ISGC 2022

N°822 / OC
TOPIC(s) : Energy

Surface organometallic chemistry for ALD growth of ultra-thin films of WS2 and their photo(electro)catalytic performances

AUTHORS

Medet ZHUKUSH / IRCELYON, 2 AVENUE ALBERT EINSTEIN, VILLEURBANNE
Clément CAMP / CPE LYON, 3 RUE VICTOR GRIGNARD, VILLEURBANNE
Siglinda PERATHONER / UNIVERSITY OF MESSINA, CONTRADA DI DIO, MESSINA
Claudio AMPELLI / UNIVERSITY OF MESSINA, CONTRADA DI DIO, MESSINA
Jules GALIPAUD / ÉCOLE CENTRALE DE LYON, 36 AV. GUY DE COLLONGUE, ÉCULLY
Corresponding author : Elsje Alessandra QUADRELLI / alessandra.quadrelli@cpe.fr

PURPOSE OF THE ABSTRACT

Elongated nanostructures with a high-aspect-ratio are known to strike a balance between large surface area and minimized charge recombination in energy conversion applications.[1] Their surface functionalization with a thin catalytic layer can significantly enhance their performance. Atomic Layer Deposition (ALD) is an established method for achieving uniform coating of high-aspect-ratio surfaces with a conformal thin to ultra-thin film. ALD is based on the succession of two (or more) different self-limiting surface reactions. Understanding the surface chemistry during ALD growth, especially in the first cycles, is important for proper selection of suitable precursors, avoidance of undesired by-products, optimization of deposition conditions as well as film quality when ultra-thin films are targeted.[1]

We here introduce a methodology of studying the surface chemistry of an ALD growth of WS2 via modeling the deposition reactions by molecular compounds in solution and on the surface of high-surface-area 3D-type substrates. The molecular model part of this method is inspired by Surface Organometallic Chemistry (SOMC),[2] which brings a large range of spectroscopic and analytic tools to gain insight into the mechanism of ALD reactions, as recently shown by our group on ulktra thin film MoS2 growth.[3]
Bis(tert-butylimido)bis(dimethylamido)tungsten (VI) (BTBMW) and 1,2-ethanedithiol (EDT) served as tungsten and sulfur precursors, respectively. BTBMW was chosen as a tungsten precursor as there was a precedent in the literature (in collaboration with us) showing successful ALD growth of WS2 while coupling with H2S.[4] EDT is an interesting sulfur alternative to H2S and provides a robust analytic handle for the molecular level monitoring of the reaction at each half-cycle. Replication of the surface chemistry in solution using a silica model, triphenylsilanol (Ph3SiOH), as well as on high-surface-area 3D silica powder as a model of silicon wafer[5,6] adds complementary molecular precision in the ALD modeling. All results are compared and contrasted with the complement XPS and Raman studies that are conducted on wafers, silica powders and triphenylsiloxy derivatives, en route to molecular level comprehension of the very first stages of WS2 growth from W (VI) precursor.
The developed ALD growth method was applied onto (semi)conducting 2D substrates like a Ti disk coated with photoactive TiO2 nanotubes. Then, the ALD-modified and pristine Ti disks were measured in photocurrent production tests.

FIGURES

FIGURE 1

Scheme of Atomic Layer Deposition

An ALD cycle (including the very first pulse on a pristine substrate) using W(=Nt-Bu)2(NMe2)2 and HSCH2CH2SH as tungsten and sulfur precursors, respectively. Insert: starting substrate anatase/rutile TiO2 nanotubes electrochemically grown on Ti disk surfa

FIGURE 2

Final WS2@TiO2/Ti

SEM micrograph of ALD-modified surface

KEYWORDS

Atomic Layer Deposition | Surface Organometallic Chemistry | Tungsten disulfide | Vapor deposition

BIBLIOGRAPHY

[1] J. Bachmann, Beilstein Journal of Nanotechnology vol. 2014, 5, 245–248.
[2] C. Copéret et al., Chem. Rev. 2016, 116, 323–421.
[3] S. Cadot et al., Nanoscale 2017, 9, 538–546.
[4] Y. Wu et al. Chem. Mater. 2019, 31, 1881–1890.
[5] O. Sneh et al., J. Phys. Chem. 1995, 99, 4639–4647.
[6] L. Nyns et al., ECS Trans. 2019, 16, 257–267.