# Photoinduced electron paramagnetic resonance study of electron traps in TiO$_2$ crystals: Oxygen vacancies and Ti$^{3+}$ ions

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Electron paramagnetic resonance (EPR) is used to identify photoinduced titanium-associated electron traps in TiO$_2$ crystals (rutile). Defect production occurs at low temperature with 442 nm laser light. Spectra with $S=1/2$ and $S=1$ are assigned to singly ionized and neutral oxygen vacancies, respectively. These oxygen vacancies have their unpaired spins localized on the two neighboring titanium ions aligned along the $c$ axis. A Ti$^{3+}$ ion next to a Si$^{4+}$ ion, a Ti$^{3+}$ self-trapped electron, and a self-trapped hole shared by two adjacent oxygen ions are also observed. Isolated substitutional Fe$^{3+}$ and Cr$^{3+}$ ions serve as hole traps. © 2009 American Institute of Physics.
[DOI: 10.1063/1.3124656]

Titanium dioxide (TiO$_2$) is a wide-band-gap semiconductor with an established record as a versatile photocatalyst.[1,2] Although this important material has been widely studied for more than five decades, a detailed understanding of the role of point defects in controlling its optical and electrical properties is still emerging.[3–7] Many of the previous investigations of defects have focused on reduced crystals where oxygen vacancies, introduced during or after growth, significantly increase the electrical conductivity.[8–11] In contrast, our current report describes results obtained from colorless (fully oxidized) TiO$_2$ crystals that contain small concentrations of doubly ionized oxygen vacancies. These doubly ionized vacancies provide charge compensation for the trace amounts of trivalent transition-metal-ion impurities that are inadvertently present. When describing the different charge states of the oxygen vacancy, we use doubly ionized ($V_O^{++}$), singly ionized ($V_O^{+}$), and neutral ($V_O^{0}$) to refer to a vacancy that is unoccupied, singly occupied, and doubly occupied, respectively, with trapped electrons.

In the present paper, electron paramagnetic resonance (EPR) is used to identify the singly ionized ($S=1/2$) and neutral ($S=1$) charge states of oxygen vacancies in TiO$_2$ crystals. These centers appear when crystals containing doubly ionized oxygen vacancies are exposed at low temperature to 442 nm laser light. Electrons trapped at the oxygen vacancies are localized on two of the three neighboring titanium ions. Additional photoinduced EPR signals are assigned to Ti$^{3+}$ ions next to Si$^{4+}$ ions, to Ti$^{3+}$ ions with no nearby defects, and to self-trapped holes shared by two oxygen ions. (Ionic notation is used for the cations.)

The two TiO$_2$ crystals used in this investigation have the rutile structure and were grown by CrysTec (Germany) and by Namiki (Japan). Their dimensions were $3.8 \times 5.0 \times 0.5$ mm$^3$ and $2.5 \times 3.5 \times 1.2$ mm$^3$, respectively. Both of the as-received samples were colorless at room temperature, having been annealed in air after growth. The EPR data were taken with a Bruker EMX spectrometer operating near 9.427 GHz. Approximately 15 mW of 442 nm light from a He–Cd laser was incident on the sample during the low temperature illuminations.

At room temperature, the as-received TiO$_2$ samples showed several narrow and intense EPR signals from Fe$^{3+}$ and Cr$^{3+}$ ions substituting for Ti$^{4+}$ ions.[12–15] With the magnetic field parallel to the $c$ axis, a signal due to Cr$^{3+}$ ions was observed at 1354 G and two signals due to Fe$^{3+}$ ions were observed at 829 and 8904 G. It is generally accepted[16] that the isolated substitutional impurities responsible for these EPR lines are charge compensated by remotely located oxygen vacancies (i.e., one doubly ionized oxygen vacancy compensates two trivalent transition-metal ions replacing Ti$^{4+}$ ions). It is also possible that some of the substitutional Fe$^{3+}$ and Cr$^{3+}$ ions are charge compensated by interstitial hydrogen in a positive charge state. Our EPR results show that the Namiki sample has a larger concentration of Fe$^{3+}$ and Cr$^{3+}$ than the CrysTec sample. From EPR, the combined concentration of these impurities is approximately one part per million in the Namiki sample and one-tenth of this value in the CrysTec sample. The increased number of Fe$^{3+}$ and Cr$^{3+}$ ions in the Namiki sample suggests that it will have more oxygen vacancies than the CrysTec sample. These EPR estimates of the absolute concentrations of Fe$^{3+}$ and Cr$^{3+}$ ions are based on a comparison with a weak pitch sample supplied by Bruker (error limits are $\pm 30\%$).

Our TiO$_2$ samples did not show EPR signals at low temperature (10 to 40 K) in the magnetic field region from 3300 to 4000 G when they were initially cooled in the dark. Subsequent illumination at low temperature, however, immediately produced easily observed trapped-electron centers. The EPR data in Fig. 1 were taken from the Namiki sample with the magnetic field parallel to the $c$ axis. Exposure of the sample to 442 nm laser light at 26 K produced three sharp EPR lines [two lines are shown in Fig. 1(a) while a third EPR line near 3958 G is not shown]. The lowest-field line

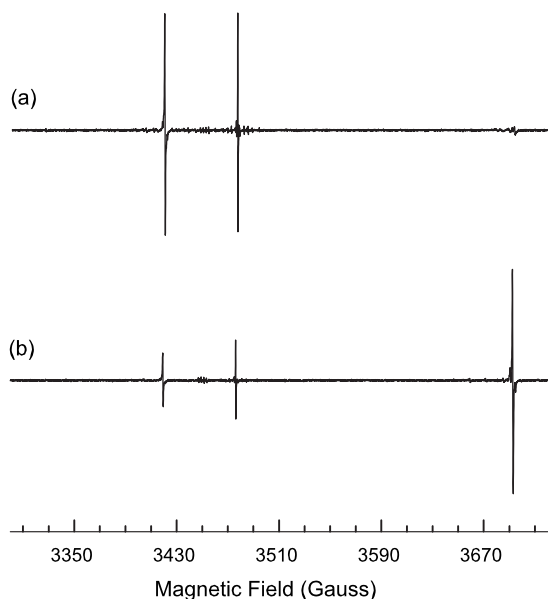a)Author to whom correspondence should be addressed. Electronic mail: larry.halliburton@mail.wvu.edu.

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FIG. 1. EPR spectra taken at 26 K from a TiO$_2$ crystal. The magnetic field is parallel to the *c* axis. (a) Upper spectrum was taken with 442 nm laser light on. (b) Lower spectrum was taken approximately 2 min after turning off the laser light.



FIG. 2. EPR spectrum of the Ti$^{3+}$−Si$^{4+}$ center taken at 26 K with the magnetic field parallel to the *c* axis. The upper and lower stick diagrams show the $^{29}$Si and the $^{47}$Ti and $^{49}$Ti hyperfine lines, respectively. Additional weak lines in the spectrum are unidentified.

near 3419 G and the highest-field line near 3958 G (not shown) belong to a $S=1$ center with $g_c=1.826$. (We use $g_c$ to denote the *g* value when the magnetic field is parallel to the *c* axis.) These two lines represent the $M_S=-1$ to 0 and the $M_S=0$ to +1 transitions. A detailed angular dependence study, to be reported later, provides complete sets of spin-Hamiltonian parameters for this and the other defects described in the present paper. We assign this $S=1$ spectrum to the neutral charge state of the oxygen vacancy ($V_O^0$). It was produced in our study when a doubly ionized oxygen vacancy ($V_O^{++}$) trapped two photoinduced electrons. The EPR angular dependence indicates that these two electrons are localized on the two neighboring titanium ions aligned along the *c* axis. We suggest that these trapped electrons form a pair of neighboring Ti$^{3+}$ ions that couple ferromagnetically to produce a spin-triplet ($S=1$) ground state. In support of our assignment, we found that a much more intense $S=1$ signal from the neutral oxygen vacancy was present at 26 K (without light) in a slightly reduced TiO$_2$ crystal (i.e., a crystal held for 30 min at 600 °C in flowing nitrogen gas). The reduction treatment creates uncompensated neutral oxygen vacancies as oxygen atoms are removed, and laser light is not needed to photoinduce the $S=1$ spectrum.

We identify the EPR signal near 3476 G in Fig. 1(a) as a Ti$^{3+}$−Si$^{4+}$ center. This is a $S=1/2$ defect with $g_c=1.938$, and is formed when a photoinduced electron is trapped on a regular Ti$^{4+}$ ion that has a substitutional Si$^{4+}$ ion at a nearest cation site along the *c* axis. Figure 2 shows the hyperfine structure accompanying this Ti$^{3+}$−Si$^{4+}$ center. In addition to the eight lines caused by the $^{47}$Ti and $^{49}$Ti isotopes, there is an extra pair of hyperfine lines separated by approximately 2.0 G and symmetrically located about the center line. The left line is slightly more intense than the right line because it is overlapped by one of four small closely spaced lines. (Note: Several weak four-line EPR spectra possibly associated with interstitial Li$^+$ or Na$^+$ ions were observed in the Namiki sample.) The extra pair of hyperfine lines in Fig. 2 requires the responsible nucleus to have $I=1/2$, and the
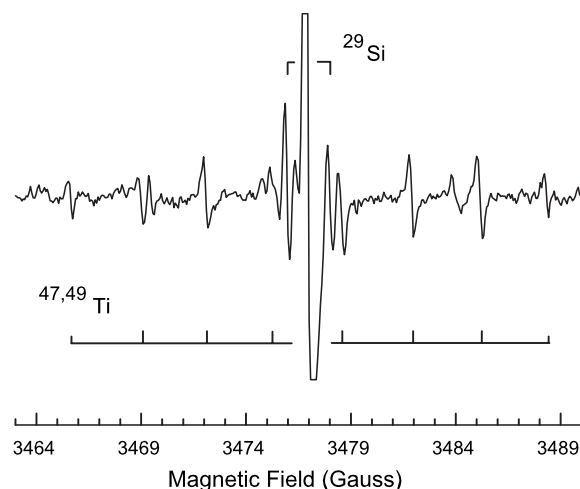
small hyperfine constant of 2.0 G suggests that this nucleus is located at a neighboring site. A comparison of the intensities of these two hyperfine lines with the intensities of the $^{47}$Ti and $^{49}$Ti hyperfine lines shows that the isotopic abundance of the $I=1/2$ nucleus must be slightly less than 5%. The only possible candidate is $^{29}$Si with an abundance of 4.67%. Elemental analyses of impurities in TiO$_2$ crystals often reveal the presence of silicon.[10,17]

Figure 1(b) shows the EPR spectrum taken at 26 K shortly after the laser light was removed from the sample. An additional line, representing a $S=1/2$ defect with $g_c=1.824$, appeared near 3693 G and quickly became the dominant signal. At the same time, the intensities of the $V_O^0$ and Ti$^{3+}$−Si$^{4+}$ signals decreased significantly. When the laser light was restored while still keeping the sample at 26 K, the line at 3693 G disappeared almost instantly and the $V_O^0$ and Ti$^{3+}$−Si$^{4+}$ signals returned to their initial intensities. We assign this signal at 3693 G to a $V_O^+$ center. Specifically, we suggest that this defect is a singly ionized oxygen vacancy with the trapped electron equally shared by the same two titanium ions that form the $S=1$ $V_O^0$ center (i.e., the two titanium neighbors aligned along the *c* axis). The $V_O^0$ center and the $V_O^+$ center have similar *g* matrices ($g_c=1.826$ and $g_c=1.824$, respectively), which supports our oxygen vacancy models. Conversion of a $V_O^0$ center to a $V_O^+$ center occurs when the shallow $V_O^0$ center thermally releases one of its two trapped electrons at temperatures near or above 26 K. In general, the equilibrium concentration of $V_O^0$ centers produced during an illumination represents a "balance" between the formation and thermal decay rates and thus depends sensitively on both the temperature and the intensity and wavelength of the light. As expected, the $V_O^0$ and $V_O^+$ centers were produced in the CrysTec sample at 26 K with 442 nm laser light, but their intensities were much lower than in the Namiki sample. This is consistent with the room-temperature EPR results that showed reduced amounts of Fe$^{3+}$ and Cr$^{3+}$ ions in the CrysTec sample. In an early study, Kerssen and Volger[10] observed the EPR spectra that we have assigned to $V_O^+$ and $V_O^0$ centers, and they proposed models for these centers that consisted of substitutional Ti$^{3+}$ ions with two nearby Al$^{3+}$ ions. Their complex models are, however, questionable because they did not observe any hyperfine splittings due to the 100% abun-
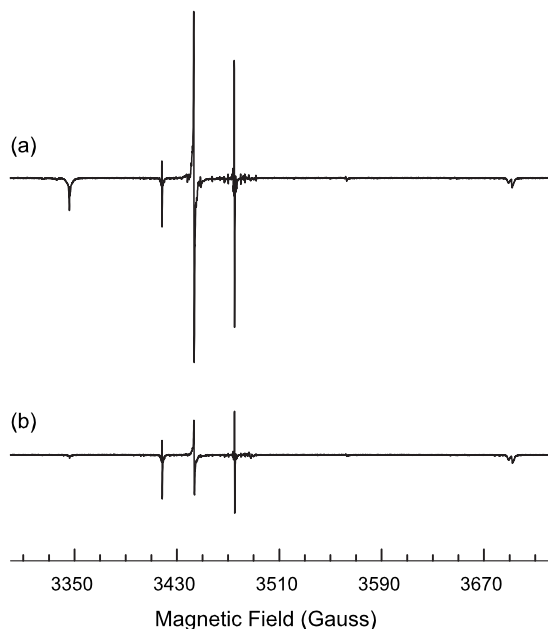
FIG. 3. EPR spectra taken at 14 K from a $TiO_2$ crystal. The magnetic field is parallel to the $c$ axis. (a) Upper spectrum was taken with 442 nm laser light on. (b) Lower spectrum was taken approximately 2 min after turning off the laser light.

dant $^{27}Al$ nuclei. It is now known[18] that an $Al^{3+}$ ion substituting for a $Ti^{4+}$ ion will trap a hole on an adjacent oxygen ion, and will not produce electronlike $Ti^{3+}$ centers.

The mechanism by which below-band-gap light (442 nm) produces trapped-electron centers in $TiO_2$ is not fully understood. The most likely scenario involves the direct excitation of electrons from $Fe^{3+}$ and $Cr^{3+}$ ions to the conduction band. The $Fe^{3+}$ and $Cr^{3+}$ ions, acting as deep singly ionized acceptors, are expected to have near-edge optical transitions (i.e., broad absorption bands) that correspond to an electron moving from the acceptor to the conduction band. A decrease of about 50% in the intensities of the $Fe^{3+}$ and $Cr^{3+}$ EPR signals occurred when the Namiki sample was illuminated at 26 K with 442 nm laser light. This decrease coincided with the production of the $V_O^0$ and $Ti^{3+}$–$Si^{4+}$ centers in Fig. 1(a). The trivalent impurity ions convert to $Fe^{4+}$ and $Cr^{4+}$ ions and serve as the compensating hole centers for the photoinduced electron centers, thus allowing the crystal to remain electrically neutral. EPR signals from $Fe^{4+}$ and $Cr^{4+}$ ions in $TiO_2$ have not been reported.

Two additional $S=1/2$ EPR centers appeared in the Namiki sample during an illumination with 442 nm laser light at 14 K. These EPR lines, shown in Fig. 3(a), are at 3345 and 3443 G when the magnetic field is parallel to the $c$ axis. The lower-field signal is holelike ($g_c=2.013$) and the higher-field signal is electronlike ($g_c=1.956$). Both of these centers had very low thermal stabilities. Their EPR signals were much smaller when the illumination occurred at 18 K, instead of 14 K. The two signals disappeared instantly when the light was removed at 18 K, but decayed more slowly (in minutes) when the light was removed at 14 K [as in Fig. 3(b)]. Neither defect could be produced with 442 nm light when the temperature was above 25 K. These signals at 3345 and 3443 G in Fig. 3 had long spin-lattice relaxation times in the 14–25 K range and were very easily saturated at higher microwave powers.

The two $c$-axis lines at 3345 and 3443 G were the dominant photoinduced EPR signals in the CrysTec sample when it was illuminated with 442 nm laser light while being held at 14 K. The $V_O^0$ and $V_O^+$ centers were much less intense in the CrysTec sample during low temperature illuminations because the crystal contained fewer oxygen vacancies. Based on their low thermal stabilities and their appearance in both the Namiki and the CrysTec samples, we propose models involving the self-trapping of photoinduced charges for the EPR signals at 3345 and 3443 G. The holelike signal has no resolved hyperfine structure, which indicates that there is no nearby trivalent cation impurity that serves to "stabilize" the hole.[18] This leads us to assign the EPR signal at 3345 G in $TiO_2$ to a "self-trapped" hole, i.e., a hole shared by two adjacent oxygen ions that have relaxed toward each other. An analogous defect has been observed in $KD_2PO_4$ crystals.[19] Similarly, we assign the signal at 3443 G to a "self-trapped" electron in the form of an isolated $Ti^{3+}$ ion, i.e., an electron trapped at a $Ti^{4+}$ ion in the otherwise perfect lattice.

In summary, doubly ionized oxygen vacancies in colorless oxidized $TiO_2$ crystals have been converted to their neutral charge state by illumination with 442 nm laser light at 26 K. The neutral oxygen vacancy ($V_O^0$) has $S=1$ with the two trapped electrons localized on the pair of titanium neighbors aligned along the $c$ axis. If the temperature is near or above 26 K, these neutral oxygen vacancies will thermally release an electron and become singly ionized oxygen vacancies ($V_O^+$) when the light is removed. This latter defect has $S=1/2$ with the one trapped electron equally shared by the same two titanium ions that form the $S=1$ $V_O^0$ center (i.e., the two titanium neighbors aligned along the $c$ axis).

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