

Interaction of Hydrogen Microwave-Induced Plasma with Titania Nanotube Arrays (TONT)

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Abstract: Experimental research of hydrogen plasma interaction with a surface of TONT is presented. Atomic hydrogen absorption results in formation of hydrides, while molecular hydrogen can be absorbed just physically. It is shown, that energy of hydrogen plasma is a major factor that defines the interaction mechanism and kinetics of the process.

Keywords: plasma, hydrogen, sorption, desorption, electrochemistry

1 INTRODUCTION

The lack of universal hydrogen-accumulating materials and hydrogen loading methods complying with the current state-of-the-art requirements stimulates various studies to be carried out in order to solve the problem. The hydrogen sorption-desorption kinetics, as well as the lifetime of hydrogen-accumulating devices, depend on the material nature, hydrogen purity and the loading method used. A thermodynamic consideration of systems containing atomic (dissociated) gases shows, that their chemical potential (effective pressure) is much higher than that of systems containing gases in their molecular state:

$$\mu_x = \mu^0 x_2(T) + \Delta G^0 + 2RT \ln p_x, \quad (1)$$

where $\mu^0 x_2(T)$ is the chemical potential of a non-dissociated gas in the standard state, p_x is the partial pressure of an atomic gas, ΔG^0 is the Gibbs standard energy for the dissociation reaction of a molecular gas:



Thus, the action of atomic gases on the surface of a solid should be more intense than that of molecular ones.

In 2003, Varghese and co-workers [1] reported high-temperature hydrogen sensing using TiO_2 nanotube arrays a few hundred nm in length, anodized in HF aqueous electrolytes. In this early work it was noted that due to chemisorption of molecular hydrogen, the electrical resistance of the TiO_2 nanotubes was highly sensitive to hydrogen as well as fully reversible; for example, for short tubes of 76 nm pore size, there is a variation in measured resistance of 103 upon exposure to

500 ppm hydrogen at 290°C. It was found that the hydrogen sensitivity of the nanotubes was highly dependent upon nanotube diameter, with 22 nm pore size nanotubes being about 200 times more sensitive than 76 nm pore size nanotubes, although the smaller pore size nanotubes have a larger surface area by only 30%.

The nanotube morphology and the wall thickness are found to invoke unique responses, as the wall thickness is comparable to the Debye length. Thus, the space charge layers are strongly modified by the dimensional features and the charge transfer associated with the chemisorption at such length scales.

The demand for highly sensitive, selective and stable hydrogen sensors has increased in recent years. Various types of hydrogen sensor technologies such as Schottky junction, fiber optic, catalytic, electrochemical field effect transistor (FET), oxide semiconductor and combinations of these, are being developed, or have been developed. Oxide semiconductor gas sensors are relatively simple and, hence, involve lower costs.

With high photocatalytic activity, strong oxidizing power, good chemical inertness, low cost and non-toxicity, large surface area, and unique optical property, nanostructured titanium dioxide TiO_2 materials offer great potential for ‘energy’ and ‘environmental’ applications in solar cells, lithium batteries, gas-sensing materials, and photocatalysis [2]. In particular, TiO_2 nanotubes have received more and more attention partially due to their specific surface area and high surface-to-

volume ratio. Structurally, TiO_2 nanotubes can be formed by rolling up one or several atomic layers along a certain crystallographic axis. Theoretical studies showed that TiO_2 nanotubes are semiconductors with a wide band gap, like their bulk phases, and their stability is enhanced as the tube diameter increases.

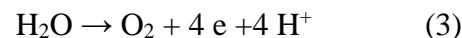
Gas sensing (especially at high temperatures and in harsh environments) is one of the most important applications of metal oxide materials, which are mechanically robust and relatively inexpensive. The high surface area and one-dimensional characteristic of nanotubes are beneficial to practical gas sensors. Recently, TiO_2 nanotube-based sensing of hydrogen has been systematically studied because of the growing importance of hydrogen in fuel cell applications, and the chemical, semiconductor and petroleum industries. It was found that at room temperature or even higher temperatures (e.g., 290°C), in response to less than or equal to 1000 ppm of hydrogen atmosphere, TiO_2 nanotubes with a mixture of both anatase and rutile phases showed a fully reversible change in electrical resistance of 3 or more orders of magnitude.

More interestingly, as compared to many conventional sensors, TiO_2 nanotubes exhibit unique self-cleaning properties after environmental contamination. It was suggested that the hydrogen sensing performance of TiO_2 nanotubes is dependent on the formation of an surface electron accumulation layer induced by the hydrogen (H) atoms chemisorption on the nanotube surface.

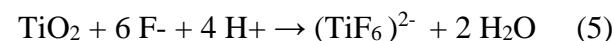
However, they are commonly operated at elevated temperatures, typically several hundred degrees Celsius, to enhance gas sensitivities and enable fast and reversible reactions. Elevated operating temperatures are not favorable for many applications, such as those involving flammable environments, biomedical applications, and those requiring low-power operation. Only a few efforts employing metal oxide semiconductors for room temperature hydrogen sensing can be found in the literature.

2 EXPERIMENTAL

Titania nanotubes were fabricated on the titanium surface by anodization method. Different conditions and the effects of voltage, water content and anodization time were investigated. In general in the absence of water in electrolytes (ethylene glycol, NH_4F) the anodization process will suffer from lack of H^+ ions and also high viscosity of the solution which leads to the formation of titanium dioxide layers only. The overall reaction for anodic oxidation of titanium can be represented as:



In the initial stages of the anodization process, field-assisted dissolution dominates chemical dissolution due to the relatively large electric field across the thin oxide layer. Small pits formed due to the localized dissolution of the oxide, represented by the following reaction, act as pore forming centers:



The pits convert into bigger pores and the pore density increases. Subsequently, the pores spread uniformly over the surface. The pore growth occurs due to the inward movement of the oxide layer at the pore bottom (barrier layer).

Investigation of TONT behavior under treatment by a beam of low-energetic partially dissociated hydrogen molecules is of particular interest. Some aspects of interaction of hydrogen with materials, used in electronics, are not clear till now and require further investigations.

A special vacuum chamber for treatment of the samples under study by atomic hydrogen beams has been constructed, in which a beam of partially dissociated hydrogen, having a density about of $1 \cdot 10^{15} - 1 \cdot 10^{17} \text{ atom} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$, was produced by a microwave generator. The power of the said generator was varied in the range of 40-60 W. The samples under study were placed in an electric heater, and the whole assembly was blown around by a flow of atomic hydrogen of the above mentioned density by means of special devices. The

period of the atomic hydrogen species, having the energy of 0.1 eV interacted with the surface was 2 to 4 hours, while the initial temperature of the samples was 25°C.

3 RESULTS AND DISCUSSION

In this paper we present results of experimental investigation of atomic and molecular hydrogen (low-energy hydrogen plasma) interaction with TONT (Fig 1, 2).

The aim of the research was to analyze a mechanism of hydrogen sorption by thin TONT arrays treated by hydrogen microwave plasma. It is shown, that it is possible to change an electrochemical activity of hydride (Fig 3,4), formed on TONT, by variation of microwave radiation power at 40 to 100 W and flow density of the molecular hydrogen through the resonator. The synthesis of metallic hydride is realized by an interaction of atomic hydrogen with surface, heated up to the temperatures not exceeding the temperature of hydride decomposition.

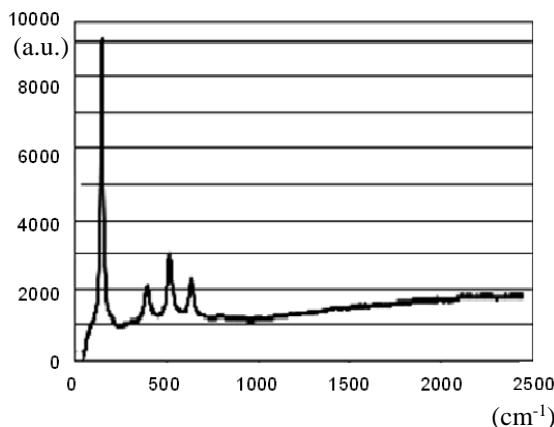


Fig.1: Raman spectra of the TONT array, calcined at 450°C, where the peaks representing anatase

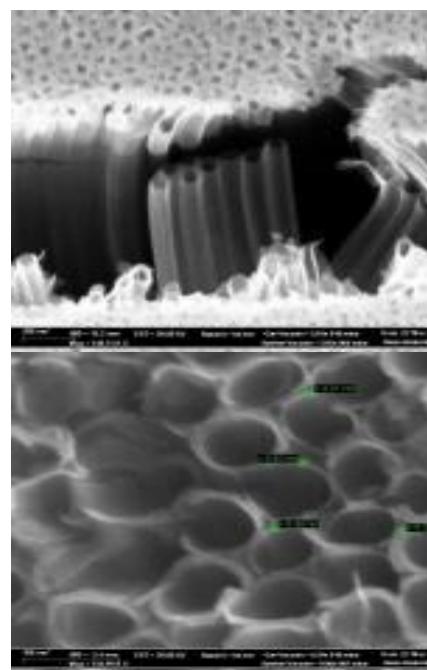


Fig.2: FESEM cross-sectional image of titanium oxide nanotube array sample

4 CONCLUSION

From the data obtained it is possible to conclude that exactly the atomization of hydrogen is the main factor in enhancing a hydrogen dissolution velocity.

On the basis of potentiodynamic cyclic iE-curves (Figs.3, 4) it has been demonstrated, that a hydrogen flow rate value through the VHF-resonator improve the electrochemical activity of TONT surface.

In addition, by the thermally stimulated desorption (TSD) method with the using of a quadrupole mass spectrometer established hydrogen evolution from samples TONT, treated with atomic hydrogen in a temperature range 200-400°C.

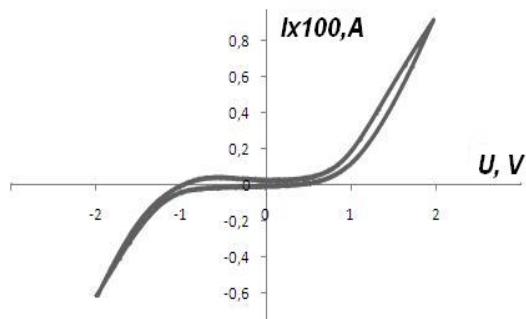


Fig.3: Potentiodynamic cyclic iE -curves in 1M KOH solution at temperature 20°C and line rate of potential 0,05 V/s(molecular hydrogen beam treatment)

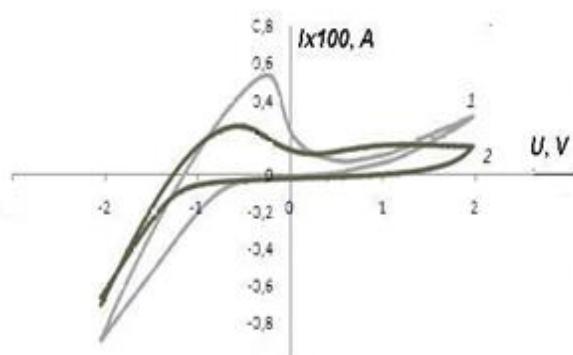


Fig.4: Potentiodynamic cyclic iE -curves in 1M KOH solution at temperature 20°C and line rate of potential 0,05 V/s (sample after atomic hydrogen beam treatment: 1- 10^{17} at./cm²·s; 2- 10^{15} at./cm²·s)

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