Applied Surface Science 285P (2013) 557–563

Contents lists available at ScienceDirect

Applied Surface Science

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

Surface and phase transformation characteristics of titanium hydride film under irradiation of pulsed ion beam

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ARTICLE INFO

Article history:
Received 14 May 2013
Received in revised form 15 August 2013
Accepted 19 August 2013
Available online 28 August 2013

Keywords:
Titanium hydride
Pulsed ion beam
XRD
Secondary ion mass spectroscopy

ABSTRACT

Titanium hydride films irradiated by intense pulsed ion beam have been investigated by using scanning electronic microscopy, surface profilometer, X-ray diffraction and secondary ion mass spectroscopy in order to explore the mechanisms of interactions between intense pulsed ion beam and titanium hydride. Three sets of titanium hydride films are irradiated respectively for several times at energy density of 0.1 J/cm^2, 0.3 J/cm^2 and 0.5 J/cm^2. Surface morphologies start to reveal a feature of intense melting and network cracks only after energy density reaches close to 0.5 J/cm^2. Additionally, desorption of hydrogen from the film has been confirmed by X-ray diffraction, and a titanium dihydride ($TiH_2(x)$) with a body centered tetragonal structure, seldom reported by researchers and formed under extreme conditions, has also been identified under this condition. Depth profile of hydrogen isotope with secondary ion mass spectroscopy seems to suggest that the bulk hydrogen isotope seems to serve as a reservoir for the drainage of top hydrogen, and its fast diffusion can quickly compensate for the exhaustion of top hydrogen isotope atoms.

1. Introduction

Titanium has long been of interest as hydrogen storage material since titanium has a high affinity to hydrogen isotopes. It is known that hydrogen absorption transforms titanium from metal (h.c.p. α-phase) to hydride (f.c.c. δ-phase), and can induce radical changes to its property [1]. Titanium deuteride or tritide is an important nuclear material used in the field of neutron generators. The stable working condition of neutron generator requires not only integrity in the macro-structure of the target but also a constant concentration of hydrogen isotopes. Therefore it is vital to evaluate the properties of the titanium deuteride film in various ways. Investigations concerning hydrogen–titanium system seem to mainly focus on the hydrogen thermal desorption spectra so as to study hydrogen desorption kinetics from metal hydride and to determine the rate-controlling step [2,3], but little is known on the evolution of its compositional changes under a much more nonequilibrium condition.

In the past two decades, the high intensity pulsed ion beam (HIPIB) technique has received extensive attention as a tool for surface modification of materials [4,5]. Compared with conventional ion implantation, IPIB irradiation into materials possesses a higher energy density with shorter pulse width and is typical of more intense thermal–mechanical effect. From such a point of view, considering the features of extreme high heating and cooling rate of IPIB, we intent to utilize IPIB as a method to evaluate the stability characteristics of titanium hydride film in order to determine a predictable behavior of the film's evolution under an extreme nonequilibrium external condition.

2. Experimental

The experimental used titanium hydride film, 2 cm in diameter and 6 μm in thickness, was pure titanium film deposited on Mo substrate, and then impregnated with deuterium under controlled temperature and pressure conditions. Experimental setups and more detailed procedures can be found in a related research [6]. Filling with deuterium other than hydrogen made it possible to study gas release with SIMS, separating it from the uncontrollable processes of hydrogen appearance in vacuum system.

The experiment was conducted on the TEMP-6 type HIPIB apparatus operating in unipolar mode [7] at the school of materials science and engineering, Dalian university of technology. A high-intensity pulsed ion source of TEMP type operated in unipolar mode was used to produce the IPIB for irradiation. A detailed description of the experimental setups is stated in reference [4]. The IPIB parameters used to treat the samples are as follows: ion beam composition of 70% proton and 30% carbon ions; ion accelerating voltage

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http://dx.doi.org/10.1016/j.apsusc.2013.08.093

of 100 kV; ion current density of 10 A/cm^2, 30 A/cm^2 and 50 A/cm^2; pulse width (FWHM) of 100 ns; shot number of 1, 5, 10.

A JSM-5600LV scanning electron microscope (SEM) was used to observe the surface morphology on the irradiated surfaces. Surface roughness was measured by using a Surfcorder SE-3H profilometer with a 2 μm-radius pinhead, where the roughness value for each case was averaged over three samples and for each sample over three measurements. Phase identification of surface layer of the specimens was performed by standard X-ray diffraction (XRD) analysis using Cu-Kα radiation. The depth profiles of hydrogen isotopes retained in the samples were analyzed by secondary ion mass spectroscopy (SIMS), using cesium ion (Cs^+) as the primary ion with the energy of 2 keV and a beam current of 4 nA to the surface normal. Dimension of the rastering area is of the order of $500 \times 500\ \mu m^2$. The morphologies of the rastered areas are profiled by a profilometer with a 2 μm-radius pinhead. The sputtering time of the samples are 14268 s and 4532 s for the virgin and irradiated sample, corresponding to 1.8 μm and 0.5 μm respectively. Sputtering rates are obtained by measuring the depth of sputtering crater divided by the total sputtering time, and are calculated as 1.26×10^{-4} μm/s, 1.06×10^{-4} μm/s and 3.31×10^{-4} μm/s.

3. Results and discussion

3.1. Surface morphologies

Fig. 1(a)–(j) displays the surface morphology of titanium hydride under IPIB irradiation. Fig. 1(a) reveals a feature of micro-protrusion on the unirradiated surface, which attributes to the deposited titanium particles in the preparation process. Glancing at it briefly, apart from the samples under irradiation of 0.5 J/cm^2, we can hardly notice any major change, except for several sparsely-populated white dots which are probably melted impurities, on the surface of titanium hydride films. However, this kind of 'peace' is disturbed when energy density is enhanced to 0.5 J/cm^2, after which some fine blurred cracks seem to come into sight after one shot, and a more noticeable indication of cracking can be ascertained under 10 shots. The accompanying white dots probably are the ablated spots resulting from the known mechanism of selective ablation [4]. Cracks are induced by the prominent thermoelastic stress raised during the rapid heating and cooling process of a near surface layer during IPIB irradiation. This large amount of network micro cracks is detected earlier compared to other related HIPIB treated materials [8,9], although their typical energy density used is significantly higher than current one. They mainly attribute to the easy-to-crack feature of metal hydride [1] and the different thermal expansions between the film and substrate when swiftly heated and cooled, which can induce extremely high internal stress. This cracking feature is noticeable, since we guess it will probably impose a positive influence on the desorption of hydrogen, facilitating its migration. To ascertain the shot impact of IPIB on films at 0.1 J/cm^2 and 0.3 J/cm^2, we have obtained the roughness profiles beneath the corresponding SEM images, although a direct compelling evidence of melting cannot be judged by SEM. As is demonstrated, except for the 0.1 J/cm^2 case, the roughness on the irradiated surface is indeed reduced to a comparatively smaller scale, which suggests that the energy density threshold for the melting of the top surface is at least beyond 0.1 J/cm^2. Generally speaking, based on current findings, energy density threshold for the melting of hydride film is beyond 0.1 J/cm^2, and cracking beyond 0.3 J/cm^2.

3.2. Evaluation of thermal mechanical effect

During the process of IPIB-target interaction, high density energy is delivered by a short pulse onto target materials, followed with rapid heating and re-solidification of surface layer at ultra-fast heating and cooling rate. We utilize finite element analysis to estimate the temperature and thermal stress field during the shot. The power function $Q(r,t)$ of IPIB and the two-dimensional heat transport equation [10] are given by:

$$Q(r,t) \approx I(t) \exp\left[-2\left(\frac{r}{R_s/2}\right)^2\right] \quad (1)$$

$$\rho C(T)\frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(\kappa(T)\frac{\partial T}{\partial x}\right) + \frac{\partial}{\partial y}\left(\kappa(T)\frac{\partial T}{\partial y}\right) \quad (2)$$

Where R_s is the full width at half maximum of ion current, and r, $I(t)$ the full length in radial direction and temporal profile of IPIB intensity; T is the temperature, and ρ, $c(T)$ and $\kappa(T)$ are the mass density, specific heat and thermal conductivity, respectively. Since the beam area is sufficiently larger than the target area, we neglect the inhomogeneous of the beamspot on the film. The $I(t)$ is approximated as an isosceles triangle during a pulse according to the measured waveform of ion current density. The volume of the film expands or is compressed with the changing temperature. However, thermal expansion of a certain cell is confined by the surrounding ones, and therefore thermal stress forms. The detailed general theory relating temperature, stress and displacement can be found elsewhere [11].

Fig. 2 delivers the finite element cross-section model diagrams of the sample. Since the thickness of the titanium deuteride film is too small compared to its width, and our consideration is mainly focused on the film other than the substrate, the mesh generator is used to mesh the model in a sequential amplification mode so as to reduce computation time. The titanium deuteride film has been evenly divided into 15 different layers with each node in the depth direction standing for 0.4 μm.

Evolution of temperature with time at the top node and temperature profiles along depth direction are shown in Fig. 3(a and b). According to calculation, the highest temperature rise at the top surface for the three groups of samples varies from 590 °C to 2400 °C.

This is, in some extent, consistent with results of SEM and surface roughness profiles, as we have known the melting point for titanium hydride is close to that of pure titanium (1660 °C) [12]. Total thermal stress along depth direction at the time of 100 ns and 200 ns is displayed in Fig. 3(c). As might be expected, thermal stress is most prominent at the surface, and increases with the enhancement of energy density. Different thermal expansion coefficients between the film and substrate have made the stress at the interface present a discrepancy, which suggests that film tends to be more badly affected than bulk one under IPIB shots, leading to the film separation form substrate. During heating stage of IPIB treatment, the surface volume is expanding due to heat absorption. However, only element expansion along normal direction is permitted without restriction otherwise is constrained by the surrounding matrix. As demonstrated in the displacement contour field (Fig. 4), the maximum value of displacement is located at the side boundaries, as only their inner sides are subjected to constraint. Besides, the surface region also takes on large displacement value, and its impact gradually spreads over to a larger scale with the conduction of heat. Consequently, as observed in SEM images, once the displacement exceeds the elastic limit, structure deformation occurs. Since the titanium hydride is typically brittle as compared to its corresponding metal [1], it is reasonable to believe that the titanium hydride film will produce numerous cracks under the shots of IPIB.