Applied Surface Science 392 (2017) 231–243

Contents lists available at ScienceDirect

Applied Surface Science

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

Interfacial engineering of two-dimensional nano-structured materials by atomic layer deposition

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ARTICLE INFO

Article history:
Received 4 May 2016
Received in revised form 18 August 2016
Accepted 11 September 2016
Available online 12 September 2016

Keywords:
Atomic layer deposition (ALD)
Two-dimensional nano-materials
Nano-architecture

ABSTRACT

Atomic Layer Deposition (ALD) is an enabling technology which provides coating and material features with significant advantages compared to other existing techniques for depositing precise nanometer-thin two-dimensional (2D) nanostructures. It is a cyclic process which relies on sequential self-terminating reactions between gas phase precursor molecules and a solid surface. ALD is especially advantageous when the film quality or thickness is critical, offering ultra-high aspect ratios. ALD provides digital thickness control to the atomic level by depositing film one atomic layer at a time, as well as pinhole-free films even over a very large and complex areas. Digital control extends to sandwiches, hetero-structures, nano-laminates, metal oxides, graded index layers and doping, and it is perfect for conformal coating and challenging 2D electrodes for various functional devices. The technique's capabilities are presented on the example of ALD-developed ultra-thin 2D tungsten oxide (WO_3) over the large area of standard 4" Si substrates. The discussed advantages of ALD enable and endorse the employment of this technique for the development of hetero-nanostructure 2D semiconductors with unique properties.

1. Introduction

The next generation of the state-of-the art electronic and advanced functional devices most likely will be based on 2D nano-materials. This is because ultra-thin 2D nano-materials possess unique structural features and outstanding properties such as ultra-high carrier mobility at room temperature ($\sim$1100 cm^{2}V^{-1} s^{-1} for 2D MoO_3) [1], outstanding optical transparency, large specific surface area and an excellent thermal conductivity [2]. They usually have thickness from one to few fundamental layers, which varies from $\sim$0.7 to $\sim$10.0 nm. Moreover, ultrathin 2D semiconductors also possess the great mechanical properties owing to the atomic thickness and in-plane covalent bonding. Combination of large lateral size, atomic thickness with ultra-high specific surface area is highly essential and desirable for many surface-based applications such as photo-catalysis, electro-catalysis, energy storage and conversion, various sensors and super-capacitors. In these applications the high specific surface area is critical parameter for obtaining outstanding properties. 2D nano-materials therefore have already become a key class of materials in condensed matter physics, chemistry and materials science. So far the improvement of their functional capabilities has been achieved by for the following scientific approaches [1–5]:

- Search for new and/or modified nano-materials with superior properties for advanced functional devices [6,7];
- Nano-architecturing the matrix of sandwich 2D nano-materials [2,8–12];
- Development of complex 2D nano-materials, including doped semiconductor nano-structures enabled optimization of the phase composition [13–18];
- Search, design and implementation of new fabrication techniques for making defect-free 2D nano-materials, providing control of their thickness, size and shape of nano-grains [19–23];
- Optimization of the existing technologies for fabrication 2D nano-crystals including improvement in existing methods of surface and post-deposition treatments [12,24–28];
- Surface modification and functionalization of the nano-architectured 2D structures through introduction of the

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http://dx.doi.org/10.1016/j.apsusc.2016.09.040
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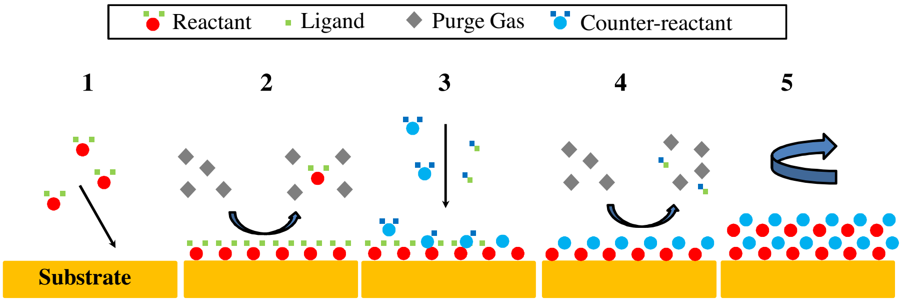

Fig. 1. Schematic view of the one cycle for a binary material in an ALD reaction.

catalytically active dopants, including nanostructured noble materials and semiconductors [29–43];

- Implementation of 1D [21,44,45] and 2D [46–53] nano-structured semiconductors and combination thereof for the development of tailored 3D nano-materials with special capabilities and properties.

It has to be admitted that the considerable efforts towards optimization of synthesis, deposition techniques and functionalities of 2D nano-materials have already resulted in essential improvements of their functional capabilities, which were supported by various publications [1,4,6,9,20,21,34,35,40,44–46,54]. In addition, during last few years the latest development in science of 2D nano-materials aims at trying to merge physical and/or chemical characteristics of individual nano-particles and nano-components into a balanced intermediate. This has been achieved through the controlled synthesis techniques developed by modern science. In this regard a wide variety of fabrication methods are available to produce nano-architectured 2D structures. However, most of them are solution-based including sol–gel [55], virus-based self-assembly [56], electrochemical deposition [57], foams and colloids [58] and aerogels [59]. In addition, chemical vapour deposition (CVD) [60] and molecular layer deposition [61] are also were widely used.

Nevertheless, many of the above-mentioned methods have inherent limitations due to the fact that they are solution-based, which can introduce solution screening, especially in high aspect ratio structures and nano-porous materials, solubility and temperature limitations. Notwithstanding great achievements in implementation of these methods, ALD, as an alternative technique, can lead to a wider variety of hybrid organic/inorganic 2D nano-materials with new and/or altered properties when compared to the individual or parent components.

Although ALD can provide great advantages in the development of 2D nano-structures, unfortunately, this method has often been overlooked in regard to the efficient tailoring of the set parameters of 2D nano-structures for such applications as photo-detectors, flexible electronics, solar cells, catalysts, displays, smart windows and various chemical and biological sensors. Therefore, we try to overlap the gap between ALD advantages in general and the existing underestimation of its functional capabilities, including surface functionalization, which ALD can contribute towards the interfacial engineering of 2D nano-materials. Thus, we are confident that topics covered by this mini-review might be of interest for researchers working in various fields.

2. ALD as an emerging deposition technology for 2D nano-materials

ALD is a cyclic vapour-phase deposition process that take advantage of temporally separated and self-limiting reactions of two or more reactive precursors. This is an advanced process for depositing ultra-thin films one atomic layer at a time. Fig. 1 broadly classified the schematic interpretation of the one cycle for a binary material in an ALD reaction [62]. In general, ALD can be presented as *pulse-purge-pulse-purge* cycle, as two precursors involved into the process. Initially, a reactant is dosed into the chamber (step 1: *pulse*). The reactant chemisorbs to the substrate, but does not react with other molecules of the same reactant. Once a monolayer of the reactant has been formed, the excess reactant is purged from the chamber with an inert gas such as N_2, Ar or other precursor such as H_2O (step 2: *purge*). The counter reactant is then pulsed into the chamber, where it reacts with the layer of original reactant on the substrate (step 3: *pulse*). Once the surface becomes saturated with the counter-reactant, the excess counter-reactant is purged from the chamber (step 4: *purge*). The surface is now primed for a new layer of reactant. Then this process is repeated until the desired thickness is achieved (step 5). In most cases, a complete monolayer is not deposited even when the surface is completely saturated with precursor due to various reasons such as hindrance from the precursor's ligands [63,64].

Usually a monolayer's thickness is dependent on the reactivity of the precursor with the surface. This results in a unique self-limiting growth mechanism with a number of advantageous features, such as excellent uniformity and simple and accurate film thickness control. The ALD technique offers unprecedented control of quality, thickness and material properties of monolayer films that are extremely "thin". One of the features of ALD technology that distinguishes it from other thin film deposition methods, is its self-limiting nature. The chemistry is such that entire surface is reacted to completion, disallowing further reactions to continue to take place. This clean and precise self-limiting feature is what enables the film's superior conformal coverage and quality. Thus, in case of ultra-thin film requirements, ALD is considered as a better choice over other deposition processes [65].

ALD was originally developed in the 1970s under the name atomic layer epitaxy (ALE) by Suntola et al. to deposit ZnS for electroluminescent displays, with the first commercial device operating in the Helsinki airport from 1983 to 1998 [66]. The more common acronym "ALD" was not widely adopted until the early 2000s as the semiconductor industry began to develop high-k (for example, HfO_2) dielectrics with the technique.

Detailed description of the recent development in ALD chemistry [60,67] and specific features covering the details of the surface chemistry for ALD [68,69] were accompanied by the wide variety of metal organic precursors [70,71], the available noble metal processes [72], the fabrication of nano-materials [73–75], reactions with polymer substrates [76] and functionalization of nano-particles [77]. Table 1 provides general overview of the existing thin-film fabrication techniques and rated for their capabilities. Considering information presented in Table 1, it is clear that ALD method has significant advantages over the other deposition techniques in terms of deposition process itself and control over various parameters of fabrication. However, poor deposition rate may be