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Ultra-thin MoO_3 film goes wafer-scaled nano-architectonics by atomic layer deposition

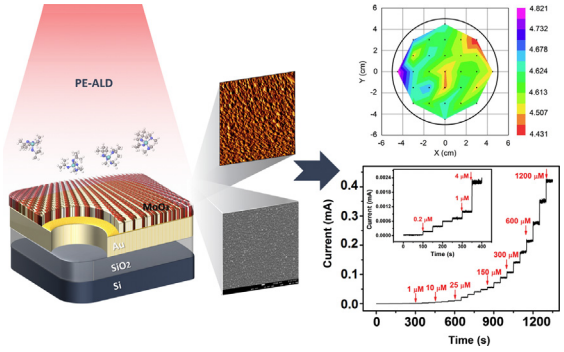
Hongyan Xu [a], Mohammad Karbalaei Akbari [b,c,*], Zhenyin Hai [b,c], Zihan Wei [b,c], Lachlan Hyde [d], Francis Verpoort [b,e,f], Chenyang Xue [g], Serge Zhuiykov [a,b,**]

[a] School of Materials Science and Engineering, North University of China, Taiyuan, PR China
[b] Ghent University Global Campus, Yeonsu-gu, Incheon 21985, South Korea
[c] Faculty of Bioscience Engineering, Ghent University, Coupure Links 653, Ghent 9000, Belgium
[d] Swinburne University, John St., Hawthorn, Melbourne, VIC 3122, Australia
[e] National Research Tomsk Polytechnic University, Lenin Avenue 30, 634050 Tomsk, Russian Federation
[f] Laboratory of Organometallics, Catalysis and Ordered Materials, State Key Laboratory of Advanced Technology for Materials Synthesis and Processing; Center for Chemical and Material Engineering, Wuhan University of Technology, Wuhan, PR China
[g] Key Laboratory of Instrumentation Science and Dynamic Measurement of Ministry of Education, North University of China, Taiyuan, PR China

HIGHLIGHTS

- Ultra-thin MoO_3 film over granular Au substrate is fabricated by PE-ALD at 250 °C.
- $C_{12}H_{30}N_4Mo$ and O_2 plasma are used as molybdenum precursor and oxygen source.
- The crystalline structure of MoO_3 nano-film is confirmed by Raman, FTIR and XPS.
- The MoO_3-based sensor shows wide linear range of 0.2 μM–1200 μM towards N_2H_4.

GRAPHICAL ABSTRACT



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ABSTRACT

From the technical and design points of view, it is quite difficult to maintain the integrity of nano-films during the deposition process to fabricate practical devices based on ultra-thin semiconductor films. Thus, defect-free wafer-scaled development of ultra-thin quasi two-dimensional (2D) oxide semiconductor films represents serious challenges. Plasma-enhanced atomic layer deposition (PE-ALD) made it possible to fabricate ultra-thin MoO_3 nano-films (4.6 nm) over the wafer-scaled granular Au electrode. The detailed ALD recipe for ultra-thin MoO_3 film was established and verified. The $C_{12}H_{30}N_4Mo$ and O_2 plasma were used as Mo precursor and oxygen source, respectively. The growth of crystalline phases was observed when the ALD temperature of 250 °C was employed. Higher ALD temperature resulted in an increase of growth rate over Au substrate (1.21 Å/cycle). The precise recipe design enabled the scalable fabrication of environmental sensors based on ultra-thin MoO_3 films with precise thickness controllability. Electrochemical sensors based on the fabricated MoO_3 nanostructures demonstrated reliable performance to hydrazine (N_2H_4) detection.

* Corresponding author at: Faculty of Bioscience Engineering, Ghent University, Coupure Links 653, Ghent 9000, Belgium.
** Corresponding author at: School of Materials Science and Engineering, North University of China, Taiyuan, PR China.
E-mail addresses: Mohammad.Akbari@ugent.be, (M.K. Akbari), Serge.Zhuiykov@ugent.be. (S. Zhuiykov).

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1. Introduction

To take advantages of newly-developed ultra-thin semiconductor films it is vital to incorporate these advanced nanomaterials onto mechanically stable, electronically conductive and chemically inert substrates [1]. The conformal deposition of few-layered oxide semiconductors over the metallic substrate is a recognized strategy to study the properties of quasi-2D oxide materials [2]. This ultra-thin film of oxide semiconductors can be considered as quasi-2D materials since the thickness of films is even smaller than the thickness of several 2D nanostructures reported previously [3]. So far, the inert metals of group Ib (Cu, Ag, Au) are the main candidates used as substrate for the deposition of ultra-thin few-layered oxide films. These metal substrates provide conformal platforms for development of versatile and stable devices for electronic, catalytic and sensing applications without altering the major characteristics of these nano-materials [2]. MoO_3 is an attractive high-*k* transition metal oxide that has been utilized in several applications including the heterogeneous catalysis [4], pseudo- [5] and supercapacitance [6], ion batteries [7], electrochemical electrodes [8], nanocomposite thermites [9], anode buffer layer for organic photovoltaics [10] and high-*k* oxide hetero-structures [11]. The motivation behind the concept of development of such ultra-thin quasi-2D oxides is attributed to unprecedented properties of these nanostructures originated from the 2D confinement and alteration of their surface activity [12]. Furthermore, the ultra-thin films of high-*k* materials can be used in various applications in which the ultra-thin insulating layers act as the main component of devices [13]. However, the most announced research activities are focused on evaluation of properties of nanostructures with the micron-sized length, synthesized either by mechanical or chemical exfoliation techniques [14] or by chemical or physical vapor deposition (CVD or PVD, respectively) [15,16]. However, these techniques experience serious challenges to successfully attain the defect-free wafer-scaled conformal deposition of ultra-thin films over the surfaces which are not smooth enough or when the substrates contains geometrical complexity [17]. Therefore, the exploration of alternative methods for design and versatile fabrication of high-performance devices is vital to fulfill the ambition of using these novel materials in everyday applications.

ALD, as an alternative to CVD, is a deposition technique based on self-limiting, self-saturated reactions, in which the precursors are introduced sequentially into the reaction chamber and typically separated in time by the inert gas purge [18]. At each individual step, a precursor is pulsed into the reaction chamber and saturates the surface by monolayer of that precursor [19]. Therefore, the chemical reactions are limited to the absorbed monolayer on surface. This step-by-step self-limiting nature of ALD cyclic mechanism facilitates the accurate control of the film thickness over the wafer-scaled substrate and guarantees the conformal deposition of thin films with high-aspect ratio dimensions [20]. Furthermore, ALD reactions take place at lower temperature ranges facilitating the deposition of ultra-thin films over the flexible substrate for applications in the flexible electronics and sensor devices [21]. These advantages placed ALD in a position to address the challenges faced during deposition of ultra-thin oxide materials.

As far as practical applications are concerned, the wafer-scaled development of ultra-thin quasi-2D oxide films would be more challenging. Hence, the conformal wafer-scaled ALD fabrication of ultra-thin oxide nanostructures with just a few nanometer thickness requires the precise design of ALD recipe and the appropriate selection of suitable precursors [22]. For example, $Mo(CO)_6$ was previously used as Mo precursor for ALD development of MoO_3 [23]. However, the thermal stability of $Mo(CO)_6$ was limited to very narrow ALD window of 152-172 °C to avoid the thermal decomposition [23]. There is also the risk of C and N contamination in nano-films due to insufficient thermal energy for fully oxidization of hexacarbonyl precursors, recognized as undesired phenomenon in the ALD process at lower deposition temperatures [24].

There was another proposed strategy to fabricate MoO_3 nano-films in which the primary Mo films were oxidized by subsequent UV/ozone exposure during the post treatment to achieve the fully oxidized MoO_3 films [10]. However, the two-step nature of this process and the employment of the halide precursor are considered as the deficiencies of this approach. Recently, successful deposition of sub-stoichiometric MoO_3 nano-film over the SiO_2 substrate was achieved by using bis (tert-butylimido)-bis(dimethylamido) molybdenum, $(N^tBu)_2(NMe_2)_2Mo$, as the metalorganic precursor in much wider ALD temperatures window of 50–350 °C [24,25]. Nevertheless, despite of all reported ALD approaches, to the best of our knowledge there is no published evidence about the wafer-scaled development of ultra-thin MoO_3 film with a few nanometer thickness over granular Au electrode focusing on fabrication of practical devices. Granular Au film acts as chemically and mechanically stable substrate for ultra-thin oxide films, providing electrical conductivity for measurements of film properties. From the practical point of view, using such advantages of Au substrate makes it possible to design and fabricate the devices based on ultra-thin oxide films [26].

In this study, the ALD recipe was designed, evaluated and improved after numerous trials and errors to achieve the conformal deposition of nano-thick MoO_3 films. The design and fabrication MoO_3-based electrodes were explained and the characterization of ultra-thin quasi-2D MoO_3 was thoroughly investigated. The developed ALD recipe is highly reproducible and the fabricated electrodes show stable detection performance. The electrochemical sensors based on ALD-developed MoO_3 nano-films demonstrated reliable sensitivity to hydrazine detection in aqueous environment. Thus, the creditability of the ALD technique as a versatile approach for fabrication of the ultra-thin oxide-based devices has been confirmed and reaffirmed.

2. Experimental section

The 4-inch Si/SiO_2 wafer (12 Ω/cm) was used as substrate, where the thickness of the native oxide was ~1.78 nm. The general fabrication process of ultra-thin MoO_3 electrodes is presented in (Table 1 in Ref. [27]). However, prior to deposition of MoO_3 thin-film, the additional ~110 nm thick SiO_2 insulating layer was applied on the Si wafers by plasma-enhanced chemical vapor deposition (CVD), (Oxford Instruments PLASMALAB 100). The resistance of wafers was measured before each deposition process (Table 2 in [27]). After that ~150 nm-thick nanostructured Au electrodes were fabricated using a custom made optical photo mask by electron beam evaporator (EBE) [Nanochrome II, Intlvac, USA)] (See Fig. 7 in [27]). The ALD of MoO_3 films was performed on Cambridge Nanotech ALD Fiji F200 apparatus using $C_{12}H_{30}N_4Mo$ (Strem Chemicals Inc., USA) as molybdenum precursor (See Fig. 1 in [27]) and O_2 plasma as oxygen source. The loading of precursors was performed in the glove-box to avoid oxygen and moisture contamination. Argon as the precursor carrier gas was used at the flow rate of 30 standard cubic centimeters per minute (sccm). To establish the optimal precursor dose and O_2 plasma duration for deposition of MoO_3 nano-films, several cases of deposition were performed at two ALD temperatures of 150 °C and 250 °C. To optimize the precursor pulse time and the O_2 plasma exposure time, the growth per cycle (GPC) was measured during ALD deposition. After each deposition cycle the variable angle in-situ spectroscopic ellipsometry measurements (J.A. Woollam M2000 DI) were carried out at the different incident angles (60°, 65°, 70°, 75°) over the wavelengths of 250–1690 nm to monitor the uniformity and to measure the thickness of the deposited MoO_3 films. The theoretical thickness of SiO_2 and MoO_3 nano-films was determined by fitting the data of spectroscopic ellipsometry using a multi-layer model (CompletEase) [28]. By measuring the GPC of MoO_3 film as the function of precursor dosing time (at constant plasma exposure time) the saturation curves of $(N^tBu)_2(NMe_2)_2Mo$ were extracted at various ALD temperatures. The same saturation curves for GPC of oxide film as the function of O_2 plasma exposure time was attained while the