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A flexible and miniaturized hair dye based photodetector via chemiluminescence pathway

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ABSTRACT

A flexible and miniaturized metal semiconductor metal (MSM) biomolecular photodetector was developed as the core photocurrent system through chemiluminescence for hydrogen peroxide sensing. The flexible photocurrent sensing system was manufactured on a 30-μm-thick crystalline silicon chip by chemical etching process, which produced a flexible silicon chip. A surface texturization design on the flexible device enhanced the light-trapping effect and minimized reflectivity losses from the incident light. The model protein streptavidin bound to horseradish peroxidase (HRP) was successfully immobilized onto the sensor surface through high-affinity conjugation with biotin. The luminescence reaction occurred with luminol, hydrogen peroxide and HRP enzyme, and the emission of light from the catalytic reaction was detected by underlying flexible photodetector. The chemiluminescence in the miniaturized photocurrent sensing system was successfully used to determine the hydrogen peroxide concentration in real-time analyses. The hydrogen peroxide detection limit of the flexible MSM photodetector was 2.47 mM. The performance of the flexible MSM photodetector maintained high stability under bending at various bending radii. Moreover, for concave bending, a significant improvement in detection signal intensity (14.5% enhancement compared with a flat configuration) was observed because of the increased photocurrent, which was attributed to enhancement of light trapping. Additionally, this detector was used to detect hydrogen peroxide concentrations in commercial hair dye products, which is a significant issue in the healthcare field. The development of this novel, flexible and miniaturized MSM biomolecular photodetector with excellent mechanical flexibility and high sensitivity demonstrates the applicability of this approach to future wearable sensor development efforts.

1. Introduction

Since the rise of environmental consciousness, chemical sensors have evolved into a powerful tool for chemical sensing, (Chen et al., 2015; Dou et al., 2009). and environmental pollution detection. An important emerging area in the field of chemical sensors is the development of inexpensive, simple sensors for chemical diagnostics, (Liu et al., 2013; Ge et al., 2013; Wang et al., 2010; Ciaffoni et al., 2013; Yu and Lai, 2013; Nie et al., 2010; Martínez-Olmos et al., 2013) and other sensing applications. (Dungchai et al., 2009; Huang et al., 2013) Such devices, if they are simple, portable, rapid, flexible, and robust, (Lin et al., 2015; Hu et al., 2013) can enable the provision of otherwise unattainable health care and other benefits to developing countries and remote communities. To be affordable, the sensors must be mass-producible from cheap, readily available starting materials and should preferably be readable without the aid of scientific instruments. Semiconductor manufacturing provides a reliable and stable platform for mass production of any designed chips. In general, however, integrated semiconductor devices with sophisticated chemiluminescence (Bi et al., 2012) analytical capabilities are still rare. Optical chemical sensors possess high sensitivity, easy operation, high accuracy, and wide detection capacity. (Ratterman et al., 2014; Salama et al., 2007; Hatakeyama et al., 2009; Wang et al., 2015; Yamamoto et al., 2013; Ruano et al., 2000; Tsafack et al., 2000; Ivanov et al., 2001; Askari et al., 2002; Song et al., 2005) In particular, luminescence-based optical chemical sensors exhibit certain advantages, including a low detection limit, insensitivity to electrical disturbance, and a wide linear working range. (Delaney et al., 2011; Borisov et al., 2008).

When developing a portable chemical sensor system, chemiluminescence and electrochemical detection mechanisms are two candidates for signal detection. The optical sensing approach has recently garnered increasing interest but is less well developed than electro-

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chemical techniques. Yen and coworkers developed an active complementary metal oxide semiconductor (CMOS) sensor array for electrochemical biomolecule detection. (Yen et al., 2014; Huang et al., 2014) Electrochemical molecular detection relies on measuring the real-time signal change due to hybridization at the interface between a metal working electrode and a conductive target analyte solution. Furthermore, Ratterman and coworkers proposed a carbon dioxide luminescent sensor based on a CMOS image array. (Ratterman et al., 2014) This design has various advantages, such as high sensitivity, wide dynamic range, and relatively inexpensive instrumentation. However, the fabrication of the CMOS optical sensor was very complicated. Several semiconductor manufacturing processes, such as impurity doping, multiple-patterning, and thin-film deposition, were required to fabricate the CMOS device. To overcome the drawbacks of the CMOS-based sensor, an alternating flexible MSM photodetector that is easily fabricated, robust, and highly flexible is proposed here. This MSM photodetector sensor has a demonstrated potential to serve as an alternative device in chemical sensing system.

Recently, photodetector technology research has been focused on developing miniaturized devices with high responsivity, low noise, short response times, high bandwidth, and high gain. (Zhang et al., 2013; Naderi and Hashim, 2012; Carturan et al., 2015; Li et al., 2014., Mohite and Rajpure, 2014; Lv et al., 2013; Song et al., 2015; Kim and Lee, 2013; Masouleh et al., 2015) Flexibility is crucial for electronic device integration and has major implications. In devices, concave and convex bending modes allow access to some otherwise unachievable performance properties. Therefore, it is necessary to accurately describe the bending behavior of flexible MSM photodetectors, which may reveal important physical mechanisms that will, in turn, improve the suitability of these devices for chemical sensing applications.

This study mainly focuses on fabrication techniques of flexible photodetector and applications to chemical sensing through luminescence. (Yang et al., 2009; Lin et al., 2009) The photosensitive element is based on a silicon wafer treated with chemical etching to endue pliability. The MSM structured flexible photodetectors were then manufactured using simple and cost-effective fabrication processes. The attained devices were immobilized with a target enzyme that catalyzed the luminescence reaction. We developed a miniaturized hydrogen peroxide sensor with outstanding flexibility that exhibited very high stability in various environments. The results presented herein provide a basis for the fabrication of cost-effective flexible photodetectors for hydrogen peroxide sensing with chemiluminescence applications. The fabrication approach used to obtain these MSM photodetectors offers flexibility for the myriad devices developed during the Silicon Era and could be used to fabricate more wearable optoelectronic and sensing devices.

2. Materials and methods

2.1. Flexible MSM photodetector fabrication process

Silicon wafers with 675-μm thicknesses (single-crystalline, p-type, boron-doped, < 100 > silicon wafers with resistivities of 1–30 Ω-cm) were chosen to develop flexible MSM photodetectors. These silicon wafers were clearly rigid and could not be used in any situation requiring curvature; however, the wafers became bendable when the thickness was decreased to less than 30 μm. To obtain 30-μm-thick silicon wafers for the fabrication and characterization of flexible MSM photodetectors, we segmented a 6-in. silicon wafer to 3 cm × 3 cm pieces and conducted etching by immersing the chips in a 40 wt% sodium hydroxide (NaOH) solution inside an etching tray. This implement was then placed in a thermostatted oil batch with a magnetic stirrer (EYELA PS-1000, Japan), and the etching temperature was maintained at 85 °C throughout the etching process. The etching process was terminated after 23 h, at which point the silicon chips were approximately 30 μm in thickness.

The flexible silicon chips were treated with an etchant solution consisting of 20 wt% sodium hydroxide (NaOH) (Sakaino et al., 2000; Gangopadhyay et al., 2006) and 50 wt% isopropyl alcohol (IPA). Anisotropic etching is an appropriate etching procedure for constructing three-dimensional structures and offers good selectivity for materials or crystalline orientations. The structure was three-dimensional pyramidal in shape and exhibited significant enhancement of light absorption. (Wang et al., 2016; Wang et al., 2016, 2013; Papet et al., 2006; Chung et al., 200 8) The chips were placed into the thermostatted oil batch with magnetic stirring, and the entire texturing process was conducted at a fixed temperature of 85 °C for 10 min.

To fabricate photodetectors with MSM structures, metal electrodes were constructed using the thermal evaporating method, and then interdigital electrode patterns were formed using interdigital shadow mask techniques. The electrodes are 50 μm in width, 2.5 cm in length, and separated from 1.5 mm for each. We used the thermal evaporator to manufacture the front electrodes with aluminum to a thickness of 0.5 μm, and the same parameters were applied to the back electrode as well but without shadow mask covering. This type of device was constructed with metal-semiconductor interfaces, but both interfaces were flexible. After the deposition of metal electrode, the flexible MSM photodetectors were assembled according to the manufacturing process shown in Scheme 1(A).

2.2. Biomolecule immobilization process and luminescence detection

The flexible MSM photodetectors fabricated according to the process mentioned in the previous section were treated with several solutions to immobilize biomolecules. The devices were immersed in 50 ml of an ethanol solution with a bifunctional aminosilane, 3-aminopropyltriethoxysilane (APTES, $C_9H_{23}NO_3Si$, 99% purity, Sigma, Great Britain), for one hour at room temperature. The weight ratio of APTES to ethanol was 1.5 wt%, and the solution was well mixed by magnetic bars. After APTES immersion, the devices were rinsed with DI water and dried with absorbent paper at least three times. Next, the samples were baked at 120 °C on a hot plate for an hour to facilitate chemical bonding and thereby increase firmness. We made up a 10 mM Biotin N-hydroxysuccinimide ester (NHS-Biotin, 98% purity, Aldrich, Japan) solution in dimethyl sulfoxide (DMSO, Fisher, USA), placed the devices in 50 ml of this solution and allowed the reaction to proceed for at least 6 h. The un-reacted NHS-biotin was removed with a rinse of phosphate buffered saline (PBS) in DI water. In addition, the flexible photodetectors were immersed in 10 ml of bovine serum albumin (BSA, 96% purity, Sigma, USA) to block nonspecific binding. The streptavidin–peroxidase polymer (Streptavidin-HRP, Sigma, USA) was diluted to 0.1 wt% with Tris-HCl buffer (pH 8.5), and then 0.5 ml of the prepared streptavidin-HRP solution was dropped onto the devices for the immobilization reaction, which proceeded at room temperature for 30 min. Due to the extraordinarily high affinity between streptavidin and biotin, the HRP enzyme was well combined with the devices. Next, we dissolved 1 wt% of 5-amino-2,3-dihydro-1,4-phthalazinedione (Luminol, $C_8H_7N_3O_2$, > 98% purity, TCI, Japan) powder in 1 M NaOH and diluted the hydrogen peroxide (H_2O_2, 30% purity, Taimax, Taiwan) solution to various concentrations in DI water. During the reaction, 0.1 ml of luminol solution was injected, mixed with 0.1 ml of the H_2O_2 solution and dropped on top of the flexible photodetectors. The luminescence reaction was catalyzed by the HRP enzyme, and the luminescence signals were detected by our flexible devices. The complete immobilization process is illustrated in Scheme 1(B).

3. Results and discussion

3.1. Device fabrication and characterization of the MSM-PD

The flexible thin silicon chips obtained, which were subsequently