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Temperature-dependent surface porosity of Nb_2O_5 under high-flux, low-energy He^+ ion irradiation

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ABSTRACT

The present study reports on high-flux, low-energy He^+ ion irradiation as a novel method of enhancing the surface porosity and surface area of naturally oxidized niobium (Nb). Our study shows that ion-irradiation-induced Nb surface micro- and nano-structures are highly tunable by varying the target temperature during ion bombardment. Mirror-polished Nb samples were irradiated with 100 eV He^+ ions at a flux of 1.2×10^{21} ions m^{-2} s^{-1} to a total fluence of 4.3×10^{24} ions m^{-2} with simultaneous sample annealing in the temperature range of 773–1223 K to demonstrate the influence of sample temperature on the resulting Nb surface morphology. This surface morphology was primarily characterized using field-emission scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM). Below 923 K, Nb surfaces form nano-scale tendrils and exhibit significant increases in surface porosity. Above 923 K, homogeneously populated nano-pores with an average diameter of ~60 nm are observed in addition to a smaller population of sub-micron sized pores (up to ~230 nm in diameter). Our analysis shows a significant reduction in surface pore number density and surface porosity with increasing sample temperature. High-resolution *ex situ* X-ray photoelectron spectroscopy (XPS) shows Nb_2O_5 phase in all of the ion-irradiated samples. To further demonstrate the length scales in which radiation-induced surface roughening occurs, optical reflectivity was performed over a spectrum of light between 200 and 1100 nm, showing a recovery of nano-scale surface damage at high sample temperatures.

1. Introduction

Over the past several years niobium (Nb) oxide micro- and nano-structures, particularly Nb_2O_5 structures, have been studied and tested for a wide range of applications including solar energy conversion [1–3], chemical catalysts [4,5], supercapacitors [6], and bio-applications [7,8]. While this is certainly a wide range of applications, every study placed a common emphasis on enhancing Nb_2O_5 surface area in a controlled manner. Particularly for bio-applications, it is important to be able to control both the surface porosity and aspect ratio of metal-oxide nanostructures [9–11]. Recently, several efforts have been made by research groups all around the world to develop highly porous Nb_2O_5 surfaces using several techniques such as electrosynthesis and anodization [12–14], phase transformation [15], thermal oxidation [16], and sol–gel processes [17,18]. In this study, we present a novel one-step ion irradiation processing technique for generating similar nano-structured Nb_2O_5 surfaces with relatively large surface area and surface porosity. This top-down approach guarantees good contact between the different crystallites and avoids electrical conductivity limitations (if required). Similar He^+ plasma-processing techniques have been used to produce nanostructures on oxidized W surfaces [19] and Fe surfaces [20] for solar water splitting applications. While W is the most widely studied material in this field (due to the relevance of He^+ ion irradiation damage to fusion applications), high-flux, low-energy He^+ ion irradiation has been known to produce various types of nanostructures in other materials such as nano-pillars and pinholes in Ti [21,22], nano-tendrils in Mo [23,24], voids and pinholes in Ta [25], and other void and nanostructure formations in Cu and Al [22].

We present He^+ ion irradiation as a novel processing technique; however, the effects of He^+ ion irradiation on Nb surfaces have previously been studied in the context of nuclear structural materials to assess Nb as a potential plasma-facing component (PFC) for nuclear fusion reactors [26–30]. In these studies, He bubble formation [26–28], surface blistering [29], and tendril-like structures [30] are observed as a result of He^+ ion induced surface modification. However, almost all of these studies use relatively higher He^+ ion energies (up to several keV) where sputtering also plays an important role. Furthermore, these studies are also primarily

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concerned with the reduction of Nb surface damage under high-flux ion irradiation instead of trying to optimize and finely tune the surface porosity and surface area. While it is understood that He^+ ion irradiation may cause certain morphological changes in Nb surfaces, none of these studies assessed the modified material's surface chemical composition or oxidation characteristics to demonstrate its relevance to applications other than nuclear structural materials. The present study will demonstrate that the generation of Nb_2O_5 micro- and nano-structures are possible with a low-energy (100 eV) He^+ irradiation process and the resulting feature sizes are tunable by tailoring the Nb temperature during ion irradiation. This may open a new pathway for solar power concentration technology, chemical catalysts, and bio-applications. In addition, surface analysis of irradiated Nb surfaces may provide some further understanding of nanostructure formation on high-Z refractory metals for nuclear applications.

2. Experimental methods

The experiments were performed at the UHFI (ultra-high flux irradiation) and IMPACT (interaction of materials with particles and components testing) surface characterization laboratories [23–25,31] at the center for materials under extreme environment (CMUXE), Purdue University. 0.5 mm-thick Nb foils (99.8% purity, annealed) were cut into 10 mm × 10 mm samples and mechanically polished to a mirror-like finish. Ion irradiation experiments were performed using 100 eV He^+ ions generated from the EH-400LE, a broad-beam End-Hall (EH) gridless ion source manufactured by Kaufman & Robinson, Inc. The Nb samples were irradiated with a constant flux of 1.2×10^{21} ions m^{-2} s^{-1} for one-hour duration, leading to a total He^+ fluence of 4.3×10^{24} ions m^{-2}. All irradiation experiments were performed inside an ultra-high vacuum (UHV) chamber with a base pressure of $\sim 10^{-7}$ Torr and a working pressure of 2.0×10^{-4} Torr. During irradiation, the Nb samples were simultaneously annealed at a constant temperature throughout each experiment at a temperature in the range 773–1223 K. For a precise temperature measurement, thermocouples were used instead of radiation thermometers; a thermal-feedback mechanism in the sample heater corrected for ion-induced heating of the Nb samples during the experiment by altering the current supplied to the heating element based on the difference between current and desired sample temperatures. Post-irradiation sample surface morphology was characterized *ex situ* by field emission scanning electron microscopy (FE-SEM). Atomic force microscopy (AFM) studies using Bruker Innova atomic force microscope were also performed on selected samples to resolve finer details of the ion-induced nanoscopic changes. To characterize changes in surface oxidation and chemical composition, X-ray photoelectron spectroscopy (XPS) was performed on a virgin and all post-irradiated Nb samples. X-rays for XPS were generated with an Mg–Kα source and electrons were detected using an Omicron Argus hemispherical analyzer with round aperture of 6.3 mm. No sample charging was observed. All XPS spectra were analyzed using commercial CasaXPS software [32]. XPS spectra were also taken from a virgin, mirror-polished sample both before and after a sputter-cleaning process to compare XPS peaks from the He^+ ion-irradiated samples to both pure and naturally oxidized Nb. The sputter-cleaning process consisted of irradiating (*in situ*) the Nb sample in a UHV environment with 1 keV Ar^+, at a flux of $\sim 10^{21}$ ions m^{-2} s^{-1}, for several minutes to remove any native Nb-oxide layers. Additionally, optical reflectivity measurements were taken for post-irradiated Nb samples to further characterize surface alterations and assess the material's relevance to solar applications. These optical reflectivity measurements were performed using a PerkinElmer 950 spectrometer with an integrating sphere of 1100 nm [33]. A combination of halogen and deuterium light was used to study a wide range of incident light wavelengths ranging from 200 to 1120 nm.

3. Results and discussion

3.1. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) studies

Fig. 1(a) depicts an FE-SEM micrograph of a virgin mirror-polished Nb surface showing relatively flat and defect-free Nb surface. Fig. 1(b)–(g) shows FE-SEM micrographs of Nb surfaces after He^+ ion irradiation with a fluence of 4.3×10^{24} ions m^{-2} as function of temperature in the range of 773–1223 K. As evidenced in Fig. 1(b), irradiations at temperatures as low as 773 K significantly alter the Nb surface. This leads to the generation of homogenously populated porous structures on the entire surface. Similar porous structures are also observed at 823 K. Note that these structures seem to resemble the early-stage formation of nano-scale tendrils or "fuzz" observed by our group in the case of Mo [23,24] and by others in the case of W [34,35], under similar He^+ irradiation conditions. The fuzzy structures are ultimately a result of sub-surface He clusters formed from the trapping of penetrating He^+ ion irradiation, which then form pressurized bubbles and erupt through the surface leaving behind dense tendril structures. In the case of Mo, fuzz is observed under similar irradiation conditions when the sample temperature is kept between 873 and 1073 K [23]. Beyond this upper temperature limit, we observe the appearance of pillar-like nanostructures. In W, this temperature window for fuzz formation is even higher (~1000–2000 K) [36]. For the present case of Nb surfaces, however, we observe large separation between nano-tendrils at temperatures above 923 K due to the growth and collapse of surface pores. In fact, around 1023 K, the main mode of surface deterioration is the appearance of a significant amount of surface pores of various sizes (Fig. 1(e)) instead of nano-scale tendrils or "fuzz" formation (Fig. 1(b)–(d)). The average sizes of these pores increase with temperature, as evidenced in Fig 1(f) and (g). Fig. 1(h) plots the surface pore number density *vs* temperature for the three highest target temperatures. The three lower temperatures (773, 823, and 923 K) were excluded from this analysis since the surface morphologies observed at those target temperatures were significantly different (nano-scale tendrils as opposed to surface pores). Note that while the average surface pore size increases with increasing temperature, the pore number density decreases. Detailed analysis of surface pore size was performed on several of the highest fidelity FE-SEM micrographs to generate pore diameter histograms shown Fig. 2. All histograms were fitted using deconvoluted Gaussian distributions to guide the eye and show existing correlations between surface pore sizes and sample temperature. For the two samples irradiated at a higher temperature (1123 and 1223 K), the histograms appear to have two separate distributions. For all three samples, there is a dominant distribution of smaller surface pores (~60 nm in diameter) as well as a second, larger distribution that has an increasing diameter with increasing temperature. The histograms reveal a sequential increase in the average surface pore diameter with target temperature for the second distribution from ~100 nm (1123 K) to ~150 nm (1223 K) while the first distribution (~60 nm) only changes slightly. At the highest temperature (1223 K), the largest observed pore size was ~230 nm in diameter. Simultaneous reduction in the surface pore number density along with an increase in average pore size suggests that the smaller pores may be agglomerating into larger surface pores. Higher temperatures during irradiation lead to enhanced mobility of He clusters trapped beneath the surface, effectively allowing for the formation of larger clusters that manifest themselves as larger pores upon surface reemission. The simultaneous exponential decrease