Chemical State Modification of 4H-SiC by Ultraviolet-Ray Aided Machining*

Masaru Takizawa,[†] Akihiro Hata, and Kei Mitsuhashi*Department of Physical Sciences, Faculty of Science and Engineering, Ritsumeikan University,
Noji-higashi 1-1-1, Kusatsu, Shiga 525-8577, Japan*

Takeshi Tanaka

*Research Organization of Science and Technology, Ritsumeikan University,
Noji-higashi 1-1-1, Kusatsu, Shiga 525-8577, Japan*

(Received 12 January 2018; Accepted 11 May 2018; Published 16 June 2018)

An ultraviolet-ray aided machining (U-RAM), which attempts to add a chemical reaction through ultraviolet-ray irradiation to a mechanical polishing, is a promising procedure to obtain a flat surface of SiC in a short time. In order to investigate how chemical states change in the U-RAM process, we have performed X-ray absorption fine structure measurements. As a result, it was found that a mixed compound other than SiO₂ was produced on the SiC surface by the U-RAM. We think that polishing efficiency of U-RAM is better than ordinary mechanical polishing because of generating the mixed compound of Si-C-O. [DOI: 10.1380/ejssnt.2018.283]

Keywords: X-ray absorption spectroscopy; Surface chemical reaction; Silicon carbide

I. INTRODUCTION

A SiC has attracted much attention as a substrate for electronic devices. In order to efficiently obtain a flat surface of SiC, many polishing procedures have been performed [1, 2]. Among them, an ultraviolet-ray aided machining (U-RAM) [3] is a promising procedure to obtain a flat surface of SiC in a short time, where an irradiated photocatalyst and fluorescent substance would provide an electron and a hole to act as oxidation/reduction reactions to the surface and a photocatalyst would also scratch the surface mechanically with abrasive grit. Previous work on the U-RAM of Al has revealed the oxidation of the Al surface [4]. Although applying the U-RAM to 4H-SiC improves a polishing rate [5], it is not clear how the surface of SiC is oxidized. In order to study the chemical state modification, we have performed X-ray absorption fine structure (XAFS) measurements of SiC during each U-RAM procedure.

II. EXPERIMENTAL

We prepared a 4H-SiC with a flat surface (commercial SiC), whose Si-plane is finished with $R_a < 0.5$ nm using chemical mechanical polishing, and then sandblasted commercial SiC to obtain a SiC with a rough surface (sandblast SiC). An U-RAM of this sandblast SiC was performed using a TiO₂ particle (~ 7 nm) as a photocatalyst and a Cathilon dye as a fluorescent substance under the irradiation of UV lamp ($\lambda = 253.7$ nm) with diamond grit (0–2 μ m), referred as U-RAM SiC. Furthermore, we continued two kinds of U-RAM procedures by exchanging grits; one with CeO₂ grit (U-RAM SiC further polished with CeO₂), the other with smaller-size diamond grit (5 nm) [U-RAM SiC further polished with Dia

(5 nm)]. In order to see an effect of the slurry and the UV irradiation, we only immersed sandblast SiC and commercial SiC in the TiO₂ and the Cathilon dye (immersed sandblast SiC, immersed SiC) under UV irradiation (immersed sandblast SiC + UV, immersed SiC + UV). As a reference, SiO₂/Si sample was also prepared.

XAFS measurements were performed at the BL-8 of SR Center at Ritsumeikan University, equipped with a grazing incidence monochromator with a varied-line-spacing plane grating. In order to obtain the depth-resolved information, XAFS spectra of the samples were simultaneously collected by total electron yield (TEY) and total fluorescence yield (TFY) through a sample drain current and a micro-channel plate detector with retarding grids, respectively. TEY spectra have the information near the surface (1–5 nm), while TFY spectra have the information mainly inside the bulk (more than 10 nm). The retarding voltage was set to –150 V for Si L-edge. In addition, set-

FIG. 1. Si L-edge TEY XAFS spectra of 4H-SiC during each U-RAM procedure. A reference SiO₂/Si XAFS spectrum is also shown.

* This paper was presented at the 11th International Symposium on Atomic Level Characterizations for New Materials and Devices '17, Aqua Kauai Beach Resort, Kauai, Hawaii, USA, December 3-8, 2017.

[†] Corresponding author: m-tkzw@fc.ritsumei.ac.jp

FIG. 2. Si L-edge TFY XAFS spectra of 4H-SiC during each U-RAM procedure.

ting the retarding voltage to -50 V enabled us to obtain more surface-sensitive (less than 1 nm) XAFS spectra by partial electron yield (PEY). The measurements were performed at room temperature under ultrahigh vacuum of $\sim 1 \times 10^{-7}$ Pa. The incident angle of SR with respect to the surface normal was set to 0° .

III. RESULTS AND DISCUSSION

Figure 1 shows the Si L-edge TEY spectra of commercial SiC, U-RAM SiC, sandblast SiC, and SiO_2/Si . For commercial SiC, the onset appears around 101.8 eV, which is a characteristic feature of 4H-SiC [6–8]. The TEY spectrum of U-RAM SiC is different from that of commercial SiC. A prominent feature appears around ~ 106 eV with a small shoulder structure starting at ~ 101 eV, as indicated in Fig. 1. This shoulder structure can be assigned to a component of SiC since the absorption onset nearly coincides with that of 4H-SiC. For sandblast SiC, the onset also appears around 101 eV and a prominent feature appears around 108 eV. As seen in the spectrum of SiO_2/Si , both the structures around 106 eV and 108 eV come from SiO_2 and the structure around 101 eV comes from Si [9]. From these results, the surface of sandblast SiC is mainly covered with SiO_2 due to the high energy collisions, and on the surface of U-RAM SiC exists not SiO_2 but other compounds besides SiC.

Figure 2 shows the Si L-edge TFY spectra of commercial SiC, U-RAM SiC, and sandblast SiC. The TFY spectra of U-RAM SiC is similar to that of commercial SiC, indicating that the chemical state of U-RAM SiC in the bulk is SiC. For sandblast SiC, two prominent features appear. One starting at ~ 101 eV, as indicated in Fig. 2, can be assigned to a component of SiC since the absorption onset nearly coincides with that of 4H-SiC. The other around ~ 108 eV can be assigned to a component of SiO_2 . Thus the chemical state of sandblast SiC in the bulk is SiC, though the structures of SiO_2 (around 106 eV and 108 eV) still appears maybe due to the rough surface.

Since other compounds were found on the surface of U-

FIG. 3. Si L-edge TEY XAFS spectra of 4H-SiC for other U-RAM procedures.

FIG. 4. Si L-edge TEY XAFS spectra of sandblast SiC with the immersion and UV irradiation.

RAM SiC, we further polished U-RAM SiC by exchanging grits. Figure 3 shows the Si L-edge TEY spectra of commercial SiC, U-RAM SiC further polished with Dia (5 nm), U-RAM SiC further polished with CeO_2 , and U-RAM SiC. The TEY spectra of U-RAM SiC further polished with Dia (5 nm) and U-RAM SiC further polished with CeO_2 is similar to that of commercial SiC. The surfaces are confirmed to be 4H-SiC free from the newly formed compound. Because SiC is harder than CeO_2 , CeO_2 grit could polish not SiC but the newly formed compound, suggested to be a brittle compound compared to SiC.

Figure 4 shows Si L-edge TEY spectra of sandblast SiC, immersed sandblast SiC, and immersed sandblast SiC + UV. For the TEY spectra of immersed sandblast SiC and immersed sandblast SiC + UV, the structure around 103–106 eV increases. Since the absorption energy nearly coincides with that of the prominent feature observed in the TEY spectrum of U-RAM SiC (Figs. 1 and 3), the same compound may be formed on the surface of sandblast SiC after the immersion and/or UV irradiation.

FIG. 5. Si L-edge PEY XAFS spectra of commercial SiC with the immersion and UV irradiation.

Figure 5 shows Si L-edge PEY spectra of commercial SiC, immersed commercial SiC, and immersed commer-

cial SiC + UV. The spectra hardly change. This suggests that only rough SiC surfaces are affected by the immersion and/or UV irradiation. Then, further polishing with CeO₂ or smaller-size diamond grits does not produce the newly formed compound because of the flat surface.

Next, we consider the newly formed compound, which appears around ~ 106 eV in the TEY spectrum of U-RAM SiC (Figs. 1 and 3). We think that the compound is a mixture of Si, C, and O. Because, it is thought that oxidation occurs on the surface of SiC, and from the previous research [10] it is confirmed that mixed compounds of Si, C, and O are produced by a thermal treatment. Although the newly formed compound is not clear at present, we think that polishing efficiency of U-RAM is better than ordinary mechanical polishing because of produced mixed compounds of Si, C, and O on the surface.

IV. CONCLUSION

We have analyzed chemical state of 4H-SiC samples by XAFS. Not SiO₂ but mixed compounds exist after U-RAM. We think that polishing efficiency of U-RAM is better than ordinary mechanical polishing because of generating the mixed compound of Si-C-O.

-
- [1] H. S. Lee, D. I. Kim, J. H. An, H. J. Lee, K. H. Kim, and H. Jeong, *CIRP Annals* **59**, 333 (2010).
 - [2] T. Akai, K. Imamura, and H. Kobayashi, *ECS J. Solid State Sci. Technol.* **6**, 265 (2017).
 - [3] T. Tanaka, *J. Jpn. Soc. Abrasive Technol.* **59**, 402 (2015) (in Japanese).
 - [4] T. Tanaka, *MEMOIRS OF THE SR CENTER RIT-SUMEIKAN UNIVERSITY* No. 17, 95 (2015).
 - [5] T. Tanaka, M. Takizawa, and A. Hata, *Int. J. Automation Technol.* **12**, 160 (2018).
 - [6] M. Tallarida, D. Schmeisser, F. Zheng, and F. J. Himpsel, *Surf. Sci.* **600**, 3879 (2006).
 - [7] G. Monaco, M. Suman, D. Garoli, M. G. Pelizzo, and P. Nicolosi, *J. Electron Spectrosc. Relat. Phenom.* **184**, 240 (2011).
 - [8] Y. F. Hu, H. Piao, J. Fronheiser, and K. Matocha, *J. Electron Spectrosc. Relat. Phenom.* **184**, 245 (2011).
 - [9] M. Kasrai, W. N. Lennard, R. W. Brunner, G. M. Bancroft, J. A. Bardwell, and K. H. Tan, *Appl. Surf. Sci.* **99**, 303 (1996).
 - [10] B. Hornetz, H.-J. Michel, and J. Halbritter *J. Mater. Res.* **9**, 3088 (1994).