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A New Hydrogen Sensor Based on a Pt/GaAs Schottky Diode

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ABSTRACT

A new hydrogen-sensitive detector based on a Pt/GaAs Schottky diode has been fabricated. The devices have been characterized by dark current-voltage and capacitance-voltage measurements, as a function of temperature and gas phase composition. At 150°C, the detection limit for hydrogen is 6 ppm in a nitrogen environment and 200 ppm in air.

In a metal-semiconductor contact, the height of the Schottky barrier depends on the work function difference between the metal and the semiconductor. In the past, it was accepted for III-V semiconductors that the barrier height was nearly independent of the metal work function, due to the high density of surface states causing pinning of the Fermi level. However, some authors have found evidence of unpinning of the Fermi level in metal/GaAs interfaces in structures fabricated on clean (100) GaAs surfaces (1).

It is known that in a catalytic metal-based Schottky diode, the barrier height decreases when the device is exposed to a hydrogen-containing atmosphere. This effect can be attributed to the decrease of the metal work function due to adsorption of atomic hydrogen at the metal/semiconductor interface (2-4). Since the diode current in a Schottky diode depends exponentially on any change in barrier height, a Pt/GaAs Schottky diode should exhibit high sensitivity to changes in the metal work function and, consequently, can be used as a simple hydrogen sensor (2).

We describe here the fabrication and characterization of a H_2 sensor based on a Pt/GaAs Schottky diode. The sensitivity of the sensor is given by the increase in capacitance observed when atomic hydrogen generated at the metal surface by catalytic dissociation reaches the Pt/GaAs interface. The change in capacitance is, therefore, a measure of the H_2 concentration present in the environment to which the sensor is exposed.

The response time of the sensor will be determined by the slowest of the successive kinetic steps involved in the global process, i.e., gas-phase diffusion of molecular H_2 towards the Pt surface, H_2 dissociative chemisorption on the metal surface, solid state diffusion of atomic hydrogen through the metal film, and finally, adsorption of atomic hydrogen at the Pt/GaAs interface. In order to ascertain which step controls the sensor response rate, we have studied the reaction kinetics via capacitance-time measurements as a function of temperature and H_2 concentration in nitrogen and air, respectively. In the following, we show that dissociation of molecular hydrogen into a weakly bound precursor state is the rate-limiting step, and that the global process has associated with it an apparent activation energy of 4.6 kcal/mol.

Experimental

The Pt/GaAs diodes were fabricated on Si-doped epitaxial GaAs (100) ($N_d = 2 \times 10^{17}, 4 \times 10^{15}$ cm^{-3}) grown by molec-

ular beam epitaxy. Platinum dots, 1000Å thick and 1 mm in diameter, were electron gun-evaporated in ultrahigh vacuum through a mask. Previously, a Au-Ge back contact had been deposited by thermal evaporation.

Experiments were carried out in a stainless steel reaction chamber, connected to a gas flow panel. The temperature of the device was determined by means of a chromel-alumel thermocouple and controlled between 25° and 200°C. Hydrogen gas was diluted with nitrogen or, alternatively, with synthetic air (20% oxygen in nitrogen). The total pressure of H_2, O_2, and N_2 was regulated under a slight overpressure (~1.5 atm). The total gas flow over the device was 500 sccm.

The devices were characterized by current-voltage and capacitance-voltage measurements in the dark as a function of temperature and gas phase composition. High-frequency C-V (1 MHz) values were obtained with a Hewlett-Packard 4280A capacitance meter. The measurement setup was computerized.

Results and Discussion

Figure 1 shows the C-V characteristics at 150°C, in N_2 and in N_2 with 1000 ppm of H_2. Plots of $1/C^2$ vs. reverse voltage indicate a Schottky barrier decrease of 0.19 eV when H_2 is diluted in a N_2 atmosphere. The I-V characteristic shows a similar behavior (Fig. 2). Following dilution of 1000 ppm H_2 in N_2 (at 150°C), there is an increase in current of about
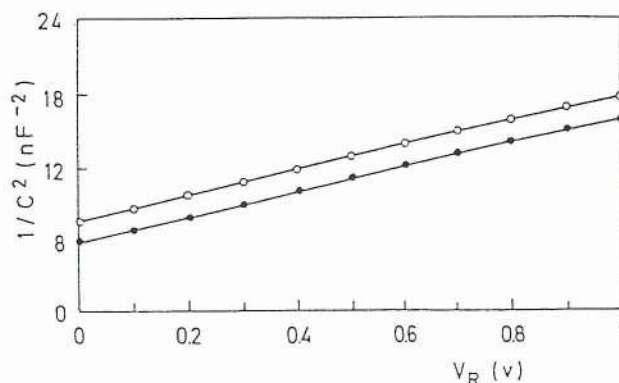

Fig. 1. $1/C^2$ vs. V plot for a Schottky diode in N_2 (○) and in 1000 ppm H_2 in N_2 (●) at 150°C. The decrease in barrier height is 0.19 eV.
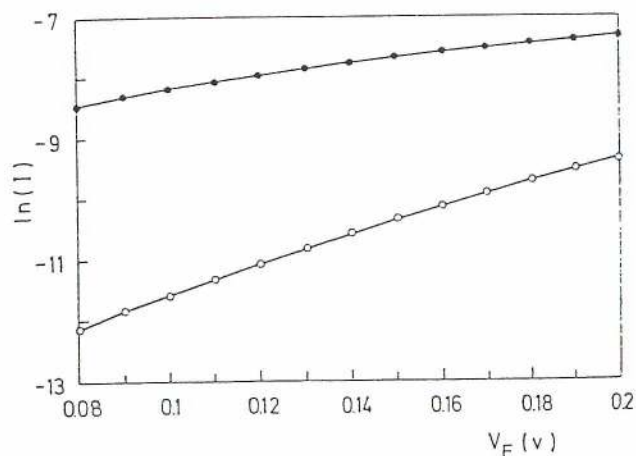
Fig. 2. Forward *I-V* characteristics of a Schottky diode in N_2 (O) and in 1000 ppm H_2 in N_2 (●), at 150°C. The decrease in barrier height is 0.15 eV.

two orders of magnitude, from 5.5×10^{-6} A to 2.3×10^{-4} A at a forward bias of 0.1V. At 50°C and 60 ppm of H_2 in N_2, a current change from 0.2×10^{-6} A to 3.2×10^{-6} A is obtained at the same forward bias. These signals are higher than those reported for Pd/GaAs Schottky barrier diodes (5). Departure from ideal diode behavior is due to series resistance effects caused by the high current value. Calculations following the thermionic emission model give a value of 0.15 eV due to 1000 ppm H_2 for Schottky barrier lowering, in good agreement with the *C-V* data obtained.

Figure 3 shows the response of the diode as a function of hydrogen concentration in synthetic air for different values of substrate temperature (measurements are made at 0.1V reverse voltage). The sensitivity as well as the linear response range increase with increasing temperature. At 150°C, a concentration as low as 200 ppm H_2 in "air" is detected and a linear response between 200 and 3000 ppm is observed. The minimum concentration of H_2 detectable in pure nitrogen atmosphere is still lower, and 6 ppm H_2 have been measured.

Kinetic studies were carried out by monitoring the capacitance of the device as a function of time, at 0.1V reverse voltage, upon introduction and removal of hydrogen in nitrogen or synthetic air. The transient response of the diode can be seen in Fig. 4; after hydrogen is turned on, it takes a certain time for the signal to change. This lag time depends on temperature and hydrogen concentration. The signal rises abruptly until it reaches saturation. After hydrogen is turned off, there is a very slow fall response; this recovery process can be activated in air, as shown in the
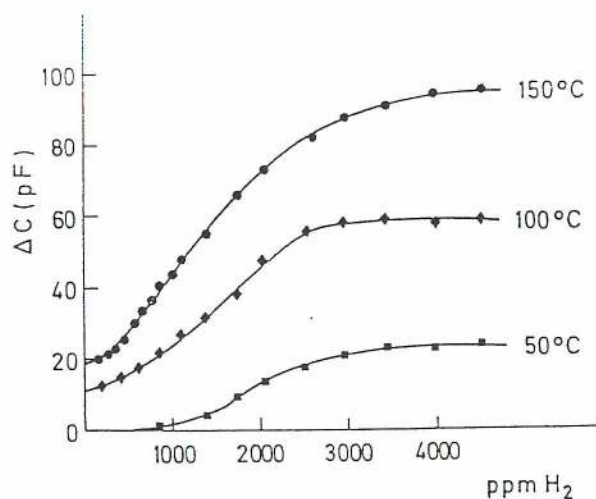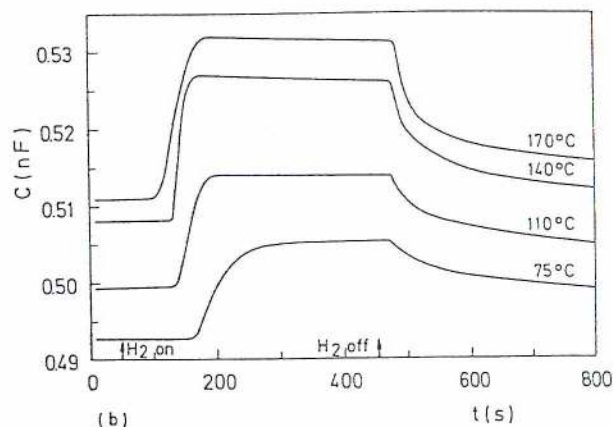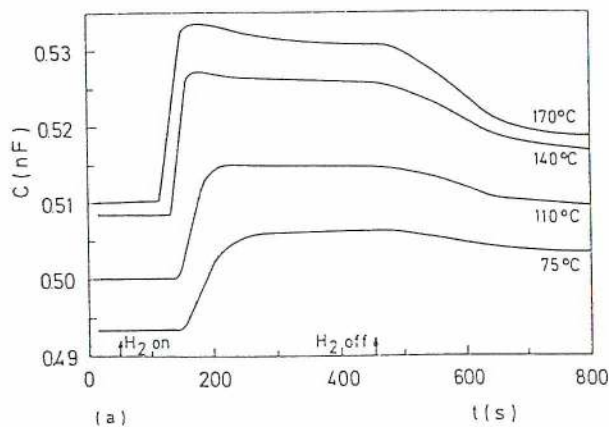

(a)

(b)

Fig. 4. Capacitance vs. time curves of a diode exposed to 1176 ppm H_2 in N_2 at different temperatures. Desorption was carried out a.) in N_2 and b.) in synthetic air.

same figure. In a N_2 atmosphere, recovery takes place through

$$2H_a \rightarrow H_2(g) \qquad [1]$$

This process is very slow, even at 150°C, indicating that the formation kinetics of $H_2(g)$ is slow. However, if O_2 is present, desorption takes place quickly due to the additional process of water formation.

Examination of the dependence on temperature of the initial rate of change of capacitance during transients, for a given gas phase composition, allowed for the determination of the activation energies associated with the processes of H_2 introduction and removal from the Pt/GaAs structure. This dependence is depicted in the Arrhenius plot shown in Fig. 5. The activation energy calculated from
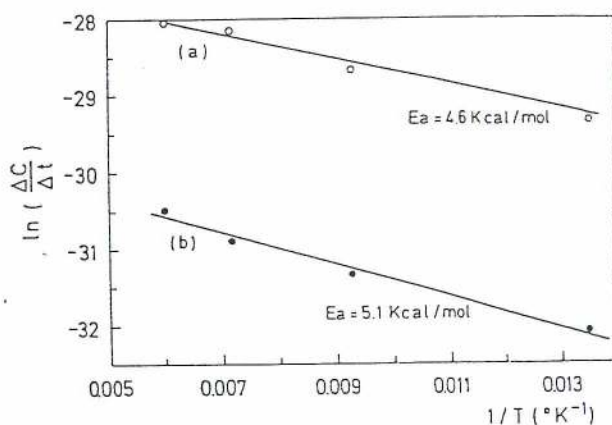

Fig. 3. Response of a Schottky diode to hydrogen concentration in synthetic air at various temperatures.

Fig. 5. Arrhenius plot for the a.) adsorption and b.) desorption of 1176 ppm H_2 in N_2 in the 75°-170°C temperature range.

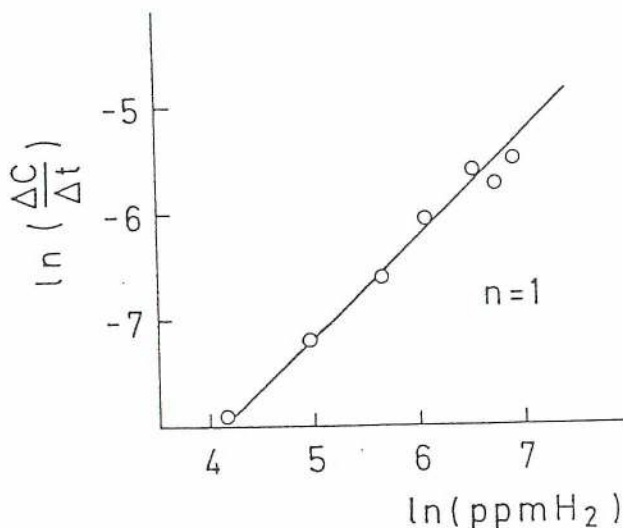Fig. 6. Dependence of H_2 introduction rate into the Pt/GaAs structure on H_2 partial pressure at 163°C.

Table I. Stability of a Pt/GaAs diode upon adsorption of 1000 ppm H_2 in N_2 over a period of 16 weeks

| | t = 0 | | t = 16 weeks | |
T (°C)	ΔC (pF)	τ (s)	ΔC (pF)	τ (s)
150	25.0	12	26.4	9
100	17.6	18	16.6	15
50	10.6	28	8.0	26

this plot for the incorporation of H_2 was 4.6 kcal/mol, and only slightly higher, at 5.1 kcal/mol, for the removal process. When the desorption process is carried out in the presence of oxygen, the activation energy decreases to 3.0 kcal/mol.

Reaction orders with respect to H_2 were determined by examining the dependence of the initial rate of change of capacitance during transients on hydrogen partial pressure at a given temperature. Figure 6 shows the dependence of the incorporation rate on reactant partial pressure of 163°C using nitrogen as a carrier gas. A linear behavior is observed in the range of H_2 partial pressures studied, irrespective of temperature.

Gas-phase diffusion of hydrogen to the Pt surface is ruled out as the rate-limiting step, since it is not an activated process. Sol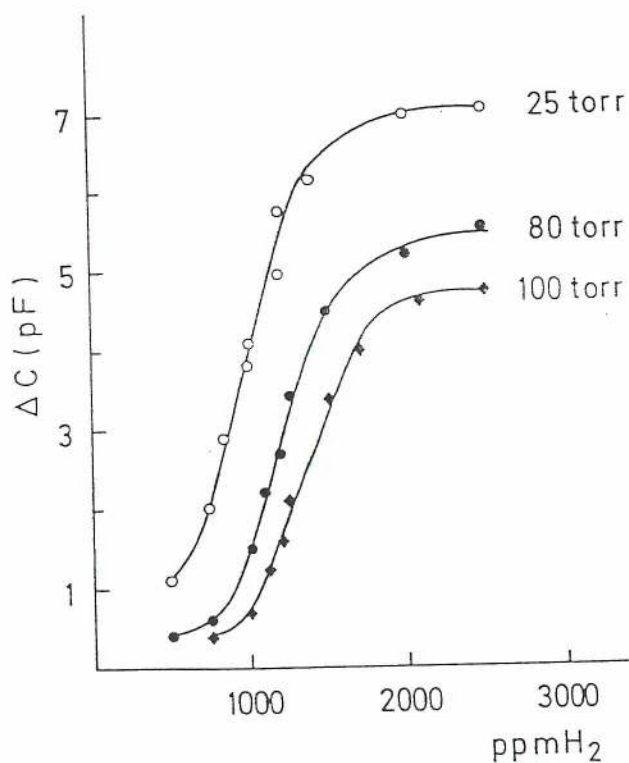id-state diffusion of atomic hydrogen in the metal ($D \sim 10^{-6}$ cm^2 s^{-1}) (6) cannot be the slowest step, because the response time of the sensor is several orders of magnitude larger than the time for hydrogen diffusion through the 1000Å-thick Pt film in the temperature range studied. As a consequence, we can assume that equilibrium between hydrogen adsorbed on the surface, H_a, hydrogen in the bulk, H_b, and hydrogen adsorbed on the Pt/GaAs interface, H_{ai}, is rapidly achieved, according to

$$H_a \leftrightarrow H_b \leftrightarrow H_{ai} \qquad [2]$$

Therefore, surface reactions leading to dissociative chemisorption of hydrogen have to be the rate-controlling step of the introduction of hydrogen into the Pt/GaAs structure. The adsorption process takes place most probably via dissociation of molecular hydrogen into a weakly bound precursor state, H', followed by the formation of a more strongly bound atomic state

$$H_2 (g) \xrightarrow{k_1} 2H' \qquad [3]$$

$$H' \underset{k_{-2}}{\overset{k_2}{\leftrightarrow}} H_a \qquad [4]$$
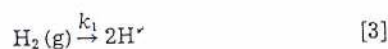
The experimentally found first-order dependence of adsorption rate on H_2 pressure, together with a low value of the activation energy, is consistent with a rate equation

$$V_{ads} = k_1 P_{H_2} \qquad [5]$$

corresponding to the adsorption through a precursor state according to [3], as the slowest step. Furthermore, it should be noted that the nearly identical values obtained for the activation energies of adsorption and desorption, respectively, indicate that the heat of adsorption is negligible as a consequence of the high coverage of the platinum surface at atmospheric pressure (7, 8).

The effect of oxygen partial pressure on the response of one of the diodes studied is shown in Fig. 7. The sensitivity decreases appreciably with oxygen concentration, due to secondary surface reactions leading to water formation, in good agreement with previous reports (4). Interferences with other gases are under investigation.

It was found that the diodes do not suffer changes in signal height for a long time. Table I shows the signal height (ΔC) and time constant (τ) for H_2 adsorption of a diode at different temperatures for 1000 ppm H_2 in N_2, over a period of 16 weeks. The time needed for the capacity change to reach e^{-1} of its final value was taken to be the time constant of the process. As can be seen in the table, the diodes proved to be quite stable for the length of time studied. Furthermore, no morphological degradation was observed in the platinum film. These characteristics make these devices advantageous with respect to Pd gate devices reported by other authors (5, 9).

Conclusions

We have fabricated hydrogen sensors based on a Pt/GaAs Schottky barrier, with a simpler design than their Si counterparts, which invariably require an intermediate insulator film to avoid reaction between metal and semiconductor. These Pt/GaAs devices have been shown to be sensitive, stable, and reproducible. At 150°C, a minimum of 6 ppm of hydrogen in nitrogen, and 200 ppm of hydrogen in synthetic air, can be detected. In air, a linear response is found up to 3000 ppm hydrogen. Measurements of I-V and C-V characteristics support the model of Schottky barrier reduction to explain the H_2 sensitivity. The devices oper-

Fig. 7. Response curve of a diode at different O_2 partial pressures (25, 80, and 100 torr). Measurements were made at 150°C and −0.1V reverse voltage.

ate over a wide temperature range and are sensitive even at room temperature. The diodes recover easily in air at 190°C, and show long-term stability.

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Technical Note

Reduced Hydrogen Cadmium Plating

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In aerospace applications, high-strength steel components (such as landing gears, fasteners, and springs) may fail mechanically (1, 2) during service from the conjoint action of stress and hydrogen embrittlement. Corrosion of steel is concomitant with production of hydrogen which may diffuse into bulk steel and cause embrittlement. Deposition of cadmium onto steel components as a sacrificial coating is a conventional practice for corrosion protection in saline environments. However, hydrogen is also codeposited with Cd during conventional electroplating and, therefore, is a cause for concern. Usually cadmium is electroplated from a cyanide bath (an aqueous solution prepared from $CdCO_3$, CdO, $Cd(CN)_2$, NaCN, and NaOH) in the industry (3).

Generally, plating is conducted with dc at low (e.g., 30 mA/cm^2) current densities and for a long time. Most significantly, the cyanide plating invariable is accompanied by hydrogen codeposition which may be responsible for hydrogen-embrittlement-related failures of cadmium-coated components.

Cadmium plating from fluoroborate electrolyte has been claimed to be less prone (4) to result in hydrogen codeposition. In a recent study Varma and Vargas (5) have emphasized a need to control the electrodeposition overpotential during the initial stage of film growth to avoid hydrogen codeposition. Study on high-rate electrodeposition of cadmium from cadmium fluoroborate solution, using pulse currents and forced electrolyte convection, provided preliminary indications that less hydrogen was deposited. This paper reports our effort, for the first time, on an almost hydrogen-free electrodeposition of fine-grained cadmium on 300 M steel substrate from fluoroborate electrolyte.

The important factors that control the rate of cadmium deposition and the quality of electrodeposits in plating are: (i) the overpotential (η) or the current density, (ii) mass-transport limitation for the cadmium ionic species in the electrolyte, (iii) the pH of the electrolyte, and (iv) the nature of the substrate surface. The electrochemical deposition of cadmium from aqueous fluoroborate electrolyte is a diffusion-controlled process, and the maximum rate for deposition is given by the limiting current density, i_{Dl}. In the dc mode it is given by the equation

$$i_{Dl} = Z F \frac{C_o}{\delta} \quad [1]$$

where Z is the number of electrons involved in the electroreduction step, F is the Faraday's Constant, C_o is the bulk concentration of cadmium ion species, and δ is the diffusion layer thickness. Here, the magnitude of i_{Dl} is limited by δ or the limitation of Cd ions that are able to reach the cathode surface. However, in the pulse method the use of high cathodic peak current pulses (~0.5-1 A/cm^2) of short duration (<0.5 ms) followed by sufficiently long rest periods and/or anodic pulses provide a number of advan-
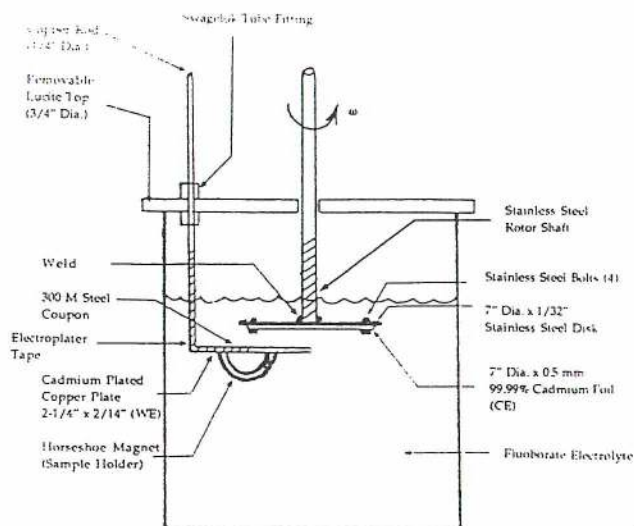
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Fig. 1. Electrochemical cell setup for pulse plating of cadmium under forced electrolyte convection.