The polarity of the Hall coefficient of the RuO₂ resistors film was always negative, and their major carrier was determined to be electron. The electron concentration of HR_RuO₂ and LR_RuO₂ were evaluated to be $n = 1.01 \times 10^{21} \text{ cm}^{-3}$ and $n = 1.57 \times 10^{21} \text{ cm}^{-3}$, respectively. The optically obtained electron concentrations of these two RuO₂ resistors were qualitatively in agreement with those obtained by the Hall effects measurement. Accordingly, the optical method we proposed here was found effective for evaluating the local electron densities in the RuO₂ resistors, although the obtained λ' was not exactly equal to real plasma edge obtained by the K-K analysis.¹⁷⁾

3.2 Qualitative analysis of the spacial distribution of the carrier density in the vicinity of Ag electrode-RuO₂ film interface.

Figure 5 shows the reflection spectra of the (a) $x = 120 \mu\text{m}$ (near the Ag-RuO₂ interface) and (b) $x = 500 \mu\text{m}$ (far from the Ag-RuO₂ interface) region of HR_RuO₂ after the durability test for 0, 192, and 874 h at 623 K; we can see the aging effect of the critical wavelength, λ' , which was peculiar in the vicinity of the Ag-RuO₂ interface. At the near interface region, λ' increased with an increase in testing time [Fig. 5(a)], while the shifts in λ' were very small in the region far from the Ag-RuO₂ interface [Fig. 5(b)]. An increase in λ' means a decrease in free-

Fig. 5. The effect of standing time on the reflectance spectra of the HR_{RuO₂} resistor; (a) is the spectrum obtained at $x = 120 \mu\text{m}$ (near the Ag-RuO₂ interface), and (b) is that at $x = 500 \mu\text{m}$ (far from the Ag-RuO₂ interface) region. The temperature and atmosphere for this durability test were 623 K and O₂, respectively. Standing times for the durability test were $t = 0, 192$, and 874 h.

electron concentration, therefore, the degradation would preferentially proceed in the vicinity of the interface during the high-temperature durability test under an elevated temperature. For specifying the thermally damaged region, we evaluated the spacial distribution of electron concentrations of HR_{RuO₂} as a function of the distance from the Ag electrode: x .

Supposing $\lambda' \simeq \lambda_p$, ω_p in Eq. (1) can be replaced as $2\pi c/\lambda'$ and the equation was rewritten as

$$n' = A \left(\frac{2\pi}{\lambda'} \right)^2, \quad A = \frac{\varepsilon \varepsilon_0 c^2 m^*}{e^2}, \quad (2)$$

where c is speed of light. Here, we defined n' as the electron concentration obtained by using Eq. (2). For the qualitative analysis of a thermal degradation of an RuO₂ resistor, we can use n' as an alternative parameter of the “real” carrier concentration n . The spacial distribution of n' of HR_{RuO₂} resistor before and after the durability test at 623 K for 192 h is shown in Fig. 6(a). The point to notice is that the bottom Ag electrode is located under the RuO₂ resistor film at the region of $x = 0-280 \mu\text{m}$, which is the hatched part of Fig. 6.

The parameter n' of an as-prepared specimen gradually increased with an increase in the distance from the electrode, x , and showed a maximum at $150 < x < 200 \mu\text{m}$, then gradually decreased and converged to a constant value at $x > 500 \mu\text{m}$, as shown in Fig. 6(a) A. This means that a high electron concentration region exists in the region of $x = 0-350 \mu\text{m}$. After the durability test at 623 K for 192 h, the spacial distribution of carrier density dramatically changed and the interface higher electron-concentration region was annihilated, as shown in Fig. 6(a).

This annihilation will lead to an increase in the interface resistance and also the increase in total electrical resistance, as is shown in Fig. 2. The originally existing high electron-concentration region of HR_{RuO₂} ($x = 0-350 \mu\text{m}$) almost coincide with the hatched region in Fig. 6, where a Ag electrode exists at the bottom of an RuO₂ film. It suggests some interaction between Ag and RuO₂ film for the formation of the high electron-concentration region. Details are discussed in the section 3.3 and 3.4.

The local electron concentration distributions of the HR_{RuO₂} resistor before and after the durability test at 493 and 523 K for 192 h are shown in Fig. 7. The interface high electron concentration region remained even after the durability test at 493 K, but it was annihilated in the test at 523 K. The thermal degradation of an RuO₂ resistor will not rapidly proceed unless it is used at over 523 K.

Fig. 6. (a) Spatial distribution of optically obtained electron concentration n' before and after the durability test at 623 K for 192 h. The n' is obtained according to Eq. (2). The hatched part ($x = 0-280 \mu\text{m}$) is the region in which the Ag electrode was located under the RuO₂ resistor film. (b) Spatial distribution of the amount of Ag diffused from the electrode before and after the durability test at 623 K for 192 h. The amount of Ag is defined as $R_{316 \text{ nm}}/R_{500 \text{ nm}}$, where $R_{316 \text{ nm}}$ and $R_{500 \text{ nm}}$ are reflectance at 316 and 500 nm, respectively. $R_{316 \text{ nm}}/R_{500 \text{ nm}} = 1$ means that no Ag was detected from the spectrum.

3.3 Origin of the formation/annihilation of interface high electron concentration region

The contributing factor that explains the formation/annihilation of the interface high electron concentration region is the formation/annihilation of the oxygen deficiency of RuO₂ due to the catalysis of the Ag electrode in contact with the RuO₂ film. For evaluation of the oxygen incoming/outgoing process from/to an Ag/RuO₂ interface, TG analysis of the Ag-RuO₂ admixture, which was the model system of the Ag-RuO₂ interface, was conducted. The temperature profile for the TG measurement was the same as that for the manufacturing process of an RuO₂ resistor and the result is summarized in Fig. 8. A gradual increase in

Fig. 7. Spatial distribution of n' (A) before and (B–D) after the durability test at 493, 523 and 623 K for 192 h. The hatched part ($x = 0\text{--}280\text{ }\mu\text{m}$) is the region in which the Ag electrode was located under the RuO₂ resistor film.

Fig. 8. Result of the TG analysis of a mixture of RuO₂–Ag pressed powder compact whose molar ratio was RuO₂:Ag = 4:1. That is the model system of an RuO₂–Ag interface. The measuring atmosphere is air, and the temperature profile is the same as that in the manufacturing process of HR-RuO₂. Process (1) of the TG curve was assigned to the oxidation of the Ag particle, and processes (2) was assigned to the decomposition of AgO_x.

weight was observed at $T > 523\text{ K}$ during heating [process (1) in Fig. 8]. This increase in weight could be assigned to the partial oxidation of Ag particles with oxygen in the atmosphere as:

Here, we suppose that some of the lattice oxygen ions in RuO₂ were also used for the oxidation of Ag and oxygen vacancies were formed in RuO₂ as follows.

where $\text{O}_{\text{o}}^{x}(\text{RuO}_2)$ and $\text{V}_{\text{O}}^{\bullet\bullet}(\text{RuO}_2)$ are lattice oxygen and the oxygen vacancy in RuO₂, respectively. Reaction (4) will proceed at an elevated temperature of $>523\text{ K}$, as will reaction (3), and excess oxygen vacancies ($\text{V}_{\text{O}}^{\bullet\bullet}(\text{RuO}_2)$) will be formed in the vicinity of near surface of RuO₂ particles. Therefore, we can speculate the formation of excess oxygen vacancies in the RuO₂ film along the interface with the bottom Ag electrode during the fabrication process of an RuO₂ resistor. Oxygen vacancies in oxides work as electron donors following Eq. (4), and this would be the origin of the interface high electron concentration region observed in the as-prepared specimen.

During the firing at 1123 K, the weight of Ag–RuO₂ admixture rapidly decreased, as shown Fig. 8. At the elevated temperature,

silver oxides are known to release lattice oxygen and turn into metallic silver with the reverse reactions of Eqs. (3) and (4).^{18)–20)} However, at the intermediate temperature during cooling, oxidative reactions as Eqs. (3) and (4) occur again, though the Ag–RuO₂ system is in the nonequilibrium state. Similar reactions are speculated to proceed at the interface between the Ag electrode and the RuO₂ film.

Judging from the negative sign of the Hall coefficient, RuO₂ films fabricated in our process show n -type conduction. The resistivity of our RuO₂ resistive film is about $5 \times 10^{-3}\text{ }\Omega\text{ cm}$ and the value is two orders of magnitude higher than those of previously reported RuO₂ films made by the sputtering technique.²¹⁾ Due to such a low carrier concentration in our RuO₂ film, its electrical conductivities would be sensitive to oxygen defect concentrations and the conductivity increases with an increase in oxygen defect concentrations accompanied by the production of free electrons. In an as-prepared specimen, the carrier concentrations are enhanced by 10% at most in the vicinity of the Ag–RuO₂ interface ($x = 0\text{--}350\text{ }\mu\text{m}$) and this modulation in electron concentrations will occur when c.a. 0.2% of the lattice oxygen ions of RuO₂ are removed. That was not an unrealistic value.

The interface high electron concentration layers observed in an as-prepared specimen were annihilated after long-term standing in the high-temperature ($>523\text{ K}$) atmosphere [Figs. 6(a) and 7]. In an as-prepared specimen, the near interface region between the RuO₂ film and the Ag electrode (the region of $x = 0\text{--}300\text{ }\mu\text{m}$) is in the nonequilibrium state and contains excess oxygen vacancies. By the annealing at $T > 523\text{ K}$, the system getting closer to the equilibrium states and the amount of excess oxygen vacancies will be decreased. As a result, the interface resistance between the RuO₂ film and the Ag electrode is enhanced. Thus, we can explain the mechanism of the increase in resistance during the high-temperature standing (Fig. 2).

Figure 6(b) shows a spatial distribution of the amount of Ag or Ag ions diffused from the Ag electrode after the durability test at 623 K, which can be evaluated by the local reflectance spectrum under the high-temperature (623 K) condition. Silver ions diffused from the electrode and they partially covered the RuO₂ film surface at the region of $x = 0\text{--}450\text{ }\mu\text{m}$. In this region, diffused Ag was worked as a supported catalyst and it may promote the diffusion of adsorbed oxygen over the Ag layer into the RuO₂ film.

3.4 Mechanical damage of the Ag electrode accompanied by the diffusion of Ag from the electrode

Indeed, one of the origins of the unexpected increase in the resistance of the RuO₂ resistor was the annihilation of the interface higher carrier concentration region as discussed in the previous section. However, mechanical damage of the Ag electrode would also proceed during long-term standing at 623 K. As shown in Fig. 6(b), Ag was diffused from the electrode to the RuO₂ film and accordingly, the Ag electrode itself was damaged.

The SEM view and the elemental map for Ag by EDX in the vicinity of the Ag–RuO₂ interface after the endurance test at 623 K are shown in Fig. 9. In an EDX map, Ag was detected over the RuO₂ film in the region of $0 < x < 450\text{ }\mu\text{m}$ and this result is consistent with the result in Fig. 6(b). In addition, an Ag-deficient region existed between the Ag electrode and the RuO₂ film. It is suggested that the Ag electrode eroded during the durability test at 623 K, and Ag ions diffused along the RuO₂ film surface, then precipitated over the RuO₂ film in the region of $0 < x < 450\text{ }\mu\text{m}$. Ag ions are known to rapidly diffuse in a borosilicate glass due to the pseudo-alkali effect resulting from Ag-alkali ion exchange.²²⁾

Fig. 9. The SEM view and elemental map of Ag by EDX in the vicinity of the Ag electrode–RuO₂ interface after the durability test at 623 K in O₂. The Ag electrode was mechanically damaged due to the diffusion of Ag to the RuO₂ surface, as illustrated in the upper panel of the figure.

However, no enhanced Ag diffusion was observed in another higher resistance specimen, whose glass phase component was much larger than that of the HR-RuO₂. Therefore, the conductive glass components in an RuO₂ resistor film will not work as the rapid diffusion pass of Ag ions, possibly surface diffusion over the RuO₂ particle network would preferentially occur.

This mechanical damage of the electrode would be another origin of the unexpected increase in resistance during the durability test; and the gradual increase in resistance at the final stage of the durability test would be caused mainly by this corrosion of the electrode, because the annihilation of the interface higher carrier concentration layer would end within 192 h in our test, as shown in Figs. 6(a) and 7.

In conclusion, we propose two possible degradation mechanisms of an RuO₂ resistor, (1) an increase in the contact resistance due to the annihilation of the originally existing higher carrier concentration at the interface between the Ag electrode and the RuO₂ film and/or (2) degradation of the mechanical contact between the Ag electrode and the RuO₂ film, which is due to the unexpected diffusion of Ag from the Ag electrode to the RuO₂ film.

4. Conclusions

In the present study, we established an alternative method for evaluating the local carrier density of an RuO₂ chip resistor as a function of the distance from an electrode–resistor film interface. This method easily and quickly provides us with location information about the degradation area of an RuO₂ resistor. It appears that the use of Ag as an electrode material has a risk of the fluctuation of contact resistance between the Ag electrode and RuO₂, whose origin is the formation/annihilation of local electron concentrations accompanied by oxidation/reduction of the Ag layer in contact with the Ag–RuO₂ interface. Corrosion of the Ag electrode would simultaneously proceed due to the diffusion of Ag to the RuO₂ layer, which is another cause of increased contact resistance.

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