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Effect of annealing and nanostructuring on pulsed laser deposited WS_2 for HER catalysis

Matteo Schenato[a], Cristy Leonor Azanza Ricardo[a], Paolo Scardi[a], Raju Edla[b], Antonio Miotello[b], Michele Orlandi[b,*], Rachel Morrish[c,**]

[a] Department of Civil, Environmental and Mechanical Engineering, University of Trento, 38123 Trento, Italy
[b] Department of Physics, University of Trento, 38123 Trento, Italy
[c] Department of Chemical and Biological Engineering, Colorado School of Mines, Golden, CO 80401, USA

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ABSTRACT

Replacement of platinum with cheap and abundant materials is a key step to enable the large scale application of water splitting schemes to produce hydrogen. Tungsten disulfide, a metal dichalcogenide showing catalytic activity toward the hydrogen evolution reaction (HER), is rapidly emerging as a cost effective alternative. In this paper we report the synthesis of WS_2 thin films with pulsed laser deposition (PLD), a versatile technique which combined with thermal treatments allows us to investigate the correlation between key material properties, such as crystallinity and morphology, with HER catalysis performance. Following FESEM, XRD, Raman and electrochemical characterization, we link increased activity with higher crystallinity, different from recently reported results for related materials such as MoS_2. An annealing temperature of 500 °C yields a markedly low onset potential of 160 mV relative to Pt metal and the introduction of nanostructuring proves a successful strategy for current density enhancement.

1. Introduction

Replacement of rare and expensive platinum group catalysts is driving the search for new earth abundant materials that will help advance the hydrogen economy. Metal dichalcogenides, such as WS_2, are emerging as promising, cost effective electrocatalysts for the hydrogen evolution reaction (HER) [1]. Tungsten disulfide consists of covalently bonded 2-dimensional W—S—W sheets that are held together by van der Waals forces. The edges of these semiconducting sheets are highly active toward electrochemical water reduction while the strong covalent bonding between tungsten and sulfur imparts good material stability in aqueous solution.

Although most reports of WS_2 electrocatalysis come from single sheet morphologies [2–4], thin films have also exhibited catalytic activity with the added benefit of large area coverage and scalable fabrication techniques [5,6]. Pulsed laser deposition (PLD) is a versatile physical deposition method that relies on laser ablation of a target material to provide uniform coverage ranging from a few nanometers up to microns in thickness. Tungsten disulfide has previously been deposited by PLD for photonic [7] and wear applications [8], but these films have not yet been tested for HER catalytic activity. One feature of PLD is that room temperature deposition can be achieved. This allows the impact of material structure to be easily investigated. While crystalline catalysts are typically stable with high conductivity, amorphous MoS_2 has shown unusually high concentrations of active sites. In some cases, it has even yielded superior performance [1]. A lingering question is whether the same behavior holds for WS_2. Deposition parameters also allow tuning of the film morphology, ranging from compact layers to nanostructured architectures such as nanoparticle-assembled coatings [9], offering a strategy to improve catalysis performance by increasing the electrode surface area.

In this report, we investigate the impact of post-deposition anneal treatments on the material properties of PLD WS_2 with a specific emphasis on film crystallinity. We then proceed to introduce nanostructuring as a tool to enhance the catalytic performance. Electron microscopy, Raman spectroscopy, and X-ray diffraction were used to monitor the films as they were heated up to 600 °C. The prepared electrodes were evaluated electrochemically as potential catalysts for the HER. Because tungsten disulfide can also act as a photocatalyst, all electrodes were deposited on

* Corresponding author. Fax: +39 0461283934.
** Corresponding author. Fax: +1 303 273-3730.
E-mail addresses: paolo.scardi@ing.unitn.it (P. Scardi), antonio.miotello@unitn.it (A. Miotello), michele.orlandi@unitn.it (M. Orlandi), rmorrish@mines.edu (R. Morrish).

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transparent conducting fluorine doped SnO_2 (FTO) substrates to facilitate future work testing light activated behavior.

2. Experimental

Tungsten disulfide electrodes were prepared by PLD on FTO coated glass substrates (Sigma–Aldrich TEC 15). A cold-pressed powder (Sigma–Aldrich) target consisting of 87% 2H phase, 6% 3R phase, and the balance elemental W (by XRD) was used for the WS_2 source. The PLD tool contains a 248 nm KrF excimer laser and the energy density for all depositions was set to about 1 J/cm^2. A detailed description of the apparatus is available elsewhere [10].

All depositions were conducted at ambient temperature with a fixed sample to target distance of 3 cm. An inert Ar atmosphere of either 30 mTorr or 300 mTorr was maintained in the deposition chamber during the process. Accordingly, samples will be labeled as LP (low pressure) or HP (high pressure) in the following discussion. Approximately 1200 pulses of 25 ns duration yielded a WS_2 thickness of ~300 nm, which is ideal for material characterization. Post deposition annealing between 300–600 °C was completed under vacuum with a 10 °C/s ramp rate and a hold time of 15 min. Longer heat treatments up to 60 min had no impact on electrode performance and times beyond 2 h are known to degrade grain boundaries [11].

Samples were analyzed in a JEOL JSM-7001F field emission scanning electron microscope (FESEM) equipped with an Oxford INCA PenteFETx3 energy dispersive x-ray (EDAX) spectrometer. An accelerating voltage of 20 keV was sufficient to survey the entire WS_2 layer. Atomic ratios were corrected according to a WS_2 powder standard surveyed under the same conditions. Raman spectra were collected at room temperature on a Horiba LabAramis instrument using a 633 nm wavelength laser configured to provide a 1 cm^{-1} resolution. Crystalline phase data was obtained from X-ray diffraction with Co-Kα source on a PANalytical X'Pert MRD diffractometer. A grazing incidence angle of 2° was used on bare silicon substrates to minimize the background signal which otherwise overlaps with reflections from the WS_2 layer. The ICDD database was used for peak identification.

Electrochemical measurements were made with a Gamry Interface 1000 potentiostat using a three-electrode cell: WS_2 on FTO (working), Pt foil (counter) and saturated calomel (reference). The chosen electrolyte was 0.1 M H_2SO_4. Potential scans were collected at a rate of 10 mV/s. For clarity, all electrochemical data was corrected for pH and reported against the reversible hydrogen electrode (RHE). The reproducibility of the fabrication technique has been evaluated by testing the performance of three electrodes for each set of conditions. Potential values are reported with a 95% confidence interval.

3. Results and discussion

FESEM micrographs given in Fig. 1 confirmed uniform coverage of the tungsten sulfide layer deposited at a low pressure of 30 mTorr. Plan view images (Fig. 1a) showed the WS_2 film consisted of smooth 100–200 nm features which are typical of pulsed laser deposition onto rough, FTO crystallites of approximately the same length scale [12]. The glass, FTO, and WS_2 layers are easily discerned in the tilted cross-sectional image (Fig. 1b). Thickness measurements of the PLD film consistently yielded 300 ± 25 nm for a set point of 1200 pulses.

A S:W atomic ratio of 1.4 ± 0.2 was estimated from quantitative EDAX surveys, which is low relative to the expected stoichiometric value of 2.0. Similar sulfur deficiencies have been reported for WS_2 deposited on to microfibers by PLD [7]. Low sulfur concentration in PLD WS_2 films may simply be a consequence of volatility differences between the two constituent elements. Sputter depositions of WS_2 will typically employ a sulfur rich WS_3 target followed by high temperature annealing in order to achieve stoichiometric layers [13]. For the application of HER catalysis, low sulfur content may not be a concern; sulfur defects and deficiencies have actually been linked to active catalytic sites in MoS_2 [14]. Vacuum annealing did not impact the WS_2 morphology as FESEM images of heat treated samples were indistinguishable from as-deposited layers (Supplementary information, Fig. S1).

A small number of 50–100 nm W metal particles were observed on the surface of the WS_2 films (Fig. 1a). The particles may have originated from the elemental tungsten in the powder target material, though their formation during deposition cannot be ruled out. Image analysis of low magnification micrographs (supplementary information, Fig. S2) indicates these particles have an area coverage of less than 0.5% and should not substantially impact surface behavior.

Raman spectroscopy was used to monitor the WS_2 layer as it was heated to 600 °C (Fig. 2). Spectra were collected from multiple regions on each sample to validate a homogeneous composition. The as-deposited sample exhibited the two primary reflections for WS_2 at 350 ($E^1{}_{2G}$) and 417 (A_{1G}) cm^{-1}along with a less intense peak at 326 cm^{-1}which has been assigned to a LA mode [15]. Tungsten disulfide spectra are notorious for containing a variety of convoluted second-order resonant features that can be corre-

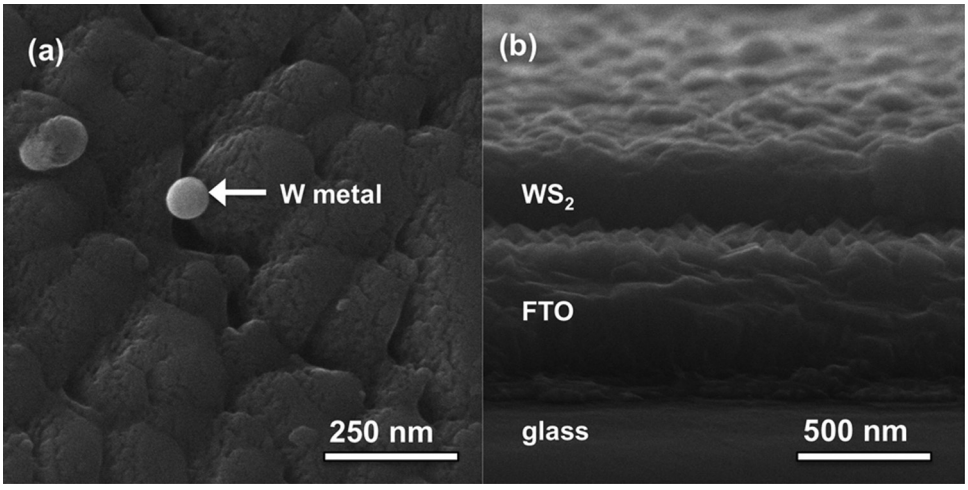

Fig. 1. FESEM images of LP PLD WS_2 (a) plan view and (b) tilted cross-section.