Photo-rewritable material based on a metal oxide

Shin-ichi Ohkoshi,*[a] Yoshihide Tsunobuchi,[a] Kazuhito Hashimoto,[b] Asuka Namai,[a] Fumiyoshi Hakoe,[a] and Hiroko Tokoro[a]

[a]*Department of Chemistry, School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, JAPAN*
[b]*Department of Applied Chemistry, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, JAPAN*

ABSTRACT

Photoinduced phase transition materials receive attention from both fundamental and technological viewpoints because they are used in high-density optical data storage. In this paper, we report a photoreversible phase transition at room temperature with a unique phase of Ti_3O_5 (hereinafter, this new phase is called λ-Ti_3O_5). The λ-Ti_3O_5 phase, which is generated by a nanoscale size effect, is a metal conductor, and exhibits a photoinduced phase transition to β-Ti_3O_5, a semiconductor. The photoreverse process from β- to λ-Ti_3O_5 is also observed. This phenomenon originates from a particular state of λ-Ti_3O_5, which is trapped at thermodynamically local energy minimum. Light irradiation causes the switching between this trapped state (λ-Ti_3O_5) and the other energy minimum state (β-Ti_3O_5).

Keywords Lambda-trititanium pentaoxide, Photoinduced metal-semiconductor phase transition

INTRODUCTION

A phase-change optical disc technology was developed for practical application in 1980s, and resulted in the commercialization of digital versatile disc (DVD) in 1990s and Blu-ray® in 2000s[1),2)]. Currently, DVD and Blu-ray® use a chalcogen alloy (*e.g.*, GeSbTe) as an optical data storage material. Various materials, including photochromic compounds, donor-acceptor stacked molecules, spin crossover complexes, cyano-bridged metal assemblies, and perovskite manganites, have been studied as next-generation high-performance optical data storage[3)]. Herein we report a unique phase of titanium oxide, λ-Ti_3O_5, which meets the requirements for optical data storage memory. This material shows a reversible photoinduced metal-semiconductor phase transition between λ-Ti_3O_5 and β-Ti_3O_5 at room temperature. This is the first demonstration of a metal oxide with a photoinduced phase transition at room temperature[4),5)].

FORMATION AND CRYSTAL STRUCTURE OF λ-Ti_3O_5

A unique phase of a titanium oxide, λ-Ti_3O_5, was obtained as two types of morphologies through different synthetic methods: one of them is λ-Ti_3O_5 nanocrystal in SiO_2 matrix and the other is a flake form of λ-Ti_3O_5 assembled by nanocrystals. The former is obtained by combining reverse-micelle and sol-gel techniques. The transmission electron microscope (TEM) image of λ-Ti_3O_5/SiO_2 shows cubic-shape Ti_3O_5 nanocrystals with a size of ca. 20 nm dispersed in a SiO_2 matrix (Fig. 1a). Moreover, the X-ray diffraction (XRD) pattern indicates a crystal structure of *C*2/*m*, which crystal structure does not correspond to any reported crystal structures of Ti_3O_5 (α-, β-, γ-, and δ-phases) (Fig. 2a).

Calcinating the anatase form of the TiO_2 nanoparticles (size = 7 nm) under hydrogen at 1200 °C produces the flake form λ-Ti_3O_5, which is black (Fig. 1b). The TEM image shows that the flake (size = 2 ± 0.5 μm) is assembled by 25 ± 15 nm nanocrystals. The XRD pattern of the sample at room temperature corresponds to the aforementioned λ-Ti_3O_5 in SiO_2, and the Rietveld analysis shows a monoclinic structure (*C*2/*m*). Variable-temperature XRD measurements demonstrate that as the temperature increases, the diffraction peaks of λ-Ti_3O_5 continuously change to α-Ti_3O_5 peaks with a crystal structure of *Cmcm*. Furthermore, heating the sample to 640 K and then cooling to 300 K causes α-Ti_3O_5 to return to λ-Ti_3O_5. Differential scanning calorimetry (DSC) measurements did not exhibit a meaningful peak, which differs vastly from the first-order phase transition between β-Ti_3O_5 and α-Ti_3O_5 in a conventional large crystal Ti_3O_5. Hence, the phase transition between λ-Ti_3O_5 and α-Ti_3O_5 is classified as a second-order type phase transition.

MAGNETIC, ELECTRIC, AND OPTICAL PROPERTIES AND ELECTRONIC STRUCTURE OF λ-Ti_3O_5

Figure 3 shows the magnetic susceptibility (χ) versus temperature (T) of the flake form λ-Ti_3O_5 as well as the χ versus T curve of a conventional large crystal Ti_3O_5. λ-Ti_3O_5 has χ values around 2×10^{-4} emu per Ti atom throughout the entire measured temperature region, suggesting that λ-Ti_3O_5 is a Pauli paramagnet due to metallic conduction. Spin-orbital coupling on Ti^{3+} ion can explain the gradual decrease below 150 K, but small amount of Curie paramagnetism (ca. 0.1%), which may be due to defects in the material, is attributed to the rapid increase below 30 K. The λ-Ti_3O_5/SiO_2 sample exhibits the same type of

χ versus T curve. The electric current versus voltage curve using atomic force microscopy in the contact mode has an electric conductivity (σ) value of ca. 3×10^{1} S cm^{-1}, indicating that λ-Ti_3O_5 is a near metallic conductor. Additionally, both the UV-vis and IR reflectance spectra indicate that λ-Ti_3O_5 possesses metallic absorption over the ultraviolet and infrared wavelength regions. In contrast, the impedance measurement and reflectance spectra suggest that β-Ti_3O_5 is a semiconductor with $\sigma = 3\times10^{-2}$ S cm^{-1} and a band gap of 0.14 eV.

The empirical relationship between the bond length and valence states gives estimated valence states for Ti(1), Ti(2), and Ti(3) in λ-Ti_3O_5 of +3.37, +3.20, and +3.53, respectively. These valence states are close to $Ti^{3\frac{1}{3}+}$, indicating that λ-Ti_3O_5 is a charge-delocalized system (Fig. 2a). This is consistent with λ-Ti_3O_5 being a metallic conductor. The electronic structure of λ-Ti_3O_5 is close to that of α-Ti_3O_5. In contrast, the valence states of Ti(1), Ti(2), and Ti(3) in β-Ti_3O_5 are +3.00, +3.79, and +3.32, respectively, which are close to the valence states for a charge-localized system of $Ti^{3+} - Ti^{3\frac{2}{3}+} - Ti^{3\frac{1}{3}+}$ (Fig. 2b). The band structures of β-Ti_3O_5 and λ-Ti_3O_5 calculated by the first-principle calculation also supported these valence states.

REVERSIBLE PHOTOINDUCED PHASE TRANSITION

When the flake form λ-Ti_3O_5 is irradiated with 532 nm pulsed laser light (6 ns, 3 shots, 1.5×10^{-5} mJ μm^{-2} pulse^{-1}) at room temperature, the irradiated area changes from black to brown (panels a and b in Fig. 4). Successively, irradiating with 410 nm continuous wave laser light (8×10^{-3} mW μm^{-2}) causes the irradiated spots to return to black (panel c in Fig. 4). Alternatively irradiating with 532 nm and 410 nm lights repeatedly induces these color changes (panels d–f in Fig. 4). The XRD pattern shows that the brown area is assigned to the β-phase (monoclinic structure of *C2/m*). Hence, the change from black to brown is due to the transition from the λ-Ti_3O_5 to β-Ti_3O_5, whereas the converse is due to the transition from the β-Ti_3O_5 to λ-Ti_3O_5. Furthermore, a similar phase transition is observed by irradiating with different pulsed-laser lights, 355 or 1064 nm.

To investigate the threshold value of laser power, a mixed sample of λ-Ti_3O_5 and β-Ti_3O_5 with ratio of 2 : 1 was irradiated with 532 nm pulsed laser light (one shot) at various laser power densities. The threshold laser power of β-Ti_3O_5 → λ-Ti_3O_5 is 2.7×10^{-6} mJ μm^{-2}, and conversely, that of λ-Ti_3O_5 → β-Ti_3O_5 is 1.0×10^{-5} mJ μm^{-2}. Such a threshold is important for recording storage media for long-lasting memory. The observed threshold values of the laser power densities used are the same order as laser power density used on DVD.

THERMODYNAMIC INTERPRETATION OF THE PHOTOINDUCED PHASE TRANSITION

The thermodynamic analysis of λ-Ti_3O_5 suggests that the present photoinduced metal-semiconductor phase transition is attributed to the phase transition from λ-Ti_3O_5, a metastable phase thermodynamically trapped at a local energy minimum state, to β-Ti_3O_5, a truly stable phase by irradiation (Fig. 5). Because metallic absorption allows λ-Ti_3O_5 to effectively absorb light over a wide wavelength range from ultraviolet to near-IR, this metal-semiconductor phase transition can be observed by irradiating with 355, 532, and 1064 nm laser lights. The reverse photoinduced phase transition from β-Ti_3O_5 to λ-Ti_3O_5 is induced by the excitation from the valence band to the conduction band on β-Ti_3O_5, and then the excited state directly changes to λ-Ti_3O_5 in the pulsed laser light irradiation experiment or thermally transits to λ-Ti_3O_5 through α-Ti_3O_5 (*i.e.*, β- → α- → λ-Ti_3O_5) in the continuous wave laser light irradiation experiment.

CONCLUSION

We reported a photoreversible metal-semiconductor phase transition at room temperature with a new phase of Ti_3O_5. This phenomenon originates from a particular state of λ-Ti_3O_5 trapped at thermodynamic local energy minimum. λ-Ti_3O_5 satisfies the operation conditions (operational temperature around room temperature, writing data by short wavelength near ultra-violet light for high memory density, and the appropriate threshold laser power to maintain long-term memory).

ACKNOWLEDGEMENT

This work was performed under the management of the Project to Create Photocatalyst Industry for Recycling-oriented Society supported by NEDO. We are thankful for a Grant-in-Aid for the Global COE Program, from MEXT Japan.

REFERENCES

1. N. Yamada, E. Ohno, K. Nishiuchi, N. Akahira, and M. Takao, ***J. Appl. Phys.***, 69, 2849−2856 (1991).
2. M. Wuttig, and N. Yamada, ***Nature Mater.***, 6, 824−832 (2007).
3. K. Nasu, *Relaxations of Excited States and Photo-Induced Structural Phase Transitions* (Springer, Berlin, 1997).
4. S. Ohkoshi, Y. Tsunobuchi, T. Matsuda, K. Hashimoto, A. Namai, F. Hakoe, and H. Tokoro, ***Nature Chem.***, 2, 539−545 (2010).
5. ***Nature Japan***, URL: http://www.natureasia.com/japan/jobs/tokushu/detail.php?id=219

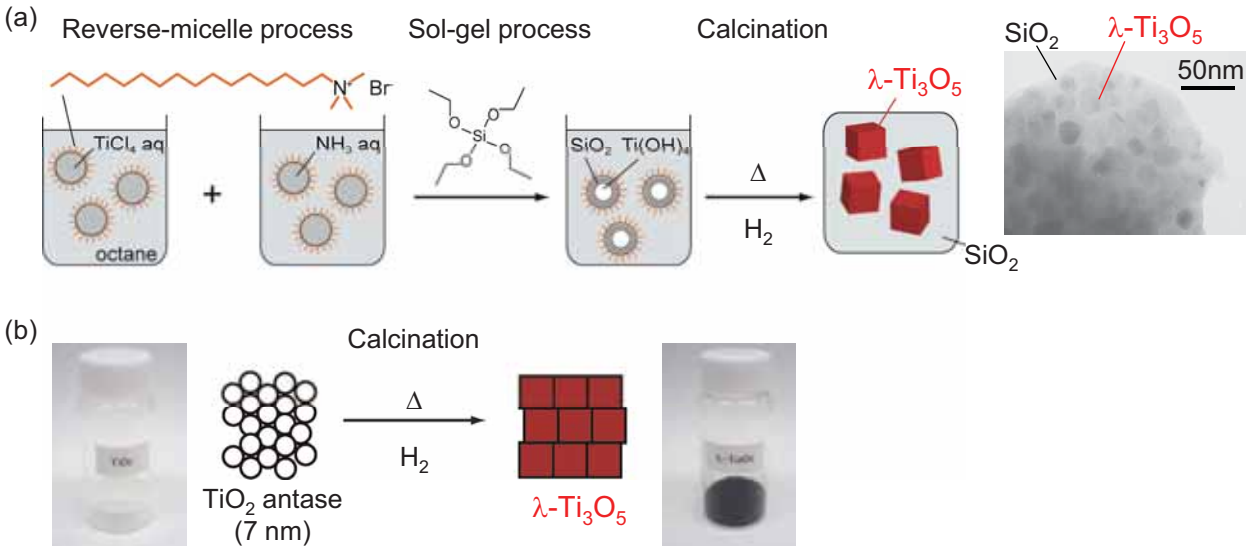
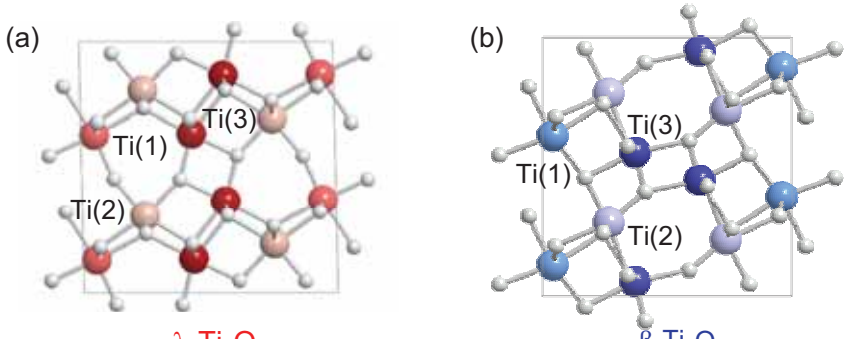


Fig. 1 (a) Schematic illustration of the synthetic procedure of λ-Ti_3O_5 nanocrystal in SiO_2 matrix using combination method between reverse-micelle and sol-gel techniques and TEM image of λ-Ti_3O_5 nanocrystals in SiO_2 matrix. (b) Schematic illustration of the synthetic procedure of flake-form of λ-Ti_3O_5.



	λ-Ti_3O_5 Charge-delocalized system	β-Ti_3O_5 Charge-localized system
	valence	valence
Ti(1)	+3.37 (≈+$3\frac{1}{3}$)	+3.00 (≈+3) S =1/2
Ti(2)	+3.20 (≈+$3\frac{1}{3}$)	+3.79 (≈+4)
Ti(3)	+3.53 (≈+$3\frac{1}{3}$)	+3.32 (≈+3) S =1/2

Fig. 2 Crystal structures and valence states of (a) λ-Ti_3O_5 and (b) β-Ti_3O_5.

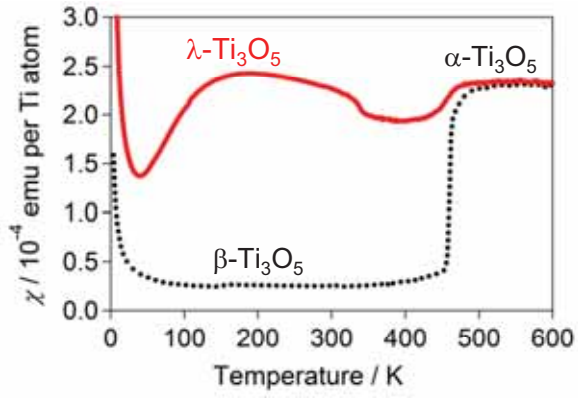


Fig. 3 χ versus T plots of flake-form of λ-Ti_3O_5 (red line) and single crystal β-Ti_3O_5 (black dotted line) under an external field of 0.5 T.

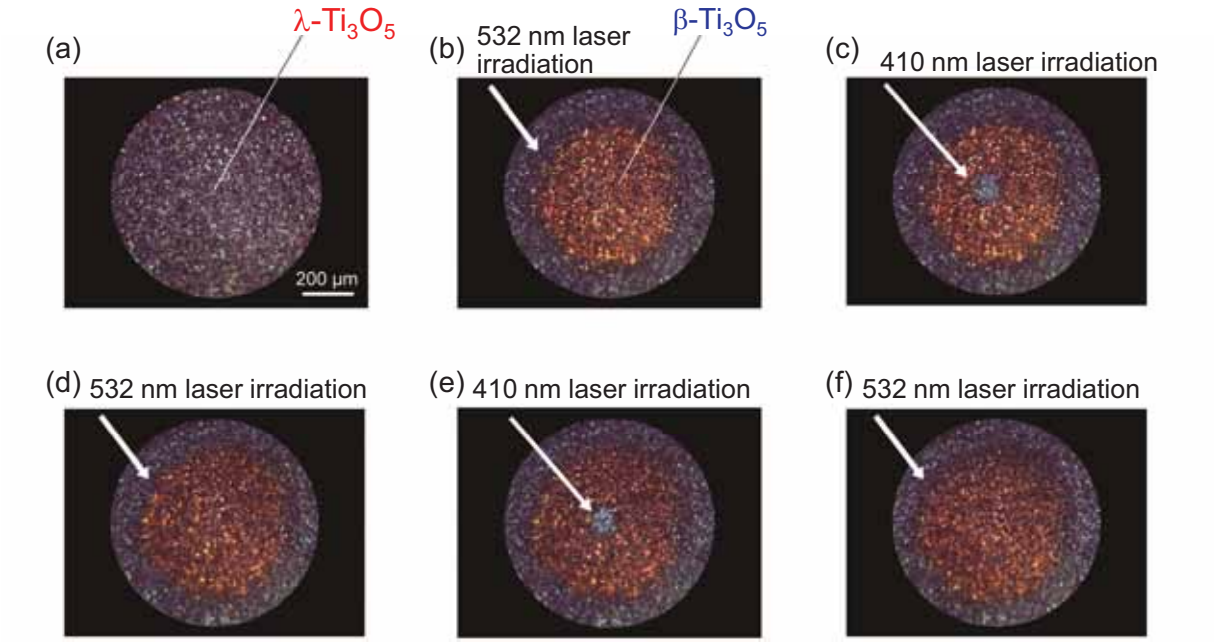


Fig. 4 Reversible photoinduced phase transition in λ-Ti_3O_5. Photographs of λ–Ti_3O_5 by the irradiation 532 nm pulsed laser and 410 nm continuous wave laser lights. When flake-form of λ-Ti_3O_5 was irradiated with 532 nm pulsed laser light at room temperature, the irradiated area changed from black (panel a) to brown (panel b). Successively, the spots returned to black upon irradiating with 410 nm continuous wave laser light (panel c). Photoinduced color changes were repeatedly observed by alternating 532 nm and 410 nm laser light irradiation (panels d-f).

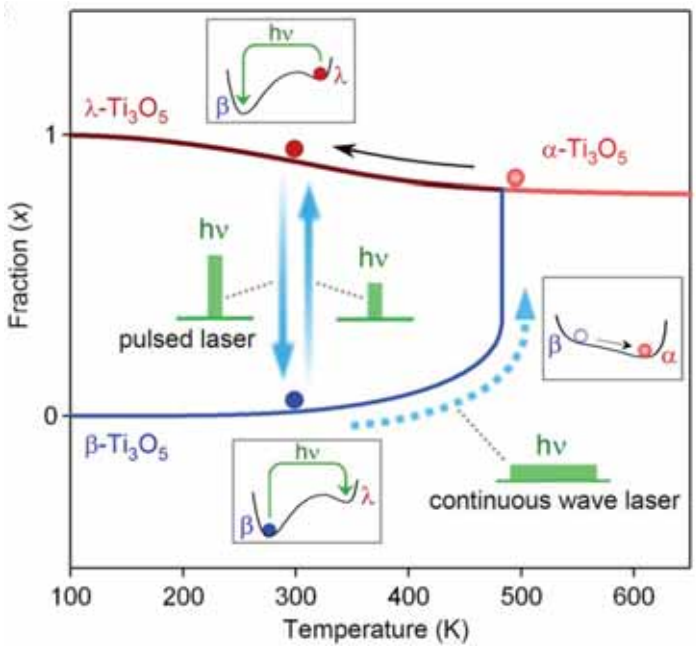


Fig. 5 Mechanism of the photoinduced phase transition in λ-Ti_3O_5. Schematic illustration of the pathways of the reversible photoinduced phase transition. Thermally populated phase versus temperature curves are described based on the *G* versus *x* plots for Ti_3O_5 nanocrystals. Red, pink, and blue lines indicate λ-Ti_3O_5, α-Ti_3O_5, and β-Ti_3O_5, respectively. The photoinduced phase transition from λ-Ti_3O_5 to β-Ti_3O_5 is attributed to the phase transition from a metastable phase to a true stable phase (downward blue arrow). In the reverse photoinduced phase transition from β-Ti_3O_5 to λ-Ti_3O_5, β-Ti_3O_5 directly transits to λ-Ti_3O_5 by the nanosecond (ns)-pulsed laser light irradiation (upward blue arrow), or thermally transits to λ-Ti_3O_5 through α-Ti_3O_5 (*i.e.*, β- $\rightarrow$ α- $\rightarrow$ λ-Ti_3O_5) by the continuous wave (cw) laser light irradiation (dotted blue arrow).