

Peeling-Off Effect and Field-Effect Modulation on Palladium-Top-Gated Indium Gallium Zinc Oxide Thin Film Transistors for Hydrogen Sensor

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Hyoung Joo Nam^{a,*} and Young Tack Lee^{b,c,*} 

^aCollege of General Education, Chung-Ang University, Seoul 06974, Republic of Korea

^bDepartment of Electrical and Electronic Engineering, Inha University, Incheon 22212, Republic of Korea

^cDepartment of Electrical and Computer Engineering, Inha University, Incheon 22212, Republic of Korea

*Corresponding author E-mail: todayonlybabo@cau.ac.kr, ytleee@inha.ac.kr

ABSTRACT

Hydrogen gas is one of the most promising future clean energy sources, which has great merits of high energy efficiency, non-pollution, and non-depletable. However, the high dangers still be remained for flammable and explosive possibility above 4 % concentrations hydrogen in ambient air. In this study, we propose a palladium (Pd) top-gated indium gallium zinc oxide (IGZO) thin film transistor (TFT) based hydrogen sensor application, reusable, reliable, and stable for above 4 % high concentrations hydrogen gas exposure. The sensing mechanism is based on the peeling-off effect of the Pd thin film came from the phase transition phenomenon of Pd hydride system formation process. The Pd top-gated IGZO TFT hydrogen sensor shows both fast response time of 30 s and recovery time of 50 s with high sensitivity of ~1,600,000 % even under the high concentration hydrogen gas condition.

Keywords: Indium gallium zinc oxide channel, Thin film transistor, Palladium, Peeling-off effect, Hydrogen sensor

1. Introduction

Hydrogen has attracted much attention for the most important future energy source due to its remarkable merits such as high efficiency, being non-depletable, and non-polluting. Despite these great advantages, hydrogen still has significant dangers due to its highly flammable and explosive properties at high concentration above 4 % in the air ambient [1–6]. In recent years, fuel cell electric vehicles using hydrogen energy have been developed and commercialized as alternative clean energy already. However, the number of hydrogen gas fueling stations is much smaller than that of gasoline and diesel fueling stations due to its potential risk of explosion [7–9]. Consequently, extensive studies have been conducted on highly sensitive hydrogen gas sensors possible to detect the little amounts of leaked hydrogen to ensure its safe use. However, studies on the detection of high hydrogen concentrations, particularly within the explosion threshold in air (> 4 %), are rare to see [10].

Palladium (Pd) is the most well-known material possible to absorb and store the hydrogen gas selectively and easily forms a Pd hydride (PdH) system (α -phase) even under the low hydrogen concentration. The absorbed hydrogen atoms can act as electron scattering sources inside the Pd thin film (TF), leading to increase resistance of the Pd TF [11,12]. Additionally, at hydrogen concentration above 2 %, excess hydrogen molecules partially accumulate within the Pd lattice, causing lattice expansion and a subsequent increase in Pd volume by creating PdH_x system (β -phase). And finally, the volumetric expansion induces a peeling-off effect of deposited Pd TF from substrate [13,14]. While such peeling-off of Pd TF is typically considered as a failure mechanism that degrades the performance of Pd-

based classical hydrogen sensor. This study explores this phenomenon to develop the high-concentration hydrogen sensor (> 4 %) based on the large-area process-compatible indium gallium zinc oxide (IGZO) semiconductor-based field-effect transistor devices.

2. Results and discussion

Figure 1 illustrates the Pd lattice schematic diagrams for hydrogen sensing mechanisms and the device schemes of two types of Pd TF-based hydrogen sensors: one is utilizing resistance variation, and the other is employing capacitance variation. When the Pd TF is exposed to a low concentration of hydrogen gas (< 1 %), Pd selectively absorbs hydrogen gas and partially forms an α -phase, which brings an additional electron scattering effect, thereby increasing the resistance of the PdH TF as shown in Fig. 1(a). Consequently, as depicted in Fig. 1(b), the extent of hydrogen exposure can be easily determined by measuring the resistance variation of the Pd TF. Figure 1(c) shows hydrogen gas detection property obtained from the variable-resistor type Pd TF sensor. On the other hand, when the Pd TF is exposed to a relatively higher hydrogen concentration above 2 %, the absorbed hydrogen atoms begin to accumulate and to form the hydrogen molecules inside the Pd lattice, called as a β -phase. This phase transition results in an expansion of the lattice parameter (a) by approximately 1.04 times, as shown in Fig. 1(d) [15–17]. Such expansion occurs in three-dimensional directions, causing volume expansion of the Pd TF, which may ultimately lead to delamination (peeling-off effect) from the substrate, particularly when adhesion is relatively weak. This peeling-off phenomenon is typically regarded as a failure mode of Pd-based hydrogen sensors. However, the formation of an unexpected gap between the Pd TF and the substrate reduces the contact area, thereby



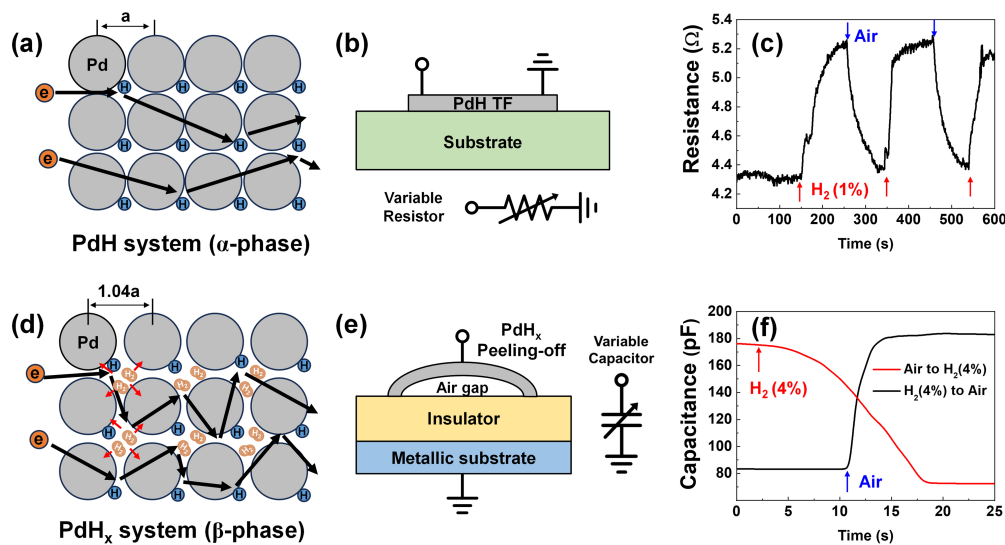


Figure 1. (a) Schematic illustration of the operating mechanism of a resistive-type hydrogen sensor based on α -phase PdH formation. (b) Cross-sectional device schematic and (c) real-time hydrogen sensing properties of α -phase PdH-based resistive sensor under cyclic exposure to 1% hydrogen and ambient air. (d) Schematic illustration of the operating principle of a capacitive-type hydrogen sensor utilizing β -phase PdH_x behavior. (e) Cross-sectional device schematic and (f) real-time hydrogen sensing properties of the β -phase PdH_x-based capacitive-type hydrogen sensor exposure to 4% hydrogen and ambient air.

enabling its application as a novel type of hydrogen sensor utilizing a variable capacitor [Fig. 1(e)]. Figure 1(f) shows the capacitance variation due to the peeling-off effect of the Pd TF deposited on a silicon substrate (red line, from air to 4% hydrogen), along with its recovery in ambient air (black line, from 4% hydrogen to Air), demonstrates the potential of this mechanism for hydrogen sensor applications.

A previous study on Pd-based capacitive-type sensors was conducted by connecting the Pd TF capacitor in series with the gate electrode of a commercial IGZO thin-film transistor (TFT). Figures 2(a) and 2(b) show the device schematic and the circuit diagram of the series connected Pd TF capacitor and IGZO TFT to convert the capacitance variation into the current signal change [10,18]. In this study, we aimed to develop a highly sensitive hydrogen sensor for the safe use of hydrogen energy. Additionally, we focused on sensor integration and large-area processing fabrication methods to enhance the reliability and stability of hydrogen sensing. To achieve this, the Pd TF itself functions as the top gate electrode of the IGZO TFT, rather than relying on the previous series-connected capacitance for device optimization. Figure 2(c) introduces the device fabrication process steps of the Pd top-gated IGZO TFT for hydrogen sensor. First, 40 nm-thick IGZO TF was deposited on cleaned substrate using RF magnetron sputtering system. And then, the IGZO active channel patterning carried out by using conventional photolithography and wet etching techniques within the dilute buffered oxide etchant (BOE) 200:1 with the etching rate of ~ 4 nm/s at room temperature (RT). After that, direct current sputtered Au/Ti (50/50 nm) electrode (S/D) electrodes were formed and patterned by utilizing a combination of photolithography and lift-off processes. The channel length and the channel width were 50 and 1,000 μm , respectively. To fabricate the 50 nm-thick Al_2O_3 gate insulator (GI) layer on it, the atomic layer deposition (ALD) system was used. And then, 50 nm-thick Pd top-gate electrode was formed in the same way as the S/D fabrication method. Finally, S/D contact via holes were created to measure the electrical properties of IGZO TFTs. For this, BOE 200:1 etchant was used for removing the Al_2O_3 GI layer above the S/D electrodes. All drain current–gate voltage ($I_D - V_G$) transfer curve and dynamic I_D characteristics were measured using a semiconductor parameter analyzer (HP 4156B, Agilent Technologies), and capacitance–voltage characteristics was measured using a LCR meter (HP 4284A, Agilent Technologies) under dark at RT.

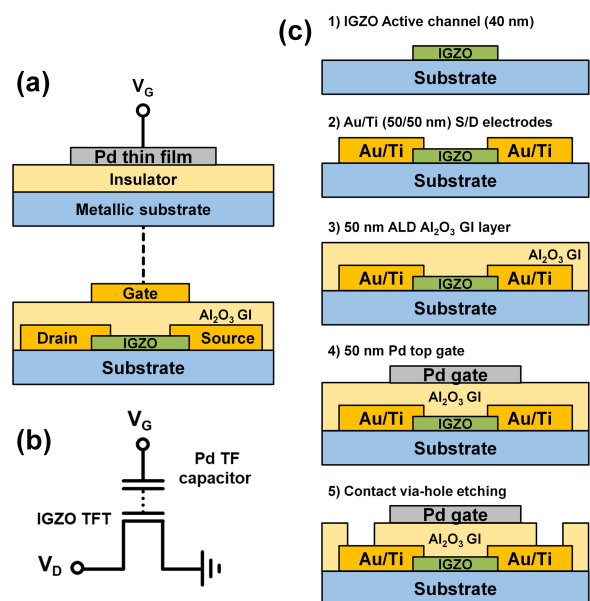


Figure 2. (a) Device schematic and (b) the suggested circuit diagram of series-connected Pd TF capacitor to gate electrode of IGZO TFT. (c) Device fabrication process steps of Pd top-gated IGZO TFT device for hydrogen sensor: 1) IGZO active channel, 2) Au/Ti S/D electrode, 3) Al_2O_3 GI layer, 4) Pd top gate, and 5) contact via-hole.

Figure 3(a) shows an optical microscope (OM) image of the as-fabricated Pd top-gated IGZO TFT. Figure 3(b) presents the $I_D - V_G$ transfer characteristics curve, the IGZO TFT hydrogen sensor was mounted in the gas chamber and operated with a printed circuit board for remoted hydrogen gas sensing measurement. The plot exhibits a I_D on/off ratio of $\sim 10^5$, along with a high drain on-current of $> 20 \mu\text{A}$ at the drain voltage (V_D) of 1 V. The inset is the cross-sectional device schematic. The 50 nm-thick Al_2O_3 GI layer, fabricated via ALD, demonstrated a subthreshold swing (SS) of 270 mV/dec and a little hysteresis loop of 0.4 V for V_G sweep of ± 20 V, confirming the high reliability of the fabricated Pd top-gated IGZO TFT array. Addition-

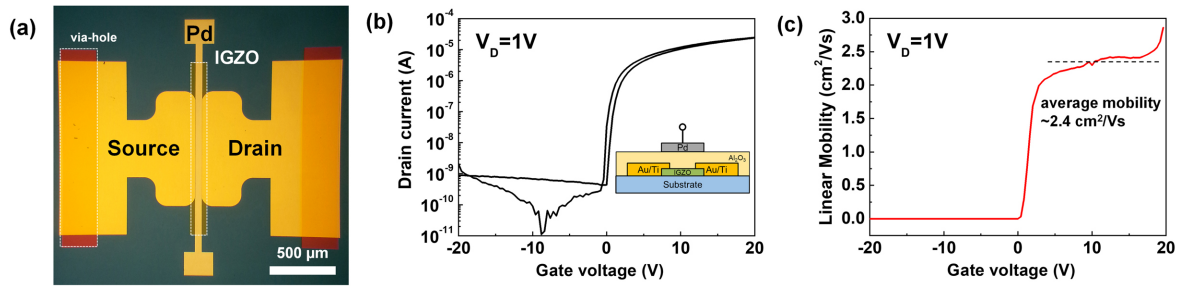


Figure 3. (a) The OM image, (b) the I_D - V_G transfer characteristics with device schematic, and (c) the μ_{lin} plots of the fabricated Pd top-gated IGZO TFT device. The scale bar is 500 μm in (a).

ally, Fig. 3(c) shows the electron mobility, calculated from the linear I_D model ($V_D \ll V_G$), where the linear mobility (μ_{lin}) was $\sim 2.4 \text{ cm}^2/\text{V}\cdot\text{s}$ by using the following equation;

$$\mu_{lin} = \left(\frac{dI_D}{dV_G} \right) \left(\frac{L}{WC_{ox}V_D} \right)$$

where the C_{ox} is oxide capacitance of the 50 nm-thick Al_2O_3 GI (dielectric constant of 7.5), W and L are the channel width and length IGZO TFT respectively.

Figure 4 illustrates the hydrogen gas sensing properties of Pd TF based IGZO TFTs. In the previous series-connected capacitive-type sensor, the Pd TF device operates as a variable capacitor in response to high concentration hydrogen exposure, while the total oxide capacitance of GI layer in the IGZO TFT is constant. Consequently, capacitance variation of Pd modulates the effective V_G ($V_{G,eff}$), applied to the IGZO TFT [Fig. 4(a)], thereby allowing real-time current-based hydrogen sensing. Figure 4(b) shows the I_D - V_G transfer characteristics of the IGZO TFT sensor employing the series-connected capacitor configuration. Each transfer measurement was performed over a duration of 20 s. As the capacitance of the Pd TF, which responds to hydrogen exposure, decreases, the $V_{G,eff}$ will be correspondingly reduced, and it leads to a positive shift in threshold voltage, degradation of the SS, and a consequent reduction in the I_D , all of which are closely

associated with key device performance such as sensitivity and responsiveness. In this study, we successfully develop the integrated hydrogen sensor by implementing a Pd top-gated IGZO TFT. Figures 4(c) and 4(d) show device schematic and OM image of the IGZO TFT after complete delamination of the Pd gate electrode following high-concentration hydrogen exposure, respectively. This device structure enables direct measurement of the hydrogen-induced response of the Pd gate electrode via current variation from the IGZO active channel, achieving integration and large-area processing for reliability and stability. Figure 4(e) shows the transfer characteristic curves of the Pd top-gated IGZO TFT displaying a direct modulation of the I_D in response to high concentration hydrogen exposure. In contrast to the series-connected Pd capacitive-type sensor, the Pd top-gated IGZO TFT exhibited a distinct behavior, where the off level of I_D sudden jumped up to 1.3 μA during the second transfer curve measurement while the I_D on current decreased to 1.5 μA . From these similar both I_D off and I_D on levels, we could conclude that this phenomenon is attributed to the peeling-off effect of Pd gate electrode, which predominantly induced a loss of gate-field effect on the IGZO channel region.

The noticeable current variation in the IGZO TFT induced by the delamination of the Pd gate electrode is attributed to the phase transition from the α -phase to the β -phase under high concentration hydrogen ambient. Figure 5(a) shows the recovery property of our Pd gate IGZO TFT sensor under the ambient air condition. The V_G sweep

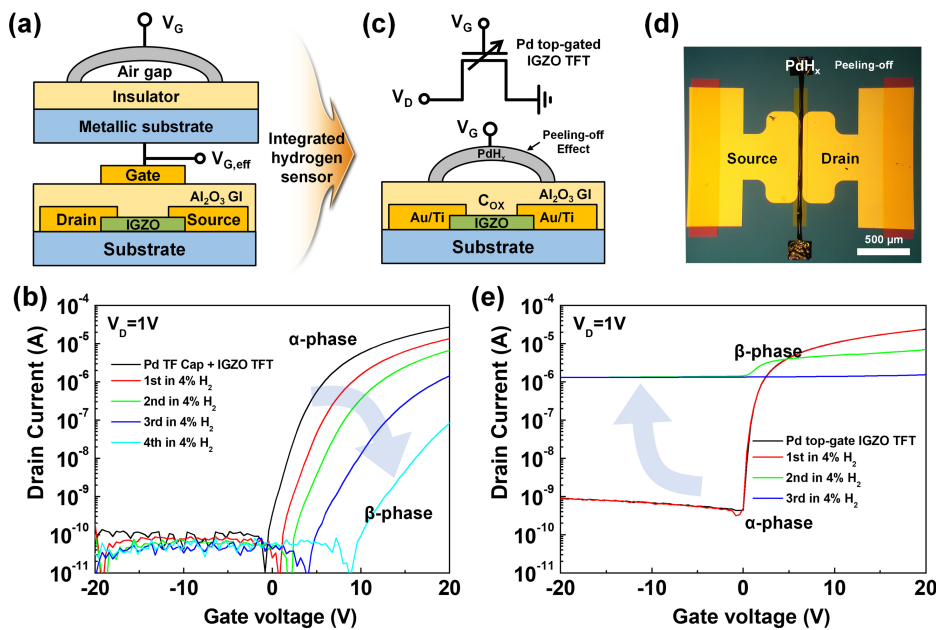


Figure 4. (a) Device schematic and (b) I_D - V_G transfer characteristic curves under high concentration hydrogen gas exposure of Pd TF based IGZO TFT hydrogen sensor. (c) Device schematic with the suggested circuit diagram and (d) OM image of Pd top-gated IGZO TFT sensor under hydrogen gas condition. (e) I_D - V_G transfer characteristic curves for 4 % hydrogen gas exposure of the integrated Pd top-gated hydrogen sensor.

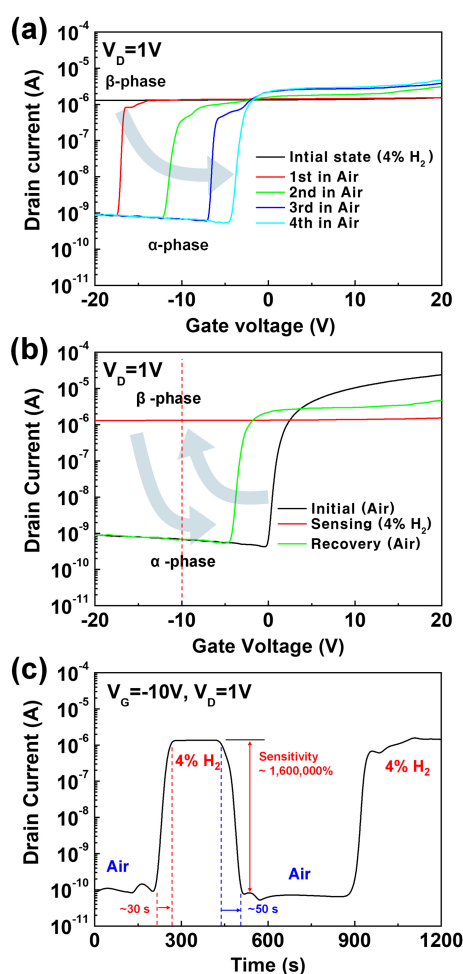


Figure 5. (a) I_D - V_G transfer characteristic curves for recovery properties (phase transition from β - to α -phase) under ambient air condition, (b) I_D - V_G transfer characteristic curves for reversible sensing properties, and (c) real-time hydrogen detection properties of Pd gated IGZO TFT sensor for 4 % high concentration hydrogen gas.

of each transfer curve was taken for 20 s. When the high concentration hydrogen is removed, the absorbed hydrogen atoms will diffuse out from the β -phase, reverting it to α -phase and even its pristine Pd electrode. As a result, the gate field-effect is restored, and the IGZO TFT regains its switching functionality. This behavior represents a reversible reaction, where high concentration hydrogen exposure induces peeling-off the Pd gate electrode, leading to the loss of the gate field effect and causing a significant I_D change. Conversely, in ambient air, the Pd gate electrode re-adheres to the Al_2O_3 GI surface, recovering the gate effect and enabling repeated use as a hydrogen sensor, as shown in Fig. 5(b). The red dashed line is the monitoring point for real-time detection. Figure 5(c) shows the real-time hydrogen sensing characteristics under fixed V_G of -10 V at $V_D = 1$ V, which shows the response time of 30 s for 4 % hydrogen gas and the recovery time of 50 s with excellent sensitivity [$S = (I_{D,H_2}/I_{D,Air}) \times 100\%$] of $\sim 1,600,000\%$, where I_{D,H_2} and $I_{D,Air}$ denote the I_D under 4 % hydrogen and air ambient conditions, respectively.

3. Conclusions

In summary, we successfully demonstrated the Pd top-gated IGZO TFT based reusable hydrogen gas sensor application method by us-

ing peeling-off effect of Pd TF for high concentration of hydrogen gas above 4 %. The peeling-off effect of Pd top gate can be realized by measuring the I_D change caused from the loss of field-effect. Therefore, this gateless IGZO channel, very similar to flat band condition, shows higher drain current level of $1.36 \mu A$ (response time of 30 s) while I_D level under air condition is 83 pA (recovery time of 50 s). Moreover, the Pd top-gated IGZO TFT sensor shows high reliability, stability, and sensitivity of $\sim 1,600,000\%$ even with reusable properties for detecting high concentration hydrogen gas sensing. Hydrogen energy should be a promising future energy source; However, high concentration hydrogen still has a bottle neck of its highly flammable and explosive. Thus, we believe our hydrogen sensor will be a significant movement for high concentrations of hydrogen exposure to ensure safe use to be a future clean energy.

Conflicts of Interest

The authors declare no conflicts of interest.

ORCID

Young Tack Lee

<https://orcid.org/0000-0003-4502-5167>

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