

Effects of hydrogen on Er/*p*-type Si Schottky-barrier diodes

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Metal Er was deposited onto $\langle 100 \rangle$ -oriented B-doped *p*-type crystalline silicon wafers, with or without plasma hydrogen treatment, to form Er/*p*-type Si Schottky barriers. The current-voltage and activation energy measurements reveal that hydrogen decreases the Schottky-barrier height (SBH) of Er/*p*-type Si by 0.10–0.12 eV, and, at the same time, the ideality factor is decreased from 1.17 to 1.08. The reason why hydrogen decreases the SBH and the ideality factor of Er/*p*-type Si and increases those of Al/*p*-type Si [Y. Q. Jia and G. G. Qin, *Appl. Phys. Lett.* **56**, 641 (1991)] is that the main role of hydrogen is either passivating or generating the defects on the metal-semiconductor interface in Er/*p*-type Si and Al/*p*-type Si, respectively.

I. INTRODUCTION

Schottky barriers (SB's) formed by metal-semiconductor contact have been widely studied in the past 50 years. However, the origin of the interfacial states at the metal-semiconductor interface remains one of the most debated problems in solid-state physics. As far as we know, few works on the effect of hydrogen on a metal-semiconductor contact have been reported. Chantre *et al.*¹ have treated the NiSi₂/*p*-type Si SB with plasma hydrogen and found a very weak effect of hydrogen on the Schottky-barrier height (SBH) (an increase of 0.01–0.02 eV). Yapsir *et al.*² found that hydrogen-ion implantation affected the electrical characteristics of the SB formed on Si in the same way as other ion implantations, i.e., increased the SBH of *p*-type Si and decreased the SBH on *n*-type Si. Thus it was thought that it was the ion-bombardment damage, rather than hydrogen, that affected the SBH. Recently, Sullivan *et al.*³ compared the SBH values for the SB formed on dilute-HF-treated *p*-type Si and that on cleaved *p*-type Si in vacuum. The difference was less than 0.02 eV. However, some other experiments suggested a hydrogen effect on the SB: Jia and Qin⁴ reported on an Al/*p*-type Si SB containing hydrogen which was formed on Si substrates incorporating hydrogen in three different ways: boiling the sample in water, exposing the sample to hydrogen plasma, and growing silicon in a hydrogen atmosphere. Compared with SB's formed on Si without hydrogen incorporation, they found an increase of 0.06–0.10 eV in SBH due to hydrogen. Liu *et al.*⁵ found that reverse-bias annealing increases the SBH of Ti/*p*-type Si formed on chemically prepared semiconductor surfaces. They thought this could be accounted for by hydrogen drifting away from the metal-semiconductor interface, so that a more uniform active dopant profile near the metal-semiconductor interface was formed. Marwick, Aboelfotoh, and Casparis⁶ reported that hydrogen can increase the SBH of CoSi₂/*n*-type Si by 0.13 eV. In this paper, we report hydrogen decreasing the SBH of Er/*p*-type Si in sharp contrast to hydrogen increasing the SBH of Al/*p*-type Si.⁴ We discuss the reason for this and believe the study

of hydrogen effects on SB's should be helpful to clarify the origin of the metal-semiconductor interfacial states.

II. THE PREPARATION OF EXPERIMENTAL SAMPLES

The initial samples used in this study were B-doped *p*-type crystalline silicon wafers (4–8 Ω cm resistivity), with $\langle 100 \rangle$ orientation and 0.5 mm thick. All Si wafers were polished mechanically on their front faces, and then were divided into two groups: one was treated with plasma hydrogen generated by rf (13.5 MHz) discharge and the other without the above treatment was used as a control. The hydrogen plasma treatment was performed for 3 h at substrate temperature of 150 °C in a pressure of 90 Pa. In order to remove the surface oxide and damage, we rinsed the samples in a 1:10 HF:H₂O solution and then polished it on the front side with deionized water to remove the SiO₂ layer and a thin Si layer about 5 nm thick. The samples were ultrasonically washed in carbon tetrachloride, acetone, and ethanol, and then Al Ohmic contacts were formed on the back faces of the samples in a vacuum chamber with a pressure of 10⁵ Torr. After putting the samples in air for 24 h, Er was evaporated to a thickness of about 1000 Å at a rate of about 1 Å/s in a Balzers UMS-500 ultrahigh-vacuum system with a pressure of 10^{−9} Torr at a substrate temperature of 40 °C. To form the SB, a mask with round holes of 0.8 mm diameter was used.

III. EXPERIMENTS AND RESULTS

The reverse-bias capacitance-voltage characteristics were measured using a HP4275 multifrequency LCR meter at 1 MHz and a fixed temperature of 298 K. Hereafter, Er/*p*-type Si (H) and Er/*p*-type Si (Ct) stand for the SB's formed on the hydrogen-plasma-treated and non-treated (control) Si substrates, respectively. In the following, we will give the detailed results for a typical pair of Er/*p*-type Si (Ct) and Er/*p*-type Si (H) Schottky diodes selected from the eight Er/*p*-type Si (H) and four Er/*p*-type Si (Ct) Schottky diodes which we have measured. The capacitance is 79.9 pF for Er/*p*-type Si (Ct), and 42.5

pF Er/*p*-type Si (H), respectively. The pronounced reduction of capacitance of the SB can be explained by the introduction of hydrogen into the Si samples; and the shallow acceptors B have been neutralized by hydrogen to become B-H pairs.

For the case of a SB diode with a series resistance Norde⁷ introduced a method which makes it possible to evaluate the SBH and series resistance using the following function of forward-bias voltage V :

$$F(V) = V/2 - kT \ln(I/A^{**}ST^2)/q, \quad (1)$$

where I is the electric current, A^{**} the effective Richardson constant (for *p*-type Si, $A^{**} = 32 \text{ A/cm}^2 \text{ K}^2$), and S the geometric area of the diode. The forward current-voltage characteristics measured at a fixed temperature of 298 K are shown in Fig. 1. Figure 2 shows the experimental results for $F(V)$ vs V for Er/*p*-type Si (Ct) and Er/*p*-type Si (H). We get the voltage V_0 at the minimum points of $F(V)$ from Fig. 2 and then the corresponding current I_0 from the forward current-voltage characteristics. The series resistance R can be determined by the following relationship:⁷

$$R = kT/(qI_0). \quad (2)$$

According to the thermionic theory of Crowell and Sze,⁸ providing that the effect of a voltage-dependent SBH has been included,⁹ the current-voltage characteristic of a SB is given by

$$I = A^{**}ST^2 \exp(-\phi_0/kT) \exp[q(V-IR)/nkT] \times \{1 - \exp[-q(V-IR)/kT]\}, \quad (3)$$

where ϕ_0 is the SBH under zero bias voltage and n the ideality factor. As $V-IR > 3kT/q$, the I - V relationship of the SB can be written approximately as

$$\ln I = \ln(A^{**}ST^2) - \phi_0/kT + q(V-IR)/nkT. \quad (4)$$

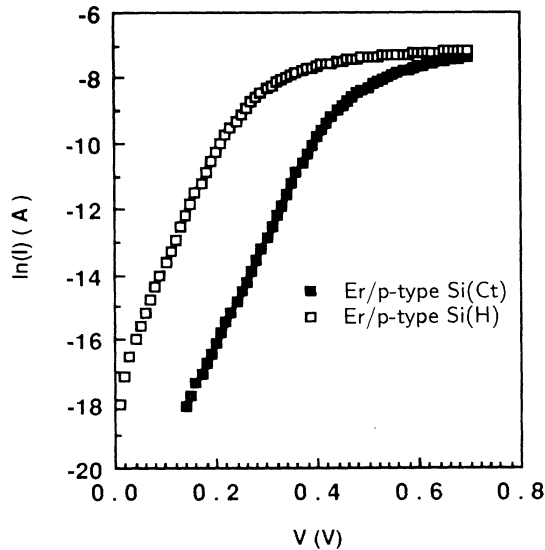


FIG. 1. $\ln(I)$ - V characteristics for Er/*p*-type Si (Ct) and Er/*p*-type Si (H).

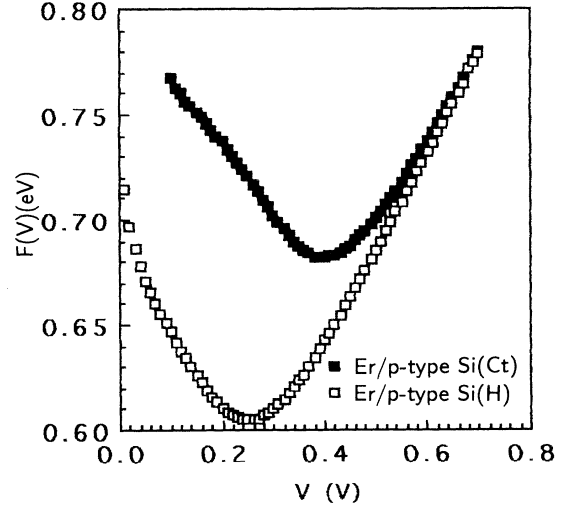


FIG. 2. Experimental plots of $F(V)$ for Er/*p*-type Si (Ct) and Er/*p*-type Si (H).

With the above determined values of R , and the experimental voltage and current values, we can determine n and ϕ_0 using the above equation. In our case, $\phi_0 = 0.81 \text{ eV}$, $n = 1.17$, and $R = 253 \Omega$ for Er/*p*-type Si (Ct), and $\phi_0 = 0.69 \text{ eV}$, $n = 1.08$, and $R = 230 \Omega$ for Er/*p*-type Si (H), respectively.

For the activation energy measurement, the following equation was used to analyze the data:

$$\ln(I/T^2) = \ln(A^{**}S) - (\phi_b - qV + qIR)/kT, \quad (5)$$

where ϕ_b is the SBH which depends on the voltage across the diode.

We measured the values of current I at different temperatures (in the range of 280–320 K) with a forward bias of 0.18 V. The maximum I in our measurement is less than $20 \mu\text{A}$, and with the above-determined values of R the qIR is therefore much less than the bias V and can be neglected in the analysis. Then the ϕ_b and A^{**} can be obtained from the slope of the straight line of $\ln(I/T^2)$ versus $1/T$ and from the intersection of this straight line with the ordinate at $1/T = 0$, respectively. The experimental results of $\ln(I/T^2)$ versus $1000/T$ for Er/*p*-type Si (Ct) and Er/*p*-type Si (H) under a forward bias of 0.18 are shown in Fig. 3. In our case, $\phi_b = 0.78 \text{ eV}$ and $A^{**} = 4.25 \text{ A/cm}^2 \text{ K}^2$ for Er/*p*-type Si (Ct), and $\phi_b = 0.68 \text{ eV}$ and $A^{**} = 9.80 \text{ A/cm}^2 \text{ K}^2$ for Er/*p*-type Si (H). For both SB's their measured effective Richardson constants are less than the value of $32 \text{ A/cm}^2 \text{ K}^2$ assumed in the current-voltage measurement. There are two probable reasons: First, the effective Richardson constants obtained from the activation energy measurement have much larger measurement error than that of SBH. Second, the actual electrical contact area is less than the geometric area of the diodes. In the current-voltage measurement, if we take effective Richardson constants from the activation energy measurement we get $\phi_0 = 0.76 \text{ eV}$ for Er/*p*-type Si (Ct) and $\phi_0 = 0.66 \text{ eV}$ for Er/*p*-type Si (H).

For Schottky diodes which we have measured SBH's

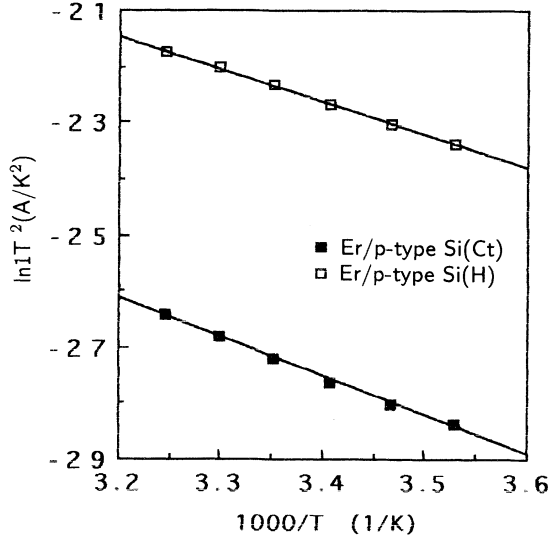


FIG. 3. Experimental results of $\ln(I/T^2)$ vs $1000/T$ for Er/*p*-type Si (Ct) and Er/*p*-type Si (H) under a forward bias of 0.18 V.

and ideality factors from the current-voltage measurement are in the range of 0.78–0.83 eV and 1.13–1.19 for Er/*p*-type Si (Ct) and 0.66–0.72 eV and 1.03–1.11 for Er/*p*-type Si (H), respectively. The SBH's measured by the activation energy measurement are in the range of 0.76–0.81 eV for Er/*p*-type Si (Ct) and 0.64–0.70 eV for Er/*p*-type Si (H). The series resistances for both Er/*p*-type Si (Ct) and Er/*p*-type Si (H) are in the range of 190–300 Ω .

IV. ANALYSIS AND DISCUSSION

In order to analyze the effect of hydrogen on Er/*p*-type Si, the SBH's and *n* factors for both Er/*p*-type Si (Ct) and Er/*p*-type Si (H) are given in Table I. The SBH's and *n* factors reported in Ref. 4 for Al/*p*-type Si SB's formed on Si substrates without and with plasma hydrogen treatment, denoted by Al/*p*-type Si (Ct) and Al/*p*-type Si (H), respectively, are also given in the table.

The SBH for Er/*p*-type Si (Ct) obtained by the *C-V* method is 0.95 eV, which is obviously higher than that measured by the current-voltage measurement and the activation energy measurement. The reason may be similar to that analyzed for GaAs SB in Ref. 10. However, the *C-V* method cannot be used for the SB containing hydrogen, where the concentration of shallow dopant varies steeply with the depth from the metal-semiconductor interface because of hydrogenation.¹¹

The current-voltage measurement reveals that hydrogen decreases the SBH of Er/*p*-type Si by 0.12 eV, and at the same time the ideality factor is decreased from 1.17 to 1.08. The activation energy measurement shows that hydrogen decreases the SBH of Er/*p*-type Si by 0.10 eV, which agrees quite well with the above result by the current-voltage measurement. But the effect of hydrogen for Al/*p*-type Si is contrary to that for Er/*p*-type Si. In Ref. 4, it has been reported that plasma hydrogen increases the SBH of Al/*p*-type Si by 0.07–0.10 eV, and the ideality factor is increased from 1.06 to 1.17.

Why does hydrogen affect the SBH and the ideality factor? Why is the effect of hydrogen on the SBH and the *n* factor for Er/*p*-type Si in sharp contrast to that for Al/*p*-type Si? We think it can be accounted for by an interaction between hydrogen and metal-semiconductor interfacial states.¹²

Monch¹³ has examined the chemical trend of the SBH's reported for 31 different metal and silicide *n*-type silicon SB's. Based on the virtual gap states (VGS) model^{14–17} and interfacial defect model,^{18,19} he argued that if the density of interfacial defects is below about 10^{13} cm⁻² then the SBH will be determined by the VGS only. When the density of interface defects is about 10^{14} cm⁻² or higher, the SBH is shifted down by 0.1 eV or more. Proceeding further, we think the SB is determined by the density of interfacial states D_s ; the larger D_s , the lower the SBH formed on an *n*-type semiconductor. D_s consists of two parts

$$D_s = D_s^V + D_s^D, \quad (6)$$

where D_s^V is contributed by the VGS and D_s^D by interfacial defects. ϕ_n and ϕ_p are the heights of the SB's formed by depositing the same metal on the same kind of semiconductor with *n*-type and *p*-type doping, and E_g is the band gap of the semiconductor. If the semiconductor surface is prepared in the same way, one expects

$$\phi_n + \phi_p = E_g. \quad (7)$$

From the above discussion, an increase in D_s can decrease the height of the SB formed on an *n*-type semiconductor. We get from Eq. (7) that the larger D_s , the greater the height of the SB formed on a *p*-type semiconductor.

It is well known that hydrogen has the ability to affect extensive defect in the bulk and on the surface of semiconductors.^{20–25} So it can be easily imagined that hydrogen can influence the interfacial defects and thus D_s^D . It is supposed that hydrogen can have two kinds of action on the defects of a metal-semiconductor interface.¹² First, hydrogen can passivate to different extents the in-

TABLE I. The SBH's and *n* factors for four different kinds of SB: (1) Er/*p*-type Si (Ct); (2) Er/*p*-type Si (H); (3) Al/*p*-type Si (Ct); (4) Al/*p*-type Si (H). [The data for Al/*p*-type Si (Ct) and Al/*p*-type Si (H) are cited from Ref. 4.]

	SBH (eV)		<i>n</i>
	Current-voltage	Activation energy	
Er/ <i>p</i> -type Si (Ct)	0.81	0.78	1.17
Er/ <i>p</i> -type Si (H)	0.69	0.68	1.08
Al/ <i>p</i> -type Si (Ct)	0.59	0.60	1.06
Al/ <i>p</i> -type Si (H)	0.69	0.67	1.17

terfacial defects, and thus cause a decrease in D_s^D . Secondly, hydrogen can create H-related interfacial defects, and thus an increase in D_s^D . More generally, the effect of hydrogen may be a combination of the above two actions; however, hydrogen cannot affect D_s^V . Which of the above two actions of hydrogen is the major one is determined by the kinds of metal and semiconductor used, and also by the fabrication technology of the SB.

Based on the above discussion, when hydrogen passivates the interfacial defects and causes a decrease in D_s^D , the height of the SB's formed on a p -type semiconductor will be lower. In our experiment, hydrogen obviously decreases the SBH of Er/ p -type Si. So for Er/ p -type Si, we think the passivation of interfacial defects is the major role of hydrogen. For Al/ p -type Si-hydrogen increases the SBH, so the generation of interfacial defects is the major role of hydrogen.

Hydrogen decreases the ideality factor from 1.17 to 1.08 for Er/ p -type Si, and increases the ideality factor from 1.06 to 1.17 for Al/ p -type Si. The change of the ideality factor can be explained by similar reasons.

Card and Rhoderick²⁶ have developed a model with two types of interfacial states which equilibrate with the metal and the semiconductor, respectively, and considered the interfacial state in equilibrium with the semiconductor to be the main one for a chemically prepared SB with an interfacial oxide layer. The model assumed that all the interfacial states in equilibrium with the semiconductor were used to analyze the practical SB in the forward direction in Ref. 27. In this case, one gets the following relationship between the n factor and D_s :

$$n = 1 + \epsilon_s \delta / \epsilon_i W + q D_s \delta / \epsilon_i, \quad (8)$$

where ϵ_s and ϵ_i are permittivity of the semiconductor

and the interfacial layer, respectively. Since the thickness of the interfacial layer δ is far less than the depletion width W in the semiconductor, the second term in Eq. (8) can be neglected in the analysis.

In our case, several preparational procedures following HF dips will produce a thin oxidized silicon interfacial layer, and Eq. (8) is thought to be suitable. For the Er/ p -type Si case, the main role of hydrogen is passivating the interfacial defects and decreasing D_s , from Eq. (8); thus the n factor is decreased. For the Al/ p -type Si case, the main role of hydrogen is creating the interfacial defects and increasing D_s ; thus the n factor is increased.

V. SUMMARY

In summary, we have reported that hydrogen decreases the Schottky-barrier height of Er/ p -type Si by 0.10–0.12 eV, and at the same time the ideality factor is decreased from 1.17 to 1.08. Jia and Qin⁴ have found that hydrogen increases the SBH of Al/ p -type Si by 0.07–0.10 eV and increases the ideality factor from 1.06 to 1.17. The above experimental results can be interpreted as follows. The SBH is determined by the interfacial state density, which consists of the virtual gap state density and that produced by interfacial defects, and hydrogen can passivate and/or generate the interfacial defects, and thus influence the interfacial state density produced by interfacial defects. The passivation of the interfacial defects is the major role of hydrogen in Er/ p -type Si, but the generation of interfacial defects is the major role of hydrogen in Al/ p -type Si.

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