



## Batch fabrication of nanogap electrodes arrays with controllable cracking for hydrogen sensing



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### ABSTRACT

Hydrogen sensor based on Pd nanogap arrays was fabricated using the swelling induced cracking method. The square hole Pd array is patterned on the polymer to define the position of the nanogaps. We discuss the influence of the size and the shape of the holes on the formed nanogaps. The structural and morphological characteristics of the metal array and the nanogaps were investigated using laser scanning confocal microscopy (LSCM) and scanning electron microscopy (SEM). To illustrate an application of the nanogap structure, the Pd nanogap array was deposited on epoxy and polyimide (PI) substrate and used as H<sub>2</sub> sensor, showing a good sensitivity and stability at room temperature. Moreover, the performance of the nanogap array on PI substrate remains stable after annealing at 80–180 °C. This effect is attributed to the high thermal stability of the PI substrate. The effective fabrication method, good sensitivity and the high stability of the Pd nanogap arrays show promising application for H<sub>2</sub> sensing.

### 1. Introduction

The detection of various hazardous vapors and gases is an important field due to the increasing threat caused by air pollution [1–6]. In particular, hydrogen (H<sub>2</sub>) draws more and more attention due to its promising application in the renewable energy field. With the help of a solar water splitting device, H<sub>2</sub> can be produced from water to feed H<sub>2</sub> fuel cells with the only byproduct being water [7–9]. Fuel cells are used in cars and busses, which is promising to reduce pollution from urban traffic [10]. However, the production, storage and utilization of hydrogen are still a challenge because of its high flammability (4–75.6% in oxygen/air), large diffusion coefficient (0.61 cm<sup>2</sup>/s) and low ignition energy (0.02 mJ) [11]. Therefore, hydrogen sensors with high sensitivity, fast response, stable and low cost are required to ensure the security [12]. And hydrogen sensor can also be used in the field of nuclear reactors, coal mines and semiconductor industry [11,13–15]. So far, a multitude of H<sub>2</sub> sensors with were demonstrated. Optical methods like laser gas analysis and plasmonic sensors can detect H<sub>2</sub> by measuring absorption or scattering spectra [16–18]. Semiconductor-based H<sub>2</sub> sensors rely on the reduction of the semiconductor caused by the H<sub>2</sub> exposure. In general, semiconductor materials are designed into nanostructures in order to increase their specific surface area and metal particles are deposited on the semiconductor surface acting as a catalytic layer, which effectively improves the sensitivity and operating

temperature [19–23]. Specifically, nanogaps in Pd have been demonstrated to be effective for improving the H<sub>2</sub> detection. The contact between Pd nanogaps electrodes would close following the H<sub>2</sub> exposure, which would result in the significant increase of the film conductivity. Numerous studies indicate that hydrogen sensors based on nanogaps display high sensitivity, fast response and high selectivity versus H<sub>2</sub> gas, which is promising for sensors fabrication [24–28].

So far, various methods were adopted to get nanogaps between the electrodes. Favier et al. fabricated nanowires by electrodeposition. The electrodeposition process introduces nanogaps for H<sub>2</sub> sensing [29]. Ibanez et al. dropped a dispersion of hexanethiolate-coated Pd nanoparticles to fabricate nanogap arrays between the Pd nanoparticles [30]. Zhao et al. deposited SiO<sub>2</sub> and Pd films on microscale silicon gaps, reducing the gaps to the nanoscale [27]. However, these methods were pointed out to be difficultly extended to fabricate hydrogen sensors over large areas [25]. Lee et al. proposed a low-cost, large-scale mechanical stretching technique in which nanocracks were formed in the metal film by the stretching of the elastomeric substrate [25,31]. This method has prospects for the fabrication of high sensitivity and low-cost hydrogen sensors. Moreover, it also provided a good idea to get nanogaps using the stretching. However, the disordered position and the orientation of the cracks may result in a hardly controlled responding behavior [27]. For this method, a soft polymer like Poly(dimethylsiloxane) is required to ensure enough strain to crack the Pd film. When

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in a high temperature atmosphere, the soft polymer will have serious deformation, which influences the performance of the hydrogen sensor [31]. Therefore, it makes sense to realize large area and low cost nanogap electrodes fabrication on substrates with high thermal stability.

In this work, hydrogen sensors based on a nanogap array are fabricated by patterning the electrodes on epoxy and polyimide (PI) substrate. The square hole array provides for stress sources and stress concentrative points. The influence of the size and the shape of the holes on the formation of nanogaps upon deformation are investigated. A higher integration level of hole arrays prevents the formation of nanogaps. We show that nanogaps can be patterned in a variety of arrangements when the hole shape changes. Furthermore, the nanogap electrode array is used for H<sub>2</sub> sensing showing a good sensitivity to H<sub>2</sub> and a stable operation at temperatures up to 180 °C.

## 2. Experimental details

### 2.1. Nanogap electrodes fabrication

Epoxy (Ausbond, crystal epoxy) was spin coated on glass substrate 1000 rpm for 18 s, followed by 2000 rpm for 45 s to reach a film thickness of 40 μm. The epoxy layer was solidified for 24 h at room temperature. A positive photoresist (Everlight Chemical Industrial Corporation, EPG 533) was spin coated onto the epoxy and pattern using photolithography. Then Cr (30 nm) and Pd (90 nm) films were successively sputtered at room temperature using the explorer multi-target sputtering system (Denton Vacuum) with 20 sccm argon (99.999%) flow rate and 0.440 Pa working pressure. The photoresist was then washed out to obtain the patterned electrodes. The distance between two adjacent holes was set to 10 μm. After this process, the patterned epoxy was immersed in ethanol for 150 s to crack the electrodes. To fabricate the nanogap electrodes that are not completely disconnected, the epoxy was replaced by PI (Minnesota Mining and Manufacturing, 98c-1) substrate. The electrodes patterned onto the PI substrate were immersed in dimethylacetamide (analytical reagents) for 24 h 3D topography measurements of the nanogap electrodes were taken using OLS4000 LEXT (Olympus). SEM images were acquired using the SU-8010 (Hitachi) microscope.

### 2.2. Characterization of H<sub>2</sub> sensor

Current-voltage measurements were performed using Keysight B2912A digital source-meter. The bias voltage was set as 0.1 V during the measurements. The H<sub>2</sub> sensing measurements were performed at room temperature using nitrogen as a carrier and vent gas. The sensor response was determined at different H<sub>2</sub> concentrations ranging from 200 to 10,000 ppm.

## 3. Results and discussion

The fabrication process of the nanogap array is illustrated in Fig. 1a, which has mentioned in our previous study [32]. Firstly, a 40 μm thick epoxy film acting as the swelling layer is spin coated on glass. Then the electrodes are patterned on the epoxy using photolithography followed by lift-off process. Palladium (Pd) is selected as the electrode material thanks to its high H<sub>2</sub> absorption capacity. A Chromium (Cr) adhesion layer was sputtered on epoxy before depositing the Pd film. The Cr layer also allows adjusting the ductility of the metal electrodes. In this work, Cr/Pd (30/90 nm) electrodes with square hole-arrays were patterned on the epoxy surface (Fig. 1a-i). The distance between two adjacent square holes was fixed to 10 μm. After the electrodes fabrication, the swelling layer is immersed into ethanol which can only permeate into the epoxy through the square hole-array. Because of the expansion of the epoxy, the electrodes edges rise up and the expansion stretches the electrodes at the necking area which result in the cracking of the electrodes, as shown in Fig. 1a-ii. Fig. 1b shows the 3D topography of the electrode

after swelling for 150 s. The epoxy exposed to ethanol undergoes an expansion and rises up, while the epoxy covered by the electrodes remains unvaried. For the electrodes, periodic bulges are generated at the necking area with a height of about 400 nm (Fig. 1c). Since the height difference between the necking areas and the undeformed regions on each bugle is almost negligible, we can safely assume that the stretches at all the necking area were identical. Simulated result shows a max strain up to 0.07 at the necking area of the electrodes after swelling in ethanol for 150 s, as shown in Fig. 1d. This stretch is strong enough to tear the electrodes and promote the fabrication of the nanogaps. When the sample is removed from the ethanol, the epoxy starts to recover its pristine volume and the nanogaps spacing shrink. Fig. 1e shows the scanning electrode microscope (SEM) image of the nanogap electrode arrays. Nanogap forms at each necking area with a width about 200 nm shows that a height differences of 400 nm is enough to crack the electrodes. Due to the high uniformity of the height difference of the bugle, the widths of nanogaps are almost the same everywhere.

For the electronic devices, high integration indicates low cost, high performance and low energy consumption. Therefore, the study of the maximum integration level of nanogaps is essential for nanogap fabrication. To get the density limit of the nanogaps, we further investigated the penetration depth and the height difference as a function of the swelling time of an epoxy film half covered by the Pd/Cr patterned film, as shown in Fig. 1f. After swelling for 5 min, the ethanol could penetrate into the epoxy covered by metal film for about 13 μm. This indicates that if the epoxy coated with a metal wire with a width of 26 μm, ethanol molecules would have been able to penetrate the epoxy under the wire. For patterned electrodes, the swelling process can be divided into two stages, as shown in Fig. 1g. Firstly, the height difference increases with the swelling time until the ethanol molecules penetrate into the epoxy under the centre of the electrodes, just as the semi-infinite metal film. At this stage, the stretch at the necking point between the electrodes increases with the time due to the increase of the height difference. After that, all the surface of epoxy swells and rises up. Since the rising speed at the centre of the electrodes is faster than the edge of the electrodes, the height difference first increases then it decreases, so that the strain at the necking point reduces. This result shows that there is a maximum stain value during the swelling. A higher integration of nanogaps would result in a smaller distance between the centres to the edge of the electrodes leading to a lower maximum strain value. To support this interpretation, square hole electrode arrays with 5 different side lengths are immersed into ethanol and the height differences are monitored at a function of the swelling time. The height differences of these samples are nearly the same before it reach the maximum value, which indicate that the size of electrodes has a very small impact on the max height change of the electrodes. And a larger side length of the square hole indicates a larger maximum height difference and swelling time to get the maximum height difference, as shown in Fig. 1h. When the side length of the hole-array is set as 10 μm, there are no nanogaps at the necking area after swelling even after swelling for 24 h. When the side length of the holes is set as more than 20 μm, nanogaps form in the necking area after swelling for the same time (Fig. S1). When the solvent is changed, its penetration speed and the polymer expansion ratio are modified, thus a different minimums distance between nanogaps can be realized. For example, the swelling using acetone results in a faster penetration speed, as only 10 s are required to get a height difference of 400 nm, while the penetrate depth is 18.5 μm. Under these conditions, a side width larger than 40 μm is required to get nanogap arrays (Fig. S2). The experimental results close interrelation between the array length and the solvent to get nanogaps and it provides a new way to prevent the cracking of metal electrodes located on the polymer when one would need to put in contact an organic solvent in subsequent processes.

The electrode cracking can also be controlled by the fillet which influences the concentrated stress. Fig. 2a shows the SEM image of electrodes arrays exposed to ethanol for 90 s. The sharp edge to sharp

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