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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 \textit{et al} [4] and Kim \textit{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
hydrogen adsorption has also been suggested [7] as a mechanism of barrier modification. Both mechanisms result in lowering of the effective Schottky barrier height, $\phi_B$. The high interface electric field makes $\phi_B$ 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 $\phi_B$ (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 $\sim 160 \mu m$, width $\sim 4 \mu m$ and thickness $<10$ nm) over an n-InP substrate of doping density $\sim 1 \times 10^{17}$ 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 ($<10$ 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 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 $\phi_B$ (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 $\phi_B$ 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 $1450 \ \Omega$ ($R_{D0}$), prior to any exposure to hydrogen. Then, 5 ppm of hydrogen is introduced into the chamber, which lowers $R_D$, saturating to 1080 $\Omega$ over approximately 15 h. Reduction in the hydrogen concentration to 1 ppm increases $R_D$ to 1180 $\Omega$.
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

\[ I = A e^{\frac{\phi_B}{kT}} \exp\left(\frac{eV}{nkT}\right) \tag{1} \]

where \(I\) is the forward bias current, \(A\) is the junction area,
\(A e^{+}\) 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 \(\phi_B\) as a
function of \(C_H\), as shown in figure 4. Both \(R_D\) and \(\phi_B\)
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 \(R_{SB}\):

\[ R_{SB}(T, C_H) = \frac{B}{AA^{+}\exp\left(\frac{\phi_B(C_H)}{kT}\right)} \tag{2} \]

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

\[ \frac{1}{R_D(T, C_H)} = \frac{1}{R_{M}(T, C_H)} \]

\[ + \frac{1}{R_{SB}(T, C_H) + g/(en_e(T)\mu_e(T))} \tag{3} \]

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, \(\mu_e\)
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
case) 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 \(\phi_B\) 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 equa-
ion (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, \(~20\%\) (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 $10^2$ ppm $< C_H < 10^4$ 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 $dI/dV$ versus $C_H$ (for $dI/dV$ against $C_H$) 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 $\phi_B$ decreases with increasing $C_H$, $dI/dV$ 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 $dI/dV$ of $\sim 2$ 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 $\phi_B$, 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 $\phi_B$ 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

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

where $\Delta \phi$ is the change in $\phi_B$ 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 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 $\sim 15$ h (5 ppm $C_H$) and subsequent response times, though much reduced, are still significant. At very 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 $\sim 20$ 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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References