Hydrogen passivation studies in Pd/*n*-GaAs devices

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Abstract. The effect of hydrogen on the current (*I*-*V*) and capacitance (*C*-*V*, TSCAP) has been studied for Pd/*n*-GaAs diodes. Hydrogenation has been found to improve ideality factor of the diode. Reverse *C*-*V* characteristics show that the number of shallow and deep donors is reduced on hydrogenation. The TSCAP measurement shows the presence of two donor states at ~0.48 and 0.72 eV which is being partially passivated on hydrogenation. The likely origin of these states is discussed.

Keywords. Hydrogen passivation; Schottky diodes; TSCAP.

1. Introduction

Hydrogen passivation of shallow and deep levels in semiconductor has been an active area of research (Haller 1991; Pankove and Johnson 1991; Myers *et al* 1992; Pearton *et al* 1992), due to the high diffusivity and chemical activity at moderate temperature (~400°C). A controlled neutralization of dopants by hydrogen has resulted in improving the opto-electronic/electronic properties of a wide variety of semiconductors including the III-V compound semiconductor (Constant *et al* 1987; Jackson *et al* 1988). Common methods of intentional introduction of hydrogen into III-V compound are: hydrogen ion implantation and heating in hydrogen plasma. The latter leads to etching and damage in the near surface region while the former introduces a large number of compensating defects in bulk. In the present study, the passivation in *n*-GaAs has been attained through a supply of low energy hydrogen giving damage free injection. For this purpose Pd/*n*-GaAs diodes were fabricated and placed in a hydrogen atmosphere at room temperature. Palladium adsorbs the molecular hydrogen and stores it as atomic hydrogen. This, in turn, diffuses from palladium film to the Pd/GaAs interface towards the bulk semiconductor. We performed similar studies on silicon (Tripathi *et al* 1989, 1992) and GaAs (Srivastava *et al* 1991; Singh *et al* 1995), and shown that hydrogen diffuses to the interface and bulk, resulting in the passivation of the deep and shallow states.

In the present communication, we have fabricated the Pd/*n*-GaAs devices and hydrogenated them in an atmosphere of molecular hydrogen and studied the electrical (*I*-*V*, *C*-*V* and TSCAP) characteristics. It is observed that the reverse leakage current and the effective donor density is reduced after hydrogenation. Two donor states have been identified from TSCAP measurement and their possible configuration discussed.

2. Experimental

The Pd/*n*-GaAs diodes were fabricated on Si doped (~10¹⁶ cm⁻³), LEC grown *n*-GaAs. The wafers were back contacted with Ni-Ge-Au. The wafers were first ultrasonically cleaned in trichloroethylene followed by acetone and then etched in a solution of NH₄OH:H₂O:H₂O₂. Palladium metal films (~1000 Å) have been deposited on the top of wafers in a vacuum of ~10⁻⁶ mbar by resistive heating technique. A suitable mask was used to give the diode area of 1.77 × 10⁻² cm². For hydrogenation, the diodes were kept in an evacuated chamber (~10⁻⁴ mbar) and then hydrogen gas was slowly passed into the chamber to achieve a pressure of 1 atm (termed as the adsorption cycle). The transient change in the diode capacitance (at zero bias) in the hydrogen ambient has been monitored at 1 MHz using a Boonton 72B capacitance meter. After the capacitance became constant in the hydrogen ambient, the diodes were exposed to air (termed as the desorption cycle) and the zero bias capacitance was recorded as a function of time. After the diode stabilized in air, the electrical measurements were carried out. The *C*-*V* measurements were carried out using a HP 4277A multifrequency LCZ meter.

3. Results and discussion

3.1 Variation in capacitance during adsorption and subsequent desorption

The variation of capacitance at 1 MHz as a function of time on Pd/*n*-GaAs diode during adsorption and desorption are given in figure 1. During adsorption, the original capacitance (point A, figure 1) increases initially and peaks after 100–110 s (peak B). After that capacitance starts decreasing and slowly equilibrates in 6–7 min

(region C). During desorption, the capacitance (region D) slowly increases and stabilizes (region E).

The initial increase of the diode capacitance in the hydrogen ambient (peak B) is understood in terms of changes in the work function of the palladium. The hydrogen gas is dissociated and adsorbed at the outer Pd surface. Hydrogen atoms then diffuse through Pd film and are adsorbed at the inner Pd surface. At this surface the adsorbed hydrogen atoms change the work function of this surface due to their dipole moments. The dipole is believed to result from the S-type adsorption of hydrogen atom inside the Pd film (Lundstrom *et al* 1975), which reduces the work function (Steele *et al* 1976). Consequently, the barrier height of the Pd/n-GaAs initially reduces, giving rise to an initial increase in the diode capacitance (regions A-B, figure 1).

The adsorbed hydrogen, having reached the interface, subsequently diffuses towards the GaAs bulk. The decrease in the diode capacitance after an initial increase is possibly due to the interaction of diffusing hydrogen with the interface and the bulk states. The diffusing hydrogen may induce the compensating interface states, which results in the reduction of diode capacitance. Some of the acceptor states have been identified previously in the hydrogenated devices from the C - V studies (Srivastava *et al* 1991).

It is observed that the capacitance becomes constant slowly with time which indicates attainment of a dynamic equilibrium by the device in the hydrogen ambient. The hydrogen diffusion in gallium arsenide may still continue but the changes produced in bulk (far from interface) cannot be monitored by zero bias capacitance measure-

ment. The capacitance voltage measurements at reverse bias would give the information about the changes occurring deep inside the depletion layer towards the bulk of gallium arsenide.

To study the desorption behaviour (regions D-E, figure 1), the device was exposed to air. The adsorbed hydrogen in Pd starts desorbing from the external surface of the palladium. Consequently, hydrogen at the Pd-internal surface tries to diffuse out through its external surface because of concentration gradient of hydrogen (Petersson *et al* 1984). The desorption of hydrogen from Pd layer and from the internal Pd layer in contact with semiconductor would give rise to an increase in the capacitance. However, there is a possible diffusion of bulk hydrogen back to the interface. The hydrogen would stay in a particular region, i.e. interfacial or bulk, depending on the availability for the sites of hydrogen bonding. After few hours the diode capacitance stabilizes in air. The net decrease in the diode capacitance after a full cycle of hydrogenation (adsorption and desorption) from its initial value, A to the final value, E can be attributed to the modifications induced by hydrogen at the interface or the GaAs bulk. The present current-voltage (I - V), capacitance-voltage (C - V) and thermally stimulated capacitance (TSCAP) studies support this.

3.2 Current-voltage studies

The current, I flowing through the Pd/n-GaAs diodes as a function of voltage (V) across it is shown in figure 2, before and after hydrogenation. It is obvious from the figure that the reverse current decreases after

Figure 1. Variation of zero bias room temperature capacitance of the Pd/n-GaAs diode during hydrogen adsorption and desorption cycle (Frequency of measurement is 1 MHz).

hydrogenation. Figure 2 represents the typical behaviour for the five diodes studied earlier. The ideality factor (η) and the barrier height (ϕ_b) for the devices have been estimated from the I - V characteristics (figure 2). For the estimation of ideality factor, the following relation (Sze 1981) has been used:

$$\eta = \frac{q}{kT} \frac{\partial V}{\partial (\ln J)} \quad (1)$$

The values of ideality factor are 1.49 and 1.09 for the

Figure 2. I - V characteristics of the Pd/n-GaAs diode before and after the hydrogenation cycle.

control (unhydrogenated) and hydrogenated samples, respectively. The change in the ideality factor on hydrogenation shows an improvement of the device. The improvement is related to the passivation of the interfacial states.

The Schottky barrier height can be estimated from the I - V studies by using the following relation (Sze 1981):

$$\phi_b = \frac{kT}{q} \ln A^* T^2 / J_0 \quad (2)$$

where A^* is the effective Richardson constant ($8.6 \text{ Am}^{-2} \text{ K}^{-2}$) and J_0 the saturation current density. The image force lowering contribution is neglected. The estimated values of ϕ_b are 0.90 and 0.92 eV for the control (unhydrogenated) and hydrogenated devices, respectively. The increase in the barrier height is known to be related with a decrease in the carrier concentration (Chin-Vincent *et al* 1990).

3.3 Capacitance-voltage studies

The capacitance-voltage studies have been carried out at three different frequencies viz. 10 kHz, 100 kHz and 1 MHz. Figure 3 gives the C - V (reverse bias) characteristics at three different frequencies. The effective donor density (N_D) has been estimated for the devices using the relation (Sze 1981)

$$N_D = \frac{2}{q \epsilon_s \epsilon_0} \frac{dV}{A^2 d(1/C^2)} \quad (3)$$

where N_D is the donor concentration, ϵ_0 the permittivity in vacuum, ϵ_s the dielectric constant of GaAs

Figure 3. Capacitance vs voltage plot of Pd/n-GaAs before and after hydrogenation at frequencies 10 kHz, 100 kHz and 1 MHz.

($\epsilon_s = 13.13$) and A the area of the diode. The calculated effective donor density (N_D) is given in table 1. Two general conclusions are obvious.

(I) Effective donor density reduces after the hydrogenation at all frequencies. The effective donor density given in table 1 is $N_D + N_{TD}$, where N_D corresponds to the ionized shallow donor density and N_{TD} the deep donor density (Milnes 1973). The reduction in the effective donor density ($N_D + N_{TD}$) after hydrogenation indicates a reduction in N_n or N_{TD} or both of them. The hydrogen passivation of shallow donors and acceptors in GaAs has already been shown by many workers and is reviewed by Pearton *et al* (1992) and Pajot (1988). Passivation of deep states by RF plasma hydrogenation (Jalil *et al* 1989) and low energy hydrogen ions (Bosacchi *et al* 1989) has also been shown.

(II) Measured effective donor density is less at higher frequencies. It is known that ionized deep states (N_{TD}) (Milnes 1973), contribute more at low frequencies. Therefore, the low frequency value of measured effective carrier concentration is a sum of N_D and N_{TD} . However,

Table 1. Effective carrier concentration at different frequencies before and after hydrogenation of Pd/n-GaAs diodes.

Frequency	Effective carrier concentration (N_D') (cm^{-3})	
	Unhydrogenated	Hydrogenated
10 kHz	3.18×10^{16}	1.16×10^{16}
100 kHz	1.80×10^{16}	9.20×10^{15}
1 MHz	8.98×10^{15}	6.20×10^{15}

N_{TD} does not contribute at high frequencies and it approximates more to N_D and hence will be lower than low frequency value. It can be found out that the value N_{TD} (deep donor density) can now be estimated by taking the difference of effective donor density at high frequency (1 MHz) and that at low frequency (10 kHz). The N_{TD} for the unhydrogenated devices is $2.28 \times 10^{16} \text{ cm}^{-3}$ and $5.4 \times 10^{15} \text{ cm}^{-3}$ for the hydrogenated devices. This shows that there is a density reduction of the deep donor states on hydrogenation which may be due to the hydrogen passivation of deep states. The involvement of such deep states in n-GaAs has also been seen by Lagowski *et al* (1982) and Pearton *et al* (1983).

4. Thermally stimulated capacitance (TSCAP) studies

In the present studies, we first filled all the traps by cooling the sample junction to $\sim 130 \text{ K}$. Then, a reverse bias (2 V) was applied and the sample was heated up to 360 K at a rate of $\sim 0.56 \text{ K/s}$. The capacitance as a function of temperature during heating cycle is shown in figure 4 for unhydrogenated and hydrogenated devices. The TSCAP curves of figure 4 show two steps in the temperature range as given below:

	1st step	2nd step
For unhydrogenated	174–228	278–302°K
For hydrogenated	177–225	286–293°K

Further, it is obvious from the above that the temperature range of the capacitance steps are narrower in

Figure 4. Thermally stimulated variation of capacitance with temperature for Pd/n-GaAs diode before and after hydrogenation.

Figure 5. $1/C^2$ vs V plot of Pd/n-GaAs diode before and after hydrogenation of the diode for which TSCAP studies are reported.

the hydrogenated case and hence it can be inferred that the distribution of trap/defect states has become sharper after hydrogenation.

The activation energy can be calculated by using the following relation (Buehler and Phillips 1976)

$$E = kT_m \ln \left[\frac{\nu k T_m^2}{b(E + 2kT_m)} \right], \quad (4)$$

where t_m is the midpoint of the TSCAP step, b the heating rate, $\nu = 10^{12} \text{ s}^{-1}$ for electron emission.

The activation energies estimated for the unhydrogenated device are 0.48 and 0.72 eV for $T_m = 201^\circ\text{K}$ and 290°K , respectively. For the hydrogenated device, the activation energies estimated are 0.48 eV and 0.72 eV for $T_m = 201^\circ\text{K}$ and 292°K , respectively.

From the magnitude of the capacitance step, the trap concentration (N_t) can be calculated using the relation (Buehler and Phillips 1976)

$$N_t \approx 2N_D \left(\frac{C_t - C_i}{C_i} \right), \quad (5)$$

knowing N_D , N_t can be calculated from the above equation.

To estimate the donor concentration (N_D), C - V measurement was done before and after hydrogenation and $1/C^2$ vs V curve was shown in figure 5. The values of N_D calculated are $4.6 \times 10^{16} \text{ cm}^{-3}$ and $2.7 \times 10^{16} \text{ cm}^{-3}$ for the unhydrogenated and hydrogenated devices, respectively. The trap concentrations estimated using above relation are: $4.4 \times 10^{16} \text{ cm}^{-3}$ and $9.1 \times 10^{15} \text{ cm}^{-3}$ for the trap energy 0.48 eV and 0.72 eV, respectively for the case of unhydrogenated device and for the hydrogenated device the trap concentration is $3.1 \times 10^{16} \text{ cm}^{-3}$ and $3.4 \times 10^{15} \text{ cm}^{-3}$ for the trap energy 0.48 eV and 0.72 eV, respectively.

The observed electron trap with energy 0.72 eV below the conduction band can be related to the well known EL2 defect (Martin *et al* 1977). The electron trap EL2 is a native defect of bulk GaAs crystals, where it occurs in large concentration (up to several 10^{16} cm^{-3}). Its formation is favoured in materials prepared under As-excess conditions as with LEC bulk crystals (used in the present study). It is ascribed to the As_{Ga} antisite defect, as suggested by many workers (Lagowski *et al* 1982; Schneider 1982; Henine *et al* 1986), but its microscopic nature is still controversial (Bourgoin *et al* 1988; Chang and Chadi 1988). The other electron trap EB6 or E3 ($E = 0.1 \text{ eV}$) is observed by Martin *et al* (1977) and Lang and Kimmerling (1975). Mircea *et al* (1976) suggested that this level might be related to the point defects or point defects/impurity complexes.

It may be noted that the concentration of both the observed states (0.72 and 0.48 eV) is found to be reduced in concentration on hydrogenation showing the partial passivation of these states. Hydrogen passivation of EL2 defect states have also been reported by Lagowski *et al* (1982), Omel'yanovski *et al* (1987) and Kang *et al* (1993) in their study using hydrogen plasma passivation.

5. Conclusions

Current-voltage, capacitance-voltage and TSCAP studies on Pd/n-GaAs diodes are reported before and after the hydrogenation cycle. Hydrogen has been found to improve the electronic quality of the diode by interfacial states' passivation. The deep bulk states at 0.48, 0.72 eV from conduction band minima have been identified from the TSCAP studies and it has been shown that their density is reduced after hydrogenation.

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