| | |
|---|---|
| Title | Surface morphology changes of silicon carbide by helium plasma irradiation |
| Author(s) | Yamashita, N.; Omori, K.; Kimura, Y.; Hinoki, T.; Ibano, K.; Lee, H.T.; Ueda, Y. |
| Citation | Nuclear Materials and Energy (2018), 16: 145-148 |
| Issue Date | 2018-08 |
| URL | http://hdl.handle.net/2433/233087 |
| Right | © 2018 Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/BY-NC-ND/4.0/). |
| Type | Journal Article |
| Textversion | publisher |

Nuclear Materials and Energy 16 (2018) 145–148

Contents lists available at ScienceDirect

Nuclear Materials and Energy

journal homepage: www.elsevier.com/locate/nme

# Surface morphology changes of silicon carbide by helium plasma irradiation

N. Yamashita[a,*], K. Omori[a], Y. Kimura[a], T. Hinoki[b], K. Ibano[a], H.T. Lee[a], Y. Ueda[a]

[a] Osaka University Graduate School of Engineering, Japan
[b] Institute of Advanced Energy, Kyoto University, Japan

ARTICLE INFO

*Keywords:*
Helium induced nanostructure
Morphology change
Silicon carbide

ABSTRACT

Silicon carbide (SiC) and its composites are candidate materials for the blanket components and for the first wall in a fusion reactor. If the SiC is used without any armor materials for the first wall, it is exposed by helium (He) plasma as well as hydrogen plasma. Characteristic surface morphology changes are reported for various materials by He plasma exposure. Thus, we exposed SiC specimens to He or simultaneous deuterium (D) and He (D + He) plasma by various conditions and then observed surface morphology changes by SEM. As a result, needle-like structures and whiskers-like structures at the tip were formed in He plasma and D + He irradiation, while only needle-like structures were formed in D plasma. Therefore, it indicated that the effects of He were attributed to form whiskers-like structures. Although the structures are different among He plasma, simultaneous D + He plasma and D plasma irradiations, sputtering is considered to be a dominant process for the formation of the structure formation. However, the effects of He atoms in the structure could also be attributed to form whiskers-like structures.

## 1. Introduction

Silicon carbide(SiC) has been proposed for the candidates as structural materials in a fusion reactor because of high strength at high temperature and low induced activity [1, 2]. When SiC is used without any armor materials for the first wall, SiC is directly exposed by hydrogen isotopes and helium (He). Several metals (tungsten, palladium, titanium and etc [3-6]) are known to form surface nanostructures of a shape of hole or fiber by helium plasma irradiation. It is known that the shape and dimension of helium induced nanostructure are dependent on fluence and surface temperature [7,8]. Besides metals, silicon surfaces irradiated by helium plasma became needle-rod-like structure [9]. However, morphology changes of SiC by helium plasma irradiation is barely reported [10].

To evaluate surface morphology changes, SiC specimens were exposed to He, deuterium (D), and mixed (He + D) plasmas. In He plasma irradiation, we investigated dependence on He fluence and specimen surface temperature. Formations of nano-scale structures were observed after the irradiations by a field emission scanning electron microscopy (FE-SEM). Classification of these structures are discussed in the beginning of Section 3. Then, dependence of nanostructure size on the total irradiation fluence (Section 3.2) and on the specimen temperature during irradiation (Section 3.3) are discussed for the He irradiation. Comparison among He, D + He and D irradiation is also discussed in Section 3.3.

## 2. Experiments

SiC specimens were fabricated by a private company using Chemical Vapor Deposition. Very high purity $\beta$-SiC was obtained which impurity content is ~100 ppb in total. As received SiC specimens were irradiated by electron cyclotron resonance (ECR) plasmas over the temperature of 593–843 K which was measured by a thermocouple touching to the back surface of the specimen. The ECR plasma exposure was performed using a linear plasma device, named LaPlex, at Osaka University, Suita. Sample temperature was controlled by a rate of coolant flow (water or air) in the sample holder which removes heat load from the plasma. In the beginning of the plasma irradiation, specimen temperatures gradually increased to the desired values. Typically, 20–30 K temperature overshooting for 3–5 min was observed, then stable temperature at the desired value was obtained. Once a steady-state condition was achieved, temperature fluctuations were within 5 K. The temperature range is consistent with the anticipated operating temperatures of the blanket plasma facing surface. Base pressure of the ECR device was $\sim 10^{-7}$ Torr with the gas filling pressure of $5 \times 10^{-2}$ Torr (He), $2.7 \times 10^{-2}$ Torr (D), and mixture of $0.3 \times 10^{-2}$ Torr (He) and $3.0 \times 10^{-2}$ Torr (D) for plasma operations. The irradiation flux and the irradiation fluence were $1.5 \times 10^{21}$ He/m$^2$s$^1$ and (1–10) $\times 10^{25}$ He/m$^2$, respectively. The incident ion energy was controlled by sample biasing and kept at 80 eV. Surface morphology changes were observed by FE-SEM (Zeiss, ULTRA55) at Kyoto University, Uji. Si/C ratio of

* Corresponding author.
*E-mail address:* yamashita-n@st.eie.eng.osaka-u.ac.jp (N. Yamashita).

https://doi.org/10.1016/j.nme.2018.06.013
Received 16 December 2017; Received in revised form 11 June 2018; Accepted 17 June 2018

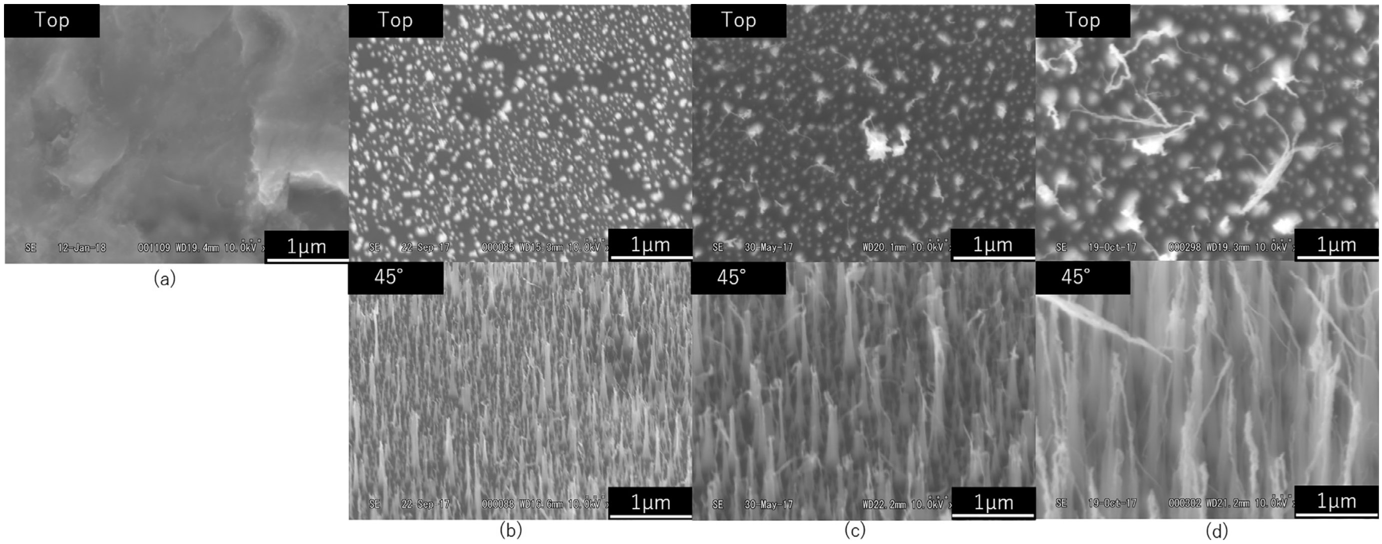


**Fig. 1.** FE-SEM micrograph of SiC surface before (a) and after irradiation by helium plasma (b) $1 \times 10^{25}$ He/m$^2$ (c) $3 \times 10^{25}$ He/m$^2$ (d) $1 \times 10^{26}$ He/m$^2$ at 783 K.

irradiated surface was analyzed by energy dispersive X-ray analysis (EDX).

## 3. Result and discussion

Fig. 1 shows FE-SEM images of SiC surface before and after He plasma irradiation. Formation of nanoscale structure was observed. The structure can be classified into two components; a needle-like structure and a whisker-like structure. Needle-like structure is a thick and straight structure grown from the base surface. In contrast, whisker-like structure is a thin and bent structure grown from tip of a needle-like structure. We studied fluence dependence and temperature dependence of the formation of these structures which are important for formation of He induced nanostructure on metals. In addition, surface morphology changes by simultaneous D + He irradiation and D irradiation were also performed to clarify He effects on the structure.

### *3.1. Size dependence of SiC nanoscale structure on the irradiation fluence*

Fig. 1 shows FE-SEM images of SiC surface before (a) and after the He irradiation fluence of (b) $1 \times 10^{25}$ He/m$^2$ (c) $3 \times 10^{25}$ He/m$^2$ (d) $1 \times 10^{26}$ He/m$^2$. Specimen temperature was kept at 783 K for all specimens. It is seen that, as fluence increased, the heights of these structures become larger. It is also seen that the erosion amounts by the irradiation, measured by mass loss, also become larger. Thus, we compared the heights of nanostructure with erosion thickness (see Fig. 2). It is found that the thicknesses of eroded layers are larger than the heights of needle-like structures. This comparison indicates that the needle-like structures are caused by an etching process of the plasma exposure. Unlike the fuzz structures, the nanoscale structures on SiC surface did not grow over the original surface. The exact formation mechanism is unclear, but both sputtering and re-deposition processes should have influences on the formation of the needle-like structures. Influences of surface migration and impurities from the sample holders also need to be considered.

### *3.2. Size dependence of SiC nanoscale structure on the specimen temperature during irradiation*

Fig. 3 shows FE-SEM images of the sample surface after irradiation at (a)593 K (b)783 K (c)843 K. Total fluence was kept at $3 \times 10^{25}$ He/m$^2$.

Both needle-like structures and whiskers-like structures at the tip were observed for the entire tested temperature range (593–843 K). As the temperature rises, whiskers-like structures became more apparent and thicker, while needle-like structures showed similar in size as summarized in Fig. 4. Hence, formation of nanoscale structures on SiC is weakly influenced by temperature, which is different from the cases for refractory metals (e.g. tungsten). The formation of He induced fuzz structures on tungsten [3] is strongly influenced by the specimen temperature during irradiation. It is known that sputtering cones, observed not only by He irradiation but by other ion species, can be formed in a wide temperature range. Thus, the formation of needle-like structures could be simply dominated by sputtering, while formation of whisker-like structures was temperature-controlled processes to some extent.

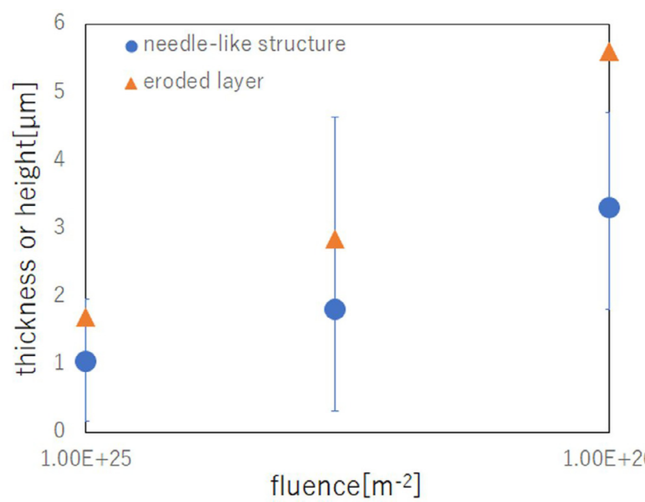


**Fig. 2.** The relationship by fluence dependence between thickness of eroded layer calculated from mass loss and heights of needle-like structure.

### *3.3. SiC nanoscale structure formation by simultaneous D + He plasma irradiation or D plasma irradiation*

Fig. 5 shows FE-SEM images of surface morphology after the simultaneous D + He (10%) plasma irradiation. Here, 10% of He content is based on the neutral gas pressure. The irradiation was performed with the specimen temperature of 743 K, incident energy of 80 eV and total fluence of $2 \times 10^{25}$ D + He/m$^2$.

The needle-like structures were observed mainly in the D + He

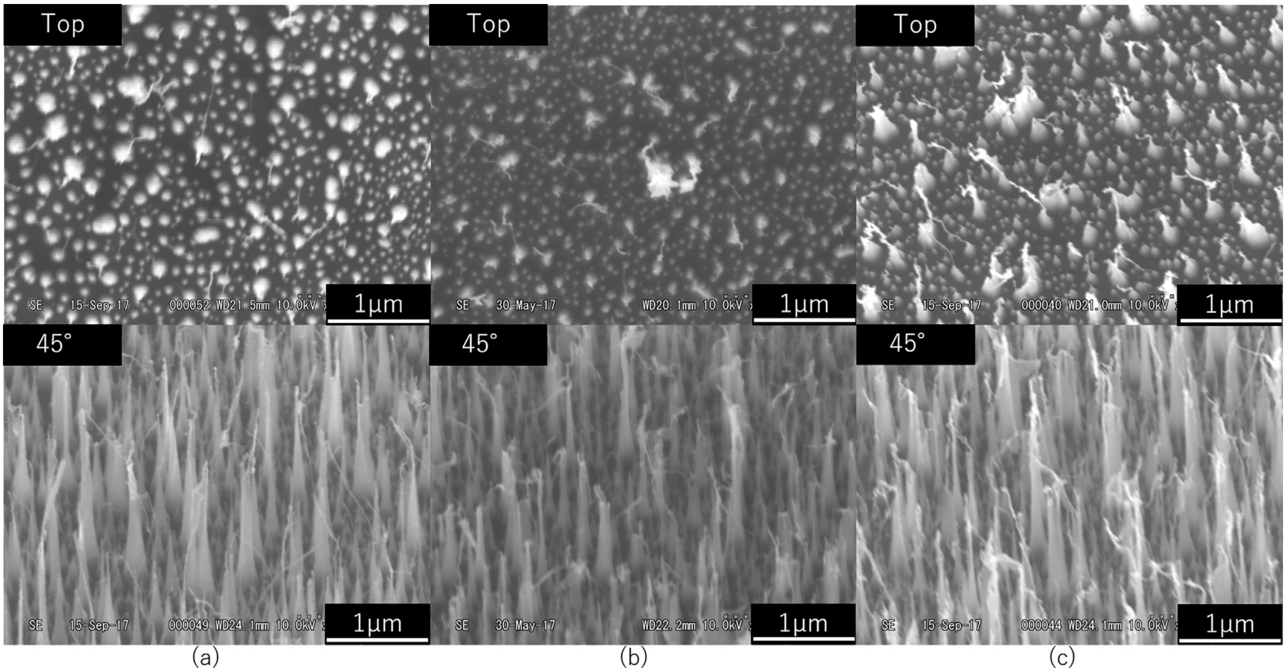


**Fig. 3.** FE-SEM micrograph of SiC surface irradiated by helium plasma (a) 593 K (b) 783 K (c) 843 K at 3 × $10^{25}$ He/$m^2$.

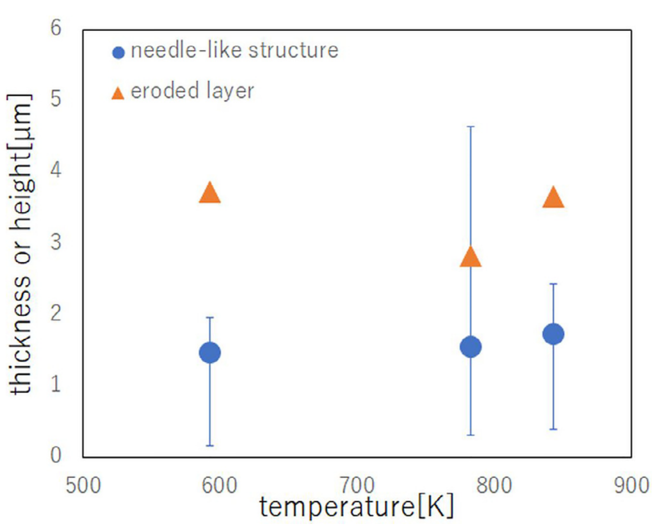


**Fig. 4.** The relationship by temperature dependence between thickness of eroded layer calculated from mass loss and heights of needle-like structure.

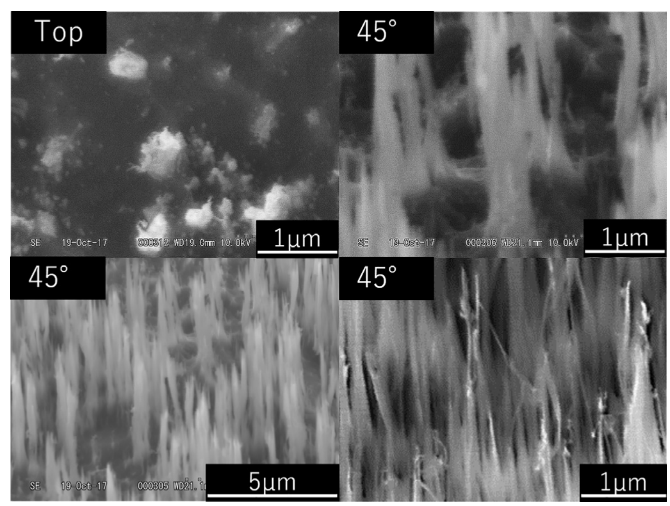


**Fig. 5.** FE-SEM micrograph of SiC surface irradiated by simultaneous deuterium and helium(10%) plasma irradiation. The specimen temperature was at 743 K and the fluence was 2 × $10^{25}$ D + He/$m^2$.

(10%) irradiation. Although the fraction of He in the irradiation is ~10%, whiskers-like structures were partially observed The fraction of whiskers-like structure is smaller than that of He irradiation for the similar plasma conditions. Thickness of eroded layer for D + He(10%) irradiation is ~3.5 µm which is more than that for the He plasma irradiation. Heights of needle-like structure are larger (~5 µm) than the thickness of eroded layer, which is different from the case for pure He irradiation. It is considered that chemical sputtering of SiC by D enhances total sputtering amount and the sputtering cone becomes higher due to redeposition of sputtered particles in case of the D + He(10%) irradiation.

Fig. 6 shows FE-SEM images of surface morphology after D irradiation. The irradiation was made with the specimen temperature of 703 K and 723 K, incident energy of 80 eV and total fluence of 2 × $10^{25}$ D/$m^2$. Only needle-like structures were observed for the pure D irradiation and the density of needle-like structures was decreased for irradiation at the lower temperature. These structures are rectilinear, and no bending nor fiber-like shapes are found. Thicker needle structures were observed which were similar to the nano-rods observed in the He irradiated Au surface as shown in [11]. The formation mechanisms of these structures are also not very certain, but sputtering erosion (physical and chemical) could play an important role. Thickness of eroded layer is ~4.0 µm which is thicker than those of He and D + He(10%) plasma irradiation cases, indicating physical sputtering by He prevails chemical sputtering by D. The whiskers-like structures were formed only when SiC was irradiated after He plasma and D + He plasma. Erosion products by chemical sputtering (D irradiation) of SiC are mainly gaseous molecules such as $CH_4$ and $SiH_4$, which are hardly deposited on the surface of nano-rods. On the other hand, erosion products by physical sputtering (He) are C or Si (mainly atoms), which are deposited on the nano-rods, which could produce whiskers-like structure. In addition, it is speculated that the effects of He were attributed to form whiskers-like structures. It is considered that whiskers-like structures were formed due to He bubbles penetrated in needle-like

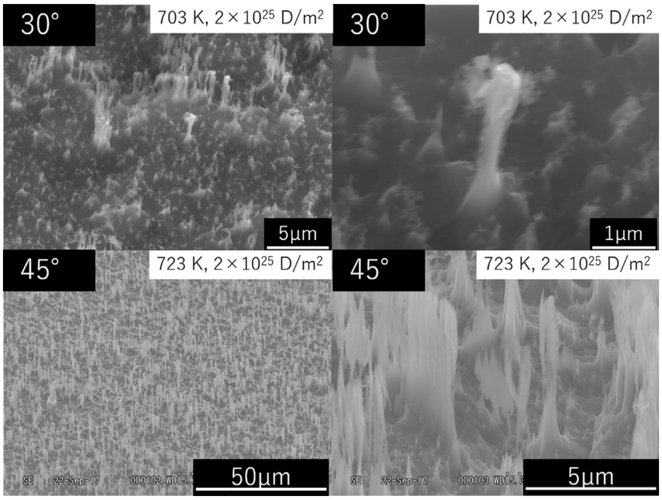


**Fig. 6.** FE-SEM micrograph of SiC surface irradiated by deuterium plasma. The specimen temperature was at 703 K and 723 K and the fluence was $2 \times 10^{25}$ D/m$^2$.

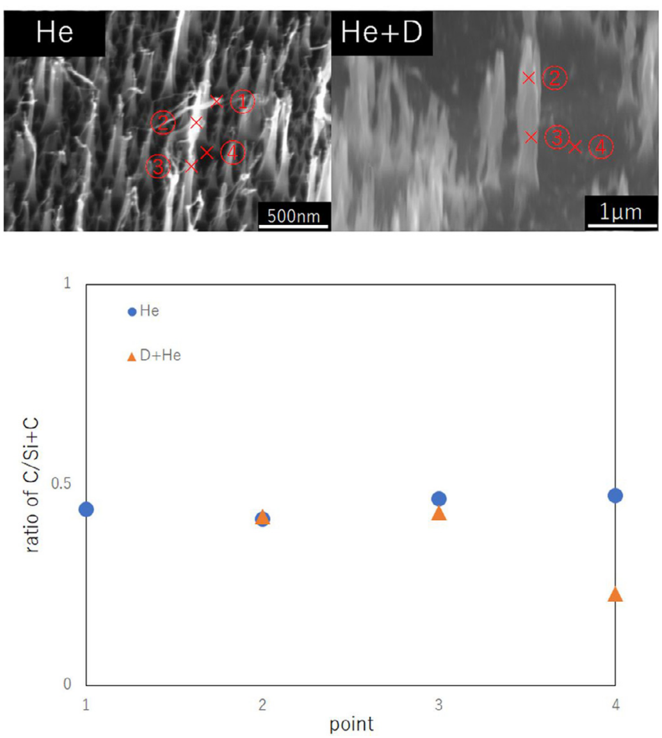


**Fig. 7.** The ratio of C/(Si + C) after (Left) helium plasma irradiation or (Right) simultaneous deuterium and helium plasma irradiation were analyzed by spot measurements of the EDX on several spots. 1: whisker-like structure 2: upper part of needle-like structure 3: lower part of needle-like structure 4: flat surface.

structures. Direct observation of He bubbles in the structure using a transmission electron microscope (TEM) will be very beneficial to support this argument. This is the first report to show the He induced unique structure, which is not simply caused by sputtering. More studies would be necessary for the formation mechanisms of the whisker-like structure on SiC by He irradiation (Fig. 7).

The atomic ratios of C/(Si + C) on the surface after he He plasma irradiation and simultaneous D + He(10%) plasma irradiation were analyzed by spot measurements with EDX. Observed spots are indicated in SEM images. Four spots are examined. Position 1–4 correspond whisker-like structure on the top of needle-like structure, upper part of needle-like structure, lower part of needle-like structure, and flat surface, respectively. Clear difference are not seen between observation points for the case of the He plasma irradiation. Apparent change is seen such that the atomic ratios of C/(Si + C) was decreased about twenty percent for the flat surface of SiC after the D + He(10%) irradiation. Chemical sputtering could be attributable to this carbon loss at this location. For the needle-like and the whiskers-like structures, a similar elemental composition with the bulk SiC is observed in both He and D + He(10%) irradiations. Although the bulk SiC beneath these structures may affect these observations, this observation also indicates that the formation of these nanoscale structures are mainly originated by sputtering. Because, if these structures are formed via atomic diffusion in bulk or surface, the composition should be influenced by the difference of diffusion coefficients between Si and C atoms.

## 4. Summary

Surface morphology changes of SiC after He, D + He or D plasma irradiation has been investigated. In case of He plasma irradiation, needle-like structures and whiskers-like structures at the tip were observed by various conditions. It is considered that sputtering process mainly dominate the formation of the needle-like structure. Both the needle-like and whiskers-like structures were also observed in D + He (10%) plasma irradiation. However, the fraction of whiskers-like structure is smaller than that of He irradiation for the similar plasma conditions. In the D plasma irradiation, needle-like structures were only observed. The ratios of C/(Si + C) on the surface after He plasma irradiation and simultaneous D + He(10%) plasma irradiation were analyzed by EDX. This observation indicates that the formation of these nanostructures are mainly determined by sputtering (physics and chemical). However, the whiskers-like structures were formed only when SiC was irradiated after He plasma and D + He(10%) plasma. Therefore, the effects of He atoms in the structure could also be attributed to form whiskers-like structures.

## Acknowledgment

This work is partly supported by the “ZE Reserch Program, IAE ZE29B-01”.

## Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.nme.2018.06.013.

## References

[1] P. Colombo, B. Riccardi, A. Donato, G. Scarinci, J. Nucl. Mater. 278 (2000) 127–135.
[2] Y. Katoh, et al., J. Nucl. Mater. 367-370 (2007) 659–671.
[3] S. Kajita, W. Sakaguchi, N. Ohno, N. Yoshida, T. Saeki, Nucl. Fusion 49 (2009) 095005–095006.
[4] P. Fiflis, M.P. Chiristnson, N. Connolly, D.N. Ruzic, Nanomater 5 (4) (2015) 2007–2018.
[5] S. Takamura, Plasma Fusion Res. 9 (2014) 140531.
[6] S. Kajita, T. Saeki, Y. Hirahata, N. Ohno, Japanese J. Appl. Phys. 50 (2011) 01AH02.
[7] T.J. Petty, et al., Nucl. Fusion 55 (2015) 09303311pp.
[8] K.D. Hammond, Mater. Res. Express 4 (2017) 104022.
[9] S. Takamura, et al., Japanese J. Appl. Phys 55 (2016) 120301.
[10] A. Hasegawa, B.M. Oliver, S. Nogami, K. Abe, R.H. Jones, J. Nucl. Mater 283-287 (2000) 811–815.
[11] Y. Ueda, et al., J. Nucl. Mater. (2018), http://dx.doi.org/10.1016/j.jnucmat.2018.04.024.