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Highly sensitive cantilever type chemo-mechanical hydrogen sensor based on contact resistance of self-adjusted carbon nanotube arrays☆

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ABSTRACT

A highly sensitive cantilever type chemo-mechanical hydrogen sensor with a novel sensing mechanism that can detect changes in contact resistance in self-adjusted carbon nanotube (CNT) arrays is described. The fabricated sensor is fully batch-fabricated on a silicon-on-insulator (SOI) wafer and is composed of two facing sets of CNT arrays, situated between a Pd-coated micro-cantilever, that serve as the electrode and counter-electrode. When the sensor is exposed to various concentrations of hydrogen at room temperature, resistance is decreased as the cantilever deforms and increases inter-CNT contact. Turning off the hydrogen re-shrinks the Pd, restoring the original cantilever position and recovering the initial resistance. The sensor can detect hydrogen diluted in nitrogen at concentrations of up to 4% and has an average response as high as −1.22% to a 0.1% concentration of hydrogen in air, which is the minimum detection limit. This sensitivity, which is much higher than in previously reported cantilever-type resistive chemo-mechanical hydrogen sensors, can be attributed to the novel sensing mechanism in which the narrow-gap between CNT arrays comprise the sensing component.

1. Introduction

Advancements in micro- and nanotechnology have led to much research in the development of high performance gas sensors. The diverse range of target detection gases includes colorless, odorless, and pollution-free hydrogen, which can serve as alternative clean energy source for automobile and spacecraft propulsion [1]. However, hydrogen is explosive when its concentration in air exceeds 4% [2], making the development of highly sensitive hydrogen sensors that can detect microscopic leakage in transfer and storage systems important in order to assure safety.

Unlike many hydrogen sensors which use metal oxide as the sensing material and are operated at high temperature [3], Pd-based sensors can detect hydrogen at room temperature with high selectivity [4,5]. Various hydrogen chemical sensors [6–9] and chemo-mechanical sensors [10–13] utilize changes of electrical resistance and volumetric expansion caused by the absorption of hydrogen at the Pd surface. The cantilever type chemo-mechanical sensor [14–18] can detect the mechanical deformation of a Pd-coated cantilever caused by volumetric expansion of the Pd as it absorbs hydrogen. Such mechanisms are suitable for use in the mass production of small footprint sensors through batch-fabrication, and their ability to change their amount of deformation based on the mechanical stiffness of the cantilever structure gives them a higher degree of sensitivity control and performance predictability than other chemical and chemo-mechanical sensor types.

In terms of sensing mechanisms, there are three different types of cantilever-based chemo-mechanical sensors: capacitive [14], optical [15–17], and resistive [18]. In capacitive sensors, additional circuitry is essential in order to reduce the influence of parasitic capacitance. Optical sensors require additional components such as photo-detectors and lasers to detect the deformation of cantilever, which results in bulkier assemblages. Resistive sensors reduce much of the additional componentry required by the other types by utilizing the closure of nanogap under a cantilever fabricated through surface micromachining techniques. When a resistive sensor is exposed to hydrogen, its cantilever deforms through closure of an approximately ten-nanometer nanogap in order to make an electrical connection with counter-electrodes. Although this process is highly sensitive and consumes low power in standby state, no sensor output is given until the first nanogap is closed, which results in the relatively high minimum detection limit of 1.5%. In

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order to reduce the minimum detection limit, it is essential to either lower the stiffness of the movable cantilever or create smaller nanogaps; both of these approaches present challenges in the fabrication processes.

Recently, we developed a highly sensitive displacement sensing mechanism that utilizes the resistance change between two self-adjusted carbon nanotube (CNT) arrays as its sensing component. The CNT arrays were synthesized on the sidewalls of the microstructures through a batch-process [19–21]. In these works, two facing sets of CNT arrays synthesized by thermal chemical vapor deposition (CVD) form a contact boundary at which, owing to the non-uniform length of each CNT, some of the CNTs are in contact while others are separated by nanoscale gaps. Utilizing this CNT synthesis process and array structure, the formation of a contact boundary with two partially contacting CNT arrays was achieved between a low-stiffness cantilever and counter-electrode. By coating Pd onto only one side of the cantilever, we could then apply this CNTs-integrated micro-cantilever into the highly sensitive chemo-mechanical hydrogen sensor described in this paper. The electrical resistance through the boundary of partial contact between the two CNT arrays—which, unlike previously reported nanogap-based chemo-mechanical sensors, has a finite initial value—changes upon exposure to low concentrations of hydrogen gas based on bending of the cantilever caused by volumetric expansion of the coated Pd layer. The chemo-mechanical sensing mechanism was validated by comparing an uncoated cantilever to one coated with Pd. The extremely small gap between the partially contacting CNT arrays and the very low stiffness of the cantilever meant that the minimum detectable limit was much lower than in previously reported cantilever-type chemo-mechanical sensors with infinite initial resistance. The repeatability and sensing range of the sensor were also measured by exposing it to both repeated introduction and high concentrations of hydrogen.

2. Design and fabrication

Fig. 1(a) shows a schematic diagram of the sensor, which is composed of a micro-cantilever connected to an anchor electrode, a counter-electrode, and two facing sets of CNT arrays integrated between the cantilever and counter-electrode. A Pd thin film for chemical reaction with hydrogen has been coated onto one side of the cantilever. Because the length of the synthesized CNTs is not perfectly identical and they are varyingly distributed, only a fraction of the CNTs are electrically connected before the sensor is exposed to hydrogen, while others form a narrow gap. Upon introduction to the sensor, hydrogen molecules become dissociated into hydrogen atoms at the surface of Pd and these are then diffused into the Pd thin film [22]. This absorption of hydrogen atoms induces a volumetric expansion of the thin film that, in turn, deforms the cantilever toward the counter-electrode, as depicted in Fig. 1(b). As the distance between each CNT array decreases, the number of CNTs that are in contact increases; through this mechanism, the contact resistance between the CNT arrays decreases [19,20]. If the supply of hydrogen is cut off, the hydrogen atoms in the Pd are desorbed and leave the Pd thin film, which re-shrinks the Pd and causes the cantilever to return to its original position and the resistance to recover to its higher initial value. The dependence of the number of hydrogen atoms diffusing into the Pd on the concentration of hydrogen naturally calibrates the degree of Pd expansion; when the sensor is exposed to higher concentrations of hydrogen, its deformation increases and, in turn, the contact resistance decreases between the CNT arrays (Fig. 1(c)) [19].

Fig. 2(a) shows a top-view of the fabricated hydrogen sensor. The fabrication process flow is shown in Fig. 2(b)–(g), which represent a cross-sectional view along the line A–B in (a). The sensor is batch-fabricated on a silicon-on insulator (SOI) wafer with a 20 μm-thick device layer, a 2 μm-thick buried oxide layer, and a 450 μm-thick handle layer. The device layer, which is heavily doped with As, has a resistivity of 0.005 Ω cm. A 400 nm-thick Al layer is deposited onto the backside of the wafer through sputtering and then patterned through lithography and wet etching in order to define backside holes. On the front side, a 2.6 μm-thick AZ7220 photoresist (PR) is patterned in order to define the cantilevers and counter-electrodes. The device and handle layers are then successively etched by deep reactive ion etching (DRIE) (Fig. 2(b)). Following DRIE, the etch masks on both the front- and backside, and the buried oxide layer are removed using a piranha solution and hydrofluoric acid (Fig. 2(c)). In order to synthesize the CNTs, a shadow mask is aligned along the device layer and then a 5 nm-thick Fe catalyst is evaporated through the mask (Fig. 2(d)). Substrate separated from the shadow mask is then loaded into a furnace and heated up while a 100 sccm nitrogen flow is introduced. When the furnace reaches 700 °C, 100 sccm of ammonia gas flow is introduced for 30 min for pre-treatment of the Fe catalyst. The CNT arrays are then synthesized by chemical vapor deposition (CVD) for 10 min using a 50 sccm acetylene flow as a carbon source (Fig. 2(e)). After it has been synthesized, the CNT arrays-integrated substrate is cooled down and unloaded from the furnace at room temperature. A second shadow mask for patterned deposition of Pd is then aligned to the substrate. Through the second mask, a 15 nm-thick adhesion layer of Cr and a 50 nm-thick Pd layer are evaporated onto only one side of the cantilever by attaching the substrate onto a jig tilted at about 45° (Fig. 2(f)). The sensor fabrication process is completed by separating the substrate from the second shadow mask (Fig. 2(g)).

During their evaporation process, Cr and Pd can be deposited not only on the sidewall but also on the top surface of the cantilever. Although Pd on the top surface might affect sensing characteristics when the volume of the Pd film expands through hydrogen absorption, the thickness-to-width ratio of the cantilever is above 2.85 and its calculated in-plane stiffness (0.022 N/m) is much lower than its stiffness in the out-of-plane direction (7.098 N/m). Accordingly, deformation of the cantilever from coated Pd expansion is far more dominant along the in-plane direction.

Scanning electron microscope (SEM) images of the fabricated hydrogen sensor are shown in Fig. 3(a). As indicated by the arrow, the Pd layer was coated onto only one side of the cantilever in this device, and the self-adjusted CNT arrays for sensing cantilever deformation were formed on the opposite side by selectively synthesizing the CNTs at the end of cantilever. We verified that the synthesized CNTs are multi-walled CNTs with the diameter of 10–20 nm by the inspection using transmission electron microscopy. An enlarged top view of the CNT arrays integrated between the cantilever and the counter-electrode is shown in Fig. 3(b). The synthesized CNT arrays completely fill the empty space between the two structures and are self-adjusted at the center of the micro-gap forming the contact boundary. This self-adjustment results from the high areal number density of CNTs and from van der Waals interactions within the CNT arrays, as reported previously [23]. The extrusive growth force of the CNTs during synthesis has extended a 5 μm-wide initial micro-gap to 15 μm, bending the flexible cantilever. While the CNT array cannot infiltrate into the opposite array, the growth of CNTs continues until the force of their growth balances the buckling resistance of the CNTs, which delivers a preload to the cantilever. Similar growth characteristics were discussed in our previous work [23]. Preload of cantilever affects the contact force between two CNT arrays. A larger contact force is applied between two CNT arrays under a larger preload, which makes an increase in the number of initially connected CNTs and therefore reduces the initial contact resistance between CNT arrays [24]. When the number of CNTs in