Hydrogen passivation studies on Pd–n-type-Si diodes

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The effect of hydrogenation on the capacitance and the infrared absorption has been studied for a Pd–n-type-Si diode. The hydrogenation reduces the carrier density by approximately 30%. The infrared spectrum after hydrogenation shows the following changes: (i) A small peak near 2340±10 cm^{-1} (corresponding to phosphorus-hydrogen bond) existing in the original sample grows and (ii) a new band near 2150–2050 cm^{-1} appears (corresponding to silicon-hydrogen bond). The growth of the silicon-hydrogen band is faster than that of the phosphorus-hydrogen band. These results show that the hydrogen passivates the donor states through the formation of phosphorus-hydrogen and silicon-hydrogen (adjacent to the substitutional phosphorus) -like species.

I. INTRODUCTION

Hydrogen passivation of shallow and deep levels in semiconductors has recently been an active area of research[1–6] due to the high hydrogen diffusivity and chemical activity at moderate temperatures ($\sim 400\,°C$). Most of the "deep" defect states in amorphous[7] and crystalline[8] semiconductors, such as the point defects,[9] metal-related deep impurity defects,[10] dislocations,[11] and grain boundaries,[12,13] can be passivated by atomic hydrogen. Further, "shallow" acceptors such as boron, aluminum, and indium in p-type silicon[1–6,14–16] and zinc in p-type GaAs (Ref. 17) get partially neutralized by exposure to atomic hydrogen. In p-type silicon the hydrogen diffuses to the substitutional acceptor sites (e.g., B, Al, and In) and sits between a silicon atom and an adjacent trivalent impurity to neutralize the threefold coordination of the acceptors. The hydrogen passivation of the deep donor (and also acceptor) and shallow acceptor states could be attained and understood by many workers[1–16] but the passivation of shallow donors could not be observed in n-type silicon by early workers. However, the hydrogen passivation of shallow donors in n-type silicon has been achieved by Johnson *et al.*[18] The calculation of energetics due to Johnson *et al.*[18] predicts that the atomic hydrogen can settle at the antibonding site of the silicon atom (that is the nearest neighbor of the substitutional phosphorus P) forming a P—Si—H linkage. The earlier passivation studies of shallow and deep impurities in silicon have been carried out either by hydrogenation through ion implantation or using hydrogen (H_2 or D_2) plasma. Both of these hydrogenation techniques involve introduction of damage in the silicon due to the injection of high-energy hydrogen. In the present study, the passivation in n-type silicon has been attained through a supply of low-energy hydrogen giving damage-free injection. For this purpose Pd–n-type-Si diodes [Pd–n-type-Si diode has been abbreviated as Pd/Si(n) later in the manuscript] were fabricated and placed in a hydrogen atmosphere at room temperature. The hydrogen adsorbed at the palladium (Pd) surface acts as a source of hydrogen supply for the passivation reaction. The effect of hydrogen on Pd/Si devices [both metal-semiconductor (MS) and metal-oxide-semiconductor (MOS) structures] has earlier been studied by several workers[19–28] and the modifications in the device characteristics have been understood in terms of the Pd work function change and/or neutralization of the boron acceptors (in p-type Si). But the interaction of hydrogen with the n-type silicon interface and bulk still remains an open question.

This paper reports capacitance-voltage and infrared absorption studies for the Pd/Si(n) diode before and after hydrogenation with a view to identifying the mechanism responsible for the decrease in donor density after hydrogenation. Detailed study of the effect of initial hydrogen adsorption (exposure to hydrogen) and subsequent desorption (exposure to air) on the zero-bias capacitance of Pd/Si(n) diodes is reported as a function of time. It has been observed that P—H- and Si—H-like species grow after hydrogenation and are responsible for the passivation of the donor impurities causing a decrease in the zero-bias capacitance of the Pd/Si(n) diode.

II. EXPERIMENT

The diodes have been fabricated on (111)-cut Si(n/n^+) wafers of resistivity 0.65 Ω cm. The thickness of the epitaxial n-type layer is 0.8 μm. The ultrasonic cleaning of Si wafers was done first in trichloroethylene and then in acetone. The wafers were given a quick chemical etch in a solution of HF:HNO_3. Excessive etching has to be avoided otherwise there is a danger of removing the entire top n layer. The wafers were then thoroughly rinsed in deionized water and dried in a clean air chamber. Palladium metal of 99.9999% purity (procured from Johnson and Matthey, U. K.) was deposited at a vacuum of $\sim 10^{-6}$ Torr. The diodes of area $\sim 7.85\times10^{-3}$ cm^2 have been realized by using a suitable mask. The thickness of the palladium film was kept $\sim$40 nm because blister formation has been reported for thinner films.[29] For hydrogenation, the diodes were kept in an evacuated

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chamber ($\sim 10^{-4}$ Torr) and then hydrogen gas was slowly passed into the chamber to achieve a pressure of 1 atm (termed 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 diode capacitance became constant in the hydrogen ambient, the diodes were exposed to air (termed the desorption cycle) and the zero-bias capacitance was recorded as a function of time. After the diode capacitance stabilized in air, detailed C-V studies were carried out with Boonton 72B and Hewlett-Packard HP4227A multifrequency capacitance meter at different frequencies (1, 10, 100 kHz, and 1 MHz).

A Perkin-Elmer spectrophotometer (model IR-783) has been used for recording ir spectra. The recording of ir spectra of the Pd/Si diodes presents a special problem since the Pd layer does not permit penetration of ir. So, for approaching the silicon interface or the bulk below the Pd layer of Pd/Si(n) diode, the ir beam was made to pass obliquely by tilting the sample.

III. RESULTS AND DISCUSSION

The values of junction capacitance in a diode with or without bias are directly related to the interfacial donor and acceptor states. It is for this reason that C-V studies have been widely used as a technique for monitoring deep and shallow interfacial states. In the present study we discuss the changes in the C-V characteristics arising out of the neutralization of the shallow donors by hydrogenation.

A. Adsorption and desorption behavior.

The values of the capacitance at 1 MHz (bias of 0 V) on the Pd/Si(n) diode as a function of time during hydrogen adsorption and desorption (as described in Sec. II) are given in Fig. 1. During adsorption, the original capacitance A increases initially, peaks after 30–40 s (peak B) and then decreases, equilibrating slowly in 4–5 h. The equilibrium value of the capacitance in the hydrogen ambient (region C) is lower than the original value, A. During desorption, a transient decrease in the capacitance occurs initially (D), and then increases giving a peak value after 6 min (peak E). The capacitance then decreases and equilibrates to a lower value (F). These observations were repeated for four diodes and broadly similar features were observed.

The initial increase of the diode capacitance in the hydrogen ambient (peak B) is understood in terms of the change in the work function of palladium. The adsorbed hydrogen atoms at the internal Pd surface reduce the work function of the internal Pd layer due to the formation of hydrogen-related dipoles at the interface.[19,20] Consequently, the barrier height of the Pd/Si(n) diode initially reduces, giving rise to the sharp increase in the diode capacitance (Fig. 1, $A \rightarrow B$). The adsorbed hydrogen, having reached the interface, subsequently diffuses towards the silicon bulk. The decrease in the diode capacitance after peak B is due to the interaction of the diffusing hydrogen with the interface and the bulk states. The diffusing hydrogen induces compensating interface state and neutralizes donorlike states, which results in the reduction in the diode capacitance at zero bias. Hydrogen will continue to diffuse into the silicon bulk if chemically active sites for hydrogen are available in the silicon. Slowly the capacitance becomes constant, which indicates a dynamic equilibrium attained by the device in the hydrogen ambient. The hydrogen diffusion in the silicon bulk still continues but the changes produced now cannot be monitored by the fixed-bias capacitance versus time

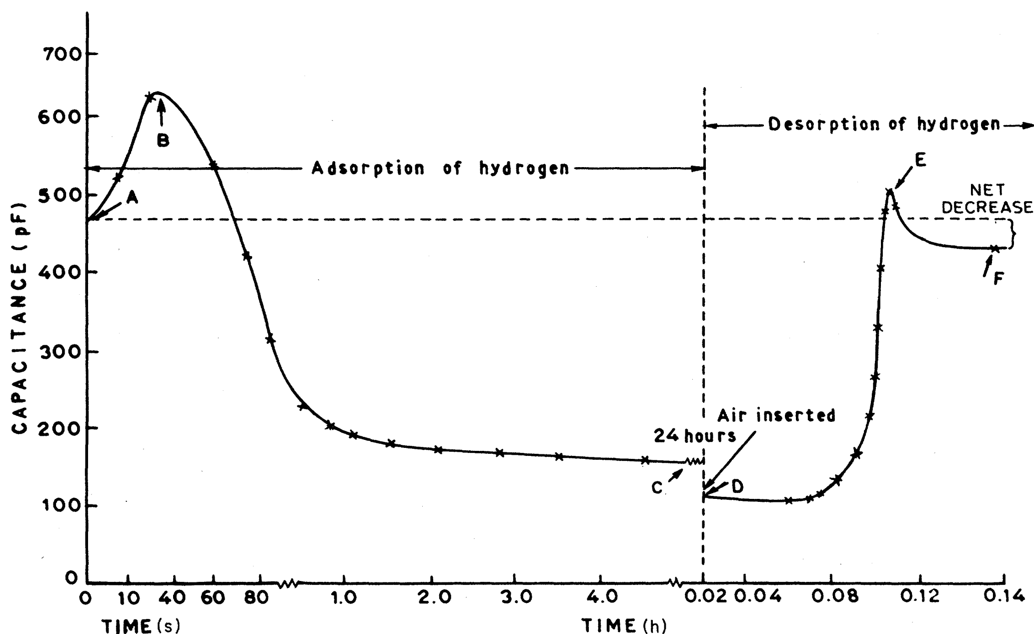

FIG. 1. Transient capacitance response of the Pd/Si(n) diode during hydrogen adsorption and desorption cycle at 27 °C (for details see text).

measurement. The capacitance-voltage (C-V) measurement will provide a better way to understand the changes occurring at the interface and silicon bulk during the above equilibrium condition (see Sec. III B).

To study the desorption behavior ($D \rightarrow F$ in Fig. 1) the device was exposed to air. The adsorbed hydrogen in the Pd starts desorbing from the external surface of Pd. Consequently, the hydrogen sites at the external surface become free. The hydrogen at the Pd-internal surface tries to diffuse out through its external surface because of the concentration gradient of hydrogen.[30] During this process the work function of the internal Pd surface returns almost to its initial value, causing a decrease in the diode capacitance (point D of Fig. 1). Further, the removal of hydrogen from the Pd internal surface withdraws some of the hydrogen diffused earlier towards the bulk, increasing the diode capacitance (point E, Fig. 1). After a 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 F can be attributed to the modifications induced by the hydrogen at the interface and the silicon bulk. Our current-voltage (I-V) and capacitance-voltage (C-V) studies reported in the following section support this.

B. *C-V* and *I-V* Studies

The following C-V studies are reported.

(i) C-V at 1 MHz for diodes (a) as fabricated—point A of Fig. 1, (b) at equilibrium in hydrogen ambient—point C of Fig. 1, and (c) after desorption—point F of Fig. 1.

(ii) Time dependence (over three days) of zero-bias capacitance at different frequencies after the diode has reached point F of the adsorption-desorption cycle of Fig. 1.

(iii) C-V at different frequencies for the diode before and after the hydrogen adsorption and desorption equilibrium cycle (point F in Fig. 1).

These results are discussed below.

Figure 2 shows the Mott-Schottky plots (C^{-2} versus V) of a Pd/Si(n) diode at 1 MHz during various stages of hydrogenation (adsorption-desorption cycles). The solid curve a shows the plot for the unhydrogenated diode. The dotted curves b and c correspond to the conditions where the diode was stabilized in hydrogen ambient and in air, respectively (point C and F of Fig. 1). As evident from the curve b, the capacitance decreases drastically for reverse bias. The carrier concentration estimated from the slope of each curve is given as follows:[31]

$$N_D = 3.6 \times 10^{16} \text{ cm}^{-3}$$

for the unhydrogenated diode (A of Fig. 1);

$$N_D = 0.7 \times 10^{16} \text{ cm}^{-3}$$

for the hydrogenated diode in hydrogen ambient (C of Fig. 1); and

$$N_D = 2.0 \times 10^{16} \text{ cm}^{-3}$$

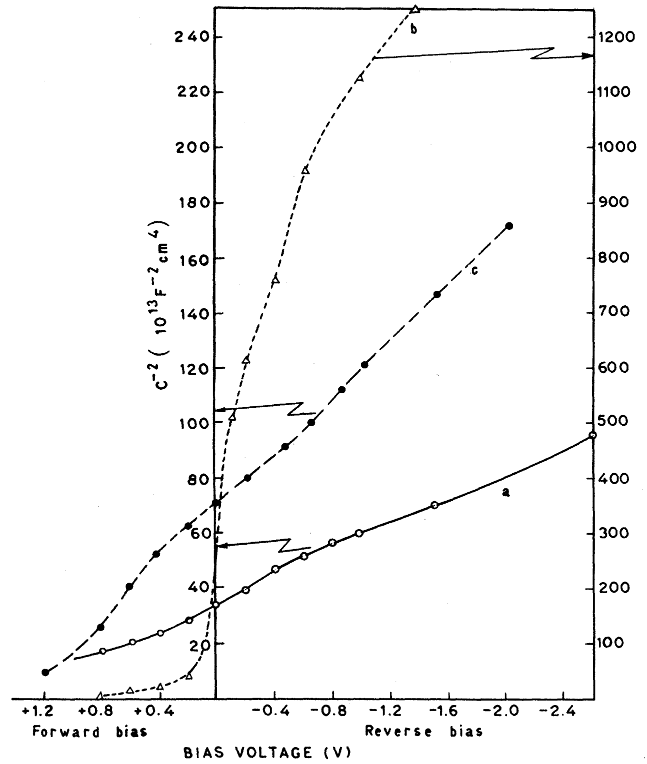

FIG. 2. C^{-2}-V characteristics of the Pd/Si(n) diode at 1 MHz during different stages of the hydrogen adsorption-desorption cycle. Curve a, before hydrogenation (point A of Fig. 1); curve b, after the hydrogen adsorption cycle in the H_2 ambient (point C of Fig. 1); curve c, after the adsorption-desorption cycle (point F of Fig. 1).

for the hydrogenated diode in air ambient (F of Fig. 1). It is observed that the carrier concentration has substantially decreased in the hydrogen ambient (curve b of Fig. 2). When exposed to air the carrier concentration increases but does not regain its original value.

A rough estimate of the barrier height from C-V studies shows that the barrier height changes in the hydrogen ambient as observed by earlier workers.[19–27] But, after desorption is equilibrated, the barrier height measured in air is approximately the same as the original barrier height. So the net decrease in the zero-bias capacitance in Fig. 1 is attributed to the decrease in the carrier concentration as a result of the modification induced by hydrogen at the interface and in the bulk of n-type silicon. The fact that there is only a negligible change in the barrier height after a complete adsorption-desorption cycle has also been checked by I-V studies.[31] The I-V characteristics of the diodes before and after hydrogenation (having reached the equilibrium at point F of the adsorption-desorption cycle shown in Fig. 1) were studied. The reverse current increased substantially while the forward current practically remained unchanged.

Figure 3 shows the frequency dependence of the zero-bias capacitance of the diodes before and after the hydrogenation cycle (point F of Fig. 1). After the hydrogena-

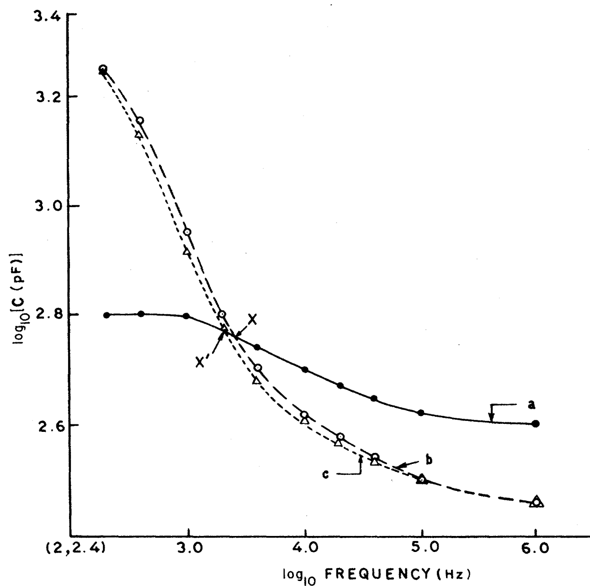

FIG. 3. Time dependence (over 3d) of zero-bias capacitance at different frequencies. Curve a, before hydrogenation (point A in Fig. 1); curve b, just after hydrogenation (point F in Fig. 1); curve c, after 3 d of hydrogenation.

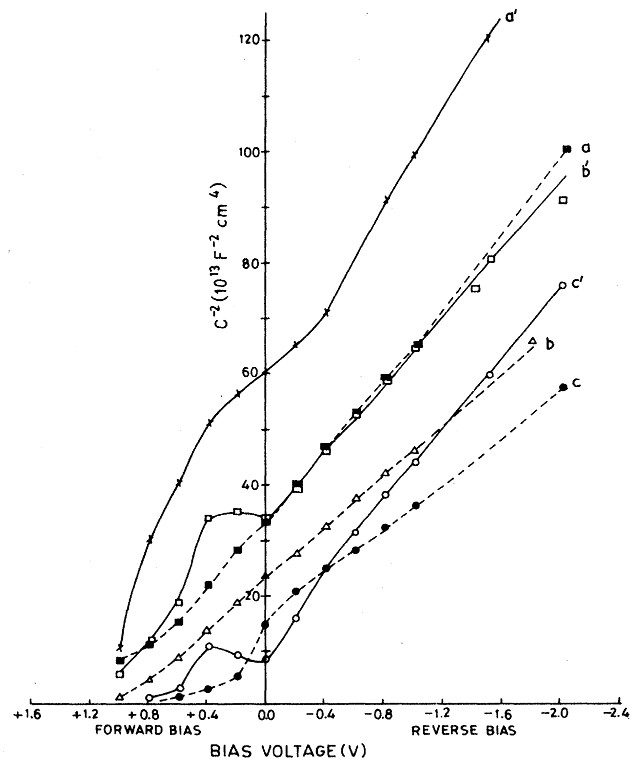

FIG. 4. C^{-2} vs V characteristic of Pd/Si(n) diode at different frequencies: 100 kHz (a is before and a is after hydrogenation), 10 kHz (b is before and b' is after hydrogenation), 1 kHz (c is before and c' is after hydrogenation).

tion cycle, the zero-bias capacitance increases below a certain frequency, whereas it decreases at frequencies higher than this (for subsequent discussion this frequency is termed as "crossover frequency"). The crossover frequency X just after reaching point F of the absorption-desorption cycle of Fig. 1 is 2.6 kHz. After 3 days, the crossover frequency X' decreases to 2.1 kHz. Generally, the high-frequency capacitance is mainly due to the shallow states while the ionized deep states contribute at the lower frequencies. Hence, hydrogenation seems to decrease shallow states while deep states are enhanced. These enhanced deep states also have a tendency to decrease (though very slowly) as evidenced by the shift of crossover frequency from $X \rightarrow X'$.

Figure 4 shows the Mott-Schottky (C^{-2} versus V) plots at 100, 10, and 1 kHz of hydrogenated (point F of Fig. 1) and unhydrogenated diodes. The behaviors near the interface ($V=0$ V) and away from the interface are quite different. The behavior near the interface ($V=0$ V) given in Fig. 4 reinforces the results given in Fig. 3, namely, the zero-bias capacitance increases (C^{-2} decreases) at a frequency of 1 kHz (curves c and c' of Fig. 4) while capacitance decreases (or C^{-2} increases) at all other high frequencies. At a reasonable reverse bias, hydrogenation increases C^{-2} at all frequencies. The estimated values of carrier concentration N_D from the Mott-Schottky plots (Fig. 4) at different frequencies are given in Table I. Two conclusions are obvious: (i) the effective carrier concentration is higher at low frequency and (ii) at all frequencies, hydrogenation decreases the effective carrier concentration. Conclusion (i) can be understood in terms of the involvement of ionized deep states[32] (N_T) which contribute to the total carrier concentration at lower frequency. Conclusion (ii), i.e., decrement of effective carrier concentration due to hydrogenation, can be understood in terms of either free-carrier concentration (N_D) or deep states density (N_T) or both.

The decrease in the carrier concentration after hydrogenation is either due to the neutralization of shallow and deep donor states or generation of acceptor-like states. The generation of acceptorlike states after hydrogenation has been detected by us earlier.[33] The estimated hydrogen-induced acceptor state density was 4×10^{10} cm^{-2}. Taking the depletion width approximately equal to 0.15 μm, this amounts to $N_A \sim 2.7\times10^{15}$ cm^{-3}. This is an order of magnitude lower than the hydrogen-

TABLE I. Carrier concentration estimated from reverse bias C^{-2} vs V plot for Pd/Si(n) diodes at different stages of the adsorption-desorption cycles.

	N_D for samples	
Frequency	Unhydrogenated (point A of Fig. 1)	After hydrogenation in air atmosphere (point F of Fig. 1)
1 MHz	3.6×10^{16} cm^{-3}	2.0×10^{16} cm^{-3}
100 kHz	3.6×10^{16} cm^{-3}	2.3×10^{16} cm^{-3}
10 kHz	5.2×10^{16} cm^{-3}	3.6×10^{16} cm^{-3}
1 kHz	6.5×10^{16} cm^{-3}	4.0×10^{16} cm^{-3}

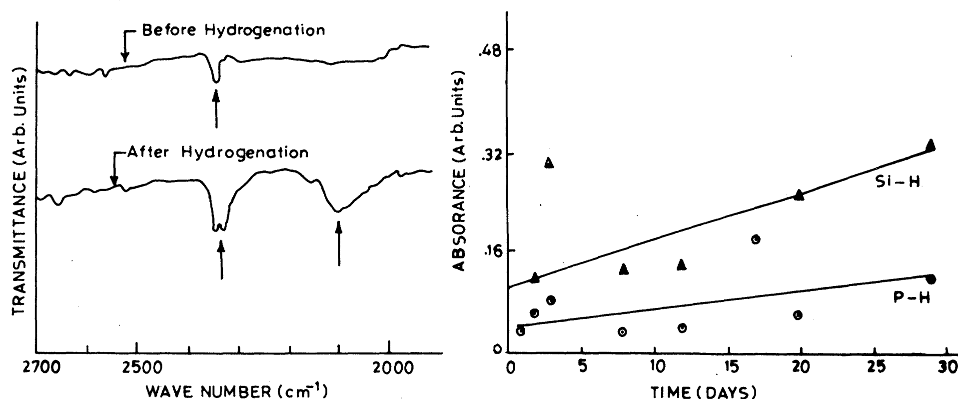

FIG. 5. (a) ir spectra of the Pd/Si(n) diode before and after hydrogenation at 27°C. (b) Growth of P-H-and Si-H-like species in the hydrogenated Pd/Si(n) diode with time.

induced reduction in the effective carrier concentration. Hence, donor-hydrogen interaction seems a dominant passivation mechanism. To identify this passivation mechanism we have carried out the ir spectroscopic studies discussed below.

C. Infrared spectroscopic studies

The typical ir spectra of the samples recorded before and after hydrogenation are shown in Fig. 5(a). On hydrogenation, the peak near 2340±10 cm^{-1}, grows, while an entirely new broad band between 2150 and 2050 cm^{-1} appears. The absorption peak near 2340±10 cm^{-1} is related to the vibrations of phosphorus-hydrogen (P-H)-like species[34] while the 2100-cm^{-1} peak is related to silicon-hydrogen (Si-H) stretching vibrations. The growth of P-H and Si-H bands are given in Fig. 5(b), which clearly shows that the growth of the Si-H band is faster than the P-H band. This is in accordance with the theoretical predictions of Johnson *et al.*[18] Generally the band between 1900 and 2200 cm^{-1} is related to the different modes of hydrogen trapping in crystalline silicon (e.g., Si-H, Si-H_2, . . .).[35,7] The total-energy calculations of Johnson *et al.*[18] show that the binding energies for H in an anti-bonding position of a Si atom which is adjacent to the substitutional P (i.e., P-Si-H) are more than that for the case of direct bonding with the substitutional P atom (P-H). However, it has been suggested that both of these configurations lead to the passivation of shallow donors in silicon. The Si-H stretching frequency in P—Si—H linkage is 2145±10 cm^{-1}, as predicted by Johnson and co-workers.[18] Part of the Si-H centers identified by the broad band (2150–2050 cm^{-1}) in our hydrogenated samples can be related to a Si-H stretch mode of P—Si—H linkage.

IV. SUMMARY

C-V, *I-V*, and infrared studies on Pd/Si(n) diodes are reported before and after hydrogenation. Hydrogen has been shown to passivate donor states through the formation of P—H and P—Si—H bonds. The passivating hydrogen was coming from the hydrogen adsorbed in Pd in the Pd/Si(n) diode. This slowly released hydrogen diffuses through Si forming Si—H or P—H linkages resulting in the passivation. The growth of Si-H bands is faster than the growth of P-H bands.

Note added in proof. We have only now become aware that A. Amore Bonapasta *et al.* have reported [Phys. Rev. B **39**, 12 630 (1989)] on a Si-H mode in P-doped silicon whose theoretical value is equal to 2149 cm^{-1}, in very good agreement with our measurement.

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