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Citation for published version (APA):

Balasubramanyam, S., Bloodgood, M. A., Zhang, Y., Verheijen, M. A., Kessels, W. M. M., Hofmann, J. P., & Bol, A. A. (2020). Synthesis of edge-enriched WS₂ on high surface area WS₂ framework by atomic layer deposition for electrocatalytic hydrogen evolution reaction. *Journal of Vacuum Science and Technology A: Vacuum, Surfaces and Films*, 38(6), [062201]. <https://doi.org/10.1116/6.0000563>

DOI:

[10.1116/6.0000563](https://doi.org/10.1116/6.0000563)

Document status and date:

Published: 01/12/2020

Document Version:

Accepted manuscript including changes made at the peer-review stage

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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- The final published version features the final layout of the paper including the volume, issue and page numbers.

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Synthesis of Edge-Enriched WS₂ on High Surface Area WS₂ Framework by Atomic Layer Deposition for Electrocatalytic Hydrogen Evolution Reaction

Shashank Balasubramanyam¹, Matthew A. Bloodgood¹, Yue Zhang², Marcel A. Verheijen^{1,3}, Wilhelmus M. M. Kessels¹, Jan P. Hofmann² and Ageeth A. Bol^{1,}*

¹Department of Applied Physics, Eindhoven University of Technology, The Netherlands

²Laboratory for Inorganic Materials and Catalysis, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, The Netherlands

³Eurofins Materials Science Netherlands B.V., High Tech Campus 11, 5656 AE Eindhoven, The Netherlands

^{*}(a.a.bol@tue.nl)

Keywords: Edge-enriched WS₂, 2D materials, hydrogen evolution reaction, electrocatalysts, atomic layer deposition

Abstract

Transition metal dichalcogenides (TMDs) are promising electrocatalysts for the hydrogen evolution reaction (HER). Several approaches have been adopted to increase the density of the catalytically active edge-sites of TMDs including the use of high surface area 3D templates. In this work, we report the implementation of high surface area WS₂ framework grown using plasma-enhanced atomic layer deposition (PEALD) as templates to support edge-enriched PEALD grown WS₂ electrocatalyst films. We show that these combined WS₂ template-electrocatalyst configurations show better hydrogen evolution reaction (HER) performance than the individual constituents. Material properties of the combined configurations including morphology and composition are investigated. A correlation between material properties and the HER performance is observed. This facile pathway could lead to a new route for creating high surface area electrocatalyst systems *via* PEALD.

I. INTRODUCTION

Electrochemical water splitting *via* the hydrogen evolution reaction (HER) is a promising route for the sustainable production of hydrogen, a potential renewable energy source.^{1,2} Well-known electrocatalysts for the HER including platinum and other precious metals are highly efficient, however, their limited availability and high cost restrict large-scale implementation.^{3,4} Recently, abundantly available transition metal dichalcogenides (TMDs) such as MoS₂ and WS₂ have shown promise as low-cost, alternative electrocatalysts for hydrogen production by HER.^{5,6} The edge-sites of these two-dimensional materials have been identified as active sites for catalysis whereas the basal planes are known to be typically inactive for catalysis.⁶ Several studies have focused on improving the HER efficiency of these materials by increasing the edge-site density through various strategies including morphology variation,³ basal plane activation,⁷ introduction of strain^{8,9} and defects,^{10,11} among others. Recently, three dimensional (3D) templates with high surface areas, *e.g.* 3D sponges,¹² carbon fibre paper,¹³ Ni foam,¹⁴ *etc.*, have been utilized to expose a higher number of catalytically active edge-sites. These high surface area 3D templates act as framework to host the TMD electrocatalyst and such templated-catalysts provide opportunities to improve the HER efficiency. In this work, we report the implementation of high surface area WS₂ framework as templates to support edge-enriched WS₂ electrocatalyst films. Various morphological configurations were realized by combining our previously established WS₂ plasma-enhanced atomic layer deposition (PEALD) processes¹⁵ that yielded either (1) edge-enriched nanoflakes or (2) high surface area, open, triangular fin structures (fins) depending on the plasma gas composition. These combined configurations resulted in consistent WS₂ growth over the 3D WS₂ templates with no interfacial incompatibilities due to material differences. We discuss how the combined configuration, shows relatively better HER performance compared to its individual counterparts.

In our previous work,¹⁵ the edge-enriched and catalytically superior “WS₂ nanoflakes” were synthesized using H₂S plasma as the PEALD co-reactant in a process that we referred to as the “H₂S process”. The high surface area “WS₂ fins” were synthesized using a H₂ diluted H₂S plasma as the PEALD co-reactant in a process that we referred to as the “H₂ + H₂S process”. For both processes, the best HER performance was obtained for WS₂ films deposited with ~100 PEALD cycles reaching ~8 nm in thickness. In this work, various process configurations were studied for HER activity by combining the above two PEALD processes sequentially. For convenience, 100 cycles of the H₂S and H₂ + H₂S processes have been designated as configurations A and B, respectively, and are considered the reference processes relative to the combined configurations (e.g. A on B). The A and B configurations acted as the building blocks to create the combined catalyst-template film configurations described in this work. Both sets of possible combined configurations *i.e.*, A on B and B on A, were studied. Of the combined configurations, the deposition of edge-enriched WS₂ nanoflakes (A) over the high surface area template (B) was the configuration expected to most significantly improve HER performance.

II. EXPERIMENT

The WS₂ films were deposited in a commercial FlexAL ALD reactor from Oxford instruments. The ALD reaction chamber consists of a 240 mm substrate table, a turbo molecular pump that enables a base pressure of 10⁻⁶ Torr, and an inductively coupled plasma (ICP) source. The chamber wall temperature was set to 150 °C and the substrate table temperature was set to 300 °C.¹⁵ In the H₂S process, the WS₂ films were deposited using the bis(*tert*-butylimido)bis(dimethylamido)tungsten precursor and a H₂S plasma as the W and S source, respectively. In the H₂ + H₂S process, the same metal precursor was used in combination with a H₂ + H₂S plasma to deposit WS₂ films. For both processes, the following PEALD step sequence was adopted: 10 s precursor dosing, 10 s purge, 3 s pre-plasma time, 30 s plasma exposure (plasma power = 500 W), and 15 s purge. Further details regarding the PEALD

processes can be found in our earlier work.^{15,16} A probe-corrected JEOL JEM-ARM200F TEM operated at 80 kV was utilized to obtain high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images. For STEM studies, WS₂ films were deposited on Si₃N₄ windows coated with 5 nm of ALD SiO₂. The film composition was determined using Rutherford backscattering spectroscopy (RBS). RBS measurements were performed at Detect 99, Eindhoven, The Netherlands, using a 2000 keV He⁺ beam. Estimating the accurate thicknesses and growth rates for the combined configurations (A on B, B on A etc,) using techniques such as ellipsometry, turned out to be complicated due to the uneven surfaces. We are improving our modelling of ellipsometry data for such combined configurations and the results will be discussed in a separate study. To give an impression about the thicknesses, the authors can comment that the thickness of configuration A on B is in between that of configuration A (~8 nm) and 2A (~16 nm). This comment can be made based on the initial thickness values obtained and the morphology evolution of the combined configurations that we have hypothesized in Figure 2.

A standard three-electrode cell set-up connected to an AUTOLAB potentiostat (model PGSTAT302N) was used to perform electrochemical measurements. PEALD WS₂ films deposited on glassy carbon substrates were used as the working electrodes. A saturated calomel electrode (Hg/Hg₂Cl₂ in saturated KCl) and a Pt wire were used as the reference and counter electrodes, respectively. All linear sweep voltammetry (LSV) measurements were carried out in (100 mL, 0.5 M) H₂SO₄ electrolyte using a scan rate of 50 mV/s. The working electrodes were rotated at 800 rpm during the LSV measurements. The number of active sites for HER were evaluated using copper underpotential deposition (Cu-UPD measurements) using the method described in our earlier work.¹⁵ All Cu-UPD measurements were carried out at a linear voltammetric scan rate of 50 mV/s in (0.1 M) H₂SO₄ and (0.002 M) CuSO₄ solution. Background correction was carried out by subtracting the charges obtained from the electrode

in (0.1 M) H_2SO_4 (cupric ions free) from the charges obtained for Cu stripping in (0.002 M) CuSO_4 solution.

III. RESULTS AND DISCUSSION

Figure 1. Top-view HAADF-STEM images (a-e) of WS_2 electrocatalyst films with various process configurations. Reference configurations A and B correspond to 100 cycles of deposition using H_2S and $\text{H}_2 + \text{H}_2\text{S}$ PEALD processes, respectively.

Top-view HAADF-STEM images of WS_2 films obtained from the reference (Figure 1 a,b) and combined process configurations (Figure 1c-e) depicting the morphological variation are shown in Figure 1. Figure 1(a) shows the edge-enriched reference configuration A (WS_2 nanoflakes) that is catalytically superior to the high surface area reference configuration B (WS_2 fins) in Figure 1(b). These two reference configurations appear quite different in surface morphology. Both configurations show a high contrast between the flakes and fins (bright features). Configuration A possesses much wider flakes, whereas configuration B has much thinner fins. These differences contribute to the overall density of the films and the number of exposed sites for catalysis. Previously,¹⁵ we observed that for both the configurations (A and B) the WS_2 layers initially grew laterally (basal-plane parallel to surface) and, then predominantly grew the vertical growth direction (forming ‘flakes and fins’) after ~ 4 nm or 60 PEALD cycles (Figure S1). The images in Figure 1(a-b) are obtained after ~ 8 nm or 100 PEALD cycles *i.e.*, after layers start to predominantly grow along the vertical growth direction.

Figure 1(c-e) show top-view HAADF-STEM images of the films with various combined configurations. These images highlight the variation in morphology when changing the configuration (e.g., A on B) and the number of PEALD cycles (the thickness of the top layer). As seen in Figure 1(c), deposition of A on B results in broadening of the fin structures remaining from the initial configuration B. This results in the film appearing more closed and implies an increase in the overall film density. Doubling the number of PEALD cycles of configuration A, *i.e.*, 200 PEALD cycles of A on B — 2A on B, led to further broadening of the fins and film densification (Figure 1d). Thus, the addition of A on B (Figure 1c-d) contributed to the overall densification of these catalyst-template configurations. Additionally, the images in Figure 1(c-d) appear similar to 32 nm films of A from (Figure S1). Cross-sectional imaging of the 32 nm films revealed a high density of edge-sites exposed on the top-surface, which was crucial for high HER activity.¹⁵ In this work, further increasing the number of PEALD cycles of configuration A (e.g., 4A on B), led to continued fin broadening (Figure S2) and further densification of the film.

A HAADF-STEM image of the reversed configuration B on A is shown in Figure 1(e). This process configuration appears to sharpen rather than broaden the fins remaining from process A as observed in the high prevalence of thin, bright lines on the tops of the fin structures from A. The B on A process appears to possess a higher film density than the reference B process, but a lower density than the A on B configuration.

Figure 2. Schematic illustration showing the evolution of individual configurations (a) A and (b) B into combined configurations (c,d) A on B and (e,f) B on A, respectively.

The hypothesized morphological evolution between configurations can be better understood from the schematic shown in Figure 2. Configurations A and B are represented in Figure 2(a) and 2(b), respectively, showing the various feature shapes (fins and flakes) extrapolated from Figure 1(a) and 1(b). The feature shapes of configurations A and B can be seen in the cross-sectional imaging in Figure S1. With the addition of configuration A on B, we predict that new horizontal and vertical growth occur starting after a few PEALD cycles of A as shown in Figure 2(c). With increasing PEALD cycles of A (Figure 2d) more vertical layers are added in line with the results observed in our previous work.¹⁵ The addition of vertical layers broadens the underlying fins from configuration B, causing a densification of the film. This results in a shift in the surface morphology to one more closely resembling that of configuration A (Figure 2a). Such a shift in surface growth can explain the surface morphology variation observed in Figure 1(c) and 1(d). This shift in surface morphology from B to A should create a higher number of exposed edge-sites resulting in increased HER activity.

A contrasting shift in surface morphology is expected with the addition of configuration B to A, Figure 2(e) and 2(f). With the addition of H₂ to the H₂S plasma in configuration B, we predict that the more uniform flakes from configuration A begin to taper and more closely resemble configuration B after a few PEALD cycles of B (Figure 2e). Tapering of the nanoflakes is mostly due to accelerated growth on sulfur-deficient surfaces and etching effects induced by the hydrogen diluted H₂S plasma (*i.e.*, H₂ + H₂S plasma).¹⁵ Continued deposition of configuration B leads to significantly tapered fin growth and relatively slow basal plane deposition, Figure 2(f). The tapering of the existing fins should increase the number of exposed edge-sites quite slowly when compared to densification of edge-exposing layers of the A on B configuration. This prediction is supported by Figure 1(e) which shows sharp fin centres and a more open surface morphology than for the A on B configurations (Figure 1b-c).

Table 1. Stoichiometry ratios (S:W) of WS₂ films for various configurations as-deduced from RBS measurements.

Configuration	S:W
A	2.2±0.1
A on B	2.0±0.1
B on A	1.9±0.1
B	1.8±0.1

With the observed shifts in surface morphology, we would also expect variations in the stoichiometry owing to the different plasmas used in A and B PEALD processes. We have previously¹⁵ shown that configurations A and B vary in stoichiometry (also shown in Table 1 here). Rutherford Backscattering spectroscopy (RBS) studies established the following S to W ratios for configurations A and B: process A yielded S-rich films with S:W=2.2, whereas process B yielded S-deficient films with S:W=1.8.¹⁵ In that study, we also related stoichiometry

to the growth and morphology for the reference A and B configurations making it an important parameter for HER activity.¹⁵

Our current RBS studies revealed that the addition of an A or B configuration to the top of each film yielded stoichiometric variation. The A on B configuration yielded overall stoichiometric films (S:W=2). On the other hand, configuration B on A resulted in the growth of slightly sub-stoichiometric films overall (S:W=1.9). It is possible, however, that the stoichiometry varies along the normal to the growth surface with configuration variation. As RBS is a bulk measurement technique, these values may represent an average of the two distinct regions as opposed to a compositionally homogeneous film. The A on B configuration may represent this stoichiometric stratification when comparing the measured stoichiometry to an average of the two reference processes. Some top configuration influence, however, can be seen on the framework in the B on A configuration for example. The slightly sub-stoichiometric nature of the B on A films shows that some etching of S atoms from the top layers of configuration A occurs resulting in a stoichiometry slightly below 2.

Considering the morphological and stoichiometry changes with configuration, it appears that the configuration order of the two combined processes (A on B and B on A) is highly significant. Configuration A appears to grow on the B framework in a manner closely resembling the growth of configuration A and leads to an overall stoichiometric composition for the combined A on B configuration. Conversely, configuration B can have a S etching component on the A framework resulting in a surface morphology more closely resembling process B and an average composition that is similar to, yet less than, the combined A on B process.

Figure 3. (a) Cathodic polarization curves (LSV) and (b) corresponding Tafel plots for the WS₂ films with configurations A on B (blue), 2A on B (red), and B on A (black).

Table 2. Figures of Merit for the HER performance of WS₂ films of various configuration: (1) overpotential required to reach a current density of 10 mA per geometric area (η_{10}) and (2) Tafel slope. The number of sites per geometric area (cm²) determined from Cu-UPD measurements for the WS₂ films are also shown. The figures of merit reported here for configurations A and B are adapted from our previous work (*Chem. Mater.* 2019, 31, 14, 5104–5115)¹⁵ with permission from American Chemical Society (ACS). Further permission related to the data in the table excerpted should be directed to the ACS (<https://pubs.acs.org/doi/abs/10.1021/acs.chemmater.9b01008>).

Configuration	η_{10} (mV)	Tafel slope (mV/decade)	No. of sites per cm ²
A	-394	122	5.6×10^{15}
A on B	-393	134	1.5×10^{15}
2A on B	-360	128	1.3×10^{15}
B on A	-538	135	5.0×10^{14}
B	-461	129	3.7×10^{14}

With the material property changes from process variation investigated, the HER performance and figures of merit were evaluated for the WS₂ films with various configurations. The HER performance was tested using linear sweep voltammetry (LSV) as shown in Figure 3(a). The

overpotential required to reach a cathodic current density of 10 mA per geometric area (η_{10}) was compared for the various configurations (Table 2). As seen from Table 2, configuration A on B exhibits a similar η_{10} of ~ -394 mV as reference configuration A, suggesting a similar HER performance. This η_{10} supports the growth pathway hypothesized in Figure 2 for the A on B configuration that results in a surface morphology similar to that of configuration A. Interestingly, configuration 2A on B exhibited a lower η_{10} of ~ -360 mV indicating that a better HER performance is achieved when the top A configuration is doubled in the number of PEALD cycles. The increase in HER performance may be attributed to the implementation of a high surface area framework (configuration B) with a more HER active surface morphology (configuration A). Further increasing the number of cycles for configuration A [*i.e.*, 3A on B (300 PEALD cycles of A on 100 cycles of B)], however, resulted in an increase in η_{10} (to ~ -420 mV) signifying a decrease in the HER performance. This decrease in performance with increasing film thickness can be a consequence of a lower number of sites exposed due to a crowding effect of vertical and obliquely aligned layers.¹⁵ Also, thicker films have been reported to offer a higher impedance for charger transfer, possibly contributing to the decrease in HER performance.^{17,18} The reverse configuration (B on A) resulted in a significant increase in the η_{10} to ~ -538 mV (Table 2). This decrease in performance most likely arises from the tapering effects which limit the number of exposed sites. These results show that the addition of configuration A to a B framework increases the HER performance and reaches an optimal activity before the performance degrades beyond 200 PEALD cycles of configuration A. The addition of configuration B to an A framework, however, had the opposite effect, decreasing the HER activity. Additionally, the Tafel slopes for the A on B, 2A on B, and B on A configurations were determined to be 134, 128, and 135 mV/decade, respectively, suggesting that the Volmer reaction was the rate-determining step for HER in all three films.^{17,19}

To help further rationalize the HER activity variations, copper underpotential deposition (Cu-UPD) was used to evaluate the number of active sites. The number of active sites was determined to be significantly higher for the A on B and 2A on B configurations ($\sim 10^{15}$ sites per cm^2) when compared to the opposite B on A configuration ($\sim 10^{14}$ sites per cm^2), see Table 2. The higher number of active sites can help explain the lower η_{10} (better HER performance) for the A on B configurations relative to B on A configuration and this correlation is similar to our previous results comparing process A to process B.¹⁵ When comparing the A on B configurations to reference configuration A, however, a seemingly anomalous behaviour is observed. The number of active sites for configurations A on B (1.5×10^{15} sites per cm^2) and 2A on B (1.3×10^{15} sites per cm^2) were both lower than the number of sites for configuration A (5.6×10^{15} sites per cm^2).¹⁵ However, the films with combined configuration possessed comparable and lower η_{10} values, respectively. This suggests that the comparable and better HER performance observed for the A on B and 2A on B configurations, respectively, does not primarily arise from an increase in active sites related to edge-site density. Electrochemical impedance can also influence the HER performance in addition to the density of active sites. However, the electrochemical impedance spectra were observed to be similar for all of these configurations (A, A on B on and 2A on B - Figure S3). It could be possible that the Cu-UPD measurements underestimate the number of active sites for configurations A on B and 2A on B. This underestimation can arise from various factors including the accessibility of the sites for Cu adsorption, clustering of Cu atoms *etc.*, however, detailed investigations are needed on this aspect to understand it better.

Although the overpotential for configuration 2A on B was significantly better compared to other configurations, the overpotential value (~ -360 mV) is relatively higher compared to other literature reports for WS_2 .^{20,21} The Tafel slopes are also on the higher side although they fall into the same category for determining the Volmer reaction as the rate-determining step. The

HER performance of our WS₂ films appears to be limited by the relatively high electrochemical impedance as the number of edge sites are comparable and/or slightly higher (depending on the configuration) to those reported in the literature.⁸ This provides further scope for improving the HER performance of WS₂ films by enhancing the intrinsic conductivity of the WS₂ films through doping, which could also be achieved by ALD.

IV. CONCLUSIONS

Using PEALD, we synthesized edge-enriched WS₂ electrocatalysts (A) on PEALD grown high surface area WS₂ framework (B). It was observed that the combined catalyst and framework configuration (A on B) showed improvements in HER performance compared to the individual components. We found that the surface morphology of this catalyst-template system depended strongly on the PEALD process used to synthesize the electrocatalyst layer (top layer). Additionally, an increase in the thickness of the catalyst layer led to a further improvement in the HER performance. These results demonstrate that PEALD is a suitable technique for synthesizing edge-enriched WS₂ catalyst-template systems for HER applications. We believe that this facile approach can be extended to other TMD-based electrocatalyst systems due to the growth similarities amongst these materials.

ACKNOWLEDGEMENTS

This work has been funded by the European Research Council (grant agreement no. 648787-ALDof2DTMDs). The authors acknowledge the technical support offered by M.

Dijstelbloem, C. van Helvoirt and J. van Gerwen. Solliance and the Dutch province of Noord-Brabant are acknowledged for funding the TEM facility. Beatriz Barcones is acknowledged for the FIB preparation of the TEM samples.

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