

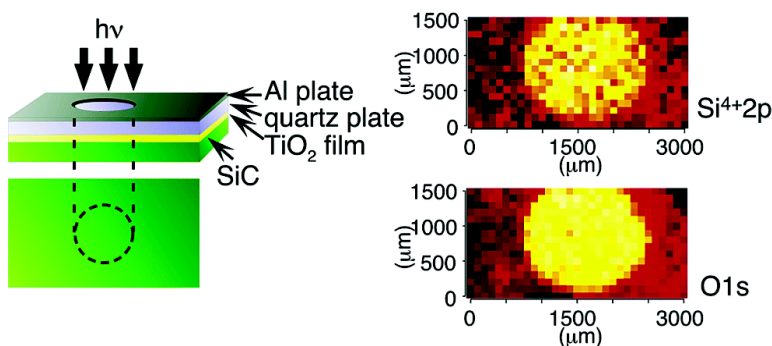
Article

Surface Treatment of Silicon Carbide Using TiO₂(IV) Photocatalyst

Yoshie Ishikawa, Yasumichi Matsumoto, Yoko Nishida, Shinichi Taniguchi, and Junji Watanabe

J. Am. Chem. Soc., **2003**, 125 (21), 6558-6562 • DOI: 10.1021/ja020359i • Publication Date (Web): 01 May 2003

Downloaded from <http://pubs.acs.org> on March 28, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 6 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

Surface Treatment of Silicon Carbide Using TiO₂(IV) Photocatalyst

Yoshie Ishikawa,[†] Yasumichi Matsumoto,^{*,†} Yoko Nishida,[†] Shinichi Taniguchi,[†] and Junji Watanabe[‡]

Contribution from the Department of Applied Chemistry, Faculty of Engineering, Kumamoto University, Kurokami 2-39-1, Kumamoto 860-8555, Japan, and Mechanical Engineering and Material Science, Faculty of Engineering, Kumamoto University, Kurokami 2-39-1, Kumamoto 860-8555, Japan

Received March 8, 2002; Revised Manuscript Received March 3, 2003

Abstract: Silicon carbide (SiC) and diamond were decomposed to CO₂(g) by the photocatalysis with TiO₂ at room temperature, although the decomposition rate of diamond was very slow. According to the XPS spectra of Si2p on the SiC surface, SiO₂ was simultaneously formed on the surface by the TiO₂ photocatalysis. The thickness of the SiO₂ formed on the SiC surface during the photocatalytic oxidation for 1 h was estimated to be about 40 Å from the depth profile of the XPS spectra using Ar etching. The SiC surface was oxidized by the TiO₂ photocatalysis even under the condition without a direct contact with the TiO₂. This indicates that the photocatalytic oxidation of the SiC occurs due to active oxygen species photogenerated on the TiO₂ surface, but not by hole produced in the valence band of the TiO₂. Moreover, a remote surface treatment system using the quartz beads coated with TiO₂ was developed for the SiC surface oxidation. Consequently, the TiO₂ photocatalysis will be very useful for the surface treatment of SiC such as photopatterning without defects and damage to the substrate because the photocatalytic reaction is carried out under mild conditions.

Introduction

Silicon carbide (SiC) and diamond are well-known as abrasive materials for grinding and polishing because of their excellent hardness. Moreover, they can also be used soon as a semiconductor material with a wide-band gap, which is very useful for some power devices.¹⁻⁷ Thus, SiC and diamond are promising materials in the precision machining and electrical industries. The surface treatment of these materials, such as chemical modification in-area and in-depth and/or nano- and micro-level etching, will be very important for developing in micro-machines and micro-devices.^{4,8-16} In general, chemical modifications such

as etching and oxide formation have been done by laser beam ablation and/or thermal oxidation at high temperature.^{1,2,12,13} On the other hand, polishing these materials has been done with some fine particles such as diamond that have excellent hardness.^{4,17,18} However, the surface treatments of SiC and diamond are very difficult under the mild conditions that are necessary for the film-type fabricated devices.^{20,21}

We now show that the surface of SiC with hard and chemically stable properties can be photocatalytically decomposed and modified using a TiO₂ photocatalyst. The SiC surface is decomposed to CO₂ and SiO₂ on its surface by the photocatalysis with TiO₂ under illumination at room temperature. This technique using the TiO₂ photocatalyst will be very useful as a nano-level surface treatment such as photopatterning under mild conditions for SiC.

TiO₂ is a famous photocatalyst that decomposes various organic compounds under illumination.²²⁻²⁹ In particular, Tat-

* yasumi@gpo.kumamoto-u.ac.jp.

[†] Department of Applied Chemistry, Faculty of Engineering, Kumamoto University.

[‡] Mechanical Engineering and Material Science, Faculty of Engineering, Kumamoto University.

- (1) Raynaud, C. J. *Non-Cryst. Solids* **2001**, *280*, 1.
- (2) Virojanadara, C.; Johansson, L. I. *Surf. Sci.* **2001**, *472*, L145.
- (3) Kosugi, R.; Ichimura, S.; Kurokawa, A.; Koike, K.; Fukuda, K.; Suzuki, S.; Okushi, H.; Yoshida, S.; Arai, K. *Appl. Surf. Sci.* **2000**, *159-160*, 550.
- (4) Zhou, L.; Audurier, V.; Pirouz, P.; Anthony, P. J. *J. Electrochem. Soc.* **1997**, *144*, L161.
- (5) Diederich, L.; Küttel, O. M.; Ruffieux, P.; Pillo, Th.; Aebi, P.; Schlapbach, L. *Surf. Sci.* **1998**, *417*, 41.
- (6) Itahashi, M.; Umehara, Y.; Koide, Y.; Murakami, M. *Diamond Relat. Mater.* **2001**, *10*, 2118.
- (7) Corrigan, T. D.; Gruen, D. M.; Krauss, A. R.; Zapol, P.; Chang, R. P. H. *Diamond Relat. Mater.* **2002**, *11*, 43.
- (8) Kiyohara, S.; Ayano, K.; Abe, T.; Mori, K. *Jpn. J. Appl. Phys.* **2000**, *39*, 4532.
- (9) Bail, E. S.; Baik, Y. J.; Jeon, D. *Diamond Relat. Mater.* **1999**, *8*, 2169.
- (10) Chen, Y. H.; Hu, C. T.; Lin, I. N. *Jpn. J. Appl. Phys.* **1997**, *36*, 6900.
- (11) Sandhu, G. S.; Chu, W. K. *Appl. Phys. Lett.* **1989**, *55*, 437.
- (12) Makhtari, A.; Raineri, V.; Via, L. F.; Franzó, G.; Frisina, F.; Calcagno, L. *Mater. Sci. Semicond. Process.* **2001**, *4*, 345.

- (13) Johnson, M. B.; Zvanut, M. E.; Richardson, O. *J. Electron. Mater.* **2000**, *29*, 368.
- (14) Strother, T.; Knickerbocker, T.; Russell, J. N. Jr.; Butler, J. E.; Smith, L. M.; Hamers, R. *J. Langmuir* **2002**, *18*, 968.
- (15) Kim, C. S.; Mowrey, R. C.; Butler, J. E.; Russell, J. N. Jr. *J. Phys. Chem. B* **1998**, *102*, 9290.
- (16) Miller, J. B.; Brown, D. W. *Langmuir* **1996**, *12*, 5809.
- (17) Grillo, S. E.; Field, J. E.; Van Bouwelen, F. M. *J. Phys. D: Appl. Phys.* **2000**, *33*, 985.
- (18) Van Bouwelen, F. M. *Phys. Stat. Sol. A* **1999**, *172*, 91.
- (19) Hirabayashi, K.; Taniguchi, Y.; Takamatsu, O.; Ikeda, T.; Ikoma, K.; Iwasaki, K. *Appl. Phys. Lett.* **1988**, *53*, 1815.
- (20) Chappel, D. C.; Smith, J. P.; Taylor, S.; Eccleston, W.; Das, M. K.; Cooper, J. A.; Melloch, M. R. *Electron. Lett.* **1997**, *33*, 97.
- (21) Kobayashi, H.; Sakurai, T.; Nishiyama, M.; Nishioka, Y. *Appl. Phys. Lett.* **2001**, *78*, 2336.

suma et al.³⁰ recently reported the photocatalytic decomposition of organic solid materials such as a polystyrene and polyethylene using a TiO₂ photocatalyst. During the photocatalytic process, the OH[•] and/or other activated oxygen species on the surface, which are produced by electrons and holes generated under illumination, act as oxidizing agents, leading to the decomposition of the organic compounds.^{29–31} These radicals also act as oxidizing agents to oxidize inorganic solid materials; solid sulfur is directly oxidized to the sulfate ion by TiO₂ photocatalysis.³² This suggests that TiO₂ may act as a photocatalyst to oxidize and decompose other inorganic solid materials consisting of carbon. In this study, a new surface treatment for SiC using a TiO₂ photocatalyst under mild conditions is demonstrated.

Experimental Section

Photocatalytic Decomposition Test of SiC and Diamond Powders by the TiO₂ Photocatalysis. SiC (Nacalai Tesque Co., Ltd., 200 μm average particle size, 0.026 m² g⁻¹ BET surface area) and diamond (Engis Co., Ltd., 0.25 μm average particle size, 20 m² g⁻¹ BET surface area) powders were used as the reactant for the photocatalytic decomposition test. TiO₂ powder (Degussa Co., Ltd., 30 nm average particle size) consisting of anatase (80%) and rutile (20%) was used as the photocatalyst in this study. The TiO₂ powder was irradiated with a 500 W Hg-lamp for 10 h before the above decomposition test so that any organic compound adsorbed on the surface of the TiO₂ powder was decomposed. The TiO₂ (1 g) and the SiC or diamond (1 g) were mixed, and then placed in a quartz vessel (1 L) filled with air. Light from the 500 W Hg-lamp was illuminated on the mixed powder. The produced CO₂ was analyzed by gas chromatography (TCD). Two types of the surface-modified diamond powder were used in this study. One had a C–O bond on the surface, which was produced by immersion in H₂SO₄–HNO₃ (9:1 v/v) solution at 80 °C for 4 h. The other had a C–H bond on the surface, which was produced by preheat-treatment in H₂ at 900 °C for 5 h. The presence of C–H or C–O bonds on the diamond surface was confirmed by FT-IR measurements.

Surface Treatment Test of SiC Substrate by the TiO₂ Photocatalysis. A 3C–SiC single crystal (111) (3 × 5 × 1 mm³) was used as the substrate to study the surface treatment using the TiO₂ photocatalysis. The SiC single crystal was etched by immersion in a HF aqueous solution to remove the surface oxide. A quartz plate coated with a transparent TiO₂ film (0.5 μm thickness), which was prepared by spin-coating at ~2000 rpm using TiO₂ sol (Nippon Soda Co., Ltd., NDC-100C, particle size of about 10 nm), was attached to the surface of the SiC single crystal, and then irradiated by the 500 W Hg-lamp, as

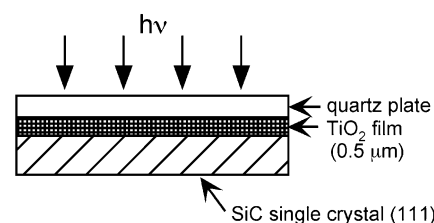


Figure 1. Model of the surface treatment system for the SiC single crystal surface.

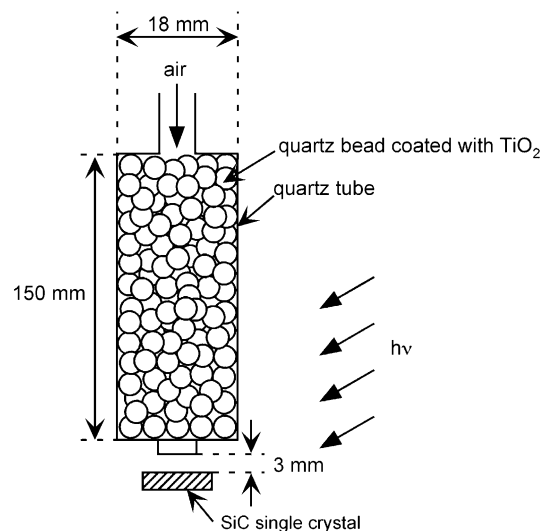


Figure 2. Model of the remote surface treatment system for the SiC single crystal surface.

shown in Figure 1. The surface of the SiC single crystal after illumination was analyzed by X-ray photoelectron spectroscopy (XPS).

A photopatterning test was carried out using the surface of the SiC single crystal. The quartz plate surface coated with the TiO₂ film was attached to the SiC single crystal. An aluminum plate with a hole (0.5 mm thickness, 1.5 mm Φ) was placed on the other side of the quartz surface during the photopatterning test (see Figure 8 (a)). The illumination was done using the 500 W Hg-lamp.

Remote Surface Treatment Test for the SiC Substrate by Flowing Air/H₂O System. A quartz tube (150 mm length, φ 18 mm) was packed with many quartz beads (φ 2 mm) coated with the TiO₂ film, and then air with various humidity was flowed into the tube at a flow rate of 1.5 L/min. The 3C–SiC single crystal was placed at the position of 3 mm apart from the outlet, as shown in Figure 2. The SiC surface as well as the tube were illuminated by the 500 W Hg-lamp for 6 h unless otherwise stated. The surface of the SiC single crystal after the test was analyzed by XPS.

Results and Discussion

Photocatalytic Decomposition of SiC and Diamond Powders by the TiO₂ Photocatalysis. Figure 3 shows the concentration of CO₂ produced in the vessel as a function of illumination time when the SiC powder was used as the reactant. CO₂ was produced in the case of the SiC/TiO₂ powder mixture, but not for the SiC powder without TiO₂ and the mixture in the dark or under illumination of light with wavelengths longer than about 440 nm, indicating that the TiO₂ photocatalytically decomposes the SiC to CO₂. The production rate of CO₂ from

- (22) Fujishima, A.; Honda, K. *Nature* **1972**, *238*, 37.
- (23) Jaeger, C. D.; Bard, A. J. *J. Phys. Chem.* **1979**, *83*, 3146.
- (24) Sato, S.; White, J. M. *Chem. Phys. Lett.* **1980**, *72*, 83.
- (25) Inoue, T.; Fujishima, A.; Konishi, S.; Honda, K. *Nature* **1979**, *277*, 637.
- (26) Wong, J. C. S.; Linsebigler, A.; Lu, G.; Fan, J.; Yates, J. T., Jr. *J. Phys. Chem.* **1995**, *99*, 335.
- (27) Goren, Z.; Willner, I.; Nelson, A. J.; Frank, A. J. *J. Phys. Chem.* **1990**, *94*, 3784.
- (28) Sopyan, I.; Watanabe, M.; Murasawa, S.; Hashimoto, K.; Fujishima, A. *J. Photochem. Photobiol. A* **1996**, *98*, 79.
- (29) Nozik, A. J.; Memming, R. *J. Phys. Chem.* **1996**, *100*, 13 061.
- (30) Tatsuma, T.; Tachibana, S.; Fujishima, A. *J. Phys. Chem. B* **2001**, *105*, 6987.
- (31) Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. F. *Chem. Rev.* **1995**, *95*, 69.
- (32) Matsumoto, Y.; Nagai, H.; Sato, E. *J. Phys. Chem.* **1982**, *86*, 4664.

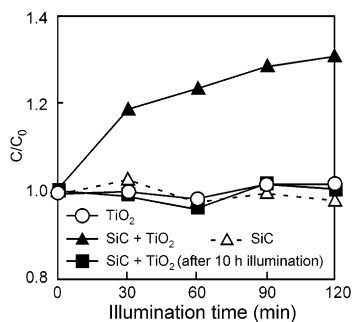


Figure 3. C (concentration)/C₀ (initial concentration, ca. 330 ppm) as a function of the illumination time for CO₂ produced in the quartz cell. SiC powder was used as the reactant.

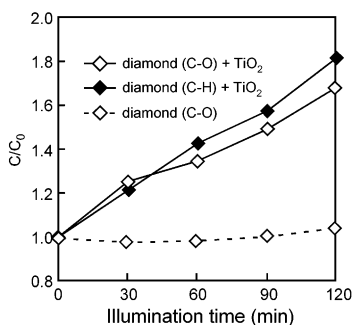


Figure 4. C (concentration)/C₀ (initial concentration, ca. 330 ppm) as a function of the illumination time for CO₂ produced in the quartz cell. Diamond powder was used as the reactant.

the SiC/TiO₂ powder mixture decreased in the cases of the illumination times longer than about 30 min, suggesting that the SiC surface was changed to SiO₂ by the photocatalytic oxidation. This was confirmed by the XPS measurement as stated in a later section. No CO₂ was produced for the mixture after a 10 h illumination, as shown in Figure 3, since the surfaces of the SiC particles were covered with the SiO₂. It was estimated that about 1.7×10^{-6} mol of CO₂ was produced in the case of the SiC/TiO₂ powder mixture illuminated for 30 min. The amount of the surface C atoms on SiC is estimated to be about 1.2×10^{-5} mol m⁻², if the decomposition surface is assumed to be the (110) plane (The cleavage plane of SiC is (110)). The total amount of the surface C atoms is calculated to about 3.2×10^{-7} mol g⁻¹ in the present test (SiC 1 g), because the SiC powder used in this study had a specific surface area of 0.026 m² g⁻¹. Consequently, it is concluded that about 530% of the surface C atoms is decomposed to CO₂ after 30 min illumination.

Figure 4 shows the concentration of CO₂ produced in the vessel as a function of illumination time when the diamond powder was used as the reactant. CO₂ was produced in the case of the diamond/TiO₂ powder mixture, but not for the diamond powder without TiO₂ and the TiO₂ powder without diamond powder even under illumination. No CO₂ was produced for the mixtures in the dark or under the illumination of light with wavelengths longer than about 440 nm. Thus, the surface of diamond was also photocatalytically oxidized to CO₂ by TiO₂ photocatalysis. The photocatalytic decomposition of diamond occurred on both the surfaces with C–H and C–O bonds, indicating that the photocatalytic decomposition of diamond does not depend on its surface composition. About 7.7×10^{-6} mol of CO₂ was produced in the case of the diamond/TiO₂ powder mixture illuminated for 2 h. The amount of the surface C atoms

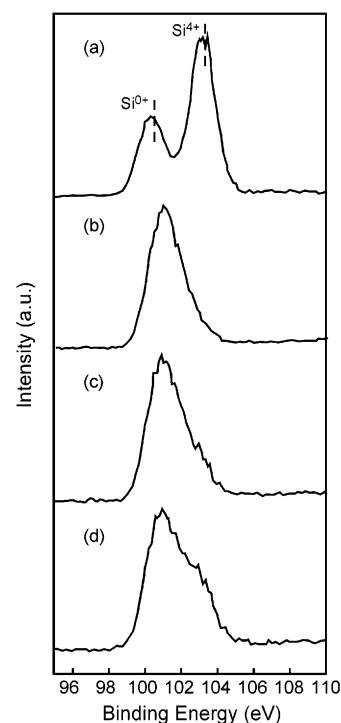


Figure 5. XPS spectra of Si2p of the SiC surface: (a) with TiO₂ under illumination; (b) with TiO₂ in the dark; (c) with TiO₂ under illumination ($\lambda > 440$ nm); and (d) without TiO₂ under illumination.

on diamond was estimated to be 3.0×10^{-5} mol m⁻², if the decomposition surface is assumed to be the (111) plane (The cleavage plane of diamond is (111)). The total amount of the surface C atoms was calculated to be about 6.0×10^{-4} mol g⁻¹, because the diamond powder used in this study (diamond 1 g) had a specific surface area of 20 m² g⁻¹. Consequently, it is concluded that only about 1% of the surface C atoms of the diamond powder is decomposed to CO₂ after 2h illumination. Both surfaces of the (100) plane of the single crystal and a CVD polycrystalline diamond (Sumitomo Electric Industries, Ltd., $5 \times 5 \times 0.5$ mm³) were scarcely etched under illumination for 200 h using the same system as Figure 1, according to atomic force microscope (AFM) observation. This is due to the slow photocatalytic decomposition rate of diamond as stated above. Probably, more intense light may be necessary for the clear photopatterning of the diamond surface.

Surface Treatment of SiC Substrate by TiO₂ Photocatalysis. Figure 5 shows the XPS spectra of Si2p of the SiC surface after various treatments for 1 h, where the surface treatment system of Figure 1 was used. Si⁴⁺ was observed at the SiC surface in contact with the TiO₂ film after illumination (a), but not for that without illumination (b). The same spectrum as for case (b) was obtained for the illumination of light with wavelengths longer than about 440 nm (c). In the case of the illumination without TiO₂ (d), a slight Si⁴⁺ was observed. This case may be due to the surface oxidation by active oxygen and/or O₃ produced by UV-irradiated air.³ For the illumination with TiO₂ (a), the atomic ratio of O/Si⁴⁺ on the surface was about 2 according to the XPS analysis, indicating that SiO₂ is formed during the photocatalytic reaction.

An aluminum metal film, whose thickness was about 15 μ m, was placed between the quartz plate coated with the TiO₂ film and the SiC substrate in order to keep a space (gap distance: 15 μ m) between the TiO₂ film and the SiC surface (noncontact),

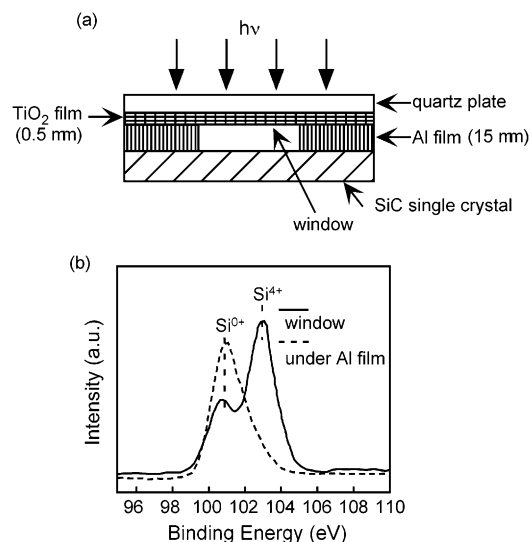
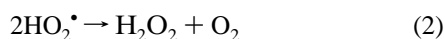


Figure 6. Model of the noncontact photocatalytic oxidation system for the SiC single-crystal surface (a) and XPS spectra of Si2p of the SiC surface treated with this system (b).

as shown in Figure 6 a. Figure 6b shows the XPS spectra of Si2p of the SiC surface after the illumination for 1 h. Si⁴⁺ was observed at the window, but not under the Al film, indicating that SiO₂ was formed on the surface of the SiC by the photocatalytic oxidation even under the condition of noncontact with the TiO₂.

Two mechanisms for the TiO₂ photocatalytic oxidation of chemical compounds have been reported. One mechanism is a direct oxidation of the reactant by photogenerated hole in the valence band. The other is the oxidation of the reactant by some active oxygen species such as OH[•], HO₂[•], O₂^{•-}, H₂O₂, and ¹O₂ produced by the reaction between H₂O and/or O₂ and the hole. In the photocatalytic oxidation of the SiC, the latter oxidation by the active oxygen species will preferentially occur, because SiO₂ was formed even under the condition of noncontact with the TiO₂ as stated above. Tatsuma et al.³⁰ reported that aromatic and aliphatic substances were oxygenated and oxidized to CO₂ by noncontact photocatalysis (gap distance: 50 μm–2.2 mm). They explain that photogenerated OH[•] and HO₂[•] on the surface of the TiO₂ will change to H₂O₂ in the first stage as follows



The generated H₂O₂ will then diffuse in the gas phase from the TiO₂ surface to the reactant surface, where the re-produced OH[•] (eq 3) under illumination oxidizes the reactant³⁰



No oxidation of SiC to SiO₂ occurred on immersion of the SiC substrate in H₂O₂ (35%) for 6 h. On the other hand, oxidation was observed after the light was illuminated on the SiC surface during the H₂O₂ immersion. Moreover, the oxidation occurred by the Fenton reaction, where the H₂O₂ solution added with FeSO₄ was used as the immersion solution to produce OH[•].³³ These results suggest that the SiC will be directly

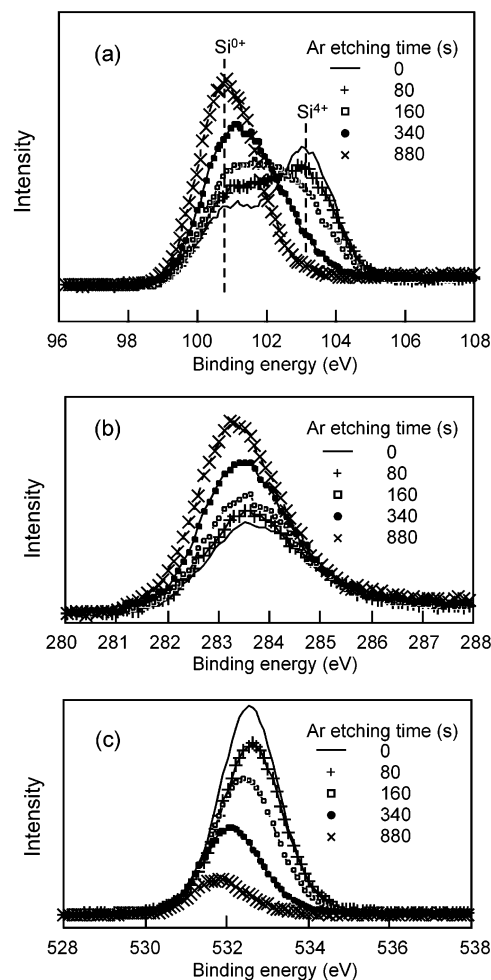


Figure 7. XPS spectra of the SiC surface after the surface treatment test under illumination for 1 h using the system shown in Figure 1: (a) Si2p, (b) C1s, and (c) O1s. The Ar etching rate is 0.5 Å/sec.

oxidized by OH[•] as denoted by eq 4. This is indirectly confirmed by a remote surface treatment test as stated in the later section

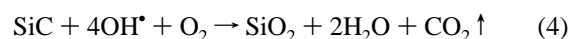


Figure 7 shows the depth profiles of the XPS spectra of Si2p (a), C1s (b), and O1s (c) of the SiC surface after illumination for 1 h, where the same system as in Figure 1 was used. By increasing the Ar etching time, the peak intensities of the Si⁴⁺-2p (shown in a) and O1s (shown in c) decreased, whereas those of the Si³⁺-2p (shown in a) and C1s (shown in b) increased. It was estimated from the Si⁴⁺-2p depth profile that the thickness of the formed SiO₂ film is about 40 Å because the etching rate was about 0.5 Å/sec. This thickness is roughly consistent with that calculated from the CO₂ production result.

Figure 8a shows the system for the photopatterning test of the SiC. Figure 8b and c respectively show the mapping of the Si⁴⁺-2p and O1s spectra on the SiC surface after the illumination. From a comparison between the system (a) and the mapping (b) and (c), it is concluded that the photopatterning of the SiO₂ formation on the SiC surface is easily accomplished by the TiO₂ photocatalysis.

Remote Surface Treatment for the SiC Substrate by Flowing Air/H₂O System. Figure 9 shows the XPS spectra of Si2p of the SiC surface treated by the remote surface treatment

(33) Fujihara, M.; Satoh, Y.; Osa, T. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 666.

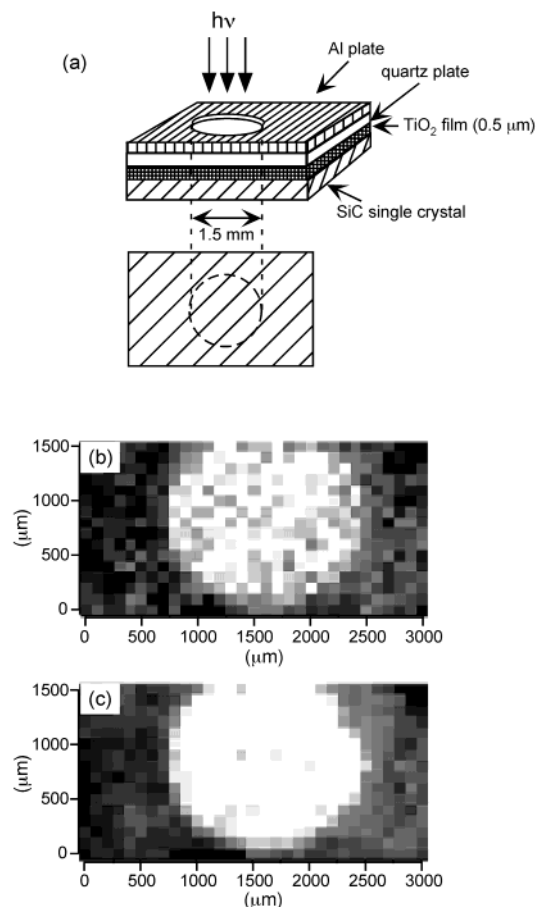


Figure 8. Model of the photopatterning test for the SiC single crystal surface (a) and peak intensity mapping of Si⁴⁺2p (b) and O1s (c) spectra of the SiC surface after the test.

system (shown in Figure 2). Si⁴⁺ was observed on the SiC surface only in the cases of air with H₂O under illumination (a)–(c). The degree of oxidation increased with an increase in RH. No peak of Si⁴⁺2p was observed in the dark treatment, the quartz beads without TiO₂ under illumination, and pure N₂ with H₂O under illumination of the quartz beads coated with TiO₂ (d). These results indicate that some active oxygen species photogenerated on the TiO₂ surface flow to the outlet of the tube and then oxidize the SiC surface and that the most of the active oxygen species will be OH[•] and/or HO₂[•] produced from H₂O for the SiC oxidation. In this case, O₂ will act to capture a produced electron or as an oxidant for oxidation of the SiC as denoted in eq 4.

In this remote system, OH[•] and/HO₂[•] photogenerated at the TiO₂ surface will not diffuse to the SiC surface, because these radicals have a short lifetime. Probably, H₂O₂ diffusion and a radical re-production mechanism will be important as stated already, since the degree of oxidation of the SiC surface is largely decreased by the suppression of light illumination on the SiC surface in the present remote system (where the quartz beads coated with TiO₂ were illuminated). Consequently, the

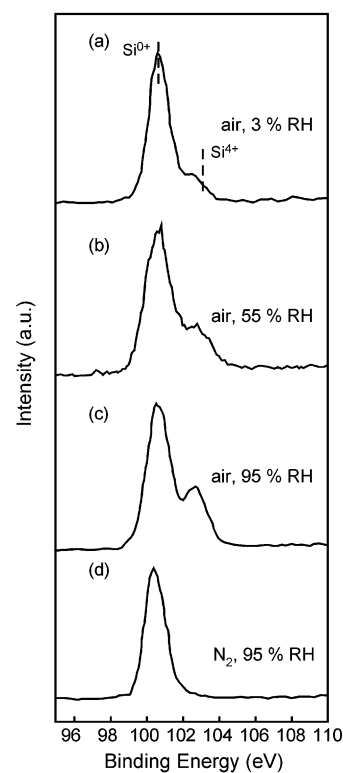


Figure 9. XPS spectra of Si2p of the SiC surface after the surface treatment under illumination by the remote system (Figure 2) using various gases: (a) air with 3% RH; (b) air with 55% RH; (c) air with 95% RH; (d) N₂ with 95% RH.

remote surface treatment system is that for the radical photogeneration using the TiO₂ photocatalysis. This system will be practically useful for the portable and moving surface treatments of the SiC and other materials under mild conditions, because the reactant surface and the TiO₂ photocatalyst are separated in position.

In conclusion, CO₂ was produced by TiO₂ photocatalytic decomposition of the SiC and diamond surfaces at room temperature. The TiO₂ photocatalysis brought about SiO₂ formation on the SiC surface, and therefore, the surface photopatterning. Thus, the TiO₂ photocatalysis will be useful for the surface treatment of the SiC surface without defects and subsurface damage, because the reaction is carried out under mild conditions. A remote surface treatment system using the tube filled with the quartz beads coated with TiO₂ was also developed. This system confirmed that the OH[•] significantly act as the oxidizing agent for the photocatalytic oxidation of the SiC surface. Moreover, this system will be practically useful for the surface treatment separating the reactant surface and the TiO₂ photocatalyst.

Acknowledgment. The present work was supported by the Research Fellowships of the Japan Society for the Promotion of Science.

JA020359I