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EPR studies on defects in sol-gel derived alumina films

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Abstract

We have studied the defect structures and mechanism for the luminescence of non-doped, Tb^{3+} -doped and $Tb^{3+}-Zn^{2+}$ codoped alumina films treated at various temperatures from 300 to 800 °C. The electron paramagnetic resonance (EPR) spectra observed before UV-irradiation are attributable to the non-bridging oxygen radicals; AI-O-O at treatment temperatures of 300-500 °C and AI-O at 800 °C. The UV-light irradiation of the non-doped alumina films gives the EPR spectra with the ²⁷Al hyperfine splitting. There exists a good correlation between the treatment temperature dependence on the light-induced EPR signal intensity of the trapped electron and the NMR peak intensity due to the five-coordinated aluminum ion. We concluded that the electron is captured at the oxygen vacancy connected with the five-coordinated aluminum. The broad EPR spectra due to the ground state of the Tb^{3+} ion were observed in the Tb^{3+} -doped and $Tb^{3+}-Zn^{2+}$ codoped alumina films. The Tb^{3+} concentration dependence of the EPR signal intensity due to the non-bridging oxygens suggests that Tb^{3+} prefers to form AI-O-Tb bonds and prevent to form a cluster of rare earth ions itself. The light-induced EPR signal of the electron trapped at oxygen vacancy next the five-coordinated aluminum was also observed for the $Tb^{3+}-Zn^{2+}$ codoped alumina film, which produced a long-lasting luminescence. The photogenerated trapped electron remained for several minutes under the room temperature. These experimental facts indicate that the five-coordinated aluminum ions act as the trapping sites to produce the long-lasting luminescence.

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1. Introduction

Long lasting luminescent materials have attracted attention [1–7] since their properties of accumulation of photon energy can be utilized in various fields such as battery-free illumination and information storage nanodevices [8–10]. Recently we reported that non-doped alumina films show a luminescence with lifetime of a few 10 ms [11], that rare earth ions can be highly doped into alumina films prepared by using aqueous sol derived from AlCl₃·6-H₂O [12,13], and that Tb³⁺–Zn²⁺ codoped alumina films show a long-lasting luminescence [11]. Based on the fact that glasses prepared by the sol–gel method exhibit defects even without X-ray, γ -ray and neutron irradiation [14,15], we hypothesized that these properties were due to the highly

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amorphous nature and defective structure of the produced alumina. To further investigate this possibility, we here examined the defect structures of alumina films using electron paramagnetic resonance (EPR) and nuclear magnetic resonance (NMR).

2. Experiment

All reagents were of reagent grade and were obtained commercially from Wako Pure Chemicals (Osaka, Japan). The preparation of alumina film by the aqueous sol-gel method was essentially identical to that previously described [11-13]. Hydrous aluminum oxide was prepared through the reaction of aqueous AlCl₃ solution with aqueous 6 M NH₃ solution. The precipitate hydroxide was aged for 12 h, then filtered and washed with pure water to remove unreacted chloride. It was then made into a clear sol by

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peptizing with acetic acid under reflux at 80 °C. Metal iondoped films were prepared as follows. The viscous sol was mixed with rare earth chloride solution to give a concentration of 1-15 mol% of rare earth ions per Al₂O₃. The sol was transferred into a plastic Petri dish. Gelation was performed in a glove box by the dehydration of aqueous sol under room temperature. The resultant films were heattreated in air at different temperatures (200–800 °C) for 2 h. ²⁷Al MAS NMR measurements were performed at room temperature on an FT-NMR spectrometer (JEOL JNM-GX270). EPR measurements were carried out at 5 K using an X-band spectrometer (Bruker ESP380E). Light irradiation for measurement of EPR spectra was produced using a high pressure Hg lamp (Ushio 500W).

3. Results and discussion

The resultant alumina films were optically transparent up to a treatment temperature of 900 °C because of the almost amorphous structure. In fact, the X-ray diffraction patterns (XRD) show only a few weak and broad bands that were assigned to a pseudo-boehmite structure at 25–400 °C, to a γ alumina (spinel) structure at 500–800 °C, and to δ and θ alumina at 900–1000 °C. Above 1000 °C, the alumina film became gradually opaque with increasing the heat-treatment temperature since the crystallization with α alumina (corundum) structure was accelerated.

We detected the five-coordinated alumina, which have a defect of oxygen, by ²⁷Al MAS NMR. Fig. 1 shows the ²⁷Al MAS NMR spectra of the alumina films heat-treated at various temperatures. The broadness of all the signals indicates that the aluminum ions are present in various environments, as reflected in the amorphousness of our alumina. There are mainly six-coordinated aluminum ions (octahedra) in the films heat-treated at relatively low temperatures. Four-coordinated aluminum ions (tetrahedra) increase and the alumina develops a spinel structure with an increase of heat-treating temperature. Signals of fivecoordinated aluminum ions were also observed. The fivecoordinated alumina is an alumina lacking oxygen, and it exists in γ alumina and other transition alumina. The signal increases with heat-treating temperature, reaches a maximum at about 550 °C, and then decreases at higher temperature. The signals of five-coordinated aluminum ions were scarcely observed for the alkoxide-derived alumina. Our alumina films derived from inorganic salt are more amorphous and oxygen-defective than the alumina derived from alkoxide.

Fig. 2 shows the EPR spectra of the non-doped alumina films heat-treated at various temperatures observed before UV-light irradiation. A weak narrow EPR signal was detected around g = 2.004 for the alumina films treated at 300 °C. The signal increases in intensity for the 500 °C-treated alumina film. If the Al atom holds the unpaired



Fig. 1. 27 Al MAS NMR spectra for the alumina films heat-treated at: (a) 300 °C; (b) 400 °C; (c) 500 °C; (d) 600 °C; and (e) 800 °C. The asterisk indicates a spinning side band.

electron or is located near the position of the electron spin, the EPR signal must be split into multi-lines because the nuclear spin of ²⁷Al, of which natural abundance is 100%, is 5/2. No apparent hyperfine structure of the EPR spectra for the 300 and 500 °C-treated alumina films was observed, suggesting that the paramagnetic site is different from those of an Al center [16,17] or aluminum-oxygen hole center (Al–OHC) [18–22]. The simple line with the g value larger than g_e (2.0023) for free electron is consistent with the oxygen hole center (Oxy) [18-20]. The Oxy defect is considered to have a structure of peroxy radicals, i.e. Al-O-O in which the distance between aluminum atom and the electron spin is long enough to neglect the hyperfine interaction with Al. When the film was annealed at 800 °C, the signal of the Oxy defect of Al-O-O disappeared and a weak broad signal appeared. The broad signal can be assigned to Al-OHC such as Al-O rather than the Oxy defect, because the large hyperfine splitting due to Al and large g-anisotropy were clearly observed. The observed spectrum could be simulated with the EPR parameters listed in Table 1.

When the alumina films were irradiated with UV-light, new EPR signals appeared as shown in Fig. 3. The EPR signal intensity drastically decreased as the treatment temperature rose above 500 °C. The non-doped alumina



Fig. 2. EPR spectra for the non-doped alumina films heat-treated at: (a) 300 °C; (b) 500 °C; and (c) 800 °C. The spectra were measured before irradiation at 5 K by using a field modulation system of 0.5 mT amplitude and 100 kHz frequency. The dotted line is a powder pattern spectrum calculated with the spin Hamiltonian parameters of the Al–O defect (Table 1) in assuming a Gaussian for a line shape. The full-width-of-half maximums (Γ) of the Gaussian function are 1.5 mT, 7.0 mT and 11.0 mT for the three principle directions of the g-tensor, respectively.

heat-treated at 300–500 °C showed luminescence, while that heat-treated at 800 °C showed almost no luminescence [11]. The good correspondence of the temperature dependences between the luminescence and EPR intensities indicates that the defect giving the multi-lines is responsible for the luminescent center in the alumina films.

We have simulated the multi-lines by the spin Hamiltonian $(\hat{\mathbf{H}}_{S})$ comprised from the anisotropic Zeeman

Table 1 Spin Hamiltonian parameters for the defects in the alumina films detected by EPR

Defect	<i>g</i> ₁	<i>g</i> ₂	<i>g</i> ₃	A ₁ (mT)	A ₂ (mT)	A ₃ (mT)
Al-O-O [°] Al-O [°] Trapped electron	2.000 2.066 2.0021	2.002 2.085 2.0021	2.010 2.220 2.0021	- <0.7 0.90	- <1.7 0.90	- 15.0 1.44



Fig. 3. Light-induced EPR spectra for the non-doped alumina films heat-treated at: (a) 300 °C; (b) 500 °C; and (c) 800 °C. The spectra were measured during UV-irradiation at 5 K by using a field modulation system of 0.5 mT amplitude and 100 kHz frequency. The dotted line is a powder pattern spectrum calculated with the spin Hamiltonian parameters of the trapped electron (Table 1) in assuming a Gaussian ($\Gamma = 0.6 \text{ mT}$) for a line shape.

 $(\mu_{\hat{B}}\mathbf{B}_{\hat{O}}\cdot\mathbf{g}\cdot\hat{\mathbf{S}})$ interaction and hyperfine interaction $(\hat{S}\cdot\mathbf{A}_{A}\cdot\hat{\mathbf{I}})$ of Al.

$$\hat{H}_{\rm S} = \mu_{\rm B} B_0 \cdot g \cdot \hat{S} + \gamma_{\rm Al} B_0 \cdot \hat{I} + \hat{S} \cdot A_{\rm Al} \cdot \hat{I}$$
(1)

where $\mu_{\rm B}$ and $\gamma_{\rm Al}$ are, respectively, Bohr magneton and magnetogyric ratio of 27 Al nuclei. **B**₀ indicates magnetic field. $\hat{\mathbf{S}}$ and $\hat{\mathbf{I}}$ stand for spin operators for unpaired electron and Al nuclear spins. When not only the isotropic hyperfine interaction but also anisotropic hyperfine interaction was taken into account, the observed multilines could be reproduced well (Fig. 3). The obtained EPR parameters are listed in Table 1. Around the central field, however, the calculated spectrum does not agree with observed one. The disagreement indicates the presence of minor defect that is not associated with Al atom. The isotropic hyperfine term, $A^{iso} (= (A_1 + A_2 + A_3)/3)$, was determined to be 1.08 mT. This value is substantially small compared with the Fermi-contact interaction for Al (98.3 mT) calculated with aluminum 3s orbital [23], suggesting that about 1% of the electron spin exists on the Al atom. The anisotropic terms $(A_n - A^{iso})$ are estimated to be $A_1^{an} = -0.18 \text{ mT}, A_2^{an} = -0.18 \text{ mT}, A_3^{an} =$ +0.36 mT. Such an axial anisotropy can be explained

within a point dipole approximation expressed as follows

$$A_{\rm an} = \frac{\mu_0}{4\pi} \gamma_{\rm e} \gamma_{\rm Al} \frac{3\cos^2\theta - 1}{r^3}$$
(2)

where γ_e is magnetogyric ratios of electron, μ_0 is permeability of vacuum, θ is the angle between the external magnetic field (\mathbf{B}_0) and the direction connecting the unpaired electron and the nearest Al atom. r indicates the distance between the electron and Al atom. A_{2}^{an} corresponds to the hyperfine interaction when θ is zero. A_1^{an} and A_2^{an} are the value of $\theta = \pi/2$. From these anisotropic terms, hence, r for the light-induced defect was calculated to be 0.16-0.17 nm. The distance almost coincides with the bond distance of Al-O calculated from the ionic radii for Al^{3+} (0.051 nm) and O^{2-} (0.132 nm). The estimated distance suggests that the light-induced defect seems to be the Al-OHC, but the g anisotropies are different from each other. While the g-values for the lightinduced defect are isotropic and smaller than g_{e} , those for the Al–OHC are anisotropic and lager than g_e [22]. Therefore, the paramagnetic center in which an electron is captured in the nearest neighboring oxygen vacancy to Al atom is a reasonable model for the light-induced defect in the alumina films. This model is similar to the F⁺-like center detected in reduced CaO-Al₂O₃ glasses [24].

The ²⁷Al MAS NMR measurements suggest the presence of the five-coordinated alumina lacking oxygen, which decreases as the treatment temperature goes up to more than 550 °C. Since the temperature behavior of the fivecoordinated alumina corresponds to the decrease of the light-induced EPR spectrum at more than 500 °C, the lightinduced defect is ascribable to an electron trapped at oxygen vacancy associated with the five-coordinated alumina. The amorphous property of the alumina films in this study has a large number of non-bridging oxygens and five-coordinated alumina ions. These defective structures may work as the trapping sites for electrons. Consequently, it is concluded that the trapped electrons at oxygen vacancy play an important role as long-lived luminescent centers.

Fig. 4 shows the Tb^{3+} doping effect on the EPR spectra for the alumina films heat-treated at 600 °C. By doping of the Tb^{3+} ions, the decrease of the signals due to Al-O was accompanied by the concomitant increase of the very broad EPR spectrum in the low field regions. The broad signal is assigned to the Tb³⁺ ion with the electronic configuration of 4f⁸, because the rare earth ions with several 4f-electrons usually show complicated resonance lines in the low magnetic field. The doping concentration of Tb³⁺ did not significantly affect the EPR spectral shape of Tb^{3+} , suggesting no drastic change of the local structure surrounding Tb^{3+} . We previously reported that Tb^{3+} and other rare earth ion-doped alumina films showed no significant luminescence quenching due to clustering of Tb^{3+} [11,25]. These facts are interpreted in terms of the greater preference for the bond formation between the defective Al-O sites and Tb³⁺ and for the dispersion of



Fig. 4. EPR spectra of: (a) non-doped; (b) Tb^{3+} (3 mol%)-doped; and (c) Tb^{3+} (15 mol%)-doped alumina films heat-treated at 600 °C. The spectra were measured before irradiation at 5 K by using a field modulation system of 0.5 mT amplitude and 100 kHz frequency.

Tb³⁺ in the alumina films. UV-irradiation of the Tb³⁺ doped film gave a weak and single EPR signal at $g \sim 2.0$. The multiple hyperfine structures due to ²⁷Al were not observed.

We also examined the Zn^{2+} ion codoping effect on the EPR spectrum, because the introduction of Zn^{2+} (or Ca^{2+}) into the Tb^{3+} -doped alumina films resulted in the long-lasting luminescence from the excited state of Tb^{3+} [25]. Although the lifetime of emission for the Tb^{3+} -doped film is ca. 2 ms, the luminescence of $Zn^{2+} - Tb^{3+}$ -codoped alumina films can be observed by naked eyes in more than 30 min after UV-light irradiation. Based on these drastic phenomena, we have proposed an electron trapping mechanism for the long-lasting luminescence [11].

During the light irradiation

$$Tb^{3+} + UV \text{ light} \rightarrow (Tb^{3+})^+ + e^*$$

e^{*} + oxygen defect center \rightarrow F⁺-like center.

After the irradiation

 F^+ -like center + phonon \rightarrow oxygen defect center + e^* $e^* + (Tb^{3+})^+ \rightarrow Tb^{3+}$ + luminescence.

During the light irradiation, Tb^{3+} is photo-oxidized to $(\text{Tb}^{3+})^+$ and generates an electron (e^{*}). The electron is trapped at the neighboring oxygen defect site. The trap depth of the oxygen defect center is shallow and broadly distributed by the structural variation owing to the codoped Zn^{2+} ions. Therefore, the electrons can be gradually

released at room temperature, and the long-lasting luminescence is realized.

Fig. 5 shows the EPR spectra of the Tb^{3+} (5 mol%)-Zn²⁺ (30 mol%) codoped alumina films treated at 800 °C before and after the UV-light irradiation. Before light irradiation only a weak signal of paramagnetic defect was observed, but an intense signal was detected after the light irradiation at very low temperatures. The multi-lines of the intense EPR spectrum were basically simulated by using the same spin Hamiltonian parameters as the trapped electron at oxygen vacancy next the five-coordinated alumina, which is observed for the non-doped alumina film during the light irradiation. The discrepancy between the calculated and observed EPR spectra around the central field implies the existence of another type of paramagnetic centers. While the multiplet EPR signal for the $Tb^{3+}-Zn^{2+}$ codoped alumina film remained somewhat by keeping the film for a few 10 min even at room temperature, the signal disappeared by heating for 10 min at 80 °C after the light irradiation. This result would indicate that the trapped electrons are thermally released from the oxygen vacancy site. The observation of the trapped electron at the oxygen vacancy by irradiation, which corresponds to F⁺-like center and is thermally recombined, verifies the electron trapping mechanism for



Fig. 5. EPR spectra of Tb³⁺ (5 mol%)–Zn²⁺ (30 mol%) codoped alumina films heat-treated at 800 °C: (a) before; and (b) after UV-light irradiation. The spectra were measured at 5 K by using a field modulation system of 0.5 mT amplitude and 100 kHz frequency. The dotted line is a calculated spectrum of the trapped electron using a Gaussian of $\Gamma = 1.2$ mT.

the long-lasting luminescence described above. The oxygen defect center is assigned to the oxygen vacancy close to the five-coordinated aluminum ion of which the energy depth is tunable by the codopant ions.

4. Conclusion

The EPR spectra due to the Al-O-O and Al-O radicals were observed before light-irradiation of the non-doped alumina films. The UV-photolysis generated the EPR signals split by the hyperfine interaction with Al. The EPR spectrum is attributed to the trapped electron at oxygen vacancy next the five-coordinated aluminum, which is the F⁺-like center. The EPR signals of the oxygen centered radicals decreased with doping of the Tb³⁺ ion. It was suggested that Tb³⁺ prefers the formation of Tb-O-Al bonds and prevents the cluster formation in the present amorphous films. The long-lived F⁺-like center was also observed for the $Tb^{3+}-Zn^{2+}$ codoped alumina film, which shows a long-lasting luminescence, by the UV-light irradiation. It is thus shown that the five-coordinated aluminum ions act as the trap center of the photo-ionized electrons.

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