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Improving Hydrogen Detecting Performance of a Pd/n-LTPS/Glass Thin Film Schottky Diode with a TiO_2 Interface Layer

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Recently, hydrogen (H_2) has extensively been studied as a new energy source. However, hydrogen is also extremely flammable with a lower explosive limit of 4% in air. Thus, one needs the fast and sensitive hydrogen sensor for operating in hydrogen environment. In the past, most of hydrogen sensors were prepared on Si or III-V compound substrates. Nevertheless, these substrate materials are also too expensive to prepare the low cost sensor for mass applications. In this study, for the first time, we successfully developed a new type low cost hydrogen sensor with an n-LTPS film (n-type low temperature polysilicon film) on a glass substrate. In this paper, we report the comparative studies of the sensor with both MS (metal/semiconductor, Pd/n-LTPS) and MIS (metal/insulator/semiconductor, Pd/TiO_2/n-LTPS) Schottky diode structures. The Pd/TiO_2/n-LTPS MIS Schottky diode shows a higher relative sensitivity ratio of and response time to that of the sensor based on Si or II-V compound. In other words, the developed MIS Schottky diode shows a higher potential as the low cost and highly sensitive hydrogen sensor.

The n-LTPS was pretreated with PH_3 gas plasma under a RF power of 90 W at 250 ℃ for 60 sec. After the treatment, the LTPS become a phosphorus (P) doped n-type polysilicon with a concentration of 3×10^{16} cm^{-3}, and has a higher surface roughness of 12.772 nm.

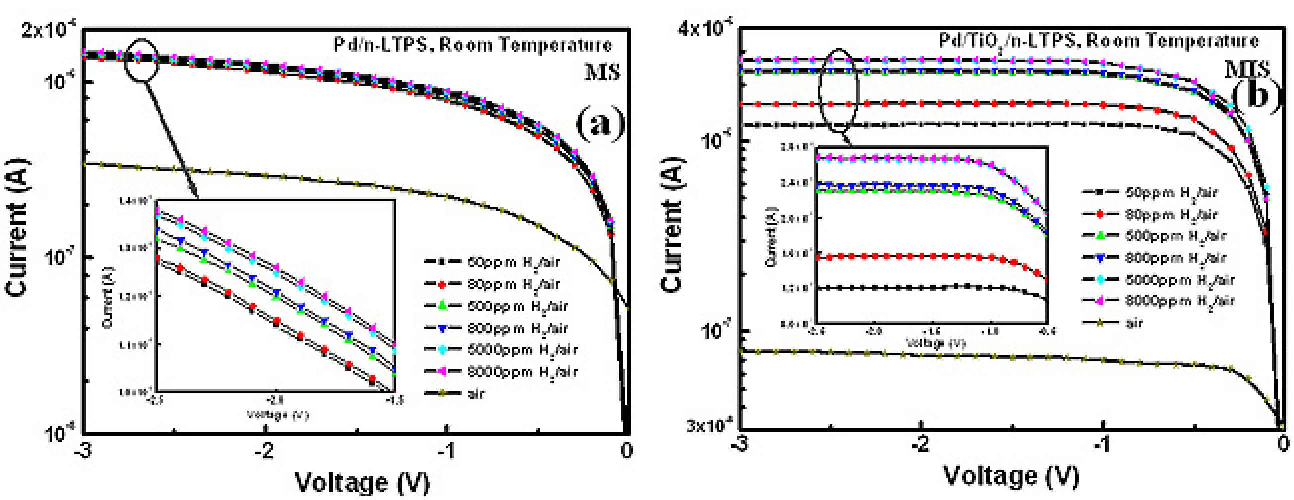

Fig. 1 Current-voltage (I-V) characteristics of (a) MS and (b) MIS Schottky diodes under various hydrogen concentrations for at room temperature.

Figure 1(a) and (b) respectively, show the measured current-voltage (I-V) characteristics of Pd/n-LTPS (MS) and Pd/TiO_2/n-LTPS (MIS) Schottky diodes in the presence and absence of hydrogen. Compared to the MS type, the MIS device manifests a higher hydrogen sensing capability. For example, under the conditions of room temperature (27 ℃), -2 V bias and 8000 ppm H_2, the MIS sample has a relative sensitivity ratio of S_r = 3504%; almost tenfold of the MS counterpart (S_r = 331.5%). The better performance can be realized from the sensing mechanism based on band diagrams shown in Fig.2 for (a) Pd/n-LTPS (MS) and (b) Pd/TiO_2/n-LTPS (MIS) diode, respectively.

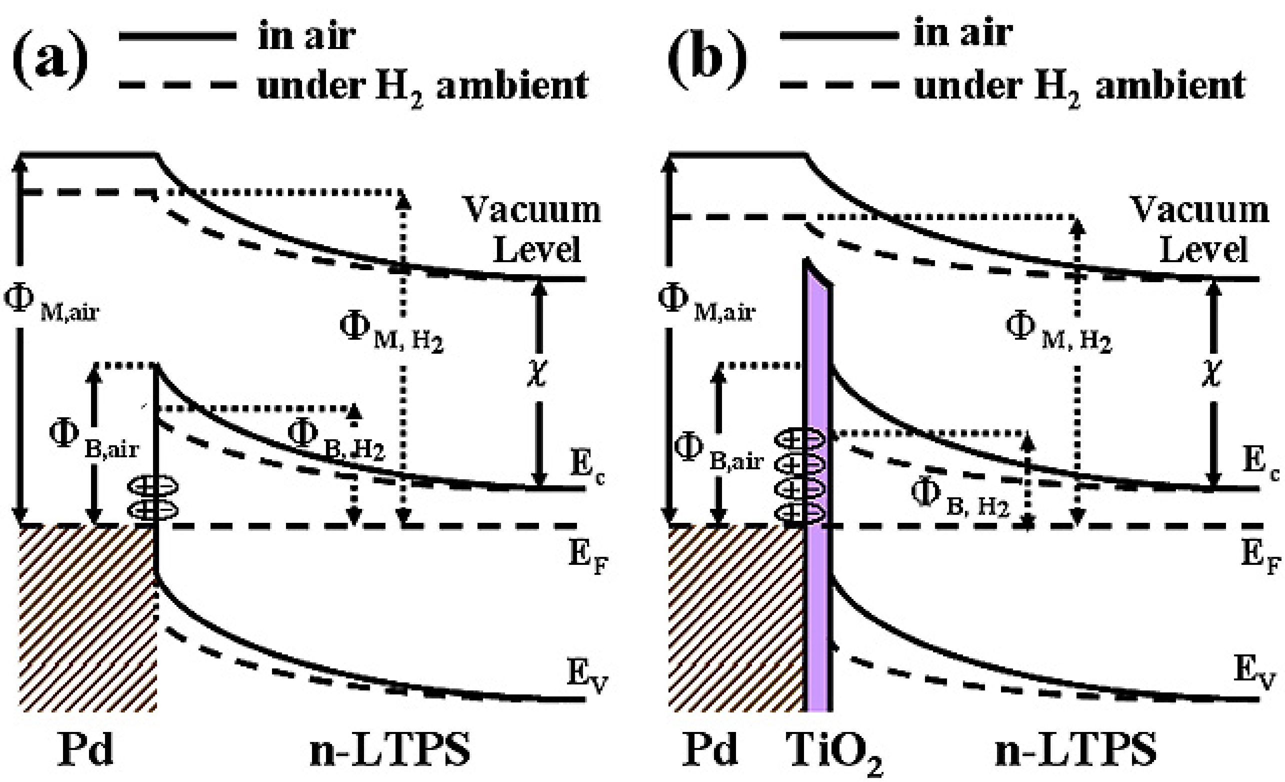

Fig. 2 Band diagrams of (a) Pd/n-LTPS (MS) and (b) Pd/TiO_2/n-LTPS (MIS) Schottky diodes in air and hydrogen atmospheres.

In the MS structure, hydrogen molecules are firstly adsorbed on the surface of the catalytic metal Pd; on there they are dissociated into hydrogen atoms, then diffuse through the thin Pd film and accumulate at the interface Pd/n-LTPS. The accumulated hydrogen atoms form a dipolar layer near the interface. It is the dipole layer to lead a shift of electrostatic potential of n-LTPS and consequently causes a significant decrease of the Schottky barrier height, thus enhancing the electrons to inject from the metal side into the n-LTPS layer. The higher hydrogen concentration causes the lower Schottky barrier height to result in a larger injection current. However, at the same time, a Pd silicide layer is formed between Pd and Si to cause the Fermi level pinning and lower H_2 sensitivity. The Fermi level pinning can be suppressed if a thin TiO_2 film is added to form the MIS structure. The thin TiO_2 oxide layer serves as a diffusion barrier against the formation of Pd silicide. Besides, the TiO_2 layer can reduce the surface state density and therefore the reverse saturation current of the Schottky barrier. As a consequent, the dependence of

Schottky barrier height variation $\Delta\Phi_B$ ($\Delta\Phi_B = \Phi_{B,\,air} - \Phi_{B,\,H_2}$) on the hydrogen concentration is enhanced. The $\Phi_{B,\,air}$ and $\Phi_{B,\,H_2}$ respectively, are the Schottky barrier height (Φ_B) under air and hydrogen atmospheres. In general, Φ_B can be calculated from;

$$\Phi_B = (\frac{KT}{q}) \ln (A A^{**} \frac{T^2}{I_0}) \quad (1)$$

,where K is the Boltzmann constant, T the absolute temperature, A the area of the diode, A^{**} the effective Richardson constant (120 AK^{-2} cm^{-2} for n-type Si), and I_0 the surface state caused reverse saturation current.

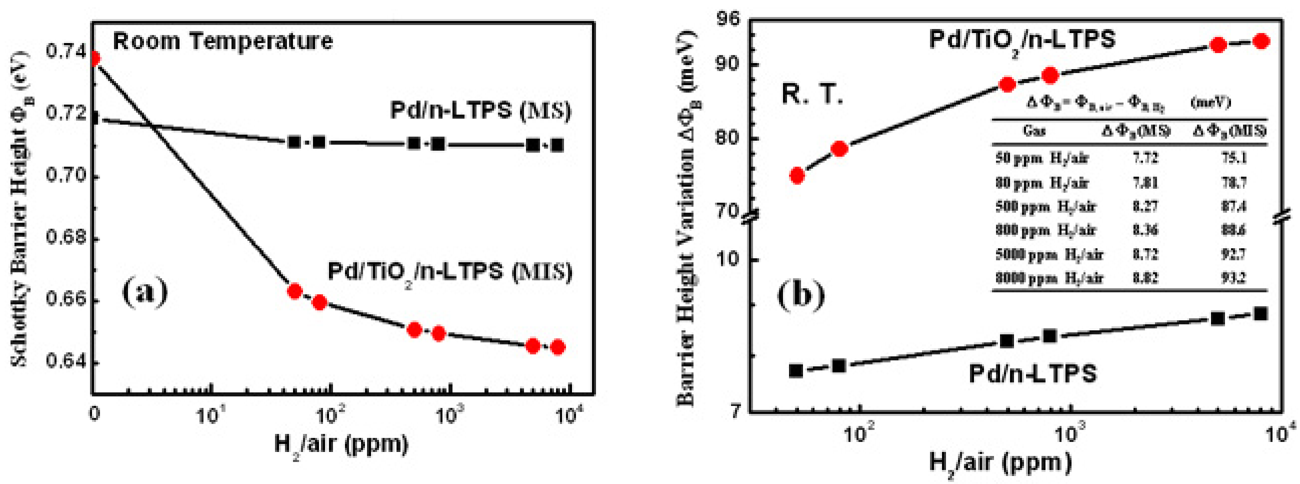

Fig. 3 (a) Schottky barrier height (ΦB) and (b) Schottky barrier height modulation ($\Delta\Phi_B$) as a function of hydrogen concentration at room temperature. The inset table in (b) lists the detailed $\Delta\Phi_B$ values.

Figure 3(a) and (b) give the calculatedΦ_B and $\Delta\Phi_B$, respectively, as a function of hydrogen concentration at room temperature. More detailed $\Delta\Phi_B$ values are listed in the inset table of Fig. 3(b). As seen, the $\Delta\Phi_B$ of both structures increases gradually with increasing hydrogen concentration, but the MIS device exhibits a relatively large $\Delta\Phi_B$. For example, under 8000 ppm H_2 in air, the $\Delta\Phi_B$ of MIS structure is 93.2 meV; almost tenfold of the MS (8.8 meV).

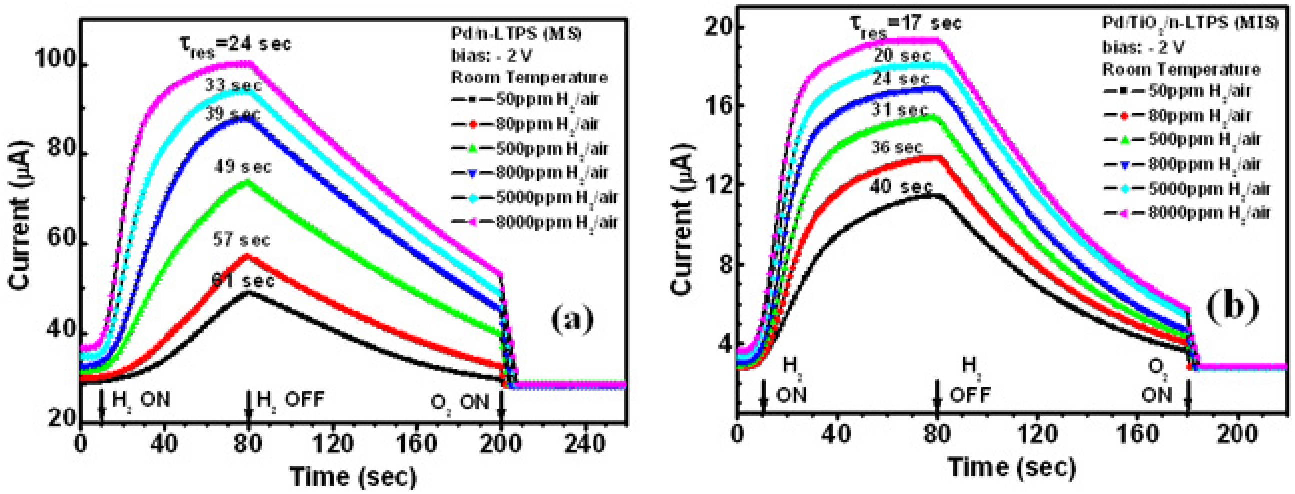

Fig. 4 Transient response curves of (a) MS and (b) MIS Schottky diodes measured at room temperature for various hydrogen concentration atmospheres under -2 V bias.

The transient response curves of the MS and MIS Schottky diodes are presented in Fig.4 (a) and (b), respectively. All of the response curves rise upon the absorption of hydrogen (H_2 ON). Based on the curves, the response time (τ_{res}) were extracted as listed in the figures. Clearly, τ_{res} decreases with increasing hydrogen concentration. Namely, at room temperature, the τ_{res} values to 50 ppm / 8000 ppm H_2 are 40 sec /17 sec, and 61sec /24 sec for the MIS and MS diode, respectively. We attribute the quicker response times of MIS to the larger barrier height modulation ($\Delta\Phi_B$). The 40 sec response time is faster than the reported values of 110 sec for a Si field effect structure sensor under 50 ppm H_2 in air ,or 27 min for a III-V compound under 48 ppm H_2 in air.

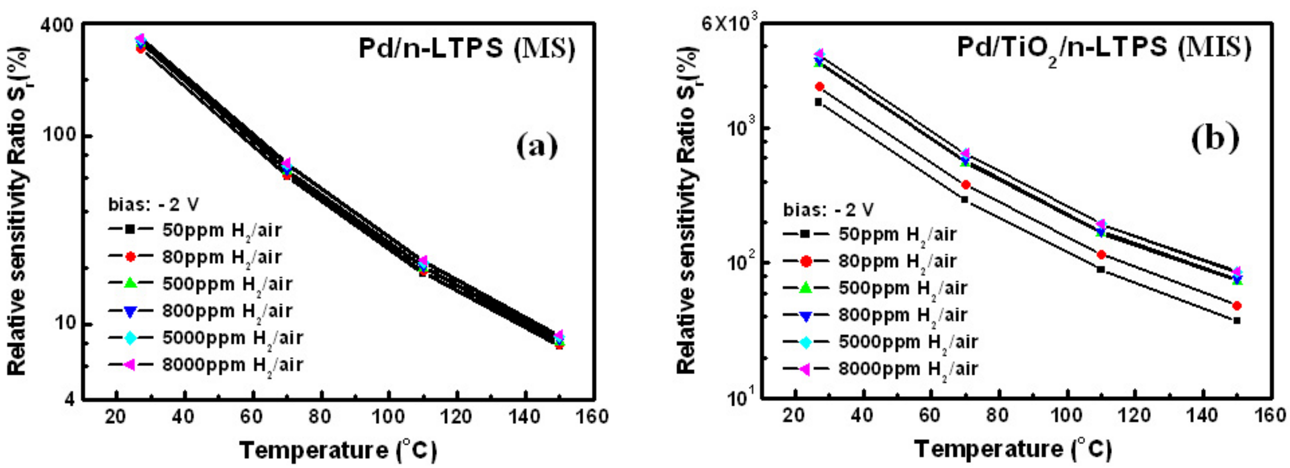

Fig. 5 Relative sensitivity ratios S_r (%) to different concentrations of hydrogen in air versus temperature of (a) MS and (b) MIS Schottky diodes operated at -2 V bias.

Additionally, the larger barrier height modulation also leads to a higher S_r value as shown in Fig. 5(a) and (b) for the developed MS and MIS Schottky diodes biased at -2 V and at room temperature, respectively. The S_r under 50 ppm / 8000 ppm H_2 concentration is 1539.6% / 3504% and 290.4% / 331.5% for MIS and MS structures, respectively. However, as the operating temperature is raised to

150℃, the S_r to 50 ppm H_2 decreases to 7.7% and 37.1% for MS and MIS types, respectively. The lower hydrogen adsorption and thus the smaller hydrogen coverage at higher temperature is attributed to the negative temperature dependence of S_r. Specifically, the S_r values of 3504% and 1539.6% to 8000 and 50 ppm H_2 of the MIS Schottky diode at room temperature are higher than the reported values of S_r = 102 ~ 103 % to 154 ppm H_2 in N_2 of the sensors prepared on Si, or a value of S_r ~ 2600% to 1% H_2 in air of a III-V compound.

In summary, the hydrogen detecting performances of the Pd/n-LTPS/glass thin film Schottky diode with and without a TiO_2 interface layer were comparatively studied. Under the conditions of room temperature and -2V bias, the addition of the TiO_2 interface layer promotes the relative sensitivity ratio from 290.4% to 1539.6% under 50 ppm H_2 ambient. The response time is also reduced from 61 sec to 40 sec. Specifically, the hydrogen detecting performances of the Pd/TiO_2/n-LTPS/glass thin film Schottky diode are better than that the reported H_2 sensors with bulk Si or III-V compounds. Therefore, the developed Pd/TiO_2/n-LTPS/glass Schottky diode shows a high potential for development and realization of a low cost and highly sensitive hydrogen sensor.