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The Pd/TiO_2/n-LTPS Thin Film Schottky Diode on Glass Substrate for Mass Market Hydrogen Sensing Applications

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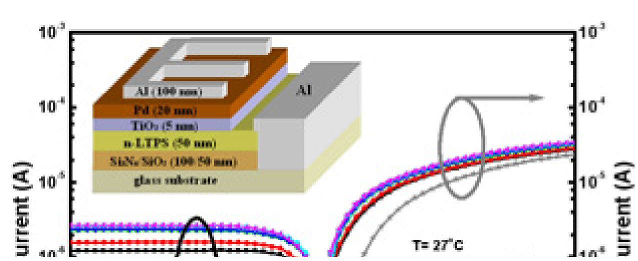
Recently, hydrogen in being considered as a new energy source for its abundance, however, hydrogen is also a colorless, odorless, and extremely flammable gas with a lower explosive limit of 4% in air. Hence, hydrogen sensors have been widely studied, and applied in many fields, such as space launch vehicles, industrial leak detection, and automobile fuel additives. Nevertheless, most of these sensors were based on electrochemical techniques, thus for compact structure and more convenient preparation, the semiconductor type hydrogen sensors prepared on Si or III-V compound substrates were also extensively studied. However, these substrate materials are expensive for fabricating low cost, room temperature sensors for mass markets. In this work, we developed a new type of low cost hydrogen-sensing device with the n-LTPS (n-type low temperature polysilicon) thin film for the purpose applications. The n-LTPS was formed by applying ELA anneal and Phosphorus (P) plasma treatment sequentially on an amorphous Si (a-Si) thin film on glass substrate. After the plasma treatment, the n-LTPS has a high doping concentration of 3×10^{16} cm^{-3} to generate a large quantity free carrier. And its surface is rough (see AFM photo in the insert of Fig. 4), so that the n-LTPS has a higher surface-to-volume ratio for adsorbing a larger number of hydrogen atoms to react, thus improving the sensing performance. The LTPS has been successfully used in preparing high-speed thin film transistor (TFT) for large area TFT-LCD or organic LED display applications. To our knowledge, this is the first time to apply the material for hydrogen sensing.

In this paper, we report both fabrication and characterization of the new sensing device with Pd/TiO_2/n-LTPS/glass structure in details. The material and preparation cost of the device are lower than that prepared with bulk Si or compound material. Specially, the developed MOS Schottky diode has a very good selectivity for hydrogen gas over other interfering gases, thus promising for mass applications in low cost and high hydrogen sensing.

Figure 1 shows the measured current-voltage (I-V) characteristics of the Pd/TiO_2/n-LTPS MOS Schottky diode under forward/reverse biases and various H_2 concentrations with HP4145B at room temperature (27 ˚C). As shown, the sensing



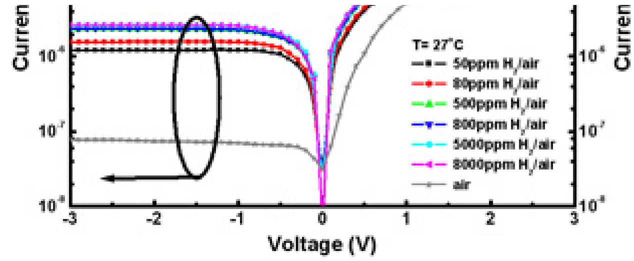


Fig. 1 Current-voltage (I-V) characteristics of the developed diode at 27 °C under both forward and reverse biases for various hydrogen concentrations ambient. Under forward, the current is high, but difference with and without H_2 ambient is small, while for reverse bias; the current curves are stable and large in difference. The insert illustrates the schematic structure of the Pd/TiO_2/n-LTPS/glass MIS Schottky diode.

currents increase with increasing hydrogen concentration for both forward and reverse biases. In air ambient, the leakage currents are lower and constant under reverse biases, in contrast to the increase with increasing forward bias. We suspect in air ambient and under reverse bias, the barrier is high (see insert of Fig. 2) thus blocking the transport of carriers, and results in a lower current. While as exposing to a hydrogen gas ambient, hydrogen molecules are adsorbed on the surface of Pd catalytic metal, and dissociated into hydrogen atoms. Subsequently the H_2 atoms diffuse through the thin Pd metal film and accumulate in the interface Pd/TiO_2 to form a dipolar layer on there. The dipolar layer builds a local field to lower the Schottky barrier height, thus enhancing the electrons to inject from the metal side into the n-LTPS layer and results in a higher current. The higher H_2 concentration causes the larger barrier lowering, consequently, the current increases with increasing the hydrogen concentration.

Figure 2 presents the transient response curves of the device operated at –2 V and 27 ˚C under the introduction (H_2/air on) and the removal (H_2/air off) of the hydrogen gas for various H_2 concentrations ambient. The measurements were repeated 5 times for each H_2 concentration ambient, with a relative standard deviation of 4-5 %. All of the response curves rise very rapidly upon the introduction of H_2/air gas (H_2/air ON). Based on these curves, the response time (τ_{res}) defined as the time for the current from initial value to 90% of the final steady state value was extracted and listed in the figure. The τ_{res} decreases with increasing the hydrogen concentration, for example, it decreases from 40 sec for 50 ppm to 17 sec for 8000 ppm. These response times are less or comparable to the reported in Si, or in III-V compound H_2 sensor. Specially, as shown in the insert, the relationship between the sensing current and hydrogen concentration is almost linear in steady state for the hydrogen concentration less than 800 ppm. Over the concentration, owing to the coverage of hydrogen atoms at the Pd-TiO_2 interface, the relation is shifted from a linear with less current change rate. Another figure of merit for a H_2 sensor is the relative signal ratio defined as $Sr(\%) = ((I_{H_2} – I_{air})/ I_{air}) \times 100\%$, where I_{H_2} and I_{air} are currents measured under hydrogen and air ambient, respectively.

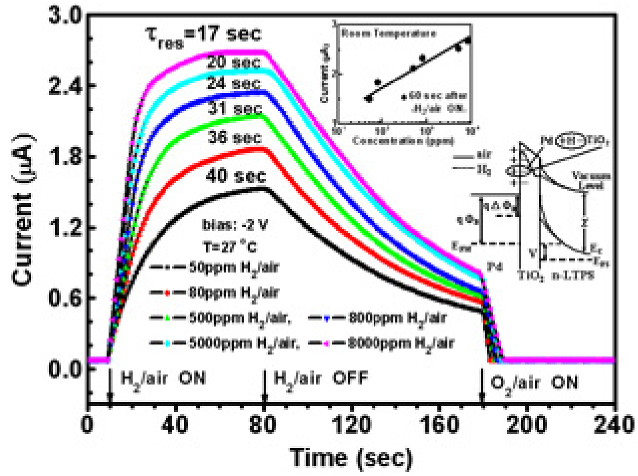


Fig. 2 Transient response curves of the developed device operated at reverse bias and room temperature for various hydrogen concentrations ambient. The response times (τ_{res}) are also listed in the figure. The insert (upper) gives the sensing current at 60 sec after introduction of hydrogen/air as a function of hydrogen concentration. While the bottoms insert shows the schematic energy band diagram of the reverse biased Pd/TiO_2/n-LTPS/glass MIS Schottky diode.

Figure 3 gives both Sr(%) (top) and τ_{res} (bottom) of the device under –2 V bias and different hydrogen concentrations ambient for various temperatures. It shows a negative dependence on temperature; for example, as the temperature is elevated from 27 ° C to 150 ° C, Sr(%) and τ_{res} decrease from 3504 to 86, and 17 to 5 sec, respectively, for the hydrogen concentration of 8000 ppm. This is because the kinetic reaction of the hydrogen adsorption is an exothermic reaction, thus according to Temkin isotherm behavior, the hydrogen coverage decreased with increasing temperature. Therefore, we suspect the negative temperature dependence of the Sr(%) to the smaller hydrogen coverage at higher temperature. It worthy to note, the Sr(%) of 3504 for 8000 ppm under room temperature is also higher than the 10^2 ~ 10^3 of the reported H_2 sensors prepared on Si, or ~ 2600 on III-V compound substrate. The shorter response time in a higher temperature is mainly caused by the higher catalytic Pd metal reaction rate, the increased hydrogen dissociation, and diffusion coefficients under high temperature.

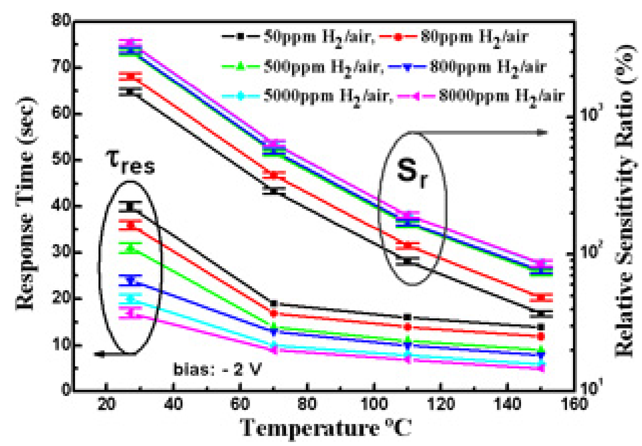


Fig. 3 Response time τ_{res} (bottom) and relative sensitivity ratio Sr (%) (upper) of the -2V biased Pd/TiO_2/n-LTPS/glass MOS Schottky diode versus temperatures for different hydrogen concentrations ambient .The τ_{res} is decreased for increasing temperature or H_2 concentration in air. The measurements were repeated 5 times for each H_2 concentration ambient, with a relative standard deviation of 4-5 %.

Moreover, as compared in Fig. 4, the Sr(%) at -2 V under 27 ° C and 8000 ppm H_2/air ambient has 7.6, 14, and 30 times over that in C_2H_5OH, C_2H_4 and NH_3 various gas ambient with same 8000 ppm in air, respectively. Thus, the device demonstrates a good selectivity for H_2 gas over other interfering gases containing H atom.

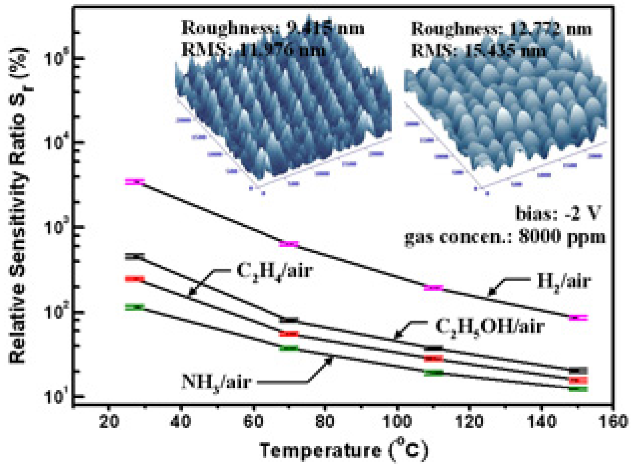


Fig. 4 Comparison of relative sensitivity ratio Sr (%) of the Pd/TiO_2/n-LTPS/glass MIS Schottky diode operated at -2V versus temperatures for H_2, C_2H_5OH, C_2H_4 and NH_3 gases ambient, respectively. The insert gives the AFM images of the LTPS films without (left) and with (right) PH3 plasma treatment. After treatment, the roughness is increased, thus the reaction area and results in higher Sr (%). The measurements were repeated 5 times for each H_2 concentration ambient, with a relative standard deviation of 4-5 %.

In summary, the hydrogen gas sensing characteristics of the Pd/TiO_2/n-LTPS /glass MOS Schottky diodes were studied in details. Under -2 V biased and room temperature, the MOS Schottky diode has a high relative signal ratio of 3504%, and fast response time of 17 sec in 8000 ppm H_2 gas ambient. These sensing abilities are better or comparable to the H_2 sensors prepared on Si or III-V compounds. In addition, in room temperature ,the developed diode shows 7.6, 14, and 30 times higher relative signal ratio in 8000 ppm H_2/air ambient over that in same concentration interference gases of C_2H_5OH, C_2H_4, and NH_3 ambient, respectively. Therefore, the developed device provides a promise for low cost mass market application hydrogen gas sensors operating at room temperature.