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FAST TRACK COMMUNICATION

High sensitivity (1 ppm) hydrogen detection using an unconventional Pd/n-InP Schottky device

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Online at stacks.iop.org/JPhysCM/23/422201**Abstract**

Hydrogen is detected using a Pd/n-InP Schottky diode in which the elongated, very thin Pd electrode is of greater resistance than the underlying semiconductor substrate. Four-probe measurements of the device resistance, as a function of hydrogen concentration, are made by contacting only the Pd electrode, with a sensitivity of 1 ppm being achieved. On hydrogen exposure the device resistance drops from an initial high value, characteristic of the Pd electrode alone, to a lower value due to a hydrogen-induced lowering of the Schottky barrier that opens up the InP substrate as a parallel current carrying channel.

(Some figures in this article are in colour only in the electronic version)

Hydrogen sensors, an essential component for the hydrogen energy industry, have drawn extensive research interest due to the vast potential market in generation, storage and transportation of hydrogen. Various types of hydrogen sensors, based on catalytic metals, i.e. Pd and Pt, have been extensively studied over the past decade. Hydrogen molecules exposed to these metals become dissociated due to catalytic action and are absorbed into the bulk of the metal resulting in detectable changes in the metal's physical and electronic properties, e.g. increase in metal grain volume and/or increase in resistance. Commercial hydrogen sensors primarily use the resistance increase of thick Pd films to measure hydrogen concentration [1], with reported sensitivities of 15 ppm and several minutes response time. Nanostructured Pd thin films have been investigated for increased sensitivity and faster response, essentially by increasing the active surface area within a given volume. Pd thin films deposited on

single wall carbon nanotubes [2] and into anodized alumina nano-wells [3] have been shown to effectively decrease the response time. Favier *et al* [4] and Kim *et al* [5] have utilized swelling of Pd grains (within nanowires) on exposure to hydrogen, and the consequent effective resistance decrease due to improved inter-grain connectivity. More recent studies on Pd nanowires have reported resistance increase on exposure to hydrogen in line with commercial sensors but with improved response time and a projected detection limit of 10 ppm [6].

Catalytic metal (Pd/Pt)–semiconductor (InP/GaAs/Si)-based Schottky diodes have also been used as hydrogen sensors. Further to adsorption by the metal, dissociated hydrogen diffuses to the Schottky interface where the strong interface electric field causes the atomic hydrogen to polarize, resulting in partial screening of the local electron affinity changing the barrier properties. Direct modification of the catalytic metal work function upon

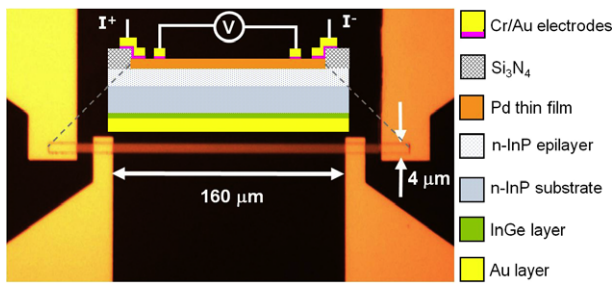


Figure 1. Optical micrograph of a Schottky device. The inset shows a schematic of the device cross-section and electrical connections for measuring R_D .

hydrogen adsorption has also been suggested [7] as a mechanism of barrier modification. Both mechanisms result in lowering of the effective Schottky barrier height, ϕ_B . The high interface electric field makes ϕ_B significantly more sensitive to hydrogen than the traditional resistance measurement techniques on Pd films. This barrier lowering is evidenced in the current–voltage (IV) characteristics by an increase in the device current (at fixed bias) on exposure to hydrogen. Several research groups have focused on this detection technique with the primary interest on increasing efficiency by varying the metal–semiconductor combination [8–12] and, crucially, the metal deposition method [13–15], in order to reduce the slow response time.

In this report we investigate the properties of a Schottky junction-based detector demonstrating a hydrogen detection capability of 1 ppm [16], equalling or exceeding that of the most sensitive (and often more sophisticated) Schottky devices reported to date. Moreover, in contrast to existing reports where detection is based on conventional IV measurements, we introduce a simpler, yet effective method of detecting changes to ϕ_B (and thus the hydrogen concentration) by ostensibly measuring the resistance of the metal electrode alone. Figure 1 shows an optical micrograph (top view) of the device used, the inset sketching the cross-section. The Schottky device is fabricated by depositing a thin Pd strip (length $\sim 160 \mu\text{m}$, width $\sim 4 \mu\text{m}$ and thickness $< 10 \text{ nm}$) over an n-InP substrate of doping density $\sim 1 \times 10^{17} \text{ cm}^{-3}$. As shown in figure 1, four metal contact pads are deposited, contacting the metal layer (for resistance measurements), along with an Ohmic back contact on InP (for complementary, conventional IV measurements across the diode); the Ohmic contact comprises a Au electrode on an InGe adlayer deposited on the InP. The devices were fabricated at the EPSRC National III-V Laboratory, Sheffield, UK.

The four top contacts are used for measuring the four-probe device resistance, R_D . The key feature here, and the crucial departure from conventional Schottky diode fabrication methodology, is that the very thin ($< 10 \text{ nm}$), elongated metal (Pd) electrode has a resistance that is greater than, or at least comparable to, the underlying InP substrate around room temperature. It is useful to first explain the device properties in terms of the R_D –temperature behaviour (we have outlined this behaviour in relation to a variety

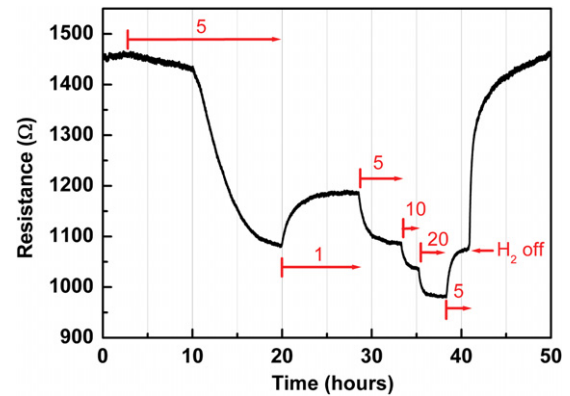


Figure 2. Graph of the device resistance, R_D , versus time for various values of hydrogen concentration in ppm.

of silicon- and III–V based Schottky devices [17] and will develop it more fully elsewhere [18]). In this scheme R_D undergoes a significant drop from high values at low temperature, where the charge carriers are confined to the resistive metal electrode, to low values at high temperature, where the semiconductor substrate has opened up as a parallel current carrying channel. In the region where R_D decreases, the charge carriers (in this case, electrons) are progressively being excited over the Schottky barrier with increasing temperature; in effect, the resistance associated with the Schottky barrier that connects the metallic electrode and the semiconductor undergoes progressive collapse. Clearly, any lowering of ϕ_B (at constant temperature) will similarly result in a greater fraction of transport through the semiconductor and thus a decrease in R_D —and this is exactly what happens in the case of hydrogen diffusing to the Schottky barrier interface region. Thus, what is required, and has been designed and implemented here, is a device that, at 300 K, sits at the edge of the resistance drop (with respect to temperature), so that a drop in R_D occurs when ϕ_B is lowered due to hydrogen exposure at room temperature.

The hydrogen detection experiments were carried out in a custom made, flow-type, ultra-high vacuum chamber fitted with two mass flow controllers adjusting the hydrogen concentration (C_H) and flow rate. Prior to any detection the chamber is evacuated to a base pressure of 10^{-8} Torr. Subsequently, hydrogen at a given C_H (mixed with nitrogen) is introduced continuously into the chamber. We have measured both R_D (figure 2) and the IV characteristics across the Schottky interface (figure 3) as a function of C_H from 1 to 5000 ppm, with the device held at a constant temperature (295 K). The overall flow rate was kept constant at 2000 sccm throughout.

Figure 2 shows the time trace of R_D for various values of C_H . The vertical lines with arrows indicate the instant when hydrogen of the specified concentration was introduced into the chamber. At the onset the device has a resistance of 1450Ω (R_{D0}), prior to any exposure to hydrogen. Then, 5 ppm of hydrogen is introduced into the chamber, which lowers R_D , saturating to 1080Ω over approximately 15 h. Reduction in the hydrogen concentration to 1 ppm increases R_D to 1180Ω

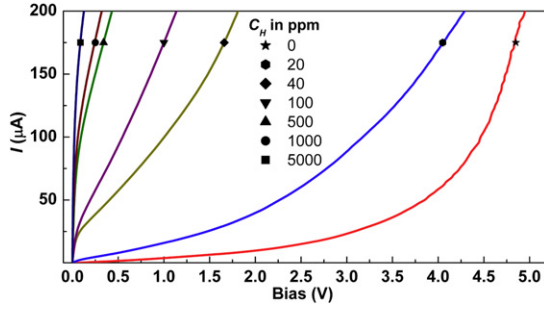


Figure 3. Typical I - V characteristics of a Pd/n-InP device at selected hydrogen concentrations.

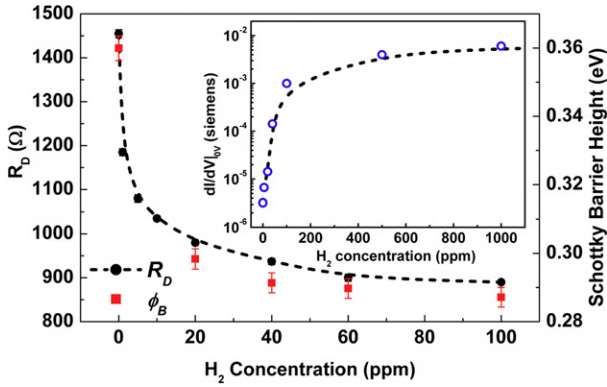


Figure 4. Calculated Schottky barrier height and saturated R_D as a function of hydrogen concentration. The inset shows the variation of $dI/dV|_0$ with concentration. The dashed lines are a guide to the eye.

with a significantly reduced characteristic recovery time of ~ 1 h. Subsequent increases in C_H show a systematic lowering of R_D , as shown in figure 2, again with a response time of ~ 1 h. Clearly the initial device response time is significantly larger than the response times observed for any subsequent changes (increase or decrease) in C_H . The variation of the saturation R_D values with C_H is plotted in figure 4. Further important features evident in figure 2 are that the hydrogen chemisorption process is seen to be entirely reversible with asymptotic R_D values appearing to be uniquely associated with specific values of C_H .

Figure 3 illustrates the experimental IV characteristics of a device at selected hydrogen concentrations. For $eV > 3kT$ they are well described by the standard thermionic emission model, with

$$I = AA^{**}T^2 \exp\left(-\frac{e\phi_B}{kT}\right) \exp\left(\frac{eV}{nkT}\right) \quad (1)$$

where I is the forward bias current, A is the junction area, A^{**} is the modified Richardson constant ($9.24 \text{ A cm}^{-2} \text{ K}^{-2}$), T is the absolute temperature, k is the Boltzmann constant, V is the applied bias and n is the ideality factor. From fits of equation (1) to the IV data we calculate ϕ_B as a function of C_H , as shown in figure 4. Both R_D and ϕ_B decay monotonically with increasing C_H , with R_D showing significantly larger percentage change.

More specifically, the relation between these quantities may be appreciated from approximate expressions for the effective Schottky barrier resistance, R_{SB} , and for R_D . First, consider the equation for R_{SB} :

$$R_{SB}(T, C_H) = \frac{B}{AA^{**}T^2 \exp\left(-\frac{q\phi_B(C_H)}{kT}\right)} \quad (2)$$

which amounts to a re-expression of equation (1) in the quasi-zero-bias limit—the reason for use of this approximation is that, in the measurement of R_D , only a very small bias of the order of a few tens of meV is developed between the contact electrodes on the device; B is a T - and C_H -independent proportionality constant. The (approximate) overall device resistance, R_D , is then given by

$$\frac{1}{R_D(T, C_H)} = \frac{1}{R_M(T, C_H)} + \frac{1}{R_{SB}(T, C_H) + g/(en_e(T)\mu_e(T))} \quad (3)$$

where R_M denotes the metal electrode resistance and the resistance of the underlying semiconductor is given by the term $g/(en_e\mu_e)$ where n_e is the electron density, μ_e the electron mobility and g a geometrical factor, L/A_S , where L is the metal electrode length and A_S is the semiconductor cross-section beneath the metal electrode. (Since the incorporation of hydrogen in the device has least effect on the semiconductor no dependence of the semiconductor resistance on C_H is included or considered below.) The full model [18] of the Schottky diode operated in the mode of figure 1 is comprised of elements of metal electrode resistance in series and a parallel set of elements of semiconductor resistance also connected in series; these sets of elemental resistances are cross-connected in a resistance network or ladder via the Schottky barrier resistance, R_{SB} . Although equation (3) constitutes a single-cell approximation, i.e. the metal electrode resistance in parallel with barrier and semiconductor resistances connected in series, it can yield a reasonably accurate description of R_D as a function of T , especially for large area devices. At $C_H = 0$ (or constant value) the zero-bias form of the expression (2) means that R_{SB} is driven purely by the thermal energy term, kT , and R_D responds accordingly, in the manner described qualitatively in the introduction. Equally, it is clear that at constant T there will be a strong dependence of R_D on C_H through the dependence of ϕ_B on C_H (described in more quantitative detail by equation (4) and the accompanying discussion). With increasing C_H , the barrier height falls and carriers are more easily excited into InP, providing a parallel conduction path which results in a lowering of R_D with increasing C_H . It can be seen that the second term in equation (3) tends towards the reciprocal of the semiconductor resistance.

The manner of the variation of R_D with C_H is of considerable interest since, superficially, it appears counter-intuitive. The largest change in R_D is observed when the device is exposed to 1 ppm hydrogen, $\sim 20\%$ (compared to the value in vacuum). Subsequent increases in C_H induce smaller changes in R_D , reducing to $<0.5\%$ for C_H change from 1000

to 5000 ppm. This indicates that, remarkably, this detection technique is most sensitive at the lowest concentrations of hydrogen. In contrast, figure 3 shows that the sensitivity of the device operated in the conventional IV measurement mode (where detection is made by monitoring change in the device current at a fixed bias) is small for $C_H < 20$ ppm, increases rapidly for $10^2 \text{ ppm} < C_H < 10^4 \text{ ppm}$ and finally saturates at very high C_H [15]. (This type of sensitivity–concentration variation is in line with Schottky-based hydrogen detection reported previously [8–15].) However, near zero junction bias there is significant change in the differential conductance (dI/dV) with C_H below 20 ppm—a plot of $dI/dV|_{0V}$ against C_H , based on figure 3, is illustrated in the inset to figure 4. The key to understanding the enhanced sensitivity at low C_H in the novel scheme described here is that the measurement of R_D effectively probes the (inverse of) differential conductance with respect to C_H . As ϕ_B decreases with increasing C_H , $dI/dV|_{0V}$ increases much more rapidly (inset to figure 4), illustrating their exponential inter-dependence. The decreasing barrier height, and thus increasing junction conductance, causes R_D to fall with increasing C_H , with the greatest change occurring for the lowest C_H values. Note, however, that the metal and semiconductor resistance terms in equation (3) determine limits on the low- and high- C_H values for R_D . Thus, while R_{SB} falls with increasing C_H , leading to a corresponding increase in $dI/dV|_{0V}$ of ~ 2 orders of magnitude across the range of 0–100 ppm hydrogen concentration, the overall decrease in R_D is only $\sim 40\%$. Nonetheless, this effect easily dominates the counter-effect of increasing Pd electrode resistance, R_M , with C_H which is the basis of simple Pd strip hydrogen detectors.

Since the physical presence of chemisorbed hydrogen atoms at the Schottky interface is essential for lowering ϕ_B , it is reasonable to argue that the lowering is proportional to the fractional interface area coverage by hydrogen [7, 15]. Also, once the interface is saturated with hydrogen no further reduction in ϕ_B is possible, resulting in a loss of sensitivity to further changes in C_H . Following the analysis of Kang and Gurbuz [7] it can be shown that the barrier height lowering is related to the environmental hydrogen concentration by

$$\frac{1}{\Delta\phi} = \frac{1}{\Delta\phi_\infty} \left(1 + \frac{1}{K\sqrt{C_H}} \right) \quad (4)$$

where $\Delta\phi$ is the change in ϕ_B at a particular C_H compared to its value prior to exposure, $\Delta\phi_\infty$ is the maximum possible change (for $C_H \rightarrow \infty$) and K is the equilibrium constant corresponding to chemisorption of hydrogen by Pd. Figure 5 shows a plot of $1/\Delta\phi$ versus $1/\sqrt{C_H}$ for two devices. The linear fits to the data indicate a good match to equation (4) and generate best fit values of K as 0.58 and 0.44 $\text{ppm}^{-0.5}$, in good agreement with earlier reports [15].

Finally, the major drawback of Schottky diode-based hydrogen detection, including the present technique, is the long response time. As seen in figure 2, the initial response time is ~ 15 h (5 ppm C_H) and subsequent response times, though much reduced, are still significant. At very

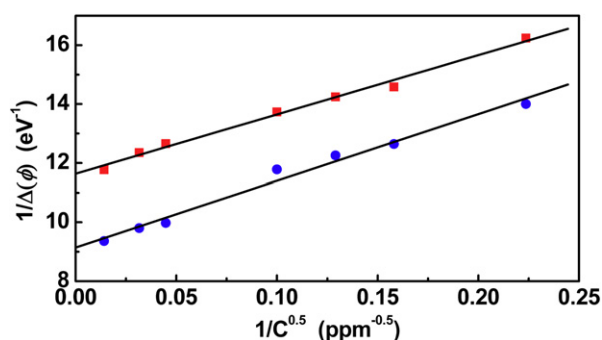


Figure 5. Plot of $1/\Delta\phi$ versus $1/\sqrt{C_H}$ for two devices. The solid lines are linear fits to the data.

low concentration hydrogen is rapidly lost due to the low concentration in the surroundings, thus making the process of uptake by adsorption at the interface extremely slow; moreover, a significant fraction of the interface has to be covered with hydrogen before being reflected in the detection mechanism. A reduction in the Schottky interface area and an increase in the volume to surface ratio of the exposed Pd are the most obvious design improvements that would potentially further increase the sensitivity of the device as well as decrease its response time. However, we reiterate the reversible nature of the detection process but note an ~ 20 h recovery time for R_D to reach its initial vacuum value at room temperature. While chamber evacuation does not accelerate the process, a simultaneous increase in device temperature to 100°C reduces the recovery time to < 2 h.

In summary, we have presented a Pd/InP Schottky junction-based hydrogen sensor utilizing a novel detection technique with a remarkably high sensitivity of 1 ppm. In contrast to conventional IV measurement a resistance measurement method is used where Schottky barrier lowering in the presence of hydrogen is reflected in a decrease in device resistance. The high sensitivity of this technique is demonstrated to be due to the sensitivity of the junction conductance to the barrier height and consequently to C_H , especially for values lower than 20 ppm.

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