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Hydrogen sensor based on palladium-yttrium alloy nanosheet

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HIGHLIGHTS

- Pd-Y sensing element was fabricated using a magnetron sputtering system and shadow mask.
- The Pd-Y compound consisted of 92% Pd and 8% Y.
- The fabrication process was simple, low-cost, and mass-production compatible.
- The sensor showed superior sensitivity, reversibility, and reproducibility to hydrogen gas.
- The device is more compact than the optical-based counterpart.

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ABSTRACT

This paper presents a hydrogen sensor based on palladium-yttrium (Pd-Y) alloy nanosheet. Zigzag-shaped Pd-Y nanosheet with a thickness of 19.3 nm was deposited on a quartz substrate by using an ultrahigh-vacuum magnetron sputtering system and shadow mask. The atomic ratio of palladium to yttrium in the nanosheet was 0.92/0.08. The fabrication process was simple and low-cost, and the sensor can be mass-produced. The experimental results show the sensor has a superior sensitivity, reversibility, and reproducibility. The resistive-based hydrogen detection mechanism in this research is much simpler and more compact compared to the optical-based detection method.

1. Introduction

Hydrogen gas is colourless, odourless, tasteless, and highly flammable. There has been a great demand for fast response and highly sensitive hydrogen gas sensors for safety and industrial application to alert the formation of potentially explosive gas and to reduce the explosion risk [1]. Presence detection and concentration measurement of hydrogen gas have over 100 years of history [1,2]. However, higher sensitivity and faster response hydrogen sensors are desirable for further safety improvement.

Hydrogen sensing element is normally made by metal or alloy, whose physical and chemical properties vary when it is exposed to hydrogen gas. A good sensing material should have high selectivity, sensitivity, and reversibility to hydrogen. Compared to other materials, such as platinum, palladium was found to have higher solubility and sensitivity to hydrogen [1,3,4]. The absorption of hydrogen molecule by pure palladium can form Pd-H hydride, leading to the changes of its physical properties, such as mass, volume, optical property, and electrical resistivity [5]. During the desorption process, the palladium thin film operates under non-equilibrium conditions. The concentration of hydrogen in the thin film is higher than that in the surface film. Due to the concentration gradient, the chemical bonds between palladium and hydrogen atoms in the thin film are broken and the hydrogen atoms move to the surface of film and are desorbed to the atmosphere. In order to gain high activation energy to break Pd-H bonds, the concentration gradient between the thin film and the exposed environment should be sufficiently high enough to provide the necessary driving force [14]. However, pure palladium film is easy to bubble and crack after absorbing and desorbing

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hydrogen for several times [6], reducing the stability and reliability of the sensor. Mechanical stress in the film and lattice expansion of palladium structure are the significant issues for further research to address [7].

In literature, there are mainly two solutions that are able to avoid the crack of pure palladium thin film after absorbing and desorbing hydrogen. The first approach is to expand the lattice of Pd before the invasion of hydrogen atoms. The expanded lattice leaves larger space for hydrogen atoms to diffuse in Pd thin film. As a result, the α to β phase transition in PdH_x is suppressed when Pd absorbs hydrogen. Liu et al. [8] found that Palladium-yttrium (Y) alloy thin film could improve the response rate and eliminate the bubble and delamination phenomena. As yttrium atom has larger radius than palladium atom, the lattice of palladium will expand after being doped by yttrium. The expanded lattice makes the diffusion of hydrogen atoms in Pd-Y alloy thin film much easier. The main advantage of his research was simple fabrication process by using DC/RF magnetron sputtering system. The deposition rates of two metals were monitored by quartz crystal thickness monitor. The surface morphology of thin film in the SEM was clean and flat.

The second approach to address the fracture issue of pure palladium film is to utilize low-dimensional structures, such as nanowire and nanoparticle [10–13]. Pd film tends to expand due to its volume increase when it absorbs hydrogen gas, leading to a compressive stress at the interface of the film and substrate [14]. Conversion of materials into nanoscale reduces crystal defects, thereby enhancing mechanical strength and reducing the fracture phenomenon. Furthermore, nanostructures have been a major research focus as high performance hydrogen sensing elements. Since nanostructures have a large surface to volume ratios, the hydrogen diffusion paths can be shortened, and absorption and desorption rates of chemical reaction are improved. Palladium nanostructures have shown promising properties, which are suitable for high speed, high sensitivity, miniature size, and low-cost hydrogen sensor [13]. However, the nanowire and nanoparticle are of great complexity to fabricate and they normally require expensive nano-fabrication facilities for mass-production.

Pd-Y alloy thin film has been used to detect hydrogen gas based on both optical and electrical methods [6–9,15]. The electrical detection method is inexpensive, easy and convenient compared to the optical counterpart [6–9]. Furthermore, palladium-yttrium based gas sensor does not require high operating temperature, which is compulsory in other popular resistive gas sensors based on tungsten oxide [16,17].

Jamshidi et al. [15] reported the hydrogen detection based on the resistance change of palladium-yttrium thin film. However, the resistance change was small due to its large thickness and unpatterned sensing element. Moreover, the results were not precise and reliable due to long time intervals of data collection.

Wang et al. [5] did research on zigzag-shaped palladium-silver thin film for hydrogen sensing based on electronic resistance change. The zigzag-shaped thin film can provide larger electrical resistance and change than unpatterned thin film. Therefore, the sensor showed higher sensitivity and reversibility. However, complex fabrication processes were required to pattern the thin film.

In this paper, we present a novel zigzag-shaped resistive hydrogen sensor based on $Pd_{0.92}$-$Y_{0.08}$ alloy nanosheet. The sensing element has an ultra-thin thickness of 19.3 nm and reasonable electrical resistance of 7 kΩ. The fabrication process of the resistive hydrogen sensor is simple and has fewer steps by utilizing shadow mask and ultrahigh-vacuum magnetron sputtering system. The proposed fabrication process is suitable for mass-production of the sensor.

2. Experiment

2.1. Sensor fabrication

Fig. 1 illustrates the fabrication process of the hydrogen sensor based on patterned Pd-Y alloy nanosheet. The substrate is a round-shaped quartz glass with 20 mm in diameter and 3 mm in thickness. First, the quartz glass substrate and shadow mask were cleaned in ethanol using ultrasonic cleaner. The shadow mask is required for patterning the alloy nanosheet to increase the nominal resistance of the sensing element. To fabricate the shadow mask, a thin plastic sheet was cut into zigzag-shaped using laser cutter (TROTEC Speedy 300™). The shadow mask was attached to the surface of glass substrate, as shown in Fig. 1 (a).

To deposit the ultra-thin film of palladium-yttrium alloy, ultra-high vacuum magnetron sputtering system (BESTEC) was utilized. Palladium and yttrium targets with purity of 99.95% were installed in the DC and RF sources of the sputtering system, respectively. The thickness of the alloy nanosheet was monitored by quartz crystal thickness monitor with a resolution of 0.1 nm. The detailed process parameters of magnetron sputtering process are listed in Table 1. A 15 nm Pd-Y nanosheet was deposited on the quartz glass substrate using BESTEC sputtering system. The Pd-Y alloy nanosheet was patterned by the zigzag-shaped shadow mask as shown in Fig. 1 (b).

However, yttrium is very easy to be oxidized when Pd-Y material is exposed to air. To avoid this problem, a thin protection film is required on the top of the Pd-Y alloy nanosheet. The pure palladium can be a good candidate because it does not react with oxygen. Therefore, the DC sputtering source continued to operate for 50 s after the RF sputtering was shut down. A thin palladium layer is coated on the surface of Pd-Y alloy nanosheet, and the thickness of the layer is 5 nm as illustrated in Fig. 1 (c). The pure ultra-thin palladium layer can allow hydrogen atoms to penetrate into the Pd-Y alloy to react, meanwhile it can reduce the probability of the contact between yttrium atoms in the alloy and oxygen atoms in air [7,8]. At last, the zigzag-shaped nanosheet was remained on the quartz glass substrate after removal of the shadow mask as shown in Fig. 1 (d).

Fig. 2 depicts a schematic diagram of the zigzag-shaped resistive hydrogen sensor. The sensing material was deposited in the middle of substrate. The material of both electrodes was same as sensing element with size of 2mm × 2mm. All the measurement and discussion hereafter are based on designs with a width of 500 μm, length of 92 mm for the zigzag-shaped nanosheet.

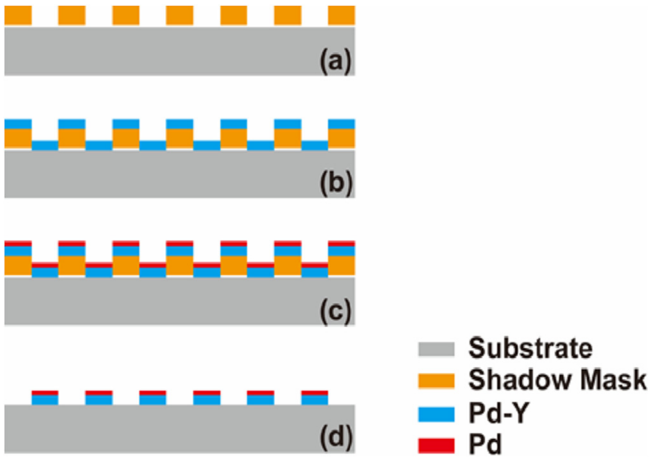

Fig. 1. Fabrication process of a zigzag-shaped Pd-Y alloy thin film on quartz glass substrate.