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# Behavior of UV-generated carriers and local structure around doped aluminum in anatase titanium dioxide

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ABSTRACT

Al-doped anatase titanium dioxide single crystals and highly Al-doped powders were prepared by chemical vapor transport and by sol-gel process, respectively. Electron paramagnetic resonance (EPR) measurement on the single crystals and powders revealed the characteristic behavior of the UV-induced carriers. The UV-induced EPR sextuplet signals originating from photogenerated holes interacting with Al were observed in both the single crystals and powders. Simulation of the powder pattern of the sextuplet signals observed in EPR measurement indicates that the local structure around the trapped hole in the powder is identical to that of the single crystals. The signal intensity under the UV irradiation and the lifetime of the sextuplets after the UV irradiation decreased with increasing Al content. Rietveld analysis of the X-ray diffraction patterns of the powders revealed that the doped Al substitutes Ti, and that the lattice volume decreases with increasing Al content. The Raman bands of the powders shifted to a higher frequency with increasing Al content. On the basis of these experimental results, the mechanism and the stability of the photogenerated hole are discussed in terms of the dependence of the local structural changes around the doped Al on the Al content.

## 1. Introduction

An existence of small amount of an element often affects the thermal or electrical properties of pure matrix; for example, a phase transition may strongly depend on impurities unintentionally included in a pure substance, and the electric conductivity of narrow-gap materials strongly depends on dopants added intentionally to the matrix. On the other hand, the hidden characteristics of impurity or dopant may become clear in a particular matrix. $TiO_2$ has received considerable attention as a highly functional material because of its non-toxicity, high chemical stability, low cost, transparency to visible light, wide band gap, high refractive index, high photocatalytic activity, its ability to decompose various organic pollutants [1,2], and superhydrophilicity [3]. Because of these desirable properties, studies on applications of $TiO_2$ have been carried out in many fields such as photocatalysis [4–7], photovoltaic cells [8], gas sensors [9,10], solar cells [11–13], lithium-ion batteries [12], energy storage devices [12], photochromic switching [12], hydrogen generation by water photoelectrolysis [14], optical emissions [4,15,16], bioimplant applications [15], and electronic devices [4]. Owing to its high reactivity, $TiO_2$ dissolves various elements, resulting in the formation of a solid solution; thus, the doping of various elements has been studied.

$TiO_2$ has three different crystalline structures; anatase, rutile and brookite. Anatase has received considerable attention because it has higher photocatalytic activity than the other modifications [17]. In anatase, every titanium is surrounded by six oxygens to form a distorted $TiO_6$ octahedron, which shares its four vertices with four neighboring octahedra [18]. The distorted $TiO_6$ octahedron, which is elongated slightly toward the crystalline *c*-axis, has two long Ti—O (Ti-$_{long}$O) bonds parallel to the crystalline (001) axis and four short Ti—O (Ti-$_{short}$O) bonds arranged locally with $S_4$ symmetry, the oxygen is connected to three titanium atoms in a planar $C_{2v}$ configuration. Our previous electric paramagnetic resonance (EPR) studies [19,20] on anatase $TiO_2$ single crystal containing Al as an impurity revealed that two pairs of UV-induced sextuplets were observed at temperatures of 30–100 K. The studies also revealed that the UV-induced holes interacting with impurity Al are persistently trapped at around Al at low temperatures. Hole trapping at Al ions in rutile $TiO_2$ was reported previously [21,22]. Because the behavior of the photogenerated hole is important for understanding of the characteristic and for improving photocatalytic activity of anatase, the UV-induced holes interacting with Al impurity has attracted much interest. Thus, we have been preparing Al-doped anatase $TiO_2$ to investigate the relationship between the behavior of the photogenerated holes and the local structure

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around Al. The phase diagram for $Al_2O_3$−$TiO_2$ [23] suggests that there is a limitation in the amount of Al that can be doped in anatase single crystal. Our experience indicated the difficulty in the growth of highly doped single crystal with the desired content suitable for its structural analysis. In sol-gel processing, precursors are mixed at the molecular level, and materials with various compositions may be formed at much lower temperatures than those in traditional preparation methods. Therefore, the application of such powderless synthesis in the $TiO_2$−$Al_2O_3$ system enables highly doped powders to be obtained.

In this study, we performed EPR, X-ray diffraction (XRD) and Raman spectroscopy measurements on the Al-doped anatase $TiO_2$ single crystals and powders, and we revealed the local structure around Al interacting with the UV-induced hole. We proposed the mechanism and the stability of the localized state of the photogenerated holes.

## 2. Experimental procedure

Al-doped anatase titanium dioxide single crystals were grown by chemical vapor transport using $NH_4Cl$ as the transport agent. Mixed rutile $TiO_2$ and $Al(OH)_3$ powders with the desired Al content ($x = 0.1$, 2 and 5 mol%) were calcined at 1400 °C and evacuated in silica glass ampules. The sealed silica glass ampules were heated in a tubular furnace with a temperature gradient for 2–3 weeks. The obtained single crystals were colorless, and their crystalline axes were determined by the X-ray back-reflection Laue method. It was difficult to grow single crystal from calcined powder which contains Al more than 5 mol%. Al-doped anatase $TiO_2$ powders with desired Al content ($x = 0.1$–10 mol %) were obtained by the sol-gel procedure. Dilute nitric acid and aluminum isopropoxide were added to titanium isopropoxide (25 mmol) dissolved in 50 ml ethanol. The solution was stirred at 80 °C for 24 h under reflux, during which it becomes transparent. Finally, the transparent solution was gelated at room temperature, and the Al-doped powder was obtained by calcining the gel at 700 °C. The measurement of XRD and Raman spectra revealed that the calcined Al-doped powders have anatase structure and that contamination with small amount of rutile is observed in the undoped powder. The powders had various composition and contained much more Al than single crystals; thus these are suitable for the investigation of the local structural changes at around Al depending on composition.

EPR measurement was performed using a Bruker ESP300E spectrometer equipped with an ER041XK microwave unit operating at the X-band frequency (9.445 GHz). Single crystals were sealed in a quartz glass tube with a Teflon sample support. The resonance field and microwave frequency were calibrated using a proton NMR field marker and a cavity wavemeter, respectively. The temperatures of the samples were controlled by a cryostat (Oxford, GFS600) and temperature controller (Oxford, ITC 503). A UV LED (Nichia, NSHU591B) with a peak wavelength of 365 nm was used as the UV light source. The XRD of the powders was measured at RT using Rigaku RINT-2500 diffractometer with monochromatic Cu $K_\alpha$ radiation. The count data were recorded in a step-scan with an interval of 0.02° in the angular range of $2\theta$ = 21-87°. Raman spectra were measured at RT using a Renishaw inVia Raman microscope with an 1800 lines/mm grating. The excitation laser was a CW Nd:YAG laser operated at 532 nm.

## 3. Results and discussion

### 3.1. EPR spectra of Al-doped anatase single crystals and powders

EPR measurement of the Al-doped single crystals was performed to confirm that Al-doped single crystals react to UV irradiation as single crystal containing impurity Al in spite of the use of high purity $TiO_2$ (4N) as the raw material. Fig. 1 shows the temperature dependence of the EPR spectrum of the 0.1 mol% Al-doped anatase single crystal under the UV irradiation in the **H** ∥ (1 0 0) configuration. The signal (singlet) observed at 3385 G in the spectrum at RT shifted to a higher magnetic field with decreasing temperature and was observed at 3393 G at 30 K. This signal observed regardless of the UV irradiation is originated from a perpetual defect. At 30–80 K, two pairs of sextuplets were observed in the range of 3320–3380 G only under the UV irradiation. The nuclear spin of Al is $I = 5/2$; thus, the sextuplets arise from a paramagnetic species with $S = 1/2$ interacting with the nuclear spin of the doped Al. Below 30 K, a singlet signal appeared at 3387 G only under the UV irradiation. This indicates that the sextuplets and singlet have a close relationship with the UV-induced carriers. These temperature dependences of the singlet and the sextuplets are independent of the amount of the doped Al in the single crystal and have high reproducibility. Angle-resolved EPR measurement was performed to determine the EPR parameters of the singlet and the sextuplets observed in the Al-doped anatase $TiO_2$ single crystals. The angular dependence of the singlet of the Al-doped anatase $TiO_2$ single crystals at 20 K indicates that g-tensor corresponding to this singlet signal has tetragonal symmetry. The resultant parameters are summarized in Table 1. These g-matrix elements are comparable to those of permanently introduced

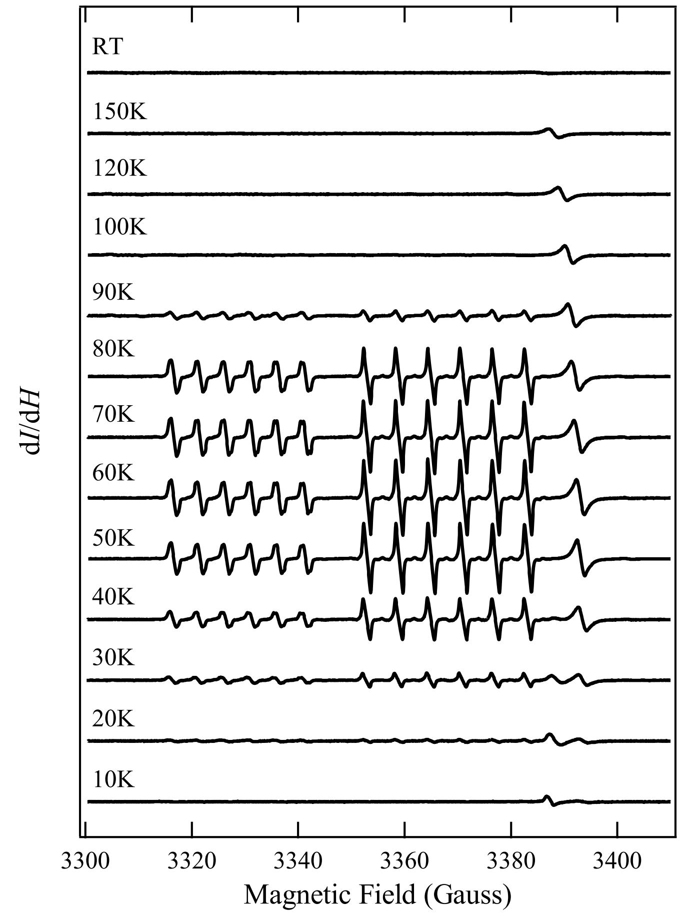


**Fig. 1.** Temperature dependence of EPR spectra of 0.1 mol% Al-doped anatase titanium dioxide single crystal under the UV irradiation in the **H** ∥ (1 0 0) configuration. The microwave frequency was operated at 9.44 GHz.

**Table 1**
g-value of the UV-induced singlet in the Al-doped single crystals observed at 20 K.

| Al content (mol%) | $g_{(100)}$ | $g_{(001)}$ |
|---|---|---|
| 0.1 | 1.9911 | 1.9619 |
| 2.0 | 1.9916 | 1.9613 |
| 5.0 | 1.9915 | 1.9625 |
| undoped [20] | 1.9929 | 1.9643 |