Conference materials
UDC 538.971
DOI: https://doi.org/10.18721/JPM.153.225

Dependence of light-addressable potentiometric sensor sensitivity on photo-induced processes in Si

A. V. Kozlowski [1] ✉, S. V. Stetsyura [1]

[1] Saratov State University, Saratov, Russia

✉ kozlowsky@bk.ru

Abstract. The effect of photoelectron processes in *n*-Si and *p*-Si during the fabrication of the "Si/SiO_2/SiNx/polyethyleneimine/glucose oxidase" sensor structure on the glucose sensitivity of a light-addressable potentiometric sensor (LAPS) depending on SiN_x thickness was investigated. It was found that the illumination of the *n*-Si-based structure during the adsorption of the glucose oxidase enzyme doubles the sensitivity to glucose compared to the adsorption of glucose oxidase in the dark, and the best effect from photostimulated adsorption is achieved at a SiN_x layer thickness of ~50 nm. At the same time, the sensitivity to D-glucose, measured in the LAPS mode, is 45% higher than the sensitivity of the capacitive sensor. Illumination of *p*-Si during glucose oxidase adsorption resulted in a slight decrease in sensor sensitivity. The results are explained by a change in the density of immobilized glucose oxidase molecules due to a change in the electrostatic forces of attraction between enzyme molecules and semiconductor upon illumination and photoinduced charge stabilization on the surface electronic states of the Si/SiO_2 and SiN_x/polyethyleneimine interfaces in the case of photostimulated glucose oxidase adsorption.

Keywords: Semiconductor, sensor structures, silicon nitride, illumination, light-addressable potentiometric sensor

Funding: This study was funded by the Russian Science Foundation (project No. 22-22-00194, https://rscf.ru/en/project/22-22-00194/).

Citation: Kozlowski A. V., Stetsyura S. V., Dependence of light-addressable potentiometric sensor sensitivity on photo-induced processes in Si, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 15 (3.2) (2022) 135–139. DOI: https://doi.org/10.18721/JPM.153.225

Материалы конференции
УДК 538.971
DOI: https://doi.org/10.18721/JPM.153.225

Зависимость чувствительности светоадресуемого потенциометрического сенсора от фотоиндуцированных процессов в Si

А. В. Козловский [1] ✉, С. В. Стецюра [1]

[1] ФГБОУ ВО «СГУ имени Н.Г. Чернышевского», Саратов, Россия

✉ kozlowsky@bk.ru

Аннотация. Исследовано влияние фотоэлектронных процессов в *n*-Si и *p*-Si при создании сенсорной структуры «Si/SiO_2/SiNx/полиэтиленимин (ПЭИ)/глюкозооксидаза (GOx)» на чувствительность к глюкозе светоадресуемого потенциометрического сенсора (САПС) в зависимости от толщины слоя SiN_x. Получено, что освещение структуры на основе n-Si при адсорбции фермента GOx увеличивает чувствительность к глюкозе в два раза по сравнению с адсорбцией GOx в темноте, а наилучший эффект от фотостимулированной адсорбции достигается при толщине слоя SiN_x ~50 нм. Освещение *p*-Si во время адсорбции GOx приводило к небольшому снижению чувствительности сенсора. Результат объясняется изменением плотности иммобилизованных молекул GOx за

счет изменения электростатических сил притяжения при освещении и стабилизацией фотоиндуцированного заряда на поверхностных электронных состояниях интерфейсов Si/SiO_2 и SiN_x/ПЭИ в случае применения фотостимулированной адсорбции GOx.

Ключевые слова: полупроводник, сенсорные структуры, нитрид кремния, освещение

Финансирование: Исследование выполнено за счет гранта Российского научного фонда № 22-22-00194, https://rscf.ru/project/22-22-00194/.

Ссылка при цитировании: Козловский А. В., Стецюра С. В. Зависимость чувствительности светоадресуемого потенциометрического сенсора от фотоиндуцированных процессов в Si // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2022. Т. 15. № 3.2. С. 135–139. DOI: https://doi.org/10.18721/ JPM.153.225

Introduction

Electrolyte/insulator/semiconductor (EIS) structures are widely used to detect nano- and bio-objects ionized in solution due to the field effect. Also, EIS-structures are used to recognize enzymatic reactions [1], viruses [2], RNA/DNA sequencing [3]. Compared to capacitive EIS-sensors, light-addressable potentiometric sensors (LAPS) have a number of advantages, such as the ability to obtain spatial and temporal charge distribution over the surface of the transducer (scanning photoinduced impedance spectroscopy), which makes it possible to visually assess the dynamics of changes in the concentration of the analyte.

Previously, we reported on the effect of photoelectron processes in a silicon substrate on the glucose oxidase (GOx) adsorption. Photostimulation of the semiconductor during enzyme adsorption led to a change in the surface concentration of adsorbed molecules, which ultimately led to an increase in the glucose sensitivity of a capacitive EIS-sensor based on the Si/SiO_2/ polyethyleneimine (PEI)/GOx structure. However, the effectiveness of photostimulated layer-by-layer adsorption of the enzyme on a semiconductor with a passivating dielectric layer of silicon nitride has not been studied before. Silicon nitride is advantageous over SiO_2 because it allows greater sensitivity to changes in H^+ in solution due to the higher density of protonated groups on the surface. However, it should be taken into account that for the photostimulated adsorption method to be effective, one should limit oneself to nanoscale insulator thicknesses.

In this work, we studied the effect of both photo-stimulated layer-by-layer adsorption (PSA) of GOx and the thickness of the dielectric layer of $Si/SiO_2/SiN_x$ structure on the sensitivity to glucose of LAPS based on $Si/SiO_2/SiN_x$/PEI/GOx structure.

Materials and Methods

The sensor structures were fabricated using single-crystal (100) Si wafers (250 μm thickness) of *n*-type ($\rho = 2 – 7\ \Omega$ cm) and *p*-type ($\rho = 9 – 15\ \Omega$ cm). Initially, the wafers were boiled in a peroxide–ammonia solution ($NH_4OH : H_2O_2 : H_2O = 1 : 1 : 4$ (vol.)) at 75ºC during 10 min. Then wafers were rinsed in deionized water ($\rho \sim 18.2\ M\Omega$ cm). Afterwards, wafers were cut into substrates of 10×10 mm^2. A 300 nm nickel layer on the rear side of the sensor structure was applied by magnetron sputtering method. The rear-side contact was partially removed to create an illumination window for the light beams. A nitride silicon (SiN_x) thin films approximately 50 and 150 nm thick were deposited on the front side Si by magnetron sputtering method (Angstrom Nexdep, USA). The SiN_x surface contains primarily silanol groups with a small percentage of silamine groups. The silanol groups in solution exist as either negatively charged Si-O- or neutrally charged Si-OH functions due to protonated-deprotonated processes. The silamine groups can exist as neutral or positively charged functions. It can be noted that isoelectric point (IEP) of the SiN_x surface is ca. pH=3.5 [4] and above this pH value the surface is negatively charged.

The glucose oxidase (GOx) form *Aspergillus niger* were used as enzyme molecules. Branched polyethyleneimine (PEI) with a molecular weight of 25 kDa was used as cationic polyelectrolyte to increase the adsorption of negatively charged GOx onto Si substrates with SiN_x layer.

The organic molecules were adsorbed onto Si substrates from the aqueous solutions during 10 min followed by rinsing in deionized water (ρ ~ 18.2 MΩ cm) during 10 min and drying in nitrogen flow. The glucose solutions were prepared by dissolving D-glucose in the working buffer. As working buffer, a 0.2 mM potassium phosphate buffer solution (pH = 7.3) containing 150 mM NaCl as an ionic strength adjuster was used. At ionic strength about of 150 mM, the 1/e distance for the exponential decay of the surface potential is approximately 1 nm. At ionic strength about of 150 mM, the 1/e distance for the exponential decay of the surface potential is approximately 1 nm. The size of the GOx molecule is 6.0×5.2×7.7 nm^3 [5]. Thus, charged GOx molecules on substrate surface would have little influence on sensor signal.

The photo-stimulated layer-by-layer adsorption technique suggested in [6] was used to adsorb GOx from aqueous solution onto $Si/SiO_2/SiN_x$ substrates covered with PEI. A halogen lamp (Philips 13186 EPX/EPV) was used to activate photoelectric processes in a silicon wafer during adsorption of polyelectrolyte molecules. The substrate was either in the dark or under illumination during the GOx adsorption, other things being equal.

Figure 1 schematically shows the experimental set-up, which has been utilised for the characterisation of LAPS with the adsorbed PEI and GOx layers. For the measurements, the prepared structure was mounted into an electrochemical cell, sealed by an O-ring and contacted on its front side by the electrolyte and Ag/AgCl reference electrode, and on its rear side by ohmic contact. The measurements have been performed at room temperature.

Before the adsorption of PEI and GOx, the pH-sensitive behaviour of the as-prepared $Si/SiO_2/SiN_x$ structure has been investigated in buffer solutions of pH 5.89–7.77 by LAPS method. For operation, a DC voltage is applied via the Ag/AgCl reference electrode. For the measuring procedure, about 0.5 mL of the working buffer or particular glucose solution was applied to the SiN_x surface, and photocurrent has been read out for after 10 min. During measurements, the substrates were illuminated from the rear side with modulated light. Red-LED (λ = 650-655 nm) is placed directly below the EIS-structure as a light source. An oscillator, which generates a 1 kHz rectangular signal, was provided the modulation of the red-light beam. After each measurement, front side region was rinsed with buffer solution.

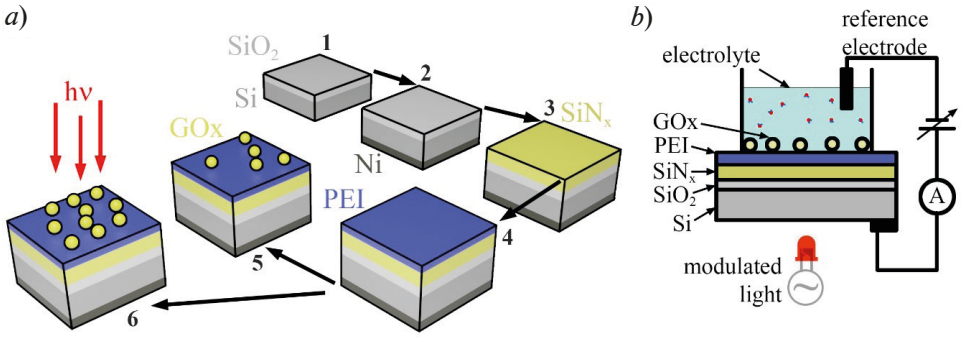

Fig. 1. Stages of fabrication a hybrid sensor structure: 1 - silicon wafer with an oxide layer after ammonia-peroxide treatment; 2 - deposition of a nickel contact and its partial etching on the rear side of the substrate; 3 - deposition of the SiN_x layer by magnetron sputtering; 4 - deposition polyethyleneimine molecules by layer-by-layer adsorption; 5 and 6 - deposition of GOx molecules in the dark (5) or under illumination (6) of semiconductor substrate (*a*). Schematic of light-addressable potentiometric sensors (*b*)

The glucose sensitivity of biosensors was studied by means of capacitance-voltage (EIS-sensor mode) and photocurrent-voltage (LAPS mode) measurements in glucose solutions with different content of D-glucose from 1 mM to 10 mM using a semiconductor device analyzer (Agilent B1500A, USA). Bias voltage was applied relative to the rear-side Si substrate.

Results and Discussion

Figure 2 shows exemplarily a typical photocurrent-voltage curves response to pH changes. With increasing pH of the solution, photocurrent-voltage curves are shifted along the voltage axis in the

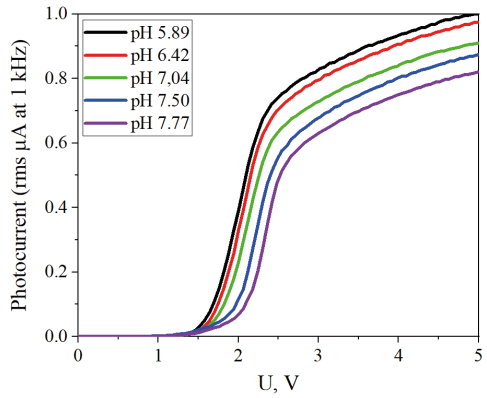

Fig. 2. Typical photocurrent-voltage curves of $Si/SiO_2/SiN_x/PEI/GOx$ sensor structures measured in 0.1 M potassium phosphate buffer at different pH-values

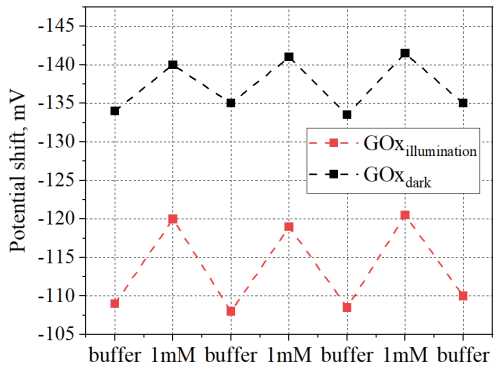

Fig. 3. Reproducibility of potential change during cyclic change of the working buffer solution (0.2 mM potassium phosphate buffer solution, pH = 7.3) by 1 mM D-glucose depending on the method of deposition of GOx molecules: in the dark or under illumination of silicon during GOx adsorption

direction to more positive voltage values. This is due to decrease in the H^+ concentration of on the LAPS surface. It was found that pH sensitivity is 1.57 times greater for a structure with SiN_x thickness of 50 nm.

It was found that for LAPS with 150 nm of SiN_x, where the GOx molecules were deposited in the dark, the sensitivity to D-glucose is 4.6 mV/mM. In the case of PSA – 7.4 mV/mM. For 50 nm of SiN_x, the D-glucose sensitivity is 6.7 mV/mM and 12.3 mV/mM for GOx deposition in the dark and PSA, respectively

The repeatability of readings of the biosensor structure during multiple measurements was also recorded. The values of the potential shift were measured during several measurement cycles. After each measurement cycle in a 1 mM D-glucose solution, the structure was washed (0.2 mM potassium phosphate buffer, pH = 7.3) and potential shift was measured again. The experiments were carried out on the structures obtained using the GOx PSA and when GOx deposited in the dark. Figure 3 shows the results of 3 consecutive cycles.

The scatter of the potential shifts for structure obtained by dark deposition of GOx is 1.3 mV or 19 %. When using PSA, the shifts are more stable: changes are less than 0.6 mV or 5.3 %. In addition, it can be seen from Figure 3 that the response to the same glucose concentration is higher for the structure obtained with GOx PSA - a change of 11.3 mV versus 5-6 mV for the structure on which GOx was deposited in the dark. The results can be explained by the change in the density of immobilized GOx molecules induced by photoelectron processes in the Si substrate during adsorption of enzyme [6].

Conclusion

It was found that the sensitivity to D-glucose of LAPS, prepared with PSA of enzyme molecules on a semiconductor substrate, twice the sensitivity of LAPS obtained without PSA. The PSA of GOx was studied for the first time for the structure of $Si/SiO_2/SiN_x$. The best effect of photostimulated adsorption was achieved with SiN_x layer thickness ~50 nm. It can be noted that PSA at the stage of adsorption of enzyme molecules to increase the stability of biosensor signal. The results were explained by photoelectron processes in a hybrid structure that occur during the adsorption of a polyelectrolyte on a photosensitive substrate.

Acknowledgments

The work was carried out at the expense of the Russian Science Foundation (project No. 22-22-00194, https://rscf.ru/en/project/22-22-00194/).

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THE AUTHORS

KOZLOWSKI Alexander V.
kozlowsky@bk.ru
ORCID: 0000-0002-3612-9776

STETSYURA Svetlana V.
stetsyurasv@mail.ru
ORCID: 0000-0002-4337-012X

Received 12.08.2022. Approved after reviewing 15.08.2022. Accepted 26.08.2022.