A Frequency-responsive Photoelectric Design for Highly Sensitive Photoelectrochemical Response Measurements

Jian Wang¹, Liping Du¹, Wei Chen¹, Ping Wang², Chunsheng Wu*¹⁺
¹ Institute of Medical Engineering, School of Basic Medical Science, Health Science Center, Xi'an Jiaotong University, Xi'an 710061, China
² Biosensor National Special Laboratory, Key Laboratory of Biomedical Engineering of Ministry of Education, Department of Biomedical Engineering, Zhejiang University, Hangzhou 310027, China
*Correspondence: C. Wu (e-mail: wuchunsheng@xjtu.edu.cn)

Abstract
A new design derived from light-addressable potentiometric sensors (LAPS) and light-activated electrochemistry (LAE) for highly sensitive photoelectrochemical sensing has been proposed. In this system, a bias voltage is applied to create a depletion layer at the semiconductor/electrolyte interface. A modulated light illuminates the sensor structure to generate electron/hole pairs and causes a detectable alternating photocurrent. The results showed a much higher signal-to-noise ratio (SNR) of the photoelectrochemical response of silicon substrates compared to that using the traditional linear sweep voltammetry (LSV) measurement. Moreover, a pH sensitivity of about 36 mV/pH was obtained analogous to LAPS with a SiO₂/Si/electrolyte sandwich structure, but with a steeper photocurrent-voltage curve due to the absence of the insulator layer. The proposed simple and low-cost sensor system can not only be used for photoelectrochemical response measurements of different semiconductors with high SNR, but also be prospective for the sensing of ions, DNA or living cells with spatial resolution.

Key words: Photoelectrochemical, frequency-responsive, high sensitivity, biosensor

Introduction
The investigation of photoelectrochemical behaviour of semiconductors to convert irradiative energy to electrical or chemical energy has gained significant attention for understanding the processes of solar cells, photosynthesis and photocatalysis. Herein, inspired by the principles of light-addressable potentiometric sensor (LAPS)¹ and light-activated electrochemistry (LAE)², a frequency responsive photoelectric system is proposed using modulated light to irradiate on a semiconductor-electrolyte structure.

Methods
In this system, double-polished silicon (100) substrates (boron doped, 1-10 Ω cm) were adopted as the research model. A diode laser (405 nm) modulated electronically (1 kHz) was used for AC photocurrent excitation. Photocurrent measurements were carried out in 10 mM phosphate buffer in an electrochemical cell consisting of a platinum electrode and an Ag/AgCl electrode as the counter and reference electrodes, respectively. AC photocurrents were measured by a lock-in amplifier while DC photocurrents were detected by a potentiostat (Fig 1).

Fig. 1. Experimental set-up for AC and DC photocurrent measurements.

Results and discussion
The results show that under the same bias voltage and laser intensity, the signal-to-noise ratio (SNR) of the produced AC photocurrent was significantly higher than that of DC output (e.g. 946 vs. 4.6 at 0.7 V, see Figs 2a and 2b). Furthermore, the silicon substrate shows a pH...
sensitivity of about 36 mV/pH (see Fig 2c), which is similar to the traditional silicon-based field-effect sensors such as LAPS with a SiO₂ insulator. On the other hand, due to the absence of insulator, the photocurrent-voltage curve was steeper and displayed a greater photocurrent resulting in a higher sensitivity of photocurrent measurements compared to the silicon substrates with oxide. The AC photocurrent kept stable in 15 min at bias voltage of 0.7 V. The proposed simple and low-cost structure can not only be used for photoelectrochemical response measurements of different semiconductors with high SNR, but also be applied for the sensing of ions, DNA or living cells.

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References

Fig. 2. Current-voltage curves of a p-type silicon substrate under 405 nm laser (red) and dark (black) measured in PBS at pH 7 (a) AC output measured with lock-in amplifier and (b) DC output measured with potentiostat; (c) AC photocurrent-voltage curves at different pH values. For AC photocurrent measurements, the laser was electronically modulated at 1 kHz.