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Fabrication and characterization of anatase/rutile–TiO₂ thin films by magnetron sputtering: a review

Sakae Tanemura, Lei Miao, Wilfried Wunderlich, Masaki Tanemura, Yukimasa Mori, Shoichi Toh, Kenji Kaneko

*Department of Environmental Technology and Urban Planning, Nagoya Institute of Technology, Showa-ku, Nagoya 466-8555, Japan
bMaterials Research Laboratory, NGK Insulators Ltd, Mizuho-ku, Nagoya 467-8530, Japan
cDepartment of Material Science and Engineering & HVEM Laboratory, Kyushu University, Higasi-ku, Fukuoka 812-8581, Japan

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Abstract

This review article summarizes briefly some important achievements of our recent research on anatase and/or rutile TiO₂ thin films, fabricated by helicon RF magnetron sputtering, with good crystal quality and high density, and gives the-state-of-the-art of the knowledge on systematic interrelationship for fabrication conditions, crystal structure, composition, optical properties, and bactericidal abilities, and on the effective surface treatment to improve the optical reactivity of the obtained films.

Keywords: TiO₂ thin film; Helicon RF magnetron sputtering; Epitaxial growth; Optical properties; Bactericidal ability; Surface treatment

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1. Introduction

The ultimate goal for the human beings living in 21st century is to establish environmentally harmonized technologies for sustainable society and energy systems. These technologies include the environmental protection,
the pollution control, 3R (reduce, reuse and recycle) of materials, the renewable and/or clean energy systems, and so on. Under the NITech 21st Century COE program on ‘World Ceramics Centre for Environmental Harmony’, we have conducted research to contribute to the designated technologies through material science and applied physics.

Since the finding of the photo-induced decomposition of water on TiO₂ electrodes by Fujishima and Honda [1] in 1971, TiO₂ has become a promising material as photocatalyst [2] to decompose and oxidize various organic and/or inorganic chemicals in waste and emission by its strong oxidation activity based on the created super oxide anion radical (O₂⁻) and ·OH radical. Its high chemical stability and inexpensive cost are the other benefits for the use of this material as photo-catalyst. This material has additionally great potential for the application to dye-sensitized photovoltaic cells [3,4], energy efficient windows and/or other optical coatings [5–7], and capacitors in LSI [8]. The wide band gap semiconductor TiO₂ exists in three different crystalline polymorphs: rutile, anatase and brookite. Among them, rutile (R-titania) and anatase (A-titania) are the most common and widely used phases in applications.

Motivated by those excellent applications of TiO₂, an increasing number of researchers, laboratories have engaged in the fabrication and characterization of TiO₂. We have recently achieved: (1) the simultaneous growth of epitaxial thin films of both A-titania on SrTiO₃ (STO) substrate and R-titania on sapphire substrates, and growth of polycrystalline A- and/or R-titania thin films on silicon and/or glass, by helicon RF magnetron sputtering [9–11]; (2) the determination of optical properties of the fabricated polycrystalline and/or epitaxial A- and/or R-titania thin films [12] and interpretation of the observed wider band-gap values [13]; (3) the evaluation of bactericidal ability by killing Escherichia coli [14]; and (4) the improvement of optical reactivity by N₂-H₂ plasma surface-treatment[15].

The scope of this review article is to summarize briefly our important research achievements on high quality TiO₂ thin films with novel physical properties among the above described ones, and gives the-state-of-the-art of the knowledge-base on systematic interrelationship for fabrication conditions, crystal structure, composition, optical properties, and bactericidal abilities, and on the effective surface treatment to improve the optical response of the obtained films.

2. Important achievements

2.1. Simultaneous growth of epitaxial thin films of A- and R-titania by helicon RF magnetron sputtering

As many applications about titanium dioxide have a broad base of high refractive index and/or high dielectric constant, fabrications of TiO₂ thin films with high refractive index have great significance for promoting applications.

| Substrates       | P_sub (Pa) | T_sub (°C) | Ar (sccm) | Target power (W) | Thickness (nm) |
|------------------|------------|------------|-----------|-----------------|----------------|
| Sapphire and SrTiO₃ | 0.1–0.25  | 300–600    | 5.8       | 160             | 150            |

In addition, epitaxial films have obviously superior optical properties compared with polycrystalline and amorphous films with lower defect concentration [16].

Epitaxial A-titania thin film on STO(001) and R-titania thin film on sapphire (110) were simultaneously grown at optimal sputtering conditions given in Table 1 by the helicon RF magnetron sputtering (ULVAC, MPS-2000-HC3) [9,10].

The epitaxial relationship was confirmed as rutile (101)//sapphire (110), (010)//(001)ₙ anatase (001)//SrTiO₃ (001), (100)ₙ/(100) by XRD pole figure plots.

The microstructure was studied by transmission electron microscope (TEM). Fig. 1(a) and (b) exemplifies the cross-sectional TEM lattice image and diffraction pattern of the epitaxial A-titania film on STO. The film can be identified as single crystal structure from the clearly defined diffraction spots. The interplanar spacings for A-titania film and STO substrate were measured from the lattice image as indexed in Fig. 1(a). The angle between A-titania (101) plane and STO (101) plane is 30° as expected, and then the A-film (101) spacing multiplied by the factor of cos 30° equal to STO (101) spacing with the precision 2.9%. This result consists with X-ray diffractometry (XRD) pole plots.

The lattice constants a and c of both A-titania and R-titania films were calculated from the d spacing obtained by spot patterns in selected area electron diffractionometry (SAED) and lattice image in TEM and the results are given in Table 2. This confirms the primitive lattice cell exhibits contraction at a and b axes while expansion at c-axis. The unit cell volume of A-titania film is shrunk from the bulk by 4.3% and that of R-titania being by 1%, respectively.

2.2. Optical properties of the fabricated epitaxial and/or polycrystalline A- and/or R-titania thin films

Optical properties, such as complex refractive indices (n-iκ; i: unit of imaginary) for a certain range of wavelength between ultra violet and near infrared, and optical band gap values E₉, are becoming quite important criteria for the selection of the applications of the fabricated films.

The results of the complex refractive index from 0.75 to 5 eV (1653–248 nm in wavelength) for the fabricated epitaxial A- and/or R-titania were obtained by spectroscopic ellipsometry (SE) (Horiba, Jobin-Yvon, UVISE), and the optical band gaps E₉ for the respective films extrapolated by Tauc plot using the obtained extinction
coefficient were reproduced [12]. Those values for polycrystalline A- and/or R-titania films grown on Si substrate by the helicon RF magnetron sputtering [9], were also compared.

The obtained real part of refractive indices $n$ in the designated wavelength range for all provided samples exemplified in Table 3 show higher values than the values cited in the recent articles for films [17,18] and for bulk ones [19,20]. Those differences are partly due to the fine crystallinity of the present samples. Comparing the dispersion relation of refractive index $n$ of epitaxial film with polycrystal one, distinct two humps in high-energy region after exceeding band gap in epitaxial A-titania and steep peak in epitaxial R-titania are characteristic [12]. This is also another confirmation of the fine crystallinity of the fabricated epitaxial films. Optical band gaps $E_g$ extrapolated using Tauc plot listed in Table 4 are about 10% larger than the bulk.

It is well-known that the optical properties of intrinsic semiconductors can be changed significantly by the application of external strain to non-degenerated state [21]. In order to understand the change of the band gap value observed in strained thin films, the density of states and the energy of the electronic orbitals depending on lattice strain are needed to be known. Ab initio simulations based on density functional theory (DFT) for calculating the electronic wave functions and their periodicity in the crystal are required. The Vienna Simulation Program (Vasp) [22], which has been successfully applied to the calculation of the surface energy, adsorption energy [23,24], and the electronic band structure [25,26] for both A- and R-titania, is employed as the most appropriate program with high reliability and reputation to obtain the correlation between lattice constants of the thin films and the optical band gap for both A- and R-titania thin films.

The calculated data are plotted in the three-dimensional graph in Fig. 2, in order to show the dependence of the band-gap ($z$-axis) on both wide range of variations of lattice constants $a$ and $c$ ($x$ and $y$-axis). Although the band gap of the bulk R-titania was calibrated to be the experimental values of 3.03 eV in the calculation procedures, the calculated band gaps from DOS calculations for bulk A-titania, and the strained A- and R-titania thin films as seen in Fig. 2 show very good agreement to the experimental values listed in Table 4. It is worth to point out that the band gap from density of states (DOS) was calculated as the gap between the O 2p-states and the Ti 3d-states. In both A- and R- titania cases, the band gap decreases with increasing $a$ and $c$, but the dependence on $c$ is less for the R-phase. The values for the thin films lie in both cases in region A, which means a slight increase in the band gap. The desired decreasing of the band gap less than 2 eV would occur in region B and D for both A- and R-titania, which means decrease of $c$-axis while increase of $a$ and $b$ axes. However, it is difficult to fabricate this kind of distorted thin films by the calculation of the total lattice energy as noticed in [13].

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Table 2

| Lattice constant | $F$ Film (Å) | $B$ Bulk (Å) | $(F-B)/B$ (%) |
|------------------|--------------|--------------|---------------|
| Anatase $(a=b)$  | 3.66         | 3.79         | -3.43         |
| Anatase $(c)$    | 9.76         | 9.51         | 2.62          |
| Anatase V        | 130.77       | 136.6        | -4.27         |
| $(a^*b*c)$       | 4.46         | 4.59         | -2.83         |
| Rutile $(a=b)$   | 3.12         | 2.96         | 5.4           |
| Rutile $(c)$     | 61.92        | 62.44        | -0.83         |
| Rutile V         |              |              |               |

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Fig. 1. (a) Cross-sectional TEM image, and (b) diffraction pattern of epitaxial TiO$_2$-anatase film on SrTiO$_3$ (100) substrate.
2.3. Evaluation of bactericidal ability

TiO₂ photo-catalyst exhibits strong oxidizing power by the generated hydroxyl radical (OH⁻) through the created hole (h⁺) in valence band and super-oxide anion radical (O₂⁻) through the excited electron to conduction band under irradiation of UV light with water and oxygen environment around TiO₂. Consequently, the irradiated TiO₂ photocatalyst can decompose and/or oxidize most of organic and/or inorganic compounds. In 1985, Matsunaga et al. [27] reported for the first time the microbiocidal effect of TiO₂ photocatalytic reaction. Since then, research work on photocatalytic killing has been intensively conducted on a wide spectrum of organisms including viruses, bacteria, fungi, algae, and cancer cells. Huang et al. [28] reported the basic killing mechanism of *E. coli* (*E. coli*) treated with TiO₂ near-UV light. Treatment of *E. coli* with TiO₂ under UV light resulted in an immediate increase in permeability to small molecules such as *p*-nitrophenol β-D-galactopyranoside on cell envelop, and the leakage of large molecules such as β-D-galactosidase from intracellular components after 20 min.

Photo-catalytic activities of TiO₂ materials strongly depend on surface morphology, crystal structure and quality. Although the killing mechanism has been widely investigated, hardly any work has systematically done on the relation of crystal structure and quality of films with bactericidal ability. So, we have conducted the study.

Bactericidal abilities have been evaluated by accounting the killed numbers of the *E. coli* colonies using film stick method under UV irradiation for both polycrystalline and epitaxial A- and R-titania thin films prepared by RF helicon magnetron sputtering [14]. The method used has been developed by the Japanese Society of Industrial-Technology for Antimicrobial Articles which being led by Prof A. Fujishima and will be employed as Japanese Industrial Standard in near future. The details of it have been described in Ref. [14]. The results are partly reproduced in Fig. 3 under the UV irradiation condition of 400 μW/cm² for 2 h. Both epitaxial and polycrystal A-titania films show bactericidal abilities, and no distinguishing difference for them. The antimicrobial activity values, of which definition is log (*C₀/C₁*), where *C₀*: colonized bacteria number without

Table 3
Values of refractive index *n* at the designated wavelength for both epitaxial and polycrystalline films

| Structure      | Rutile Polycrystalline | Rutile Epitaxial | Anatase Polycrystalline | Anatase Epitaxial |
|----------------|------------------------|------------------|-------------------------|-------------------|
| *n* at 500 nm  | 2.849                  | 2.843            | 2.657                   | 2.637             |
| Maximum *n* at 400–800 nm | 3.182(400)             | 3.173(400)       | 2.898(400)              | 2.892(400)        |
| Maximum *n* at 250–1600 nm | 3.952(330)             | 4.142(320)       | 3.605(320)              | 3.79(330)         |

Table 4
Band gap of the anatase and rutile films by Tauc plot in comparison to the bulk

| Structure      | Polycrystalline rutile film | Polycrystalline anatase film | Epitaxial rutile film | Epitaxial anatase film | Bulk rutile | Bulk anatase |
|----------------|-----------------------------|------------------------------|----------------------|-----------------------|-------------|-------------|
| Band gap *E₉* (eV) | 3.34                        | 3.39                        | 3.37                  | 3.51                  | 3.03        | 3.20        |

Fig. 2. Calculated band gap width in (eV) as a function of the lattice constants *a* and *c* in (pm = 0.001 nm) for (a) A-titania and (b) R-titania. The dots mark the experimental data points for bulk and thin films on Al₂O₃ and/or SrTiO₃, respectively.
UV irradiation; and $C_1$: colonized survival bacteria number with UV irradiation, are given in Table 5. The maximum value is 1.28 for single crystal anatase irradiated at 400 $\mu$W/cm$^2$ for 2 h. On the other hand, no bactericidal ability is found for R-titania films. One possible reason for the poor photocatalytic effect of R-titania film might be its energy potential lower than the potential required for the generation of super-oxide anion radical (O$_2^-$) which leads to its weaker reduction capability. For the identification of the precise bactericidal mechanism for the designated thin films, the further investigation about the lifetime of excited electron and the created hole by femto-second laser spectroscopy will be needed.

2.4. Improvement of optical reactivity by N$_2$–H$_2$ plasma surface-treatment

TiO$_2$ has photo-activity only under ultraviolet (UV) light, whose energy is greater than the band gap of TiO$_2$ ($\sim$ 3 eV), and this limits its application greatly. It is well-known that the introduced lattice defect such as substitution of atom at the site by foreign atoms and/or creation of vacancies, and the interstitial substitution of foreign atoms, resulted in the narrowing of band gap in the case of intrinsic semiconductors since 1974 by Watkins [29]. Many papers report doping TiO$_2$ lattice with various transition metals [30–32] can improve the photo activity of TiO$_2$ and extend its absorption edge into the visible-light region. On the other hand, others report doping of non-metal substances like S [33] and N [34, 35] into TiO$_2$ lattice is better than transition metals due to the thermal instability or an increase in the carrier-recombination centers occurred in the latter system. Asahi et al. [34, 35] recently calculated the density of states (DOSs) of A-titania with O substitution by dopants C, N, F, P or S by the full potential augmented plane wave formalism in the framework of the local density approximation. They found that the substitution of dopant N was the most effective because its $p$ states contribute to the band-gap narrowing by mixing with O 2$p$ states. Also this was identified by their evaluation of photo-catalytic activity for A-titania thin films [34] and powder [35] which were fully substituted by doped N.

In a heterogeneous photo-catalysis system, photo-induced molecular transformations or reactions take place at the surface of a catalyst [36]. We have applied plasma-surface-treatment to surface modification of A-titania thin film [15]. The used experimental system installed two modes of either DC reactive magnetron sputtering or plasma-surface-treatment in the single vacuum vessel. A-titania polycrystal thin films were firstly prepared on glass substrate heated at 500 °C with 1200 Å in film thickness by DC reactive magnetron sputtering from Ti metallic target in an Ar+O$_2$ mixed gas under the total pressure 0.5 Pa (the sample being named as No. 1), then the sample No. 1 was successively surface-treated by the plasma of N$_2$–H$_2$ mixed gases with the volume ratio of 1:3 under the total pressure 14 Pa at 400 °C for 2 h (sample No. 2) and additionally anneal-treated in N$_2$ gases at 400 °C for 2 h (sample No. 3).

Table 5

| Condition 1 | Condition 2 |
|-------------|-------------|
| (400 $\mu$W/cm$^2$, 2 h) | (800 $\mu$W/cm$^2$, 1 h) |
| Single-crystal anatase | 1.28 | 0.75 |
| Polycrystal anatase | 1.18 | 0.96 |
The optical absorption spectra show that the absorption edges of Nos. 2 and 3 films shifted from 363 nm (3.4 eV) to 428 nm (2.9 eV), 354 nm (3.5 eV) to 428 nm (2.9 eV), respectively, while the absorptance increase by 16 and 26%, respectively, for the two corresponding samples in comparison with No. 1 in Fig. 4a. The optical band gaps of three corresponding samples are extrapolated by Tauc plot using extinction coefficient $k$ for the surface layers. The values are 3.4 eV for No. 1 and 2.9 eV for No. 2, respectively, which of them agree well with absorption results although the surface layer of No. 3 sample shows metallic behavior at the lower energy region ($\approx 2.5$ eV) as shown in Fig. 4b.

XPS results revealed the formation of TiO$_2$-$_{x}$N$_x$ and TiN in the surface layer with about 120 Å in depth for the both surface-treated samples (Nos. 2 and 3). SIMS also detected the high concentration of N element at the surface of the samples Nos. 2 and 3. N-doping was proved as N substituted O in TiO$_2$ by XPS Ti 2p and N 1s spectra, and this substituted N-dopant to TiO$_2$ lattice contributed to the band-gap narrowing which led to a significant red shift of the absorption edge to the visible-light region. Consequently, N$_2$–H$_2$ plasma-surface-treatment was proved to be an effective way for improving the optical reactivity of TiO$_2$ thin film.

3. Conclusion

Epitaxial A- and R-titania thin films were simultaneously grown on STO and sapphire substrates at optimal sputtering conditions, and the epitaxial relationship was determined as rutile (101)//sapphire (110), (010)//(001)$_s$, anatase (001)//SrTiO$_3$ (001), (100)//(100)$_s$ by XRD. TEM observation confirmed the epitaxial film growth of single crystalline anatase and rutile structure with slight lattice distortion compared with bulk. Through calculating lattice constant, the films were identified as contraction at $a$ and $b$ axes while expansion at $c$-axis.

Based on complex refractive indices $n$ and $k$ measured by spectroscopic ellipsometry, very high refractive indices at the designated wavelength range were confirmed. The optical band gaps $E_g$ extrapolated using Tauc plot were about 10% larger than the bulk. The ab initio calculation of the optical band gap of TiO$_2$ thin films depending on lattice constants has verified that the wider band gap observed is due to the expansion of $c$-axis and the contraction of $a$ and $b$ axes for both A- and R-titania thin films in comparison with bulk TiO$_2$. The desired decreasing of the band gap less than $2$ eV would occur in a certain distorted region for both A- and R-titania, which means decrease of $c$-axis while increase of $a$ and $b$ axes. However, it is difficult to fabricate this kind of distorted thin films by the stability of the total lattice energy as previously noticed.

Bactericidal abilities were evaluated by accounting the numbers of killed E. coli colonies using film stick method under UV irradiation for both polycrystalline and epitaxial A- and R-titania thin films. Both single and polycrystal A-titania films showed bactericidal abilities, and no distinguishing difference for them in the designated experiment. The maximum antimicrobial activity value was 1.28 for single crystal A-titania at the irradiation of UV with 400 μW/cm$^2$ for 2 h. On the other hand, no bactericidal ability was found for R-titania films in this work.

The improvement of the optical reactivity for A-titania thin films by N$_2$–H$_2$ plasma-surface-treatment was succeeded. The absorption edges obtained from UV/VIS/NIR spectrophotometer for plasma-treated sample and plasma plus anneal-treated one shifted from 363 nm (3.4 eV) to 428 nm (2.9 eV), and 354 nm (3.5 eV) to 428 nm (2.9 eV), respectively, while the absorptance for two corresponding samples increased by 16 and 26%, respectively, in comparison with the as-deposited sample. N-doping was proved as N substituted O in TiO$_2$ by XPS, and this substitutional N-doping to TiO$_2$ lattice contributed to the band-gap narrowing which led to a significant red shift of the absorption edge to the visible-light region. Consequently, N$_2$–H$_2$ plasma-surface-treatment was an effective way for improving the optical reactivity of TiO$_2$ thin films.

From those achievements, we can safely conclude that epitaxial and/or polycrystalline TiO$_2$ thin film with good crystal quality and high density fabricated by RF helicon
magneteron sputtering is feasible to apply to solar cell material, photo-catalyst, waveguiding material, capacitor for DRAM device, and optical functional coating, and being prospective as an industrial material.

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References

[1] A. Fujishima, K. Honda, Nature 238 (1972) 37.
[2] A. Fujishima, K. Honda, Bull. Chem. Soc. Jpn 44 (1971) 1148.
[3] B. O’Regan, M. Gratzel, Nature (Lond.) 353 (1991) 737.
[4] A. Hagfelt, M. Gratzel, Chem. Rev. 95 (1995) 49.
[5] C.G. Grankvist, Materials Science for Solar Energy Conversion Systems, Pergamon Press, Oxford, 1991.
[6] P. Jin, L. Miao, S. Tanemura, G. Xu, M. Tazawa, K. Yoshimura, Appl. Surf. Sci. 212–213 (2003) 775.
[7] G.S. Brady, Materials Handbook, 10th ed., McGraw-Hill, New York, 1971.
[8] Y.H. Lee, Vacuum 51 (1998) 503.
[9] L. Miao, P. Jin, K. Kaneko, S. Tanemura, in: H.J. Gao, H. Fuchs, D.M. Chen (Eds.), Proceedings of Eighth IUMRS International Conference on Electronic Materials: Advanced Nanomaterials and Nanodevices, IOP, 2002, p. 943.
[10] L. Miao, S. Tanemura, P. Jin, K. Kaneko, A. Terai, N. Nabatova-Gabain, J. Cryst. Growth 254 (2003) 100.
[11] L. Miao, P. Jin, K. Kaneko, A. Terai, N. Nabatova-Gabain, S. Tanemura, Appl. Surf. Sci. 212–213 (2003) 255.
[12] S. Tanemura, L. Miao, P. Jin, K. Kaneko, A. Terai, N. Nabatova-Gabain, Appl. Surf. Sci. 212–213 (2003) 654.
[13] W. Wunderlich, L. Miao, S. Tanemura, M. Tanemura, P. Jin, K. Kaneko, A. Terai, N. Nabatova-Gabain, R. Belkada, Int. J. Nanosci. 2004; (in press).
[14] L. Miao, S. Tanemura, Y. Kondo, M. lwata, S. Toh, K. Kaneko, Appl. Surf. Sci. 238 (2004) 125.
[15] L. Miao, S. Tanemura, H. Watanahe, Y. Mori, K. Kaneko, S. Toh, J. Cryst. Growth 260/1–2 (2004) 118.
[16] J. Aarik, A. Aidla, H. Mandar, T. Uustare, M. Schuisky, A. Harsta, J. Cryst. Growth 242 (2002) 189.
[17] C.C. Ting, S.Y. Chen, J. Appl. Phys. 88 (8) (2000) 4682.
[18] M.H. Suhail, G. Mohan Rao, S. Mohan, J. Appl. Phys. 71 (3) (1992) 1421.
[19] D.C. Cromerney, Phys. Rev. B 87 (1952) 876.
[20] H. Tang, F. Levy, H. Berger, P.E. Schmid, Phys. Rev. B 52 (1995) 7771.
[21] Foreexample: T. Yamaguchi, Semiconductor Physics, Asakura Publish, Tokyo, 2001. P. 101.
[22] G. Kresse, J. Hafner, Phys. Rev. B 47 (1993) 558; J. Kresse, J. Hafner, Phys. Rev. B 49 (1994) 14251.
[23] S.P. Bates, G. Kresse, M.J. Gillan, Surf. Sci. 409 (1998) 336.
[24] S.P. Bates, G. Kresse, M.J. Gillan, Surf. Sci. 385 (1997) 386.
[25] R. Asahi, Y. Taga, W. Mannstadt, A.J. Freeman, Phys. Rev. B 61 (11) (2000) 7459.
[26] B. Poumellec, P.J. Durham, G.Y. Guo, J. Phys.: Condens. Matter 3 (1991) 8195.
[27] T. Matunaga, R. Tomoda, T. Nakajima, H. Wake, FEMS Microbiol. Lett. 29 (1985) 211.
[28] Z. Huang, P.-C. Maness, D.M. Blake, E.J. Wolfum, S.L. Smolinski, W.A. Jacoby, J. Photochem. Photobiol. A: Chem. 130 (2000) 163.
[29] G.D. Watkins, Lattice defects in Semiconductor, IOP, London/Bristol, 1974. Pp. 1–22.
[30] H. Yamashita, Y. Ichihashi, M. Takeuchi, S. Kishiguchi, M. Anpo, J. Synchrotron. Rad. 6 (1999) 451.
[31] J.M. Herrmann, J. Disdier, P. Pichat, Chem. Phys. Lett. 108 (1984) 618.
[32] E. Borgarello, J. Kiwi, M. Granzlet, E. Pelizzetti, M. Visca, J. Am. Chem. Soc. 104 (1982) 1996.
[33] T. Umebayashi, T. Yamaki, H. Itoh, K. Asai, Appl. Phys. Lett. 81 (3) (2002) 454.
[34] R. Asahi, T. Morikawa, T. Oohkai, K. Aoki, Y. Taga, Science 293 (2001) 269.
[35] T. Morikawa, R. Asahi, T. Oohkai, K. Aoki, Y. Taga, Jpn J. Appl. Phys. 40 (2001) L561.
[36] A.L. Linsebgler, G. Lu, J.T. Yates, J. Chem. Rev. 95 (1995) 735.