Solar Energy Materials & Solar Cells 93 (2009) 1885–1895

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

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

Application of WO_3 thin films for enhancement of photolysis in AgCl

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ARTICLE INFO

Article history:
Received 20 February 2009
Accepted 7 July 2009
Available online 25 July 2009

Keywords:
Photochromism
Hydrogen
Silver nanoparticles
WO_3
AgCl

ABSTRACT

A double-layer AgCl–WO_3 structure was employed to produce photochemical hydrogen for doping of an AgCl film. Atomic photochemical hydrogen, detached under the action of light from hydrogen donor molecules, previously adsorbed on the WO_3 surface, migrated through the WO_3 film into the AgCl film, which provided doping of the AgCl surface and yielded hydrogen sensitization simultaneous to illumination and yielded the enhancement of photochromism in the AgCl films. The atomic hydrogen played the role of a reducing agent and triggered the formation of sensitization centers on the halide surface, which in turn facilitated the growth of silver clusters and colloids under the action of light. The double-layer AgCl–WO_3 structure realizes the idea of two-stage catalysis: first the oxide surface catalyses hydrogen production under the action of light, then the photochemical hydrogen atoms act as catalysts during the photolysis of the halide.

1. The functions of WO_3 relative to atomic hydrogen

1.1. WO_3 as a catalyst for photodetachment of hydrogen atoms

WO_3 belongs to the family of "hydrogenphilics", loving hydrogen materials, capable of accommodating and transporting great amounts of hydrogen atoms. The interest in WO_3 increased with the pioneering work by S.K. Deb [1], which initiated intensive investigations of electrochromism and photochromism in this oxide [2 and Refs. therein,3,4].

WO_3 thin films can also play the role of a catalyst in photochemical hydrogen detachment reactions, if specially selected organic molecules (hydrogen donors) are adsorbed on the WO_3 film surface; hydrogen atoms being detached from the adsorbed molecules as the result of excitation of the WO_3 film surface by photons with the energy exceeding the oxide forbidden energy gap and transfer of surface excitation to the adsorbed molecules [5–9].

When the WO_3 surface absorbs n light quanta with energy exceeding the oxide band gap n electron-hole pairs are generated in the oxide:

$$WO_3 + n(h\nu) \rightarrow WO_3 + n(h^+ + e^-) \quad (1)$$

Very often methanol is used as a hydrogen donor, like in this study, and for the one of the photogenerated holes, according to [8,9], it is possible to write

$$h^+ + (CH_3OH)_{ads} \rightarrow H^+ + (\dot{C}H_2OH)_{ads} \quad (2)$$

The hydrogen transfer between the donor molecule and the oxide surface yielded a scavenge of the hole and formation of a $\dot{C}H_2OH$ radical, which in fact is an exchange of the photogenerated hole for a proton. This in turn makes the life time of an electron, photogenerated together with the hole, indefinitely long, since scavenging of the hole makes recombination impossible. This electron is localized at W atom giving rise to the formation of a lower-valency cation

$$W^{6+} + e^- \rightarrow W^{5+} \quad (3)$$

The number of photogenetrated electrons and protons continuously grows under illumination and hydrogen tungsten bronzes are formed:

$$WO_3\ (RH_n)_{ads} + h\nu \rightarrow H_xWO_3(RH_{n-x})_{ads} \quad (4)$$

where $(RH_n)_{ads}$—is the adsorbed molecule (hydrogen donor), H_xWO_3—the hydrogen tungsten bronzes [2]. Thus, the method used makes it possible to achieve doping of the WO_3 with electrons and protons, or in other words doping with electron–proton plasma.

1.2. WO_3 as a material to provide doping by hydrogen atoms

Under illumination the concentration of the injected particles grows and the electron–proton plasma front moves from the film surface into the film depth, which implies the possibility of transporting of the electron–proton excitation to some other materials that could be in contact with the WO_3 films.

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doi:10.1016/j.solmat.2009.07.003

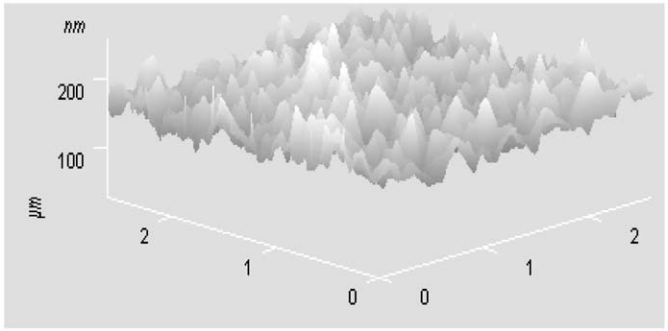

Fig. 1. Three-dimensional atomic force image of the WO_3 film surface. The scales along the *X* and *Y*-axes are given in μm, whereas along the *Z*-axis in nm. Film thickness $d = 1$ μm.

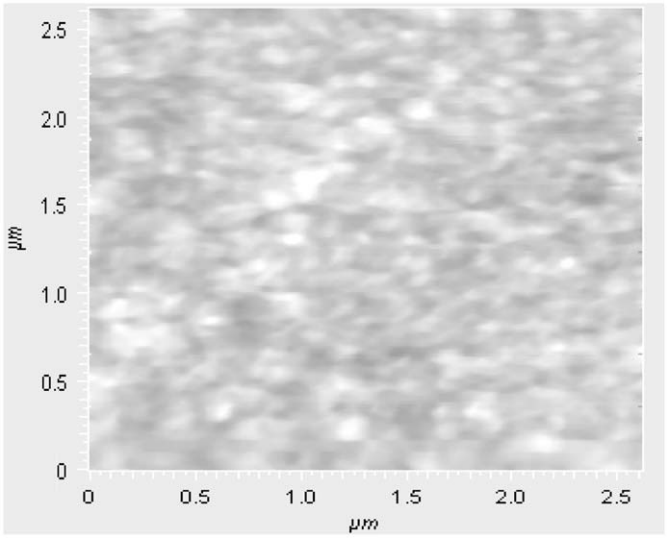

Fig. 2. Two-dimensional (*XY*-plane) atomic force images of the WO_3 films surface. The scales along the *X*-axis are given in μm. Film thickness $d = 1$ mm.

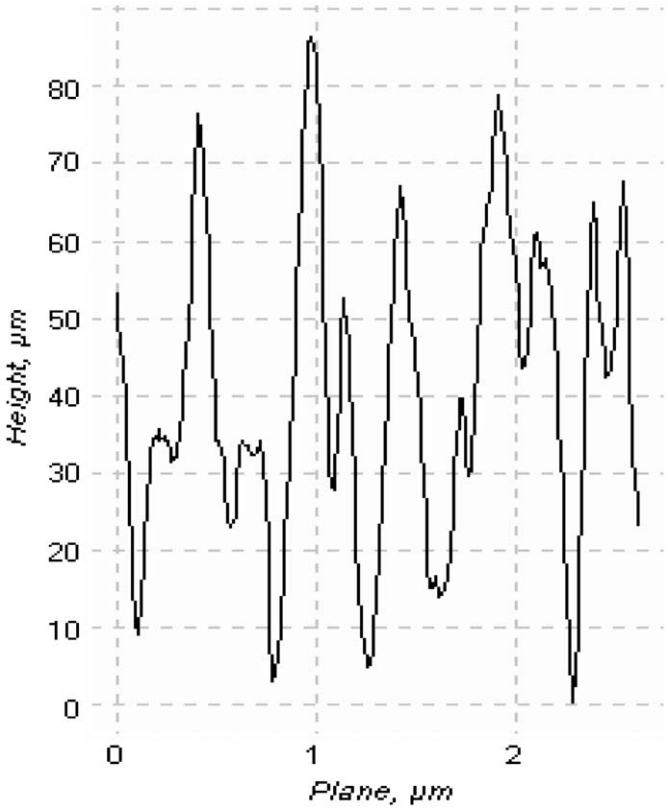

Fig. 3. Two-dimensional cross-section of the atomic force image in the *XZ* plane of the WO_3 film surface. The scales along the *X*-axis are given in μm, whereas along the *Z*-axis in nm. Film thickness $d = 1$ mm.

For this purpose double-layer structures can be prepared; WO_3 being the upper layer of the double-layer structure, whereas the other layer is a hydrogen acceptor material whose doping with hydrogen atoms should be carried out. Demands of compatibility predetermine the regime of depositing for the WO_3 layer: namely, it must be deposited onto the hydrogen acceptor at room temperature.

Meanwhile, there are various technologies of WO_3 thin film preparation, but the films prepared by evaporating WO_3 powder onto unheated substrate possess many interesting specific properties, which is worthwhile to elucidate.

These WO_3 films were found to be nanocomposites, whereas the absence of long-range order was confirmed by X-ray analyses. For this reason, the films can be characterized as "quasi-amorphous".

Morphology of the WO_3 films, prepared by evaporating WO_3 powder onto unheated quartz substrates, was studied here with the help of a "Smena-B" atomic force microscope (NT-MDT-company). To make the role of the WO_3 nanostructured film visual, the full set of characteristic atomic force images is presented here. Fig. 1 shows three-dimensional atomic force images, Fig. 2 shows two-dimensional images in the XY plane, and Fig. 3 shows two-dimensional cross-sections in the XZ plane for 1-μm-thick WO_3 films. One can observe the friable film structure with the grains of ~50 nm average size. The films possess a high porosity with an average of ~50 nm pore diameter and ~100 nm depths, where the adsorbed molecules get the degrees of freedom in arrangement on the surface. They can freely move, rotate, and bond to the film surface (Figs. 2 and 3); the surface is essentially heterogeneous, which has exceptionally high chemical reactivity for definite number of surface centers [8,9]. Thus, the investigated films are nanosized and macroporous with a rough and highly disordered fractal surface, which provides high adsorption capacity.

These films have ~0.8 of the density of the bulk [1]. The same tendency is observed for the refractive index *n*, which is $n = 2.2$ against $n = 2.5$ for bulk WO_3 [1].

The highly disordered WO_3 have maximal efficiency in hydrogen transfer reaction. They provide hydrogen transfer even at very low temperatures; the reaction is tunnelling proton-coupled electron transfer (PCET) [10], whereas fluctuative preparation of the energy barrier diminishes it. The mechanism was described in detail elsewhere [8,9].

The WO_3 films have very small electron mobility, which ranges within between 0.03 and 0.2 $cm^2/V\,s$ [11]; the electron diffusion coefficient is determined as $D = 0.0025 \pm 0.0006\ cm^2\ s^{-1}$ [12]. The photogenerated electrons have a great inclination to localization via Anderson, electron–phonon, and electron–electron mechanisms of localization [11].

The electron work function φ for the WO_3 films is $\varphi = 4.3$–4.9 eV [13–18]. This is a relatively low value as compared with many other materials. A typical scheme of the electron energy band diagram for the double-layer structure consisting of an n-type semiconductor (hydrogen acceptor) with a higher value of φ and the WO_3 layer is shown in Fig. 4.

The electron flow occurs from the WO_3 layer to the hydrogen acceptor when the double-layer structure is produced; the surface