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Wafer-scale two-dimensional ALD-developed α-MoO_3 for ultra-sensitive, stable and selective hydrogen peroxide sensing

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Abstract:
Two-dimensional (2D) wafer-scale α-MoO_3 films with thickness of 4.9 nm were fabricated via atomic layer deposition (ALD) technique. The developed MoO_3 films were composed of flat nanoparticles with the average size of about 35 nm and possessed layered orthorhombic phase (α-MoO_3). The electrochemical sensor based on these 2D α-MoO_3 films exhibited the greatest sensitivity of 168.72 $\mu A \cdot mM^{-1} \cdot cm^{-2}$ to hydrogen peroxide (H_2O_2) amongst all the others MoO_3 electrochemical sensors reported-to-date and presented extremely wide linear detection range of 0.4 μM - 57600 μM with the lowest detection limit of 0.038 μM at the signal to noise ratio of 3. Furthermore, due to extremely thin nature of 2D α-MoO_3 films ultra-fast response/recovery time was achieved with response/recovery time range of 0.45/0.5 s - 1.5/1.95 s under the concentration range of 0.4 μM - 50000 μM. Additionally, the superiority with great long-term stability, excellent selectivity and high reproducibility was also achieved among the different 2D α-MoO_3 samples. The 2D α-MoO_3 films fabricated via ALD technique in this work represent a great opportunity for development of the high-performance electrochemical sensors based on 2D transition metal oxides.

Key words: α-MoO_3, two-dimensional materials, atomic layer deposition, electrochemical sensing, hydrogen peroxide.

Introduction

The sensitive and selective measurement of H_2O_2 with high convenience and accuracy is of practical importance in biomedicine, food security, and environmental protection [1]. In various measurement techniques the non-enzymatic electrochemical detection method has been created and applied in numerous fields, owing to its unique merits like real-time detection, simplicity high sensitivity and low cost [2]. Over the past few years, 2D nano-materials have been proven to be highly desirable for the developing of excellent electrochemical sensor owing to their large surface-to-volume ratio, confined atomic thickness, special electronic and mechanical properties [3].

Among these 2D nanomaterials, molybdenum compounds have played a significant role and molybdenum trioxides (MoO_3) have shown intriguing physical and chemical properties, as well as exciting prospects for variety of applications [4]. However, to the best of our knowledge, the utilization of 2D MoO_3 nanomaterial for the fabrication of electrochemical H_2O_2 sensor has not yet been reported.

ALD technique is a surface controlled layer-by-layer process based on self-limiting chemical reactions and can deposit large-scale conformal dense nano-films with precise thickness and component control at the relatively low temperature [5]. Therefore, in this work, Ultra-thin α-MoO_3 films were deposited on the Si/SiO_2 wafers by ALD technique and their electrochemical behaviors for H_2O_2 detection were thoroughly investigated.

Experimental

Ultra-thin α-MoO_3 films were developed on the Au/Cr films deposited on Si/SiO_2 wafers (1 kΩ cm) by ALD technique using the cross flow reactor of Savannah S100 (Ultratech/Cambridge Nanotech) with $(NtBuN)_2(NMe_2)_2Mo$ and oxygen plasma gases as the molybdenum precursor and oxygen precursor, respectively. After many times test and optimization under various deposition temperatures ranging from 100 to 350 °C and different pulse duration and purge time, the wafer-scale ALD-fabricated 2D α-MoO_3 films

with thickness of 4.9 nm were developed. After the deposition, the wafers were diced into 1.0 x 1.0 cm pieces and the fabrication process was schematically presented in Fig. 1.

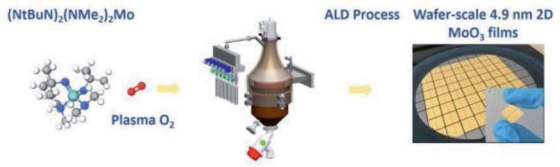

Fig. 1. Graphical scheme of the development of 2D α-MoO_3 films.

Results and Discussion

In order to evaluate the linear response range, sensitivity and the limit of detection of 2D α-MoO_3 films for the H_2O_2 detection, chronoamperometric measurements at various H_2O_2 concentrations were carried out. Fig. 2(a) shows the typical steady-state current-time (i-t) response plot with continuous addition of different concentration of H_2O_2 into the stirring phosphate buffered saline solution approximately every 50 s at the optimal oxidation potential of 0.5 V. As expect, well-defined stepwise increment in the current responses was observed upon the addition of H_2O_2. The linear detection to H_2O_2 range from 0.4 μM to 57.6 mM (correlation coefficient = 0.9991) of α-MoO_3 films calculated from the calibration curve (current versus concentration) was obtained in Fig. 2(b), which is an outstanding wide linear detection scale range from nanomolar to several millimolar. Besides, according to the equation of "*sensitivity=slope/surface of the electrode*" and "*low detection limit=3S_b/sensitivity*" [6], where S_b is the standard deviation of the blank signal, the 2D α-MoO_3 films showed the greatest sensitivity of 168.72 $\mu A \cdot mM^{-1} \cdot cm^{-2}$ with a low limit of detection of 0.038 μM at the signal to noise ratio of 3. The measured results demonstrated that the ALD-fabricated 2D α-MoO_3 films in this work are superior for extremely sensitive H_2O_2 detection.

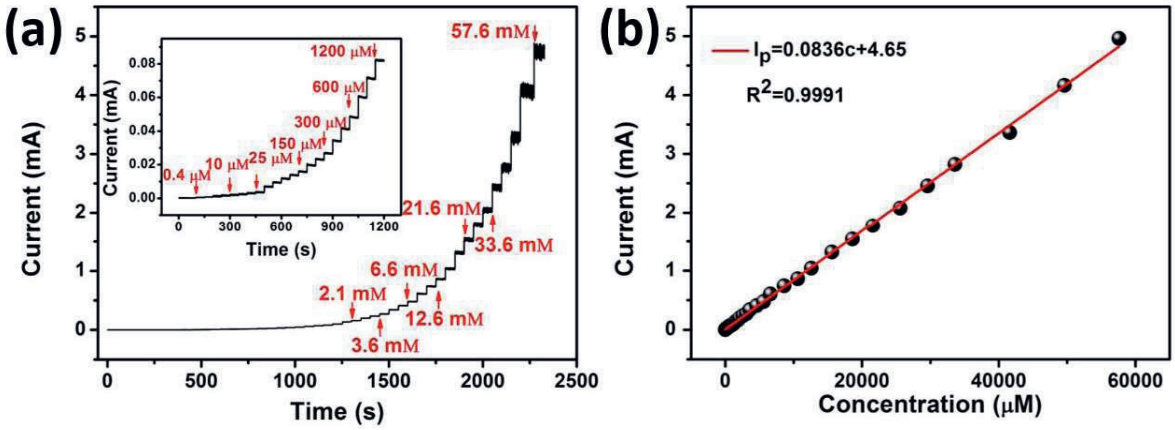

Fig.2. Chronoamperometric current response of 2D α-MoO_3 films to the changes H_2O_2 concentration from 0.4 μM to 57.6 mM in 0.1 M PBS; Inset: Chronoamperometric current response to lower concentration range of 0.4-1200 μM; (b) Corresponding linear plot of the current versus H_2O_2 concentration.

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