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Morphology Changes of Metal Surfaces Irradiated by He Plasma and Effect of Nitrogen Injection
ヘリウムプラズマ照射による金属の微細化と窒素導入による表面改質効果

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Surface morphology change occurs on various metals by irradiating He plasma. The morphology change leads to changes of physical parameters such as high surface area and optical absorptance. The He plasma irradiated metals can be used for catalytic materials. In this study, we investigated the surface modification of tantalum by the exposure to He plasma. Furthermore, we investigated effects of N injection to metals under irradiate He-N_2 mixing plasma using the linear plasma simulator NAGDIS-II.

1. Introduction

Photocatalysis is paid attention as one of the methods that can utilize solar energy effectively. Until today, photocatalysis was studied actively. TiO_2 has been mainly used until now, and catalytic reactions have been identified mainly with UV light. According to wavelength distribution of solar energy, most of them have longer wavelength than UV light. Hence, visible light responsive photocatalyst is desired in order to use solar energy effectively. One of the methods to fabricate visible light responsive material is to dope nitrogen (N) on TiO_2 [1]. Also, tantalum compounds have high optical absorptance in region of visible light, tantalum attract much attention as visible light responsible photocatalyst [2]. In addition, it was clearly identified that formation of fiberform nanostructure on the surface improves the property as photocatalyst [3]. Recently, it was experimentally found that He plasma irradiation to various metals, such as titanium, tungsten, nickel, molybdenum, iron, and so on leads to the formation of fiberform nanostructures [4].

In this study, we investigated the change of the tantalum surface morphology and forming condition to nanostructure on the surface under He plasma irradiated. And we conducted irradiation of He-N_2 mixing plasma to Ti to form nanostructures on the surface and N doping into material at the same time.

2. Experimental setup

The substrate materials were tantalum and titanium provided by Nilaco Co. with 99.95 % purity and 0.1 mm thickness, 99.5 % purity and 0.3 mm thickness, respectively. Irradiation of He plasma or He-N_2 mixing plasma was conducted in the linear plasma devices NAGDIS-II (Nagoya Divertor Simulator). In order to control the sample temperature and the incident ion energy, which are thought to be important to form nanostructure, samples were electrically biased and plasma parameters were changed. The typical electron density and temperature of the He plasma was on the order of 10^{18} to 10^{19} m^{-3} and 5 eV, and the ion flux was on the order of 10^{21} to 10^{22} $m^{-2}s^{-1}$. The surface is heated by the plasma bombardment. A water cooling stage is used when it is necessary to sustain the temperature sufficiently low. The surface temperature was measured by a radiation pyrometer. After the plasma irradiation, the surface modification of samples were observed by scanning electron microscope (SEM). To investigate the N dope state of samples, we use X-ray photoelectron spectroscopy (XPS).

3. Results and discussion

3.1 *Tantalum experiment*

Fig.1 shows the SEM micrographs of the samples after He plasma irradiation. On the surface of Fig.1(a), neither hole nor nanostructure is observed. On the surface of Fig.1(b) and 1(c), He bubbles and holes are formed. Consequence of various parameters irradiation, three types of surface morphology changes are found to be observed: no changes, large size of holes (larger than around 100 nm) and smaller size of holes (smaller than around 100 nm). Holes and He bubbles are thought to be important for formation nanostructure. The relationship between the surface morphology and irradiation parameters is shows in Fig.2. It is shown that the surface morphology changes depend on the irradiation parameter such as incident ion energy and surface temperature. In particular, the surface temperature has strong effect to surface morphology changes and the size of holes formed on the surface. Moreover, requirements for formation holes on the surface are observed in the surface temperature around 800-900 K.

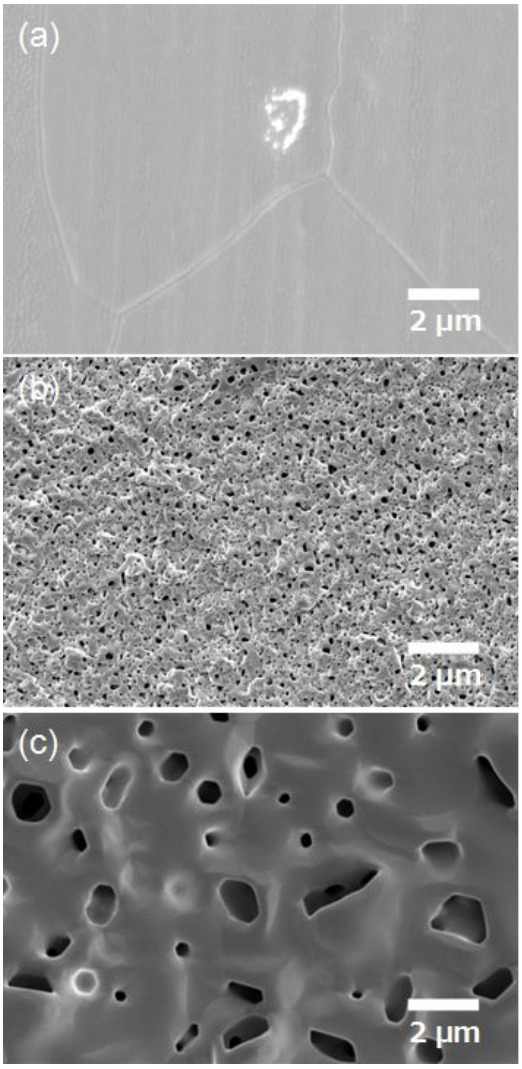

Fig.1. SEM micrographs of tantalum exposed to He plasma under the condition shown in Table 1.

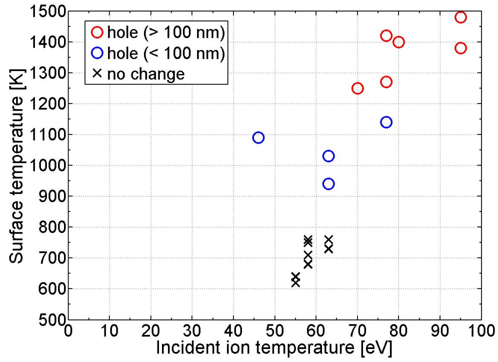

Fig.2. Relationship for the surface morphology and plasma parameters (incident ion energy and surface temperature)

3.2 *Titanium experiment*

Exposure conditions to plasma for titanium samples are shown in Table 1. The incident ion energy and ion flux were measured with a Langmuir probe. Fig. 3 shows XPS spectra of irradiated samples with different gas mixture ratios. It is clearly seen that N is doped on Ti. And gas ratio and irradiate time affect the fraction of N on Ti. It is suggested that the plasma process is effective N doping method.

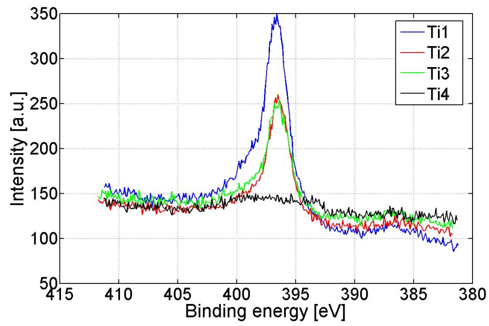

Fig.3. XPS of TiO_2 of after irradiate plasma with Table 1 parameter.

References

[1] T. Yoshida, S. Muto: MRS-J **33** 339-344 (2008).
[2] M. Hara, G. Hitoki, *et. al.*: Catal. Today **78**, 555 (2003).
[3] S. Kajita, T. Yoshida, *et. al.*: J.Appl. Phys. **113**, 134301(2013).
[4] S. Kajita, D. Kitaoka, *et. al.*: Applied Surface Science **303** 438–445 (2014).

Table 1. Experimental parameters of the plasma irradiation to Ti

	Ti1	Ti2	Ti3	Ti4
Incident ion energy	70 eV	70 eV	70 eV	87 eV
Ion flux	5.5×10^{22} $m^{-2}s^{-1}$	5.5×10^{22} $m^{-2}s^{-1}$	5.5×10^{22} $m^{-2}s^{-1}$	3.6×10^{22} $m^{-2}s^{-1}$
Fluence	2.0×10^{26} m^{-2}	2.0×10^{26} m^{-2}	2.0×10^{26} m^{-2}	2.0×10^{26} m^{-2}
Time	3600 s	1800 s	3600 s	3600 s
Temperature	580 K	610 K	640 K	700 K
Surface modification	-	-	-	Nano cone
Gas ratio (He:N_2)	3:1	3:1	1:1	Only He