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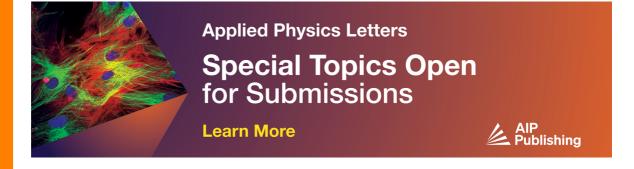
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Band gap narrowing of titanium dioxide by sulfur doping

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Titanium dioxide (TiO_2) doped with sulfur (S) was synthesized by oxidation annealing of titanium disulfide (TiS_2). According to the x-ray diffraction patterns, TiS_2 turned into anatase TiO_2 when annealed at $600\,^{\circ}$ C. The residual S atoms occupied O-atom sites in TiO_2 to form Ti—S bonds. The S doping caused the absorption edge of TiO_2 to be shifted into the lower-energy region. Based on the theoretical analyses using *ab initio* band calculations, mixing of the S 3p states with the valence band was found to contribute to the band gap narrowing. © 2002 American Institute of Physics. [DOI: 10.1063/1.1493647]

Titanium dioxide (TiO₂) has received attention as a promising material for photochemical applications and as a photocatalyst because of its excellent functionality, longterm stability, and nontoxicity. Nevertheless, TiO₂ becomes active only under ultraviolet (UV) light, whose energy is greater than the band gap of TiO_2 ($\sim 3.0 \text{ eV}$). The effective utilization of visible light occupying the main part of the solar beams is one of the important subjects for the increased utility of TiO2. In previous studies, in order to improve the photoreactivity of TiO2 and to extend its absorption edge into the visible-light region, doping of various transition metal cations has been intensively attempted.³⁻⁶ Except for a few cases, 5,6 however, the photoactivity of the cation-doped TiO₂ decreased even in the UV region. This is because the doped materials suffer from a thermal instability or an increase in the carrier-recombination centers.³

Recently, some groups have demonstrated the substitution of a nonmetal atom such as nitrogen $(N)^{7-10}$ and fluorine $(F)^{11-13}$ for oxygen (O). Lee *et al.*⁷ fabricated the N-doped TiO_2 films on a silicon substrate by metalorganic chemical vapor deposition using titanium tetra-isopropoxide and nitrous oxide. Asahi *et al.*^{9,10} showed that N doping shifted the absorption edge to a lower energy, thereby increasing the photoreactivity in the visible-light region. On the other hand, F doping in TiO_2 was carried out by gas-phase HF treatment at high temperatures, 11 a sol–gel technique, 12 and ion implantation. 13 The photocatalytic performance of the F-doped TiO_2 was enhanced due to reduction of the recombination rate of the photogenerated charge carriers. 12

In contrast, we expected that the substitution of sulfur (S) at the O sites could significantly modify the electronic structures of TiO₂ because S has a larger ionic radius compared to N and F. However, there have been few reports regarding S doping into TiO₂ except by Gonbeau *et al.*¹⁴ and

regarding S doping into TiO_2 except by Gonbeau *et al.*¹⁴ and

Hebenstreit *et al.*^{15,16} We incorporated S into TiO₂ by the oxidation of titanium disulfide (TiS₂) and then discussed the doping effect on the optical-response properties. This study shows that the S doping into the lattice of TiO₂ contributes to the band gap narrowing.

The structural and optical properties of the oxidized TiS_2 powders were investigated by x-ray diffraction (XRD) analysis, x-ray photoelectron spectroscopy (XPS), and diffuse reflectance spectroscopy (DRS). In order to make the S-doping effect clear, we performed *ab initio* band calculations based on the density functional theory¹⁷ using the full potential linearized augmented plane wave method.¹⁸

Morikawa *et al.*¹⁰ reported that the N-doped TiO₂ was synthesized by oxidative annealing of TiN powder. Likewise with TiN, TiS₂ is oxidized in air and transformed into TiO₂.^{19,20} In the present method, the TiO₂-based polycrystalline powder samples, including S substituted for O, were prepared by heating the TiS₂ powder (High Purity Chemicals Laboratory Co., Ltd.) at 300 °C or 600 °C for 5 h in air. After the annealing, the color of the samples changed from black to gray (300 °C) and to white (600 °C).

Figure 1 shows the XRD patterns (Cu $K\alpha$ and λ = 1.542 Å) of the annealed samples and standard powders of pure TiS₂ and anatase TiO₂. When annealing at 300 °C, the pattern exhibited both the anatase TiO₂ and TiS₂ structures, indicating a mixture of anatase TiO₂ and TiS₂. As shown in Fig. 1 (b), a single phase of anatase TiO₂ appeared in the patterns of the sample annealed at 600 °C. Although the peak of rutile TiO₂ (110) was also observed in these two patterns, it was weak enough to be ignored here. It is considered, therefore, that the sample annealed at 600 °C is the anatase TiO₂-based polycrystalline powder.

Figure 2 shows the XPS spectra (Mg $K\alpha$ and $h\nu$ = 1253.6 eV) of the sample annealed at 600 °C and pure TiO₂ for the S 2p core level. The S 2p state had a broad peak because of the overlap of the split sublevels, the 2 $p_{3/2}$ and

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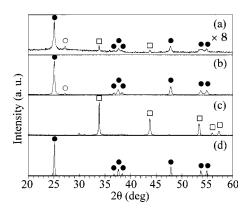


FIG. 1. X-ray diffraction patterns of TiS_2 annealed at (a) 300 °C or (b) 600 °C for 5 h in air. This also represents the patterns of pure (c) TiS_2 and (d) anatase TiO_2 for comparison. ($\Box TiS_2$, \bullet anatase TiO_2 , \bigcirc rutile TiO_2).

 $2p_{1/2}$ states, with separation of 1.2 eV by spin-orbit coupling.²¹ As seen in the spectrum [Fig. 2(a)], two peaks were observed around 168 eV and 160 eV for the annealed sample. According to Ohinishi et al. 22 and Sayago et al., 23 for the adsorbed sulfur dioxide (SO₂) molecules on a TiO₂ surface, the typical peak of the S 2p state lay between 166-170 eV. Thus, the higher-energy peak can be ascribed to surface S atoms adsorbed as SO2 molecules, which were generated through the decomposition and oxidation of TiS2 in our case. Furthermore, the amorphous titanium oxysulfide, where S atoms bond to Ti, exhibited an S2p peak around 160–163 eV. ¹⁴ Hebenstreit et al. ^{15,16} also reported that S 2p peak appeared at 162 eV when S atoms replaced O atoms on the TiO₂ (110) surface. These previous studies undoubtedly indicate that the lower-energy signal is associated with S forming Ti—S bonds in TiO2. A trace amount of S atoms would remain in the annealed sample as either a TiS2 compound or homogeneously distributed substitutional atoms at the O sites.

The optical absorption is represented by the Kubelka–Munk function 24 calculated from the DRS spectra. Optical absorption spectra of the samples are shown in Fig. 3. Compared to anatase $\rm TiO_2$, the absorption edge was shifted to the lower-energy region in the spectrum of the sample annealed at 600 °C. The most possible mechanism to account for the observed absorption shift might involve O vacancies produced by thermal treatment, which form localization levels

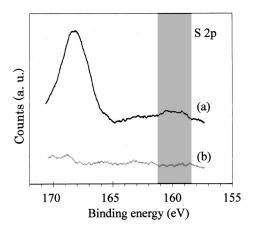


FIG. 2. X-ray photoelectron spectra of the S 2p state of (a) TiS $_2$ annealed at 600 $^\circ C$ and (b) anatase TiO $_2$ as the standard.

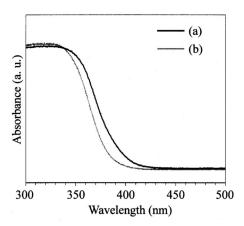


FIG. 3. Diffuse reflectance spectra of (a) TiS_2 annealed at 600 °C and (b) anatase TiO_2 powder as the standard (also annealed at 600 °C).

within the band gap. ²⁵ However, this possibility can be excluded, because we also annealed the standard powder at $600\,^{\circ}$ C in order to ignore the thermal effect. Also, the sample spectrum completely differs from that of TiS₂ whose optical absorption starts from a much lower-energy region of about 0.5 eV. ^{26,27} This suggests that TiS₂ does not exist after the annealing at $600\,^{\circ}$ C.

Combining the above XRD, XPS, and DRS results, we conclude that S was incorporated into the O site of the TiO_2 lattice by the oxidative annealing of TiS_2 . Importantly, the band gap narrowing was successfully achieved by S doping into TiO_2 .

In order to investigate the doping effects on the electronic and optical properties of TiO_2 , we analyzed the band structures of the S-doped TiO_2 by *ab initio* band calculations using the super-cell approach. Based on the experimental results, the calculation model consisted of two unit cells of anatase TiO_2 , where one S atom is replaced with one O atom. The density of states (DOS) of the pure and S-doped TiO_2 , $TiO_{2-x}S_x$, is shown in Fig. 4. In the pure TiO_2 crystal, the valence band (VB) and conduction band (CB) consist of both the $Ti\ 3d$ and $O\ 2p$ orbitals. Because the $Ti\ 3d$ orbital is split into two parts, the t_{2g} and e_g states, the CB is divided into the lower and upper parts. When TiO_2 is doped with S, the S 3p states are somewhat delocalized, thus greatly contributing to the formation of the VB with the $O\ 2p$ and $Ti\ 3d$ states. Consequently, the mixing of the S 3p

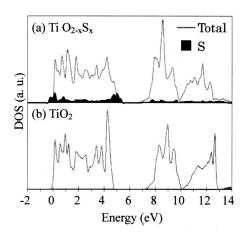


FIG. 4. DOS for (a) S-doped TiO2 and (b) pure TiO2.

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states with VB increases the width of the VB itself. This results in a decrease in the band gap energy due to S doping. The calculated band gap energies were 1.4 eV for $\text{TiO}_{2-x}S_x$ and 2.3 eV for TiO_2 . Our calculation results consistently confirm that the S atoms doped into the substitutional site of TiO_2 are effective for the band gap narrowing.

In conclusion, the TiO_2 -based polycrystalline powder doped with S was synthesized by oxidation heating of the TiS_2 powder. The substitution of S for O was found to cause a significant shift in the absorption edge to lower energy. The analysis using the *ab initio* band calculations showed that the band gap narrowing due to the S doping originates from mixing the S 3p states with VB, leading to an increase in the VB width.

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