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A Novel Pt/$In_{0.52}Al_{0.48}As$ Schottky Diode-Type Hydrogen Sensor

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Due to the issues of petroleum crisis and environmental protection, hydrogen gas becomes more and more important as a new and clean energy source and has been employed in industrial applications. However, the properties of autoignition and explosion might be a safety concern when the hydrogen concentration exceeds 4.65 vol. % in air. Therefore, a high-performance hydrogen sensor is required to detect and monitor the leak of hydrogen gas.

In this work, a novel Pt/$In_{0.52}Al_{0.48}As$ Schottky diode-type hydrogen sensor is fabricated and presented. Based on the catalytic activity and high work function of Pt metal, the studied device is expected to exhibit wide temperature operating regimes. Moreover, the studied device shows advantages including simple device structure, easy fabrication process, high sensitivity, fast response, and easy operation. It is worth to note that this device shows a significant advantage of widespread and stable reverse voltage operating regime which demonstrates the promise for high-quality hydrogen sensor applications. This excellent performance is not observed in the previously reported Schottky diode-type hydrogen sensors.

The schematic cross section of the studied device is depicted in Fig. 1. The typical current- voltage (I-V) characteristics under the applied forward and reverse biases, at 30°C and 160°C, are illustrated in Fig. 1. Obviously, good electrical properties and rectifying behaviors are demonstrated under both air and hydrogen-containing ambience. The increase of currents both under forward and reverse biases are caused by the lowering of the effect ive Schottky barrier height. The hydrogen sensing me chanism can be interpreted as follows. First, hydrogen molecules are dissociated into hydrogen atoms by the catalytic Pt metal. Then, hydrogen atoms diffuse toward the Pt/$In_{0.42}Al_{0.58}As$ interface. The hydrogen accumulation and formation of a dipolar layer at the Pt/$In_{0.52}Al_{0.48}As$ interface, caused by the built-in electrical field, changes the effective work

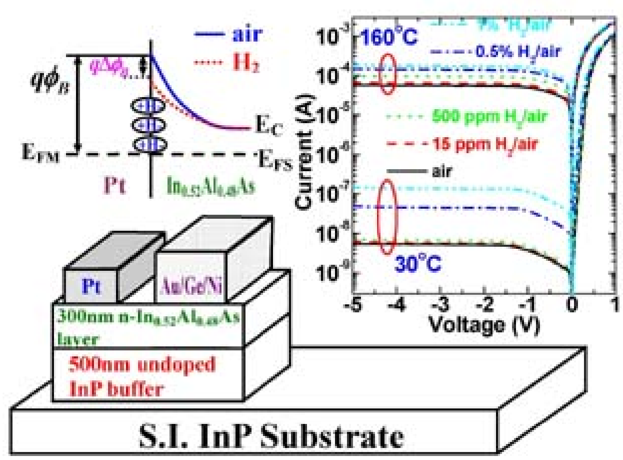


Fig. 1 Schematic cross section and corresponding energy band diagram of the studied Pt/$In_{0.52}Al_{0.48}As$ Schottky diode-type sensor. The typical current-voltage characteristics under the applied forward and reverse voltages, at 30 and 160°C, are also illustrated.

function of Pt metal and barrier height of the Schottky contact as seen in Fig. 1. Also, this effect can be proven by the current increment in Fig. 1. It is observed that the studied device can detect a very low hydrogen concentration of 15 ppm H2/air, even at temperatures up to 160°C. This value is much lower than the 1/10 of lower explosion limit (LEL) as an alarming level for gas sensors. Experimentally, based on the thermionic emission model and the Norde method, the calculated Schottky barrier height ϕ_B values are 736, 734, 731, 729, 723, 681 and 649 meV in air and under hydrogen concentrations of 15, 200, 500 ppm, 0.1, 0.5, and 1% H2/air, respectively, at 30°C.

In order to investigate the hydrogen-sensing performance, the relative sensitivity ratio Sr(%) is defined as:

$$S_r(\%) = \left(\frac{I_{H_2}}{I_{air}} - 1\right) \times 100\% \quad (1)$$

where I_{H2} and I_{air} are currents measured under hydrogen-containing ambiance and air, respectively. The relationship between the relative sensitivity ratio Sr(%) and applied voltage at 30°C is illustrated in Fig. 2. Clearly, the stable and flat curves are found under an applied reverse voltage between -0.5 and -5V for all introduced hydrogen gases. A high Sr(%) value, under the 1% H2/air gas at 30°C, of about 2600% is obtained at -0.5V. However, the Sr(%) is drastically decreased by the increase of applied forward bias. The decrease of Sr(%) can be attributed to the presence of resistance limited region (resistance effect). The positive concentration dependence of Sr(%) is caused by the occupancy of more hydrogen adsorption sites at the Pt/ In0.52Al0.48As interface under higher concentrations of hydrogen which leads to the increase of the number of dipoles (i.e., hydrogen atoms). The lower Sr(%) under lower concentrations of hydrogen (<1000 ppm H2/air) may also be caused by adsorbed oxygen which effectively blocks the hydrogen dissociation and adsorption.

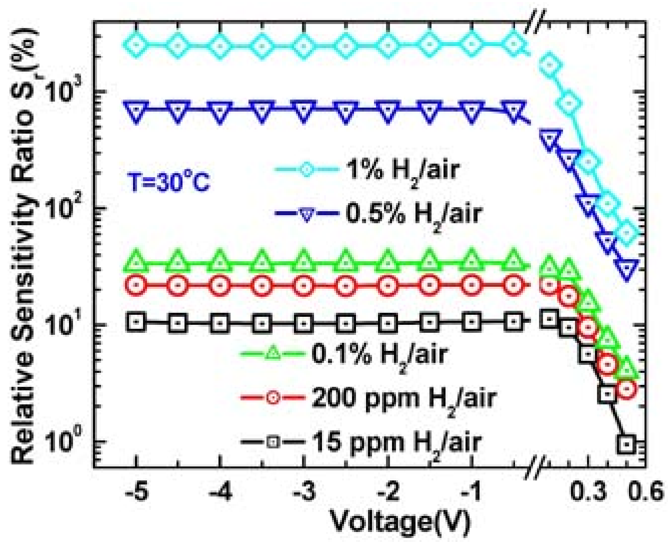
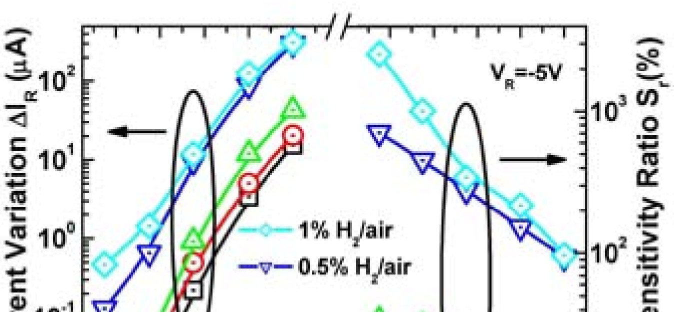


Fig. 2 Relative sensitivity ratio Sr(%) as a function of applied voltage under different-concentration hydrogen species at 30°C.

Figure 3 shows the reverse current variation ΔI_R and Sr(%) versus temperature under different hydrogen gases. The reverse voltage is fixed at -5 V. As shown in Fig. 3, an interesting phenomenon is observed that the temperature dependence of ΔI_R is contrary to that of Sr(%).



The ΔI_R value, under the 1% H2/air gas, is increased from 0.47 to 310 μA once the temperature is increased from 30 to 200°C, while the corresponding Sr(%) value is reduced from 2543 to 96.5%. The variation of ΔI_R at 30 and 200°C approaches 2.8

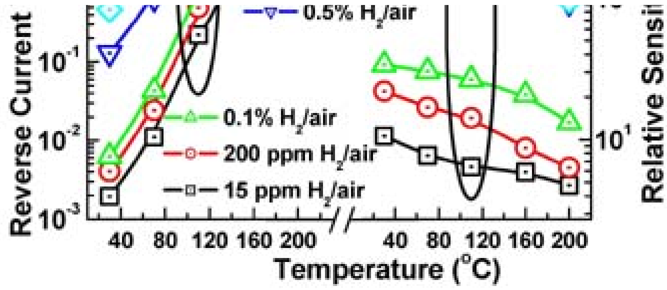
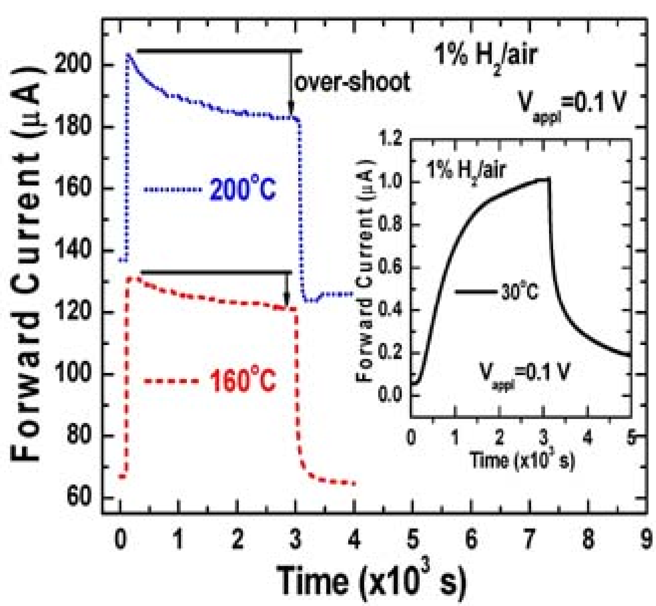


Fig. 3 Reverse current variation ΔI_R and relative sensitivity ratio Sr(%) versus temperature under different hydrogen-containing gases. The applied reverse voltage is -5 V.

order in magnitude under the 1% H2/air gas. The negative temperature dependence of Sr(%) is due to the lower hydrogen coverage at higher temperature. This causes the lower Schottky barrier height variation $\Delta\phi_B$ as mentioned above and therefore the smaller Sr(%) value. Iair is deeply influenced by thermal effects because Iair is a function of temperature. ΔI_R, and thus Sr(%), are also influenced by thermal effects but only indirectly through decreased sticking coefficient of H2 with increased temperature. Therefore, the trend of ΔI_R shows the positive temperature dependence. In addition, the small differences of Sr(%) and ΔI_R at higher temperature reveal the quasi-saturated phenomena of Sr(%) and ΔI_R under high concentrations of hydrogen. Consequently, the device can be operated under widespread reverse voltage (0~-5V) to obtain improved hydrogen sensing characteristics.

Figure 4 shows the transient response curves under the 1% H2/air gas at 160 and 200°C. The inset shows the transient response curve at 30°C. The applied voltage is fixed at 0.1 V. Good hydrogen sensing behaviors are observed upon exposing to the introduction and removal of 1% H2/air gas. An over-shoot phenomenon is observed at higher temperature (>90°C). This abnormal phenomenon can be attributed to the formation of hydroxyl species and water on the Pt metal surface. They reduce the hydrogen adsorption sites and cause the decrease of interfacial hydrogen coverage. In this work, the response and recovery time constants τ_a and τ_b are defined as the time needed to reach the inverse exponential value (e^{-1}) of the final steady-state currents under hydrogen-containing atmosphere and air, respectively. Both τ_a and τ_b decrease with increasing the operating temperature. The calculated τ_a (τ_b) values under the 1% H2/air gas are 758.5 (303), 2 (25), and 1.5 (20) s at 30, 160, and 200°C, respectively. The shorter response time means the device is suited to be operated at high temperature for fast response.

In conclusion, a novel hydrogen sensor based on a Pt/$In_{0.52}Al_{0.48}As$ Schottky diode has been fabricated and demonstrated. Good I-V characteristics and temperature-dependent behaviors under different-concentration hydrogen gases were found. The studied device showed significant features, under the reverse bias, including high Sr(%) value (about 2600%), large current variation (310 μA), wide temperature regime (30~200°C), widespread reverse voltage operating regime (0~-5V), and stable hydrogen sensing properties. Based on the advantage of integration compatibility with InP-based electronic devices, the studied Pt/



$In_{0.52}Al_{0.48}As$ Schottky diode-type hydrogen sensor provides the promise for micro-electro-mechanical system (MEMS) and high-performance sensor array applications.

Fig. 4 Transient response curves under the 1% H2/air gas at 160 and 200°C. The inset shows the transient response curve at 30°C. The applied voltage is fixed at 0.1 V.