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Effect of Cr_2O_3 and NiO dopants in α-Al_2O_3 on its electrical conductivity under electron irradiation

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Abstract

The electrical conductivity of single crystals of α-Al_2O_3 doped with Cr_2O_3 (0.03–2.5 wt%), NiO (0.75 wt%) plus Cr_2O_3 (0.03–0.15 wt%), and NiO (0.75 wt%) has been measured under 1 MeV electron irradiation at 300 K to investigate the effects of the concentration of impurity and of the depth of impurity levels in forbidden bands on the radiation induced conductivity (RIC). The RIC of Cr_2O_3 and/or NiO doped α-Al_2O_3 decreases with increasing concentration of Cr_2O_3 and/or NiO dopants. The electrical conductivity of 2.5 wt% Cr_2O_3 doped α-Al_2O_3 is smaller than any other doped materials tested. The dose rate exponent for Cr_2O_3 doped α-Al_2O_3 is smaller than that for NiO plus Cr_2O_3 doped material, due to deeper trapping centers of Cr (5.8 eV from the conduction band) than those of Ni (2.0 eV). Doping impurities with deep trapping centers are most effective for suppressing RIC.
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1. Introduction

Radiation induced conductivity (RIC) and radiation induced electrical degradation (RIED) in ceramic insulators are believed to play critical roles in the assessment and selection of materials. Alpha-alumina (α-Al_2O_3) is one of the most promising materials for insulators and windows in fusion devices [1,2], especially in the international thermonuclear experimental reactor (ITER). It is, therefore, necessary to evaluate the electrical conductivity and to understand the mechanism of the electrical conductivity of α-Al_2O_3 in radiation fields.

It has been suggested theoretically [3,4] and experimentally [4] that impurities in α-Al_2O_3 suppress RIC. In Refs. [3,4], however, it does not specify what nature of impurities affect the RIC in α-Al_2O_3. In addition, few systematic studies have been done for the effect of impurities on the RIC in α-Al_2O_3, although many studies have been carried out under different radiation fields [5–15]. Thus it has not been determined that what nature of impurities effectively suppresses RIC. In order to get insights into the effect of impurity atoms, their concentration and impurity levels in forbidden bands on RIC, effects of Cr_2O_3 and NiO dopants in α-Al_2O_3 have been investigated under 1 MeV electron irradiation.

2. Experimental

Single crystals of α-Al_2O_3 (Nakazumi Crystal Laboratory) doped with 0.75 wt% NiO, with 0.75 wt% NiO plus 0.03–0.15 wt% Cr_2O_3, or 0.03–2.5 wt% Cr_2O_3 were used as specimens. The size of specimens was 5.5 mm diameter and 0.3 mm thick. The center, guard and ground electrodes were made on the specimens by vapor deposition of titanium in a vacuum pressure of 10^{-4} Pa. The diameter of the electrodes were as follows: 2 mm for the center electrode, 3.5 mm (inner) and 4.5 mm (outer) for the guard, and 4.5 mm for the ground electrode. A specimen holder developed for in situ measurements in a high voltage electron microscope (HVEM) (JEM-1000) [16] was used. Irradiation was performed with a 1 MeV electron flux of 1.0×10^{19} e/m^2 s (6.2×10^4 Gy/s and

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1.1×10^{-9} dpa/s) in a HVEM at the HVEM Laboratory, Kyushu University. The electrical conductivity was measured under a DC electric field of 300 kV/m at 300 K with or without electron irradiation using a Hewlett Packard HP4339A high resistance meter.

3. Results and discussion

Fig. 1 shows the electrical conductivity of Cr_2O_3 doped α-Al_2O_3 at 300 K as a function of electron flux. The electrical conductivity of undoped α-Al_2O_3 is also shown in Fig. 1. The electrical conductivity increases with increasing electron flux. The electrical conductivity of Cr_2O_3 doped α-Al_2O_3 under irradiation decreases with increasing content of doping Cr_2O_3 and is smaller than for the undoped material at the same electron flux. The values of electrical conductivity of 0.03, 0.05, 0.15 and 2.5 wt% Cr_2O_3 doped α-Al_2O_3 at the maximum electron flux of 9.0×10^{17} e/m^2 s are 2.6×10^{-7}, 1.8×10^{-7}, 1.4×10^{-7} and 8.7×10^{-9} S/m, respectively, in contrast to the value of 5.9×10^{-7} S/m for undoped α-Al_2O_3. That means doping with Cr_2O_3 suppresses the RIC in α-Al_2O_3. The decrease in the electrical conductivity with doping Cr_2O_3 results because the Cr levels in forbidden band capture the carrier electrons excited by irradiation.

The electrical conductivity of NiO doped and NiO plus Cr_2O_3 doped α-Al_2O_3 is shown in Fig. 2 as a function of electron flux. In Fig. 2 the electrical conductivity of undoped α-Al_2O_3 is also included. The electrical conductivity increases with increasing electron flux, being smaller than that of the undoped material. At the flux of 1.0×10^{18} e/m^2 s the values of electrical conductivity are 2.4×10^{-7}, 2.1×10^{-7} and 7.5×10^{-8} S/m for NiO doped, for NiO plus 0.15 wt% Cr_2O_3 doped and for NiO plus 0.03 wt% Cr_2O_3 doped α-Al_2O_3, respectively, against the value of 7.0×10^{-7} S/m for undoped α-Al_2O_3.

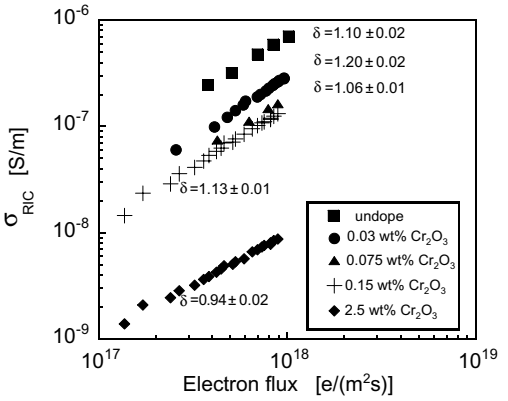

Fig. 1. The electrical conductivity of a single crystal of α-Al_2O_3 doped with Cr_2O_3 as a function of electron flux. That of undoped α-Al_2O_3 is also included in this figure.

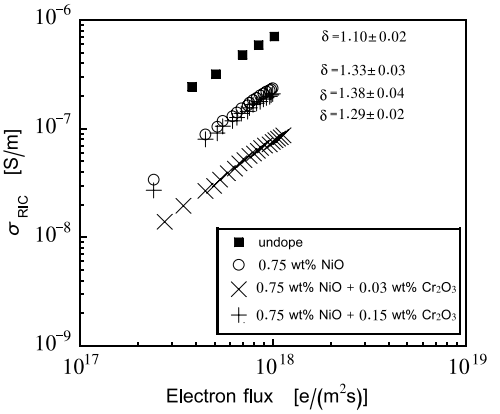

Fig. 2. The electrical conductivity of a single crystal of α-Al_2O_3 doped with Cr_2O_3 plus NiO as a function of electron flux. That of undoped α-Al_2O_3 is also included in this figure.

The electrical conductivity of NiO plus Cr_2O_3 doped α-Al_2O_3 is smaller than that of NiO doped material, indicating that RIC is effectively suppressed by Cr_2O_3 doping rather than NiO doping although it is suppressed by only NiO doping. This means that Ni and Cr levels formed in the forbidden band capture the carrier electrons excited by irradiation and that the electrons are captured more effectively by Cr levels than Ni levels. In the case of NiO plus Cr_2O_3 doped α-Al_2O_3, the electrical conductivity does not decrease with increasing Cr_2O_3 concentration although it decreases with increasing the content of Cr_2O_3 in the case of only Cr_2O_3 doping, which means that the carrier electrons are not captured only by Cr levels. From the results in Figs. 1 and 2, the electrical conductivity of 2.5 wt% Cr_2O_3 doped α-Al_2O_3 is smaller than any other doped material.

Fig. 3 shows the electron flux dependence of electrical conductivity of undoped, 2.5 wt% Cr_2O_3 doped and NiO plus 0.15 wt% Cr_2O_3 doped α-Al_2O_3. The electrical conductivity of all specimens is smaller than the limiting conductivity (10^{-6} S/m) of the insulator for magnetic coils at the dose rate of 3000 Gy/s (5.6×10^{16} e/m^2 s) near the first wall in ITER. In particular, the electrical conductivity of 2.5 wt% Cr_2O_3 doped α-Al_2O_3 is smaller than any other doped material, being smaller than the limiting conductivity (10^{-6} S/m) of the insulator for magnetic coils at dose rates less than 5.0×10^6 Gy/s (9.3×10^{19} e/m^2 s). The electrical conductivity of NiO plus Cr_2O_3 doped α-Al_2O_3 is, however, greater than that of undoped material and the limiting conductivity (10^{-4} S/m) for general insulators in fusion reactors at greater than 5.0×10^6 Gy/s.

The electrical conductivity σ under irradiation is empirically expressed by the following relation,

$$\sigma = \sigma_0 + k\phi^{\delta},$$

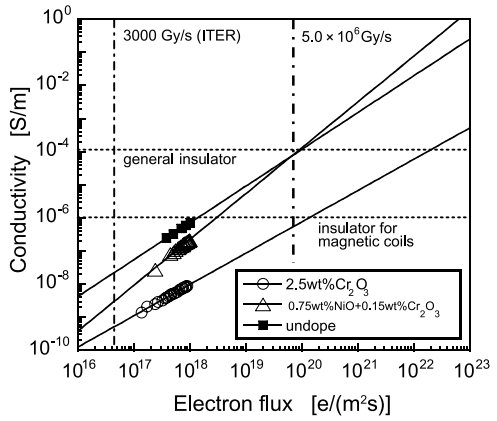

Fig. 3. The electron flux dependence of electrical conductivity of undoped, 2.5 wt% Cr_2O_3 doped and NiO plus Cr_2O_3 doped single crystal of α-Al_2O_3. A upper and lower dotted lines show the allowed limiting conductivity of 10^{-4} (general insulators) and 10^{-6} S/m (insulators for magnetic coils), respectively. A left dash-dotted line shows the dose rate (3000 Gy/s) around the first wall in ITER.

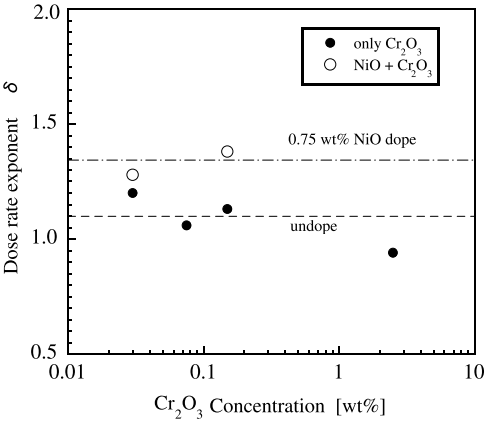

Fig. 4. The Cr_2O_3 concentration dependence of dose rate exponent, δ, for Cr_2O_3 doped and for 0.75 wt% NiO plus Cr_2O_3 doped single crystal of α-Al_2O_3 at 300 K. Dotted and dash-dotted lines indicate the δ for undoped and for 0.75 wt% NiO doped α-Al_2O_3, respectively. The experimental errors of δ are included within the diameter of open and closed circles.

where σ_0 is the conductivity in the absence of radiation, k a constant, ϕ the electron flux and δ a dose rate exponent. The values of δ for 0.03, 0.075, 0.15 and 2.5 wt% Cr_2O_3 doped α-Al_2O_3 are 1.20 ± 0.02, 1.06 ± 0.01, 1.13 ± 0.01 and 0.94 ± 0.02, respectively, as indicated in Fig. 1. Values for 0.75 wt% NiO doped, for 0.75 wt% NiO plus 0.03 wt% Cr_2O_3 doped, and for 0.75 wt% NiO plus 0.15 wt% Cr_2O_3 doped α-Al_2O_3 are 1.33 ± 0.03, 1.29 ± 0.02 and 1.38 ± 0.04, respectively, shown in Fig. 2. These contrast to the value of 1.10 ± 0.02 for undoped material. The values of δ are greater than 1.0, suggesting that the carrier electrons are excited from not only the valence band but also from impurity (Cr and/or Ni) levels to the conduction band. The values of δ for NiO doped α-Al_2O_3 are greater than that of Cr_2O_3 doped α-Al_2O_3, which suggest that the electrons in Ni levels are excited more than in Cr levels.

Fig. 4 shows the Cr_2O_3 concentration dependence of δ at 300 K. In Fig. 4, an open and closed circles show the δ for Cr_2O_3 doped and for NiO plus Cr_2O_3 doped α-Al_2O_3, respectively, and dotted and dash-dotted lines indicate the δ for undoped ($\delta = 1.10$) and 0.75 wt% NiO doped ($\delta = 1.33$) α-Al_2O_3, respectively. The values of δ for Cr_2O_3 doped and for NiO plus Cr_2O_3 doped α-Al_2O_3 increase due to doping Cr_2O_3 and/or NiO except for 0.75 and 2.5 wt% Cr_2O_3 doped material. The value of δ for Cr_2O_3 doped α-Al_2O_3 is smaller than that for NiO plus Cr_2O_3 doped material, decreasing with increasing Cr_2O_3 concentration in contrast to increasing the value for NiO plus Cr_2O_3 doped α-Al_2O_3.

Theoretical models for the electrical conductivity under irradiation indicate that the value of δ changes due to the existence of shallow and deep trapping centers between the conduction and the valence bands [3,4]. It has been reported that Ni and Cr dopants in α-Al_2O_3 form impurity levels at 2.0 and 5.8 eV above the valence band, respectively [17]. The values of δ for Cr_2O_3 doped α-Al_2O_3 are smaller than that for NiO plus Cr_2O_3 doped α-Al_2O_3 due to deeper trapping centers of Cr than those of Ni. The decrease in the value of δ for Cr_2O_3 doped α-Al_2O_3 with doping Cr_2O_3 is due to the increase of trapping centers of Cr. The values of δ for NiO plus Cr_2O_3 doped α-Al_2O_3 increase with increasing Cr_2O_3 concentration, which means that the δ value is dominated by the concentration of the shallow trapping centers of Ni. Thus doping with a high concentrate of impurities with deep trapping centers in α-Al_2O_3 is needed to give to be small value of δ.

It is concluded that high concentration doping using an impurity with deep trapping centers is most effective for suppressing the electrical conductivity under irradiation.

4. Summary and conclusions

In this study, the electrical conductivity of Cr_2O_3 and/or NiO doped α-Al_2O_3 was measured at 300 K with or without 1 MeV electron irradiation in a HVEM. The results obtained are summarized as follows:

(1) The RIC is more suppressed as the amount of Cr_2O_3 and/or NiO doping is increased.
(2) The value of the dose rate exponent for Cr_2O_3 doped α-Al_2O_3 is smaller than that for NiO plus Cr_2O_3 doped material due to deeper trapping centers of

Cr (5.8 eV from the conduction band) than those of Ni (2.0 eV).

(3) Doping using an impurity with deep trapping centers is most effective for suppressing the RIC of α-Al_2O_3.

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