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

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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 (Tj) of SiC devices (upward of Tj = 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 × 10−2 Ω cm and with high chemical stability,3) and it is used as a basic material for metal-glace 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,5) 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.6)–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.6)–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.9) 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 ωp, which is simply expressed by

\[
\omega_p = \sqrt{\frac{4\pi n_e e^2}{m_0}}
\]
\[ \alpha_p = \sqrt{\frac{n\epsilon^2}{2E\mu_m^*}} \]  

where \( n \), \( \epsilon \), \( \epsilon_0 \), 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 \( \alpha_p \) is closely related to the electron concentration of \( n \), and using this relation of \( \alpha_p \propto \sqrt{n} \), one can evaluate \( n \) as a function of \( \alpha_p \).

The objective of the present study is to obtain the spatial distribution of the local electron concentrations of an RuO\(_2\) resistor, especially in the vicinity of the electrode-resistor 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 spatial resolution of our optical method is less than 20 \( \mu \)m 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 RuO\(_2\) 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 RuO\(_2\) 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 frit 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 RuO\(_2\) film, a conductive component (RuO\(_2\)), PbO-B\(_2\)O\(_3\)-SiO\(_2\) 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 RuO\(_2\) resistor was illustrated in Fig. 1. Two prototypes with different resistances were provided: a high-resistance type (HR.RuO\(_2\)) and a low-resistance type (LR.RuO\(_2\)). The resistance of an RuO\(_2\) resistor was controlled by controlling the ratio of the amount of conductive component to glass frit. A high-resistance type resistor; HR.RuO\(_2\), whose component ratio between conductive component and glass frit 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 RuO\(_2\) resistor film was finished to an optical flat (roughness \( \sim 0.5 \) \( \mu \)m) using polishing film sheets. The high-temperature durability test was conducted in a tube furnace at 623 K in an O\(_2\) gas stream for 192 and 874 h. The environmental condition for the durability test was conducted in a tube furnace at 623 K in an O\(_2\) gas stream for 192 and 874 h. The environmental condition for the durability test was almost fully dense and > 0.6 wt% of impurities was not detected by the EDX analysis. 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In this measure-ment, the contribution of the interface resistance between the Ag electrode and the RuO\(_2\) 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 \(+8\) 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.RuO\(_2\) or LR.RuO\(_2\) 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 \( \mu \)m and its position: \( x \) (distance from the Ag–RuO\(_2\) 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 \( \lambda = 2000 \) nm was about 2.7 \( \mu \)m. For a better S/N ratio of spectroscopy, the minimum spot size should be 15–20 \( \mu \)m square. For our purpose, a higher spatial resolution to the \( y \) direction (along the Ag–RuO\(_2\) interface) was not necessary, and then we expanded the dimension of an optical spot to 20 \( \times \) 200 \( \mu \)m; the spatial resolution to the \( x \) direction was determined to 20 \( \mu \)m. Optical characterization was conducted before and after the long-term durability test at 623 K in a O\(_2\) 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 RuO\(_2\) 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 Ag\(_{\text{I}3\text{d}}\) which was observed at \( \lambda = 316 \) nm and the amount of Ag were defined as \( R_{316\text{nm}} \) and \( R_{500\text{nm}} \), respectively. If we reverse the direction of the vertical axis, this graph would indicate the amount of Ag over an RuO\(_2\) surface as a function of the distance from the electrode.

2.3 Admixture of Ag and RuO\(_2\) powder as a model system of Ag–RuO\(_2\) interface

As described later, the solid-state reaction between the Ag electrode and the RuO\(_2\) 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–RuO\(_2\) interface, we prepared an admixture of Ag and RuO\(_2\) powder with a molar ratio of 1:4 and analyze its thermal gravity (TG). The admixture of RuO\(_2\) and Ag powder was uni-axially pressed into a disk. The large interface area between Ag and RuO\(_2\) particles is guaranteed. Therefore, this system was considered to be a model system of a Ag–RuO\(_2\) 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.RuO\(_2\) and LR-RuO\(_2\).

3. Results and discussion

Figure 2 shows the degradation degree of the resistance of an RuO\(_2\) resistor; HR.RuO\(_2\) 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 an O2 gas stream at 623 K. Temperature coefficient of resistivity (TCR) (×10^-4 K^-1) before and after the durability test, shown in brackets.

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 135 Ω with a temperature coefficient of resistivity (TCR) of 309 × 10^-4 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 × 10^-4 K^-1 after the durability test for 874 h.

Fig. 3. Reflectance spectra of a local area (20 × 200 μm) of the as-prepared RuO2 resistor, HR.RuO2. (a) near the Ag–RuO2 interface (x = 40 μm) and (b) far from the interface (x = 460 μm). x (μm) is the distance from the electrode, which was defined in Fig. 1.

The critical wavelength at which the reflectance spectra 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 absorption 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 polycrystalline RuO2 films.14-16 In addition, a sharp absorption peak at λ = 316 nm was observed in the spectrum of the near interface region ([x = 40 μm 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 obtained by the K-K analysis,17 we conducted following experiments. We checked the reflectance 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.

Fig. 4. Reflectance spectra of a (a) high-resistance product (HR.RuO2) and (b) low-resistance product (LR.RuO2).

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 × 200 μm) of the as-prepared HR.RuO2 resistor (a) near the Ag–RuO2 interface (x = 40 μm: x is the distance from the electrode) and (b) far from the interface (x = 460 μm) 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 absorption 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 polycrystalline RuO2 films.14-16 In addition, a sharp absorption peak at λ = 316 nm was observed in the spectrum of the near interface region ([x = 40 μm 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.

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Supposing the Drude model, the carrier concentrations were calculated using the Eq. (1) and m* = 9.11 × 10^-13 kg (electron rest mass) and e = 1. The results are 1.21 × 10^21 cm^-3 for HR.RuO2 and 1.41 × 10^21 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 n = 1.01 × 10^21 cm^-3 and n = 1.57 × 10^21 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 reflectance spectra of the (a) x = 120 μm (near the Ag–RuO2 interface) and (b) x = 500 μm (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-
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 spatial distribution of electron concentrations of HRRuO₂ as a function of the distance from the Ag electrode: x.

Supposing \( \lambda' \simeq A \rho \), \( \omega_0 \) in Eq. (1) can be replaced as \( 2\pi c/\lambda' \) and the equation was rewritten as

\[
n' = A \left( \frac{2\pi c}{\lambda'} \right), \quad A = \frac{\varepsilon_0 e^2 m^*}{\hbar^2}, \tag{2}
\]

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 spatial distribution of \( n' \) of HRRuO₂ 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 \( x = 0-280 \mu m \), 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 \( 150 < x < 200 \mu m \), then gradually decreased and converged to a constant value at \( x > 500 \mu m \), as shown in Fig. 6(a) A. This means that a high electron concentration region exists in the region of \( x = 0-350 \mu m \). 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 HRRuO₂ \( (x = 0-350 \mu m) \) almost coincided 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 HRRuO₂ 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. 5.](image)

![Fig. 6.](image)

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
Here, we suppose that some of the lattice oxygen ions in RuO$_2$ 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 K) atmosphere [Figs. 6(a) and 7]. In an as-prepared specimen, the near interface region between the RuO$_2$ film and the Ag electrode (the region of $x = 0$–300 $\mu$m) is in the nonequilibrium state and contains excess oxygen vacancies. By the annealing at $T > 523$ 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 RuO$_2$ 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 RuO$_2$ film surface at the region of $x = 0$–450 $\mu$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 RuO$_2$ 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 RuO$_2$ 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 RuO$_2$ 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–RuO$_2$ interface after the endurance test at 623 K are shown in Fig. 9. In an EDX map, Ag was detected over the RuO$_2$ film in the region of 0 < $x$ < 450 $\mu$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 RuO$_2$ film. It is suggested that the Ag electrode eroded during the durability test at 623 K, and Ag ions diffused along the RuO$_2$ film surface, then precipitated over the RuO$_2$ film in the region of 0 < $x$ < 450 $\mu$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 layer 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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