A Low-Energy Room-Temperature Hydrogen Nanosensor: Utilizing the Schottky Barriers at the Electrode/Sensing-Material Interfaces

Peng Zhang, Abhilash Vincent, Amit Kumar, Sudipta Seal, and Hyoung Jin Cho

Abstract—The hydrogen-sensing performance of a nanosensor integrating interdigitated electrodes with a gap of 100 nm and indium-oxide-doped tin dioxide nanoparticles is investigated at room temperature. The nonlinear behavior observed from the I/V curves of the sensor in air atmosphere indicated the presence of a Schottky barrier contact at the electrode/sensing-material interface. The linear I/V response obtained in hydrogen atmosphere suggested that the Schottky barrier height could be modulated in the presence of hydrogen. At a low applied voltage of 0.4 V and 0.09-vol% hydrogen gas exposure, a very large sensitivity of ∼2300 and a short response time of ∼127 s were recorded.

Index Terms—Hydrogen sensor, interdigitated electrodes (IDEs), In_2O_3-doped SnO_2, Schottky barrier.

I. INTRODUCTION

WITH THE concerns of the safety issues of hydrogen energy, hydrogen sensors have been investigated in the decade [1]–[9]. Among the various types of hydrogen sensors, chemiresistor-based hydrogen sensors have been widely used due to the advantages of well-established fabrication and detection methods [3]–[5]. Fast response, low energy consumption, and low detection limit are the major critical factors to the hydrogen sensors. As the temperature decreases, the activation energy required for the gas–MOS reaction increases. This brings technical challenges in achieving both fast response and high sensitivity at room temperature. In this letter, we present a hydrogen nanosensor integrating gold (Au) interdigitated electrodes (IDEs) and indium oxide (In_2O_3)-doped tin dioxide

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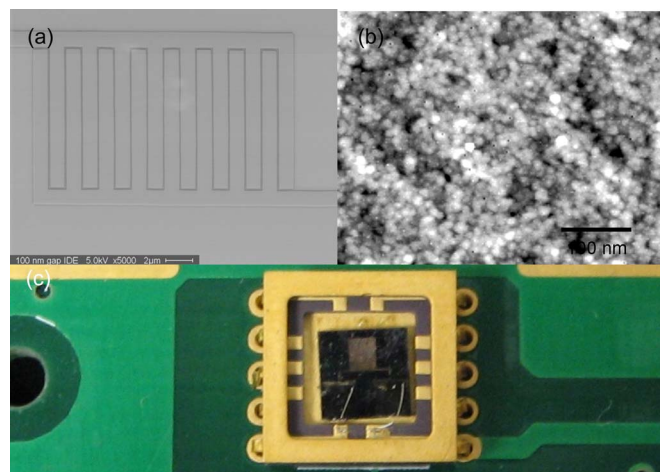
Fig. 1. (a) SEM image of the IDEs. The gap, the width, the length, and the number of fingers of the IDEs are 100 nm, 1 μm, 10 μm, and 8, respectively. (b) AFM image of the In_2O_3-doped SnO_2 hydrogen-sensing film. (c) Packaged H_2 sensor device.

(SnO_2) nanoparticles and the influence of the Schottky barriers at the electrode/sensing-material interface on hydrogen sensing.

II. SENSOR DESIGN AND FABRICATION

The sensor platform with Au IDEs was fabricated by e-beam lithography in Fig. 1(a). The hydrogen-sensing material (6.5-mol% In_2O_3-doped SnO_2 nanoparticles) was prepared by a sol-gel process [4] and was coated on the Au IDEs with a film thickness of 120 nm. The sensor shows a high reproducibility. The surface morphology of the nanostructured coating is shown in Fig. 1(b). Doping SnO_2 with In_2O_3 increases the oxygen vacancy and then improves the sensing capability [4]. Platinum (Pt) nanoclusters were sputtered on the sensing material as a catalyst, and the sensor sample was heat treated at 400 °C for an hour to control the film density and grain size and ensure a good adhesion between Pt clusters and the sensing film [4].

III. RESULTS AND DISCUSSION

Before an electrical field is applied, at the interface of the IDEs and the sensing material, free-electron transfer occurs from the sensing material to the Au electrodes due to the different work functions of the materials until the thermal equilibrium is reached. This generates electron depletion layers (also known as Schottky barriers) at the interfaces. Meanwhile,
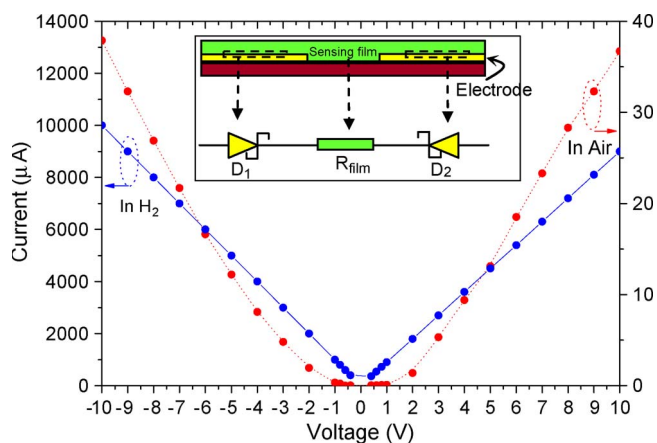
Fig. 2. (Inset) Proposed model based on the Schottky barrier assumption and I/V curves of the nanosensor tested in air and in 0.09-vol% H_2 atmosphere. The electrode/material interfaces are considered as Schottky diodes (D_1 and D_2). The sensing material (In_2O_3-doped SnO_2) is considered as a uniform resistor in air atmosphere. The graph was obtained after 20 min when the sensor was exposed to air and hydrogen atmosphere.
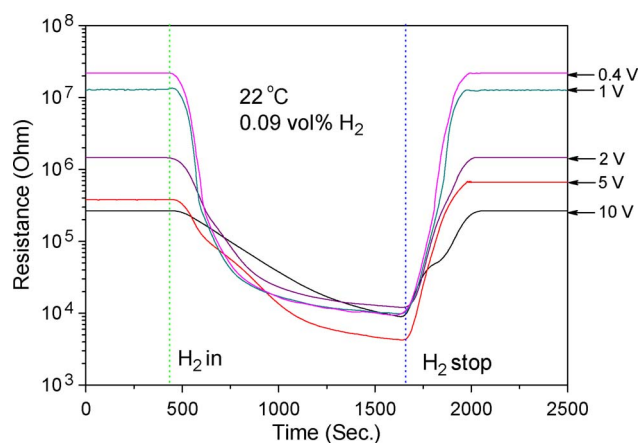

Fig. 3. Resistance change at various applied voltages from 0.4 to 10 V. The initial resistances in air atmosphere decreased with increasing voltages. At 0.4 V, the sensor exhibited the fastest response (127 s), the highest sensitivity (2300), and the lowest energy consumption (7 nW) in 0.09-vol% H_2 at room temperature.

in air atmosphere, oxygen molecules adsorbed on the surface of the sensing film pick up the electrons from the conduction band of the sensing material and push the electron depletion layer at the interface into the sensing film further. Therefore, the sensor shows high electrical resistance in air. If the Au-electrode/sensor-material interface is considered as a Schottky diode, the equivalent circuitry of the sensor could be modeled as two Schottky diodes which are connected back to back with a series resistance (In_2O_3-doped SnO_2 material) in between, separating the diodes (inset in Fig. 2). In order to simplify the analysis, here, we will discuss only the case of two electrodes as it is possible to expand the results to represent the whole IDEs. In Fig. 2, when an electric potential is applied, if one diode (D_1) is forward biased, the other diode (D_2) is considered reverse biased due to the symmetry of the sensor structure. At the reverse-biased interface, the electron depletion layer is extended further into the sensing material. In this condition, only a limited amount of electrons can travel from the negatively biased Au electrode to the sensing material by tunneling and/or thermal emission before the breakdown happens. This makes the measured current very small in magnitude. The electronic conductivity behavior of the sensor in air atmosphere is confirmed from the I/V characteristic measurements conducted on the sensor in air (Fig. 2). At a low applied voltage (< 2 V), the current was constrained by the reverse-biased Schottky diode, and a limited current flow (< 100 nA) was observed. When the applied voltage was larger than 2 V, the current increased dramatically, implying the breakdown of D_2, and the current was then controlled by the resistance in series originating from the sensing material. Fig. 2 also shows the I/V characteristics of the sensor measured at 0.09-vol% H_2. A linear trend in the I/V characteristics was obtained in the range from 0.4 to 10 V. It is believed that the Schottky barriers are responsible for the nonlinear behavior in the I/V curves obtained in air, whereas those are reduced or even vanished in the presence of H_2, resulting in a linear trend. When H_2 is introduced to the sensor, the dissociated hydrogen atoms could accumulate at the electrode/sensing-material interfaces and be

polarized. This could cause the formation of a dipolar layer at the interface. The presence of the excess of charge states at the interfaces is known to effectively reduce the Schottky barrier height [6].

Fig. 3 shows the resistance changes of the sensor during H_2 sensitivity tests at applied voltages varying from 0.4 to 10 V. The sensor exhibited different performance at different working voltages. The sensor exhibited both the highest sensitivity ($R_{air}/R_{hydrogen} =\sim 2300$, where R_{air} and $R_{hydrogen}$ are the measured resistances in air and in hydrogen gas, respectively) and the fastest response (~127 s, the time frame when R_{air} drops by one order of magnitude) at 0.4 V. The effect of applied voltages on the sensor performance could be explained by the Schottky diode model proposed in Fig. 2 (inset). When the applied voltage is 0.4 V, the current from the sensor would be limited by the reverse-biased Schottky diode (D_2) in air, and therefore, the initial resistance is very large. On the other hand, in H_2, given the reduced effect of the Schottky barriers at the interfaces, the measured resistance is mainly from the series resistance between the diodes. It should be noted that the resistance of the sensing material can also decrease in the presence of H_2 [4]. When the applied voltage is above 2 V, breakdown happens (inset in Fig. 2) at the Schottky diode D_2 (in air), and the initial resistance of the sensor (determined by the series resistance of the sensing material) then decreases. The measured initial resistance of the sensor in air at 2 V was 1.1 MΩ, which was much smaller than that (22 MΩ) of the sensor working at 0.4 V. It is clear from Fig. 3 that an increase in the applied voltage close to 2 V or above reduces the sensitivity of the sensor dramatically. During dynamic testing in H_2 atmosphere, Fig. 3 shows that, before the sensor resistance drops to its saturated value, it first follows an exponential decay (due to the disappearance of the Schottky barriers at the interface) and then a linear decrease (due to the surface chemical reactions in the sensing material). Due to the huge R_{air} at the low applied voltage of 0.4 V, the calculated energy consumption ($W = U^2/R_{air}$, where U is the applied voltage) of the 100-nm-gap sensor was as low as 7 nW. This makes
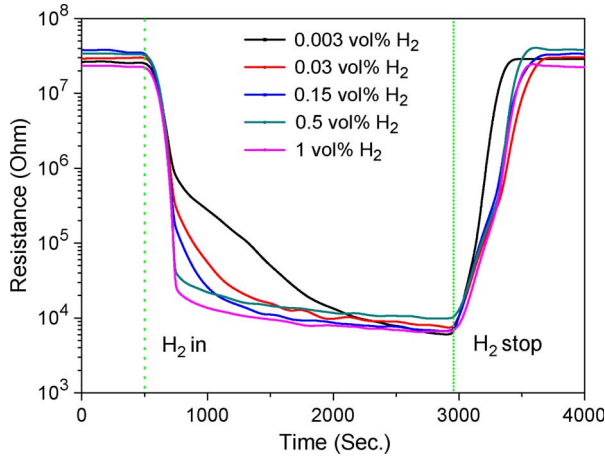
Fig. 4.   Sensor response in 0.003- to 1-vol% H_2 at 0.4 V and 22 °C.

the sensor more suitable for the applications where power is considered as one of the most precious commodities, such as spacecraft missions.

The sensor performance at 0.4 V and in various H_2 concentrations is shown in Fig. 4. The detection range of the sensor is wide from 0.003 to 1 vol%. The interesting observation is that the sensor shows similar sensitivity at all the concentrations (provided that enough time is given to reach the saturation). It might be due to the vanishing of the Schottky barriers at the interfaces. After enough concentration of H_2 reaches the interface, the film resistance does not change significantly.

Based on the proposed model, the response time of the sensor working at 0.4 V depends on how fast the hydrogen atoms could diffuse to the interfaces to lower the Schottky barrier height instead of the reaction rate between the hydrogen gas and the sensing material since most of the resistance drop comes from the Schottky barriers at the interfaces.

When the Knudsen diffusion coefficient (D_k) and the reaction rate constant κ (from the Arrhenius equation) are compared, the temperature effect is usually less prominent in D_k than κ since D_k is proportional to $T^{1/2}$ [7]. Here, D_k and κ are [7]

$$D_k = \frac{4r}{3}\sqrt{\frac{2RT}{\pi M}} \tag{1}$$

$$\kappa = A \cdot \exp\left(\frac{-E_k}{RT}\right) \tag{2}$$

where r is the pore radius of the sensing film, R is the gas constant, T is the temperature, M is the molecular weight, E_k is the activation energy, and A is the preexponential factor.

Therefore, at low temperatures, particularly at room temperature, the gas-diffusion-controlled response time should become shorter than the gas–material-reaction-controlled one. The Schottky-diode-based hydrogen sensors have shown a fast response at low hydrogen concentrations and low temperatures

since even a smaller concentration of the hydrogen could lower the Schottky barrier height significantly [6].

Compared to other Schottky-diode-type hydrogen sensors [8], [9], the presented sensor shows an order of magnitude higher sensitivity (2300) and a shorter response time (127 s) at room temperature due to the vanishing of the Schottky barriers in H_2. It is worthwhile to mention that Schottky barriers may exist at the Pt/sensing-material interface as well, even though they do not directly influence the sensing characteristics.

IV. CONCLUSION

We have fabricated and characterized a nanogap hydrogen sensor. A model based on the assumption of Schottky barriers at the electrode/sensing-material interface has been proposed and discussed over the I/V characteristics measured in both air and H_2 atmospheres. The sensor showed improved performance at the low applied voltage of 0.4 V among other conditions by utilizing the Schottky barriers at the electrode/sensing-material interfaces. Fast response (127 s), high sensitivity (2300), and low energy consumption (7 nW) were observed in 0.09-vol% H_2 at room temperature. Moreover, a wide detection range from 0.003- to 1-vol% H_2 indicates that the sensor could be used for the early detection of hydrogen leak.

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