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Surface modification of titanium using He plasma

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ABSTRACT

Helium plasma irradiation to metals could be a potential novel surface modification method in nanoscale. In this study, systematic helium plasma irradiations to titanium were conducted in low ion energy (<100 eV) and high fluence (>10^{25} m^{-2}) regime. From the surface analysis by scanning electron microscopy and transmission electron microscopy, various types of morphology changes, i.e. nanocone, pinhole, porous structure, and rough surfaces, were identified. The experimental conditions that control the various morphology changes are revealed from the aspect of the incident ion energy and the surface temperature. Based on the observations, it is thought that helium bubble growth, surface diffusion, and physical sputtering played important roles for the morphology change.

1. Introduction

Titanium (Ti), its oxide, and alloys have been paid attention in various fields including photocatalysis [1–3], biomedical application [4], and structural material for nuclear fusion devices [5]. Nanostructures are highly promising for application materials, because they would increase the surface area and reactivity for photocatalysis [6] and improve bioactivity of biomaterial [7]. And recently, nanoscale surface modifications of metals by helium (He) plasma irradiation have been attracted attention, and the discussion of its application has been initiated [8–10].

Historically, the interaction of He to Ti has been investigated using especially high energy (higher than 60 keV) low flux ion beams. The higher energy ion beam irradiation forms He bubbles near the surface [11,12]. The breakthrough came in mid-2000's from basic material research in nuclear fusion field. It was found that significant morphology changes and growth of fiberform nanostructures occur with low energy (<100 eV) He plasma irradiation to tungsten (W) at elevated temperatures [13,14]. The low energy He plasma irradiation has been conducted to other metals such as molybdenum (Mo) [14,15], nickel, stainless steel, titanium, and iron [9]. It has been revealed that various morphology changes in nanoscale occur by the exposure to He plasma under certain conditions. However, different from W and Mo, for which the effects of He plasma irradiation have been extensively investigated, the relation between the irradiation conditions and morphology changes has yet to be fully revealed for other metals.

In this paper, focusing on the plasma surface modification of Ti, He irradiation experiments will be conducted. Compared with conventional He ion implantation experiments, notable differences are in the incident ion energy and the He ion flux/fluence. Typically, in this study, the incident ion energy is more than two to three orders of magnitude less and the He ion flux is three to four orders of magnitude greater than those in the previous He ion implantation experiments. Previously, formation of nanocone and fiberform nanostructures on Ti by He plasma irradiation were presented [9]. This study will systematically investigate the morphology changes on Ti by conducting He plasma irradiation with various experimental conditions. Based on the experimental results, we will discuss the candidate mechanisms to lead the morphology changes by the He plasma irradiation. It is shown that the He bubble growth and physical sputtering could be major key players for the morphology changes.

2. Experimental setup

Experiments were conducted in the linear plasma devices NAGDIS-I and NAGDIS-II. In both the devices, He plasma was produced in steady state by a direct current arc discharge. Magnetic field, of which the strength is approximately 0.1 T, is formed by solenoidal coils and suppresses the radial diffusion of the plasma

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to form high density plasmas. A heated LaB_6 disk was used for cathode material, and copper was used for anode. The density of the He plasma was on the order of 10^{18} to 10^{19} m^{-3} and the He flux was on the order of 10^{21} to 10^{22} $m^{-2}s^{-1}$. In both the devices, turbo molecular pumps are used for vacuuming and the background pressure was 10^{-5} Pa. The He pressure during the discharge was in the range of 0.1–1 Pa. These devices were originally developed to simulate the divertor region in fusion devices, in which materials and high density plasmas were interacted [16], and have also been utilized for general plasma surface modification studies [14,8].

The Ti sample was equipped on a water cooling stage. Because the heat flux from the plasma is considerably high, it is necessary to cool the sample to control the surface temperature, T_s, rather than heating. The incident ion energy, E_i, was controlled by changing the biasing voltage of the sample. Since the space potential was almost zero, the biasing voltage almost corresponded to E_i. The surface temperature was measured with a radiation pyrometer.

3. Results and discussion

3.1. Incident ion energy and surface temperature dependence

He plasma irradiations were conducted at E_i of less than 100 eV. Several different types of morphology changes were observed. Here, we show typical surface temperature dependence when the temperature was approximately 800 K. Fig. 1(a), (b), and (c) shows the SEM micrographs of the He irradiated Ti surfaces at the incident ion energy of 12, 58, and 89 eV, respectively. The surface temperature and the He ion fluence were in the ranges of 770–800 K and 2.4–5.3 × 10^{25} m^{-2}, respectively. The experimental conditions correspond to case (i)–(iii) summarized in Table 1. When the incident ion energy was 12 eV, no significant morphology changes were identified on the surface. At 58 eV, pinholes were observed on the surface. These pinholes were formed probably by the growth of He bubbles beneath the surface. Similar as the annealing experiments of He irradiated copper, on which pinholes were observed, the pinholes were formed when grown He bubbles reached the surface [17]. At 78 eV, nanocones were formed on the surface. The width of the nanocones was approximately 100 nm. Physical sputtering is likely to be an important process to form nanocones. The mechanisms to lead the formation of nanocones will be discussed later.

Fig. 2(a)–(c) shows the SEM micrographs of the Ti surfaces irradiated by He plasmas under the conditions (iv)–(vi), respectively, shown in Table 1. The incident ion energy was ∼ 75 eV and the He ion fluence were in the range of 2.6–6.0 × 10^{25} m^{-2}. The surface temperature was changed from 550 to 1200 K.

Table 1
Irradiation conditions used in the experiments.

	E_i [eV]	T_s [K]	Fluence [m^{-2}]
(i)	12	800	3.1 × 10^{25}
(ii)	58	800	2.4 × 10^{25}
(iii)	78	770	5.3 × 10^{25}
(iv)	75	550	6.0 × 10^{25}
(v)	73	850	2.6 × 10^{25}
(vi)	75	1200	4.9 × 10^{25}
(vii)	75	850	1.3 × 10^{25}
(viii)	83	860	2.1 × 10^{25}
(ix)	70	1000	3.1 × 10^{25}
(x)	74	550	2.0 × 10^{25}
(xi)	72	520	3.3 × 10^{25}
(xii)	90	600	1.5 × 10^{25}
(xiii)	69	800	3.0 × 10^{25}
(xiv)	70	810	3.2 × 10^{26}

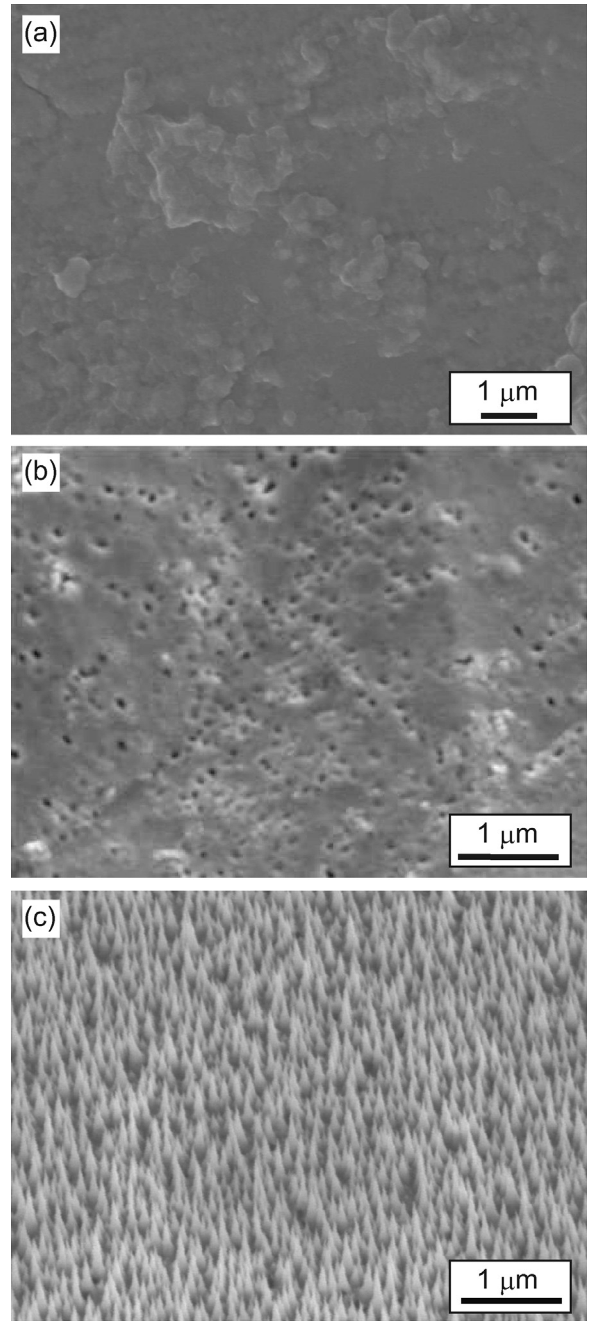

Fig. 1. SEM micrographs on Ti surfaces exposed to He plasmas in the energy range of 12–78 eV. In (c), the sample was tilted 45°. The irradiation conditions of (a), (b), and (c) correspond to the cases (i), (ii), and (iii), respectively, shown in Table 1.

At 550 K, the surface had cone shaped structures. The width of the structure was several hundreds of nanometers. When the temperature was increased to 850 K, large holes and small white spots, which are nanocones, as shown later, are observed on the surface. When the temperature was increased to 1200 K, no fine structures remained on the surface and rough surface appeared.

Fig. 3(a) and (b) shows the cross sectional TEM micrographs of the samples (v) and (vi), respectively, prepared by focused ion beam (FIB) milling process. The thickness of the sample was approximately 200 nm. Fig. 3(a) shows the nanocones with a sharp head. The base width and the height of the cones were approximately 200 and 500 nm, respectively. From Fig. 3(a), it is seen that many bubbles exist inside the cone structure. The size of the largest bubbles is approximately 20 nm. There are many small bubbles with