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Ultraviolet-visible absorption spectra of N-doped TiO₂ film deposited on sapphire

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The optical-response properties of nitrogen(N)-doped titanium dioxide (TiO₂) films are investigated by means of a combination of ultraviolet-visible absorption spectroscopy and first-principles density-functional calculations. The TiO₂ films were epitaxially grown on the sapphire substrate by the pulsed laser deposition method. The doping of N atoms was achieved by 70 keV of N⁺ ion implantation, followed by postirradiation heat treatment at 550 °C for 2 h in air. We find that when 5×10^{16} (1×10^{17}) N ions/cm² were implanted into the epitaxially grown TiO₂ film, the absorption edge is reproducibly shifted to lower energy by about 0.06 (0.12) eV together with a significant optical absorption extending into the visible-light region. These experimental data can be explained by our calculated band structure of N-doped TiO₂, where the bands originating from N 2*p* states locate above the valence band edge, while the band gap narrowing due to the mixing of N with O 2*p* states is 0.04 eV. © 2006 American Institute of Physics. [DOI: 10.1063/1.2400099]

I. INTRODUCTION

For photocatalytic and photoelectrochemical applications such as waste-water purification, bactericide, self-cleaning, and antifogging, titanium dioxide (TiO₂) has been known as the most important material because of its high catalytic activity, excellent stability, and nontoxicity.¹⁻¹⁶ However, a high intrinsic band gap of TiO₂ (3.2 eV for the anatase structure and 3.0 eV for the rutile structure) allows only absorption of the ultraviolet part of the solar irradiation. Since this part has a small fraction (~4%) of the incoming solar energy on the earth's surface, it is of considerable interest to extend the optical absorption of the TiO₂-based systems to the visible-light part having the maximum amount of energy of the solar spectrum. Such effective utilization of visible light can be achieved by reducing the intrinsic band gap of TiO₂. For this, several approaches such as doping of various transition metal cations¹⁻³ and synthesis of reduced TiO_{2-x} (Refs. 4 and 5) (i.e., formation of the oxygen vacancy) have been proposed. The performance of various transition metal dopants, however, is limited by thermal instability and increase of carrier-recombination centers,² whereas reduced TiO_{2-x} photocatalysts lower the photocatalytic driving force because of the formation of oxygen vacancy states between the valence and conduction bands of TiO₂.⁵

Recently, an approach has been introduced to broaden the optical response of TiO₂ by doping with various anionic dopants such as nitrogen (N),⁶⁻¹¹ carbon(C),¹²⁻¹⁴ sulfur(S),¹⁵ and fluorine (F) (Ref. 16) atoms. Asahi *et al.*⁶ showed that the N dopant induces a significant shift of the photoabsorption edge to lower energy, therefore yielding a dramatic im-

provement over undoped TiO₂ in its optical absorption and photocatalytic activity for visible light. On the basis of their analysis of the density of electronic states, Asahi *et al.*⁶ concluded that the substitutional doping of N for O in the anatase TiO₂ crystal produces a band gap narrowing by mixing of N 2*p* states with O 2*p* states. In a while, Irie *et al.*⁷ observed that quantum yields for the decomposition of gaseous 2-propanol on N-doped TiO₂ are significantly greater under ultraviolet light irradiation compared with visible-light irradiation. Therefore they suggested that the visible-light response in N-doped TiO₂ might be due to N 2*p* states isolated above the valence band edge of TiO₂. The photoelectrochemical measurements of Lindgren *et al.*⁸ found not only the presence of N 2*p* states within the band gap but also the little change of the conduction band edge. Recently, our density-functional theory (DFT) calculations confirmed that substitutional N impurities induce the formation of localized states just above the O 2*p* valence band.¹⁷

For N doping to TiO₂, treatments with N₂/H₂ mixed gas plasma¹⁸ and N₂⁺/Ar⁺ mixtures¹⁹ have been recently conducted for the sputter-deposited film¹⁸ and single crystal¹⁹ materials. In the present study we prepared epitaxial TiO₂ thin films grown by the pulsed laser deposition (PLD) method. For N doping we implanted N⁺ ions onto the deposited TiO₂ films. Using ultraviolet-visible absorption spectroscopy we observed that the N-doped TiO₂ films exhibit not only a reduction of the band gap but also a significant optical absorption ranging over the visible-light region. In order to understand the mechanism of the observed redshift we carried out first-principles density-functional theory calculations to obtain the band structures of undoped and N-doped TiO₂ crystals. We assumed a perfect anatase TiO₂ crystal structure with the substitution of N for O. On the basis of our calculated band structure of TiO_{2-x}N_x, we provide an explanation for the observed experimental data.

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II. EXPERIMENTAL AND CALCULATIONAL METHODS

TiO₂ thin films were deposited onto the sapphire substrate with an optical finish slightly off the (0001) plane. The film deposition was conducted in a vacuum chamber with a base pressure of 10⁻⁸ Torr by ablating the TiO₂ target using Nd:YAG (yttrium aluminum garnet) laser. The film thickness, determined by profilometry, was around 500 nm. We prepared both stoichiometric and understoichiometric TiO₂ thin films by controlling oxygen gas into the deposition chamber. In order to produce a stoichiometric TiO₂ thin film, we introduced 6N purity oxygen gas into the chamber through a mass-flow control manifold, with an ambient gas pressure of 10⁻³ Torr. The film was also deposited without flowing the oxygen gas into the deposition chamber during the film deposition to fabricate an understoichiometric TiO₂ thin film. During the film deposition, the temperature of the sapphire substrate was held at 350 °C. X-ray diffraction was performed in the range of 10° < 2θ < 50° to investigate the film epitaxy. N ions of 70 keV were implanted into the deposited film. The ion dose was in the range between 5 × 10¹⁶ and 2 × 10¹⁷ ions/cm². Here, we produced N ions using a multistep process. N ions are initially formed by extracting electrons from N atoms in a plasma. As they are passed through a mass-analyzing magnet, only singly charged ions (i.e., N⁺) can be selected. The beam of N ions is then accelerated using a potential gradient column. Using a series of electrostatic and magnetic lens elements, the N ion beam is scanned over the sample in a work chamber. Base and working vacuum pressures of the chamber in the ion implanter were 2 × 10⁻⁶ and 2 × 10⁻⁵ Torr, respectively. After the ion implantation, postirradiation annealing was conducted at 550 °C for 2 h in air. Ultraviolet-visible light spectroscopy for the TiO₂ thin films was monitored in the absorption mode before and after the ion implantation.

In order to examine the band gap narrowing in N-doped TiO₂, we calculate the band structure of TiO_{2-x}N_x by first-principles DFT. Here, we assumed an anatase TiO₂ crystal structure with the substitution of N for O. Such a N-doped TiO₂ system was simulated by using the supercell geometry with four unit cells of anatase TiO₂, where one O atom is replaced by one N atom. Therefore, 3.125 at. % of the O sites in the anatase TiO₂ crystal is replaced by N (i.e., TiO_{2-x}N_x, where x=0.0625). We performed first-principles DFT calculations using norm-conserving pseudopotentials²⁰ and the local-density approximation (LDA).²¹ The electronic wave functions are expanded in a plane wave basis set with a cutoff energy of 60 Ry. The **k** space integration was done with four **k** points in the Brillouin zone of four unit cells. All atoms in N-doped TiO₂ were allowed to relax along the calculated Hellmann-Feynman forces until all the residual force components were less than 1 mRy/bohr.

III. RESULTS AND DISCUSSION

The deposited films were highly epitaxial with an anatase structure, because only (004) peak at 38° in 2θ except for a peak from the sapphire substrate was found in the diffraction pattern [Fig. 1(a)].¹⁸ The full width at half maximum (FWHM) of the (004) peak was 0.29° in θ [Fig. 1(b)]. The

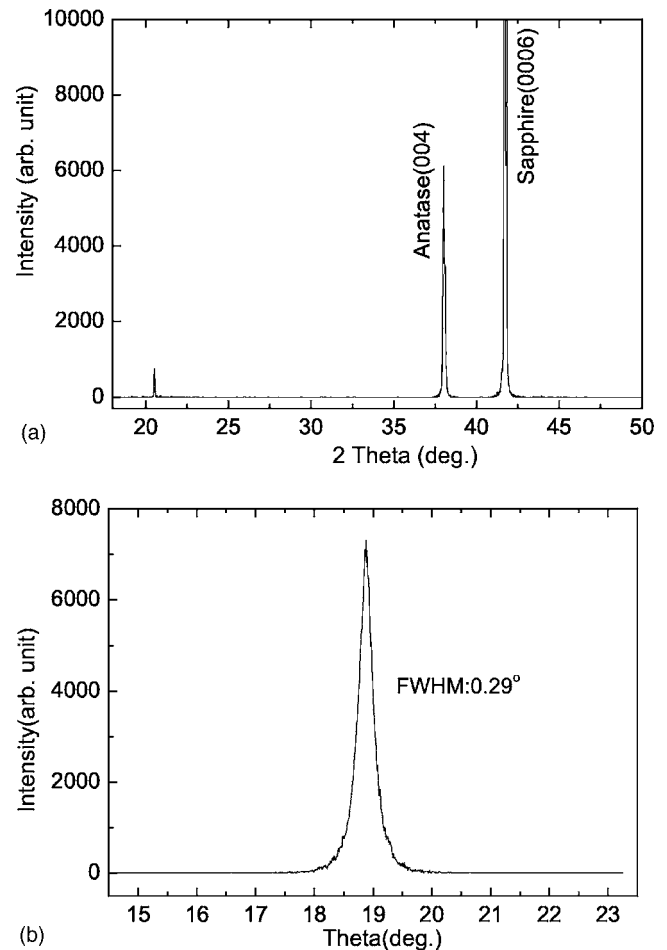


FIG. 1. $\theta/2\theta$ XRD pattern of TiO₂ film deposited onto sapphire substrate by ablating the TiO₂ target using Nd:YAG laser (a) and the rocking curve through the (004) diffraction (b).

FWHM was almost the same when the N-ion-implanted sample was annealed at 550 °C for 2 h in air. The TiO₂ film appeared visually transparent when the film was grown in the presence of oxygen, but the film exhibited yellow color when the film was grown without the oxygen gas introduction. We believe that this change in color is due to the color centers caused by the oxygen vacancies in the deposited TiO₂ film. As computed by the transport of ions in matter (TRIM) software, the N implanted depth into anatase TiO₂ is about 128 nm. Considering the diffusion of the implanted N during annealing at 550 °C for 2 h, the implanted depth should be more than 128 nm. However, we believe that the spectra obtained in this work reflect the sensitized depth less than the film thickness of about 500 nm.

Figure 2 shows the difference of the light absorbance between the films prepared with and without oxygen gas introduction. The absorption threshold of the latter film shifts to longer wavelength by about 27 nm compared with that of the former film, implying a difference in the band structures of the two TiO₂ films. Certainly, a longer absorption shift in the latter film should be attributed to the oxygen deficient TiO₂ (TiO_{2-x}). In Fig. 1 we estimate the redshift of the understoichiometric film to be about 0.13 eV, indicating that our synthesized TiO_{2-x} has a band gap reduction of 0.13 eV. Thus, we can say that reduced TiO_{2-x} will be very much

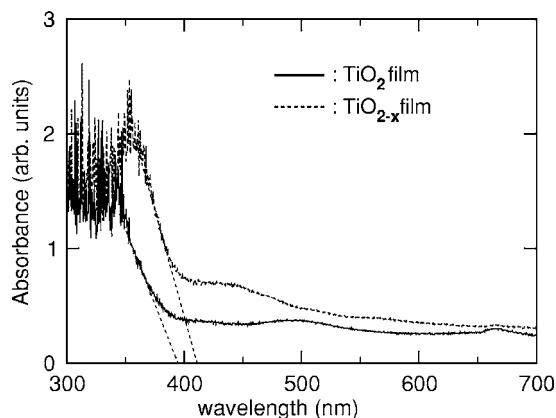


FIG. 2. Photoabsorption spectra of the TiO₂ films prepared with and without oxygen gas introduction. For absorbance the arbitrary units are used in log scale.

sensitized to the visible light. Previously, several approaches such as doping of various transition metal cations¹⁻³ and synthesis of reduced TiO_{2-x} (Refs. 4 and 5) have been proposed to increase the photoactivity and quantum efficiency (= number of photoformed products/number of incident photons). However, the reduced TiO_{2-x} photocatalysts lower the photocatalytic driving force because of the formation of oxygen vacancy states between the valence and conduction bands of TiO₂.⁵

The light absorbances of undoped and doped TiO₂ films as a function of the wavelength are plotted in Figs. 3 and 4, respectively. The results for the TiO₂ films prepared with and without oxygen introduction are given in Figs. 3 and 4, respectively. In Fig. 3, the film implanted with N ions of 1×10^{17} ions/cm² has more threshold shift as well as more photon absorbance in the visible region compared with that with 5×10^{16} ions/cm². From the tangent lines in Fig. 3, we estimate that the former (latter) sample has a redshift of 0.12 (0.06) eV. As shown in Fig. 4, when N ions of 1×10^{17} ions/cm² are implanted into the film prepared in the absence of oxygen, we obtain a redshift of about 0.08 eV. Both results obtained with and without oxygen introduction imply that N ion implantation into the epitaxially grown TiO₂ film followed by heat treatment improves photoabsorption regardless of the film stoichiometry.

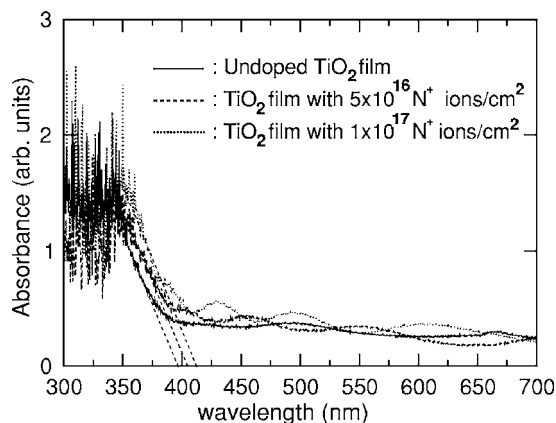


FIG. 3. Photoabsorption spectra of undoped and N-doped epitaxially grown TiO₂ films prepared with oxygen introduction. Two different ion implantations are given.

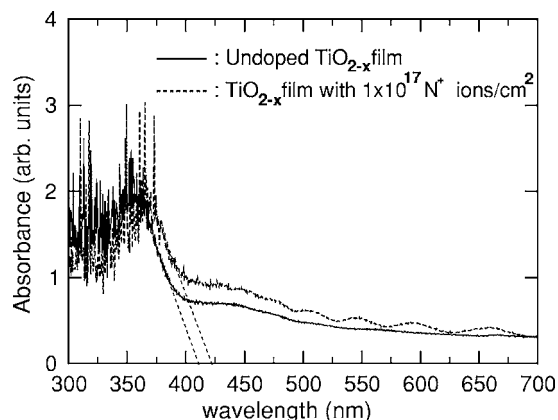


FIG. 4. Photoabsorption spectra of undoped and N-doped epitaxially grown TiO₂ films prepared without oxygen introduction.

As compared with the nearly stoichiometric TiO₂ sample, we find that N doping to the synthesized TiO_{2-x} exhibits a total band gap reduction of as much as 0.21 eV. This fact may imply that N-doped TiO_{2-x} will be very much sensitized to the visible light. However, the photocatalytic activity of N-doped TiO_{2-x} might be lowered by oxygen vacancy states formed between the valence and conduction bands of TiO₂. Thus, it is likely that a sizable modification of the band structure caused by oxygen deficient TiO₂ or metal doping²² would not be always desirable for the photocatalytic behavior of TiO₂.

We note that the photoabsorption of our N-doped TiO₂ film prepared in the presence of 6N purity of oxygen gas was very reproducible though its threshold shift is somewhat small. This may be predominantly attributed to the fact that only N⁺ ions among various ion species were selected for the implantation through the mass-analyzing magnet and the N⁺ ions were implanted into the epitaxially grown TiO₂ film, which is a single crystalline. We also note that N ion bombardment onto a TiO₂ film surface may cause the surface to be amorphous as well as understoichiometric due to a preferential sputtering of O atoms.²³ In order to recrystallize the amorphous film and also to recover the reduced TiO_{2-x} surface, the postirradiation annealing was conducted in air at 550 °C. As mentioned above, the x-ray diffraction peak of anatase (004) showed almost the same FWHM as that acquired from as-deposited TiO₂. Therefore, we believe that the redshifts reflect predominantly the N-doping effects and are not significantly associated with the lattice damage. In contrast with the present result, Diwald *et al.*¹⁹ reported that a blueshift took place in a rutile TiO₂(110) single crystal by reactive N₂⁺ and Ar⁺ sputtering and subsequent annealing at 900 K in ultrahigh vacuum. This sample treatment differs from the present work where we used epitaxially grown anatase TiO₂ and subsequent annealing in air.

Various sample preparations employed in the present work will provide a standard condition for producing the reproducible light absorption properties of N-doped single crystalline (epitaxially grown) TiO₂ films. Although the reduced TiO_{2-x} film prepared without introducing the oxygen gas into the deposition chamber showed a significant redshift, it will not be the standard condition because of its

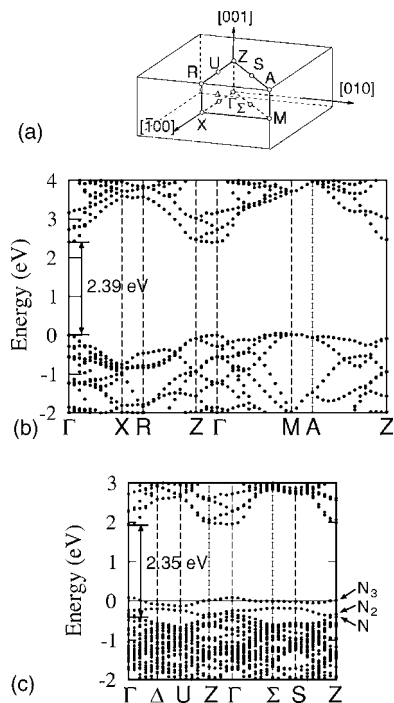


FIG. 5. Calculated band structures of (b) undoped and (c) N-doped TiO_2 along high-symmetry lines of the irreducible Brillouin zone. The Brillouin zone for the tetragonal Bravais Lattice is given in (a). In (b) the valence band maximum is taken as the energy zero, while in (c) the energy zero represents the Fermi level. The values in (b) and (c) denote the energy difference between the lowest Ti $3d$ band and the highest O $2p$ band.

lower efficiency in the photocatalytic activity mentioned above. It is noticeable that more redshift was observed with increasing N ion dose. This implies that modification of the band structure of the TiO_2 film is controllable by changing the ion dose.

To provide an explanation for the observed experimental data, we calculate the band structure for a perfect anatase TiO_2 crystal involving N substitution for O, which may simulate well the structure after N ion implantation followed by heat treatment. The calculated band structures of undoped and N-doped TiO_2 are shown in Figs. 5(a) and 5(b), respectively. For undoped TiO_2 we find a minimum band gap at the Γ point with a magnitude of 2.39 eV, which is largely underestimated compared with the experimental²⁴ value of 3.2 eV. Such a large underestimation ($\sim 25\%$) of the band gap is the well-known shortcoming of the LDA. For N-doped TiO_2 the three bands [N_1 , N_2 , and N_3 in Fig. 5(b)] originating from N $2p$ states are located slightly above the valence band maximum of TiO_2 . The charge character of these band gap states, shown in Figs. 6(a)–6(c), reveals that the N_1 , N_2 , and N_3 states represent p_z , p_x , and p_y characters of N p orbitals, respectively. Here, it is notable that the N $2p$ states show a weak interaction with the neighboring Ti and O atoms. We find that the charge densities of the topmost O $2p$ state and the lowest Ti $3d$ state in N-doped TiO_2 are almost equal to those [Figs. 6(d) and 6(e), respectively] in undoped TiO_2 .

Our band structure of N-doped TiO_2 shows that the energy gap between the highest O $2p$ band and the lowest Ti $3d$ band is 2.35 eV, slightly smaller than that ($E_g=2.39$ eV) of

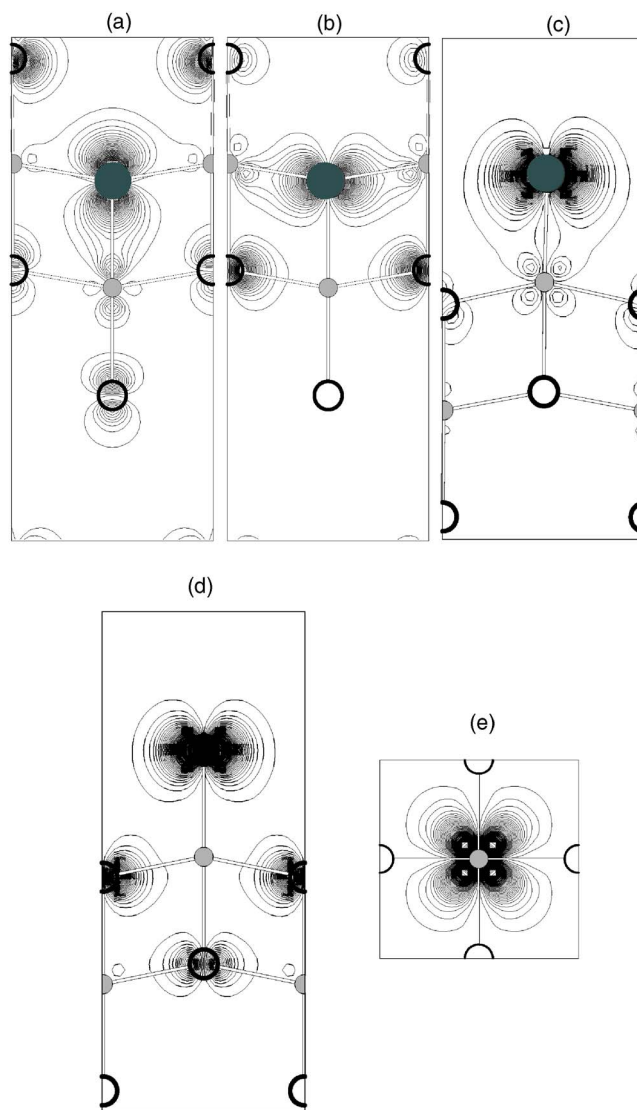


FIG. 6. (Color online) Charge characters of (a) the lowest N $2p$ state, (b) the middle N $2p$ state, (c) the highest N $2p$ state, (d) the O $2p$ state, and (e) the Ti $3d$ state at the Z point of the Brillouin zone. The charge densities of (a), (b), and (c) [(d) and (e)] were obtained from doped [undoped] TiO_2 . The plots in (a) and (b) [(c) and (d)] are in the vertical xz [yz] plane containing the impurity atom, while that in (e) is drawn in the horizontal xy plane containing Ti. Contour spacings are $0.002 e/\text{bohr}^3$.

undoped TiO_2 . Thus, N-doped TiO_2 shows a band gap narrowing of 0.04 eV. When we consider the underestimation of the LDA band gap compared with the experimental one, our theoretical band gap narrowing of 0.04 eV agrees well with our observed 0.06–0.12 eV shift of the absorption edge. It is worthwhile to note in Fig. 5(b) that the energy difference between the highest N $2p$ state and the conduction band minimum is 1.88 eV. This energy difference, if the above-mentioned LDA error ($\sim 25\%$) is corrected, is estimated as 2.51 eV (equivalent to 494 nm wavelength), thereby extending optical absorption into the visible-light region as observed in our experiment. This estimated value agrees well with a recent photoabsorption result of Nakamura *et al.*,¹¹ where the energy difference between the highest N $2p$ state and the Ti $3d$ state was estimated as 2.45 eV. It is notable that such corrected energy difference between the highest N $2p$ state and the conduction band minimum is exactly the

same as the estimated band gap (~ 2.5 eV) from the N_2 -annealed $TiO_{2-x}N_x$ sample in Ref. 25. Thus, we believe that the D_2 level observed in Ref. 25 would be caused by the N-induced states located above the valence band edge. Of course, we do not exclude the possibility of a significant change of the band structure at a high N concentration used in Ref. 25, where the x value was 0.2373 for the N_2 -annealed $TiO_{2-x}N_x$ sample. The comparative agreement between theory and experiment implies that most N atoms replace the O atoms in the TiO_2 matrix. We believe that this N substitution for O can be obtained by the sample preparation that singly charged N ions are implanted into the single crystalline TiO_2 , followed by postirradiation heat treatment in air.

IV. SUMMARY

We have presented the optical-response properties of N-doped epitaxially grown anatase TiO_2 film by a combination of ultraviolet-visible absorption spectroscopy and first-principles density-functional theory calculation. Our experiment shows not only that N ion doping causes the absorption edge of the epitaxially grown TiO_2 film to be shifted to lower energy, but also that the optical absorption was extended more into the visible-light region as the ion dose increases. We obtained the very reproducible ultraviolet-visible absorption spectroscopy data through the sample preparation that the TiO_2 films epitaxially grown on the sapphire substrate were N^+ ion implanted and then heat treated in air at 550 °C for 2 h. Our calculated band structures of N-doped TiO_2 , which was simulated by one substitution of N for O within four unit cells of anatase TiO_2 , are well consistent with the experimental data, implying that most implanted N atoms might occupy the O sites in the TiO_2 films. We conclude that the very reproducible and controllable photoabsorption behavior of the N-doped TiO_2 film can be obtained by controlling the ion dose with the following four conditions; the film preparation in the presence of oxygen gas in the deposition chamber, the film epitaxy, singly charged N ion implantation, and postirradiation heat treatment.

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