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Selective and Reliable Ampometric H_2O_2 Sensor based on Au-ZnO Heterostructure Electrode

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Summary:
Au-ZnO heterostructures were fabricated on the 4-inch SiO_2/Si substrates by the atomic layer deposition (ALD) technique for their subsequent use as sensing electrodes in amperometric H_2O_2 sensor. The results showed that the sensors based on Au-ZnO heterostructures possess high sensitivity of 0.53 $\mu A \mu M^{-1} cm^{-2}$, excellent long-term stability, wide linear H_2O_2 detection range of 1.0 µM to 120 mM, low limit of detection (LOD) of 0.78 µM and excellent selectivity at the normal operation conditions.

Keywords: Heterostructures, Au-ZnO, H_2O_2, amperometric chemical sensor, atomic layer deposition

Introduction

Development of 2D heterostructures for the usage in electrochemical sensors has been an established trend during last decade of the 21st century. Several technologies have been dominated in this trend including RF sputtering, chemical vapor deposition, hydrothermal method, solvothermal method, thermal evaporation, sol-gel, mechanical exfoliation etc. However, ALD, as an emerging technology, has not yet been fully exploited its features towards the development of reliable electrodes for the measuring devices. There are several reasons for that including relatively high costs, availability of precursors, specific ALD temperature window for deposition, lack of reliable recipes etc. Nevertheless, the advantages of ALD are far superior to the existing capabilities of other techniques. ALD is the only one technology, which enables fabrication of conformal, defects-free semiconductor 2D films and their heterostructures on the wafer scale with precise control of the thickness of sensing electrode during fabrication at the Ångstrom scale.

2D Au-ZnO heterostructures for H_2O_2 sensors were ALD-fabricated on the Si/SiO_2 wafer with Au electrodes. After deposition, all wafers were diced into the sensor segments of ~1.0x1.0 cm for further annealing and characterization (Fig. 1). Experimental data for variable angle spectroscopic ellipsometric measurements of ALD developed ZnO with the thickness of 1.3 nm is presented in Fig. 1(right). All fabricated Au-ZnO samples were annealed in air for 3 h at 250°C with the heating rate of 0.5°C/min for improvement of their crystallinity.

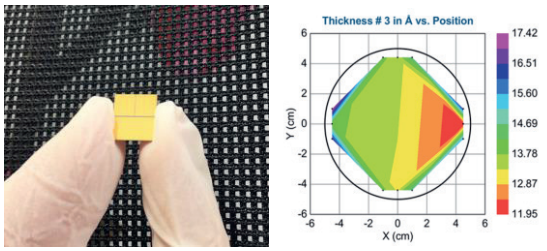

Fig. 1. Optical image of the 1.0 cm^2 sensor structure (left) and the spectroscopic ellipsometric mapping of thickness of ZnO nanofilms in Å on 4-inch Si/SiO_2 wafer (right).

Results

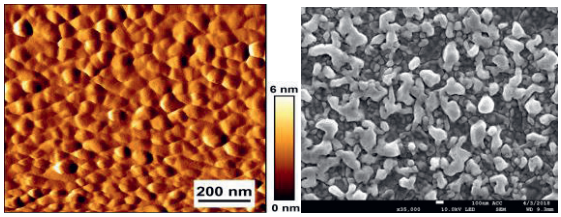

Fig. 2. AFM image of bare Au electrode (left) and SEM image of Au-ZnO heterostructure after annealing at 250°C.

Fig. 2 depicts AFM measurement of the flat Au electrode prior to annealing and SEM image of Au-ZnO heterostructure in which the initial thickness of ZnO films was 1.3 nm. SEM shows a rough ZnO surface compared to similar thickness 2D WO_3 and TiO_2 nanofilms after annealing. It is clearly visible that ZnO nanofilms owning to their extreme thin thickness (1.3 nm) were aggregated and agglomerated into island-like Au-ZnO

heterostructures with the average size of the particles of approximately ~50-100 nm.

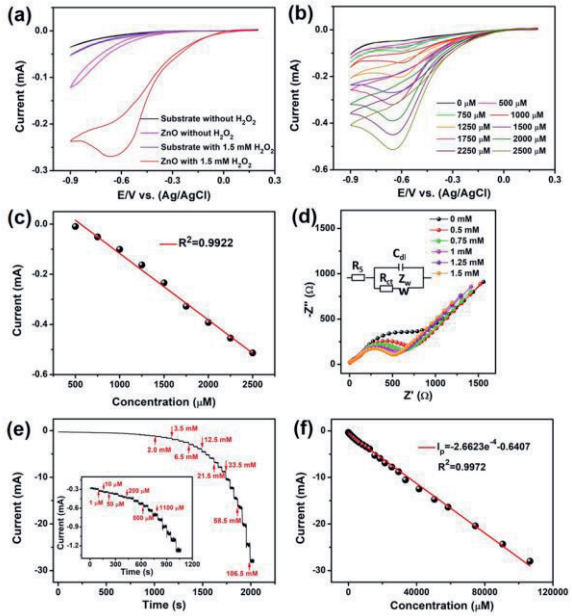

Fig. 3. (a) Measured CVs for the blank sensor substrate and Au-ZnO electrode at the absence and presence of 1.5 mM H_2O_2; (b) CV curves of ZnO with the different concentrations of H_2O_2. (c) Corresponding linear plot of the current peak versus H_2O_2 concentration, (d) Nyquist plots of 1.3 nm thick ZnO with various H_2O_2 concentrations of in 5 mM $K_4Fe(CN)_6$, (e) Chronoamperometric current response of Au-ZnO-based sensor to the changes of H_2O_2 concentration, (f) Corresponding linear plot of the current versus H_2O_2 concentration.

Improvement in H_2O_2 detection was clearly observed between the blank substrate and the sensor based on Au-ZnO heterostructure, as depicted in Fig. 3a. In order to understand it further, experiments continued with CV measurements at the different H_2O_2 concentrations (Fig. 3b) until the upper detection limit of 120 mM was established. The peak current was found to be linearly proportional to the increase of H_2O_2 concentration (Fig. 3c), which indicated the efficient electro-catalytic activity of Au-ZnO heterostructures without any fouling effect and indirectly reflected fast electron transfer reactions on the Au-ZnO heterostructures. Noteworthy, EIS measurements, presented in Fig. 3d, shown that the Nyquist semicircle becomes smaller and the R_{et} value gradually decreased as the measuring H_2O_2 concentration increased, indicating improved electron transfer rate. Moreover, in order to evaluate the linear response range, sensitivity and the LOD of H_2O_2, chronoamperometric measurements at various H_2O_2 concentrations were carried out for the Au-ZnO heterostructures. Fig. 3e shows typical current time dynamic response at changes of concentration from 2.0 μm to 106.5 mM. H_2O_2 was added approximately every 50 s. The inset image displays the lower concentrations range from ~1.0 μM to 1100 μM. From *i-t* curves, the response time to the different H_2O_2 concentrations for all measurements was found. In fact, 2D Au-ZnO heterostructures showed fast response time and all steady-states were achieved within ~2.0 seconds. The corresponding calibration curve for H_2O_2 detection by 2D Au-ZnO heterostructures is presented in Fig. 3f. Heterostructures demonstrated remarkable linearity in chronoamperometric responses to the changes of H_2O_2 concentration from ~1.0 μm to 120 mM with the correlation coefficient higher than 0.99.

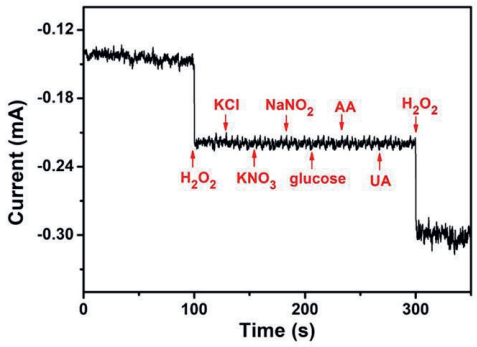

Fig. 4. Interference study of the H_2O_2 sensor based on Au-ZnO heterostructure at the presence of 10 μM H_2O_2 and 1.0 mM of different interfering chemicals at 25°C.

Responses of 2D Au-ZnO-heterostructures to the different interfering agents including glucose, KCl, $NaNO_2$, AA, UA, KNO_3 are clearly displayed in Fig. 4. It should be stressed that the concentration of the additional chemicals was about 100 times higher (1000 μM) and about 50 times higher for glucose (500 μM) than the existing H_2O_2 concentration (10 μM). It is evident from this figure that the sensor based on 2D Au-ZnO heterostructures is almost insensitive to all added chemicals.

Conclusions

ALD-developed Au-ZnO heterostructures have clearly demonstrated high performance towards H_2O_2 sensing, especially at the low concentrations levels. Specifically, our amperometric sensor exhibited not only high sensitivity of 0.53 $\mu A \mu M^{-1} cm^{-2}$ within a wide H_2O_2 concentrations range from 1.0 μM to 120 mM, but also rapid response/recovery time (~2.0 s), low LOD of 0.78 μM and excellent selectivity and long-term stability compared with the sensors based on micro-structured ZnO and other semiconductor oxides. Au-ZnO interface enabled considerable *surface-to-volume* ratio in electrode, which allowed the measuring chemical agent to reach the inside of the heterostructure more easily.