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Separation of Hydrogen from Water Molecules by Ion Implantation into Thin Ti Films

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The potential of hydrogen as primary gas source has generated considerable interest in hydrogen separation technologies. In the present work, the method of ion implantation has been used to separate hydrogen from energetic water molecules penetrating into Ti films. According to the results of the present study, the technique and method of implantation are capable of splitting water molecular ions into their constituent atoms with accommodation of oxygen and hydrogen atoms in interstitials of Ti film.

The experimental distribution profiles are fitted with the simulated results based on the analysis of solutions of rate equations including processes of molecular ion implantation and diffusion. The dominant mechanisms transporting incident particles from the surface into the bulk are discussed. The obtained results are compared to literature data on the widely studied titanium—hydrogen bulk system. The experimental and simulation results are in consistency that molecular ions upon entering the substrate break up into constituent atoms and separation of hydrogen occurs.

Keywords: Hydrogen, Water plasma, Ion implantation, TiO₂.

PACS numbers: 81.15 Cd, 68.47Gh, 81.65Mg, 66.30jj

1. POLICY OF THE PROCEEDINGS

Conventional energy resources, which are being used to meet most of the world's energy requirements, have been depleted to a great extent. It is therefore necessary to produce an alternative fuel that should in principle be pollution-free, storable, and economical [1]. The main advantage of hydrogen is its environmentally friendly properties but hydrogen is not a primary fuel. Many techniques for hydrogen separation are in use or under study, such as pressure swing adsorption [1], cryogenic separation [2], catalytic purification [3], and selective diffusion through membrane interfaces [4]. Although steam reforming of natural gas, coal gasification and water electrolysis are the most important industrial processes for hydrogen production today [5-9], chemical water decomposition is anticipated to play a significant role in hydrogen production in the future. Hydrogen purification and separation has been identified as a bottleneck in the development of the advanced hydrogen technologies.

This study presents the new technological concept of hydrogen production using method of water vapour plasma ion immersion implantation of molecular ions into nanocrystalline membranes. Water molecular splitting into hydrogen (H₂) and oxygen (O₂) using magnetron water vapour plasma is an ideal way to generate clean and sustainable hydrogen as energy carrier. Thermodynamically, water splitting into H₂ and O₂ is an uphill reaction, accompanied by a large positive change in the Gibbs free energy ($\Delta G = 238$ kJ/mol) [2, 10]. Also water-vapor plasmas attract attention as working media for lasers, light sources and efficient sources of UV radiation, especially in the range below 200 nm [11-15].

The main processes of the suggested technology are following: (i) the generation of water vapour plasma at 5-10 Pa pressure; (ii) the implantation of molecular ions extracted from the water vapour plasma with en-

ergies of 1-5 keV into nanocrystalline (the grain size in the range 40-90 nm) membranes, and (iii) the spatial separation of H and O atoms in the bulk of thin (2-5 μm thick) nanocrystalline membranes using nanomaterials permeable along grain boundaries for H atoms, or high ionic conductivity oxides.

The main advantages of the considered technology are following: (i) the ecologically clean technology, (ii) the atomization efficiency is close to 100 %, takes place at room temperature and without expensive catalysts as the new water atomization method is based on the processes of electron and nuclear interaction between energetic molecular ions and membrane atoms, (iii) the separated hydrogen is pure and additional purification process is avoided, and (iv) the technology is flexible and easy controllable.

2. EXPERIMENTAL TECHNIQUE

Titanium films of $1.5-2~\mu m$ thicknesses were prepared in vacuum by means of ion beam sputter deposition at room temperature under Ar atmosphere at the pressure of 2 Pa on silicon substrates.

The irradiation of Ti films has been performed by molecular ions extracted from plasma generated in water vapor at the pressure of 10-100 Pa by applying $0.2{-}0.5$ kV pulsed voltage.

Samples were located at different sites of PVD -75 vacuum chamber: (i) at distance 1-2cm from magnetron outside its sputtering zone (case A), and (ii) on the surface of Ti magnetron cathode (case B). In case A, ion current density was in the range of $10~\mu\text{A/cm}^2$ and in case B: $1\text{-}2~\text{mA/cm}^2$.

XRD measurements using a Bruker D8 diffractometer with a Cu-Ka radiation were performed before and after irradiation in order to investigate the effect of water molecular ion implantation on the film microstructure. The surface topography of as-deposited and hydro-

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genated films was analyzed by scanning electron microscopy (SEM, Joel JSM-5600). The distribution profiles of oxygen and hydrogen in titanium films after hydrogenation were measured using glow discharge optical emission spectroscopy (GDOES, Spectrum Analytic GMBH).

3. EXPERIMENTAL RESULTS

3.1 XRD analysis

Fig. 1 includes the typical XRD patterns of the asdeposited Ti film and after different durations of irradiation.

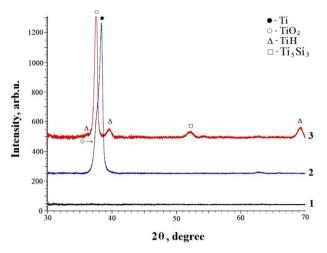


Fig. 1 – XRD patterns of Ti films before hydrogenation (curve 1) and after low intensity ion flux (case A - $10~\mu\text{A/cm}^2)$ during 45 min (curve 2) and high-flux ion irradiation (case B - $1\text{-}2~\text{mA/cm}^2)$ during 60 min (curve 3)

X-ray diffraction pattern of the as-deposited thin Ti film (curve 1) demonstrates the amorphous nature of the film.

After irradiated by ions extracted from water vapour plasma during 45 min (curve 2) show one wide and asymmetric peak which is interpreted as superposition of two peaks – Ti [002] at 38.41° and TiO₂ [004] at 37.39°. It may be concluded that the plasma discharge partially oxidized the titanium film transferring it to a rutile structure after 45 min of plasma treatment under low-flux ion irradiation (case A).

In case of high-flux ion irradiation (curve 3) during 60 min, the characteristic peak of Ti at 38.41° is not present, instead the single peak of TiO_2 [012] at 37.47° together with small peaks of titanium hydride phase have been identified: TiH [111] at 35.59° , TiH [002] and TiH [113] at 39.39° and 69.10° , respectively. The fact that no crystalline titanium oxide phases after high-flux ion irradiation were indexed can be an indication that oxygen transport can be completely separated from hydrogen transport and integral effects might be important.

3.2 GDOES (Spectrum Analytic GMBH) analysis

Fig. 2 includes the distribution profiles of oxygen (curve 1 and 2) and hydrogen (curve 3 and 4) across the thickness of Ti film irradiated by water plasma ions under different intensities of irradiation: case A - 10 $\mu\text{A}/\text{cm}^2$ (O curve 1, H curve 3) and case B - ion current density was in the range of 1-2 mA/cm² (O curve 2, H curve 4).

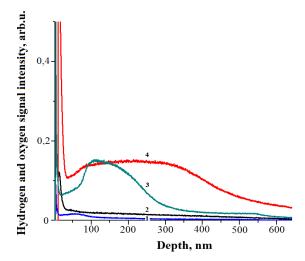


Fig. 2 – Distribution profiles of H (curve 3 - 10 $\mu A/cm^2;$ curve 4 - 1-2 mA/cm²) and O (curve 1 - 10 $\mu A/cm^2;$ curve 2 - 1-2 mA/cm²) atoms in plasma treated Ti films.

It is seen that hydrogen depth distribution in Ti film depends on the irradiation intensity. Oxygen distribution profiles in Ti film are very similar after low and high-flux irradiation.

GDOES analysis demonstrated that under implantation of ions extracted from water vapor plasma hydrogen atoms are separated at the surface of Ti film and most of the hydrogen diffuse into the bulk.

3.3 SEM surface views

Fig. 3 includes SEM surface views of Ti film before hydrogenation and after different flux ion irradiation.

The studies of surface roughness on a nanometric scale revealed that surfaces of Ti film after water plasma treatment become rough. SEM surface views support the assumption about accommodation of H_2 at film-substrate interface.

4. DISCUSION

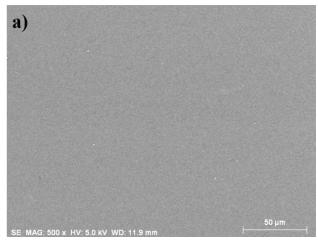
Proposed scheme of H_2 separation shown in Fig. 4. Thin Ti film is eventually transformed into TiO_2 under water plasma treatment (Fig. 4 a). All the time the surface is under continuous water vapor condensing conditions and simultaneous arrival of atomic and molecular species from plasma in neutral and ionized states. The water molecules at the interface dissociate

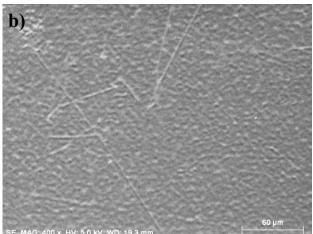
into H⁺ and OH⁻.

The split hydrogen atoms occupy the interstitials (Fig. 4 b). From interstitials hydrogen moves into grain boundaries and is distributed along the entire thickness of Ti film as has been registered experimentally by GDOES technique (Fig. 2.).

H atoms move deeply into the bulk without formation of hydrides (Fig. 4. b). If concentration of hydrogen is low, the hydrogen forms α phase which is not registered by XRD (Fig. 1 curve 2). The β phase of titanium hydride was registered in XRD patterns (Fig. 1, curve 3) when concentration of hydrogen exceeded the limit of solubility in Ti.

Taking into account titanium's high affinity for hydrogen, are absorbed by the titanium, and consequently are stored in the bulk (Fig. 4 c).





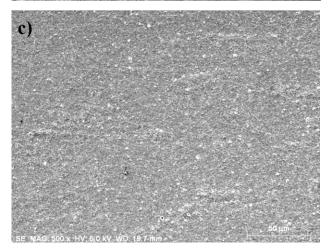


Fig. $3-{\rm SEM}$ surface views and surface topography profiles of plasma treated Ti films: a) – before hydrogenation; b) – after low-flux ion irradiation (case A) and c) after high-flux ion irradiation (case B)

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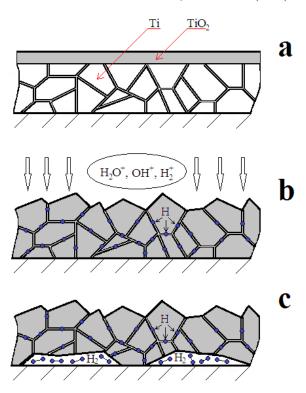


Fig. 4 - Scheme of H₂ separation

5. CONCLUSIONS

Energetic (0.3-0.5 keV) water molecular ions are split into constituent elements (H and O atoms) under molecular water ion irradiation in the near-surface region of target material.

Separated oxygen atoms form Ti-O bonds; thin 0.4 μm thick Ti film is transformed into TiO_x at ion current density about 1-2 mA/cm² in 2-3 min.

Broken hydrogen atoms are approximately homogeneously distributed across entire film thickness and stay in interstitials.

It is suggested that hydrogen atoms accommodate at film interface forming H₂ molecules.

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