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DOPING DEPENDENCE OF THE BARRIER HEIGHT OF PALLADIUM–SILICIDE SCHOTTKY-DIODES*

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Abstract—Capacitance-voltage and current-voltage measurements have been used to determine the barrier height of palladium–silicon Schottky diodes. All diodes were heat-treated to form palladium silicide and the doping range of the silicon was varied in the range 5×10^{15} cm^{-3} to 2×10^{18} cm^{-3}. The zero-electric-field (flat-band) barrier height was found to be independent of doping concentration in the above range, having a value $0{\cdot}75 \pm 0{\cdot}01$ eV. On the other hand the zero-bias barrier height is more electric-field dependent than the predictions of the usual image-force theory. However, the results are well described by an additional barrier lowering term of the approximate form $\Delta\phi = -x_m\epsilon_m$ where ϵ_m is the maximum junction electric-field and x_m a characteristic length in the region of 20–40 Å.

Résumé—On a utilisé les mesures du voltage capacitif et de la tension du courant en vue de pouvoir déterminer la hauteur d'arrêt des diodes de Schottky au palladium–silicium. Toutes les diodes ont été traitées à la chaleur pour obtenir un siliciure de palladium et on a varié la hauteur d'induction du silicium entre 5×10^{15} cm^{-3} et 2×10^{18} cm^{-3}. On a trouvé que la hauteur de barrière du champ électrique nul de bande rectangulaire était indépendante de la concentration de l'induction entre les mesures indiquées plus haut et que sa valeur est de $0{\cdot}75 \pm 0{\cdot}01$ eV. D'autre part la hauteur de la barrière de polarisation nulle est plus dépendante électriquement qu'il ne l'était prévu par la théorie normale image-puissance. Neanmoins, les résultats sont bien décrits par une formule additionnelle d'abaissement de la barrière de la forme approximative suivante: $\Delta\phi = -x_x\,\epsilon_m$ dans laquelle ϵ_m représente le champ électrique maximum de jonction et x_m représente une longueur caractéristique se situant vers 20–40 Å.

Zusammenfassung—Zur Bestimmung der Barrierenhöhe bei Palladium–Silizium Schottkydioden wurden Kapazitäts- und Strommessungen in Abhängigkeit von der Spannung verwendet. Alle Dioden wurden einer Temperaturbehandlung unterworfen, um Palladiumsilicid zu bilden. Die Dotierung des Siliziums wurde zwischen 5×10^{15}/cm^3 und 2×10^{18}/cm^3 variiert. Die Flachbandbarriere (verschwinden des elektrisches Feld an der Phasengrenze) ergab sich in diesem Bereich unabhängig von der Dotierungskonzentration zu $0{,}75 \pm 0{,}01$ eV. Andererseits ist die Barriere stärker vom elektrischen Feld abhängig als es die übliche Theorie mit Bildkraft vorhersagt. Die Ergebnisse werden besser beschrieben mit einem zusätzlichen Term, der die Barriere erniedrigt. Dieser hat näherungsweise die Form $\Delta\phi = -x_m\epsilon_m$, wobei ϵ_m das maximale elektrische Feld im Übergang und x_m eine charakteristische Länge im Bereich von 20 bis 40 Å bedeuten.

1. INTRODUCTION

THE BARRIER height of metal–semiconductor diodes is generally found to show a larger decrease with increasing electric field than expected from the simple theory involving only a correction to the barrier height due to the image force. Evidence of the additional barrier lowering is provided first, by non-saturation of the reverse current with increasing reverse bias, second, by a reduced slope of the forward $\log(J)$ vs. voltage characteristic corresponding to a value of n in the empirical diode equation of greater than unity and, third, by a considerable discrepancy between the barrier height obtained by capacitance–voltage measurements and from the current vs. forward-voltage.

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Such effects were originally attributed to the presence of a thin oxide layer between the metal and the semiconductor[1–3]. But more recently silicon Schottky-diodes have been made using a metal, such as Pt, which, upon heat treatment, forms a metallic silicide thus penetrating a small distance into the silicon and removing at least the majority of any oxide film originally present [4]. An X-ray diffraction analysis of Pd-silicide : Si diodes has been recently carried out by Kircher[5]. This has shown that the silicide is formed at a temperature of 200°C or greater and has the composition Pd_2Si. However, the additional barrier lowering is still observed and therefore some mechanism other than an oxide film must contribute to the field dependence of the barrier lowering.

The existence of a dipole layer at the interface between a metal and a semiconductor in intimate contact was first suggested by Heine[6]. From basic quantum-mechanical considerations he showed that a negative charge is created at the surface of the semiconductor as a fundamental consequence of penetration of the metal wave-functions into the forbidden band of the semiconductor. The latter form electronic states which become occupied by free electrons from the metal within the energy range between the semiconductor valence band edge E_v and the metal Fermi-level, E_{Fm}. This charge decays exponentially, in a direction normal to the surface, into the semiconductor and therefore is of the form

$$N_s = N_s^- \exp(-x/x_0) \tag{1}$$

in which N_s^-, the surface charge density, is approximately given by

$$N_s^- = \rho(E)(E_{Fm} - E_v)/q$$

with $\rho(E)$ the average density of surface states per unit energy, and q the electronic charge. From band structure considerations Heine deduced that $x_0 \geq 3$ Å and $\rho(E) \geq 3{\cdot}5 \times 10^{14}/\text{cm}^2$, for the $\{111\}$ surface of silicon.

This model was first applied by Parker *et al.*[7] to describe the reverse-voltage characteristics of *n*-GaAs : Al diodes. When allowance was made for quantum-mechanical reflection of electrons at the barrier, excellent agreement between experiment and theory was obtained for $x_0 = 5$ Å.

Quite recently Andrews and Lepselter have used a similar model to describe the behavior of several metal–silicide diodes[8, 9], again obtaining good agreement.

The theoretical and experimental evidence for the existence of a dipole layer at the metal–semiconductor interface, for truly intimate contact, is therefore quite good.

In the following section we describe the effect of a negative charge, bound to the interface, upon the barrier height. The experimental results for palladium–silicide diodes, of several different *n*-type impurity concentrations, are described in relation to the model in Section 4.

2. NEGATIVE CHARGE MODEL

Figure 1(a) shows the two charge distributions in the semiconductor, in a direction normal to the surface, caused by: (i) the normal depletion region of uniform charge density equal to the number of donor atoms N_D, extending to a distance a from the surface; and (ii) by electrons bound to surface states, having a distribution in the x-direction given by relation (1). The potential resulting from this distribution is shown in Fig. 1(b). To eliminate some confusing negative signs in subsequent equations the electron charge is taken to be positive,

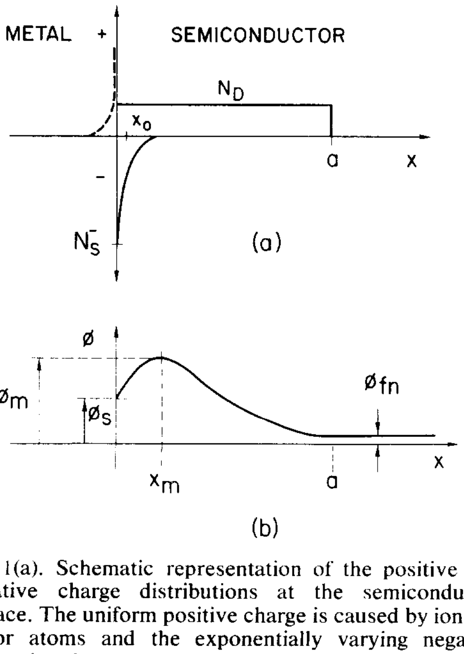

Fig. 1(a). Schematic representation of the positive and negative charge distributions at the semiconductor surface. The uniform positive charge is caused by ionized donor atoms and the exponentially varying negative charge by electrons trapped in interface states. (b). The potential profile resulting from the charge distributions (a).

hence the potential profile is not inverted with respect to the normal band diagram. The zero of potential is set equal to the Fermi level in the metal and the potential of an electron just inside the semiconductor is defined as ϕ_s. The maximum barrier height ϕ_m is displaced by the negative charge to a distance x_m from the surface. In this respect the negative charge has a similar effect to the image force. The barrier height ϕ_m and also x_m are easily derived from the solution of the one-dimensional Poisson equation, with the help of some simplifying assumptions.

First we assume that the zero-electric-field, or 'flat-band', barrier height ϕ_{B0} is a constant, independent of doping concentration. Second, that the depletion region thickness a and the maximum electric field ϵ_m at the junction are independent of the presence of the negative charge, being given therefore by the usual relations

$$a = \sqrt{\left[2\left(\phi_{B0} - \phi_{Fn} - \frac{kT}{q} - V\right)\Big/\alpha\right]} \quad (2)$$

and

$$\epsilon_m = \alpha a, \qquad \left(\alpha \equiv \frac{qN_D}{\epsilon_s}\right). \quad (3)$$

Here ϕ_{Fn} is the Fermi potential in the bulk of the n-type semiconductor, V the applied voltage and ϵ_s the semiconductor permittivity, $(\kappa\epsilon_0)$. Finally, we assume x_0 in (1) to be very much less than a. All those assumptions will later be seen to be justified.

Making the substitution $\beta = qN_s^-/\epsilon_s$, the solutions for x_m and ϕ_m are obtained from the following two relations, respectively:

$$\beta x_0 e^{-x_m/x_0} - \alpha(a - x_m) = 0 \quad (4)$$

$$\phi_m = \phi_{B0} - \alpha x_m(a - x_m/2) - \beta x_0^2 e^{-x_m/x_0}. \quad (5)$$

The change in barrier height ($\Delta\phi = \phi_m - \phi_{B0}$) with electric field is obtained from (3) and (5), namely,

$$\Delta\phi = -\epsilon_m x_m - \beta x_0^2 e^{-x_m/x_0} + \frac{\alpha}{2} x_m^2. \quad (6)$$

The n-value of the forward log (current) vs. voltage characteristic may be expressed by the relation [10]

$$\frac{1}{n} = 1 - \frac{d\phi_m}{d\epsilon_m} \cdot \frac{d\epsilon_m}{dV}.$$

Some manipulation of relations (3), (4) and (5) shows that

$$\frac{d\phi_m}{d\epsilon} = -x_m \quad \text{and} \quad \frac{d\epsilon_m}{dV} = -1/a, \quad (7)$$

therefore

$$\frac{1}{n} = 1 - \frac{x_m}{a}. \quad (8)$$

Including the additional small contribution to the n-value, arising from the image force, the complete expression for n becomes

$$n = \left[1 - \frac{x_m}{a} - \frac{\Delta\phi_s}{2\alpha a^2}\right]^{-1}. \quad (9)$$

In this relation $\Delta\phi_s$ is the barrier height lowering due to the image force; it is given in turn by

$$\Delta\phi_s = \sqrt{\frac{q\epsilon_m}{4\pi\epsilon_s}}. \quad (10)$$

To obtain the total barrier lowering as a function of electric field this contribution must also be included along with $\Delta\phi$ from (8) so that the 'effective' barrier height ϕ_B is given by

$$\phi_B = \phi_{B0} - (\Delta\phi + \Delta\phi_s). \quad (11)$$

3. EXPERIMENTAL

All diodes were delineated by conventional oxide masking and photolithography. Approximately 200 Å of palladium was evaporated onto the exposed silicon surfaces at a pressure of 10^{-8} Torr. After stripping the resist and Pd from the oxide, the wafers were heated to 550°C for 10 min in vacuum to form the metallic Pd-silicide. Ohmic contacts of Sb-doped Au were also formed adjacent to the diodes in the same heating cycle. The contact areas were subsequently electroplated with gold alloy and individual diodes were mounted on TO 46 headers for measurement. The diode areas were in the range $(0{\cdot}9–2) \times 10^{-5}$ cm^2.

Two types of measurement were performed in order to determine the barrier heights at zero-electric-field and at zero-applied voltage.

Measurement of the capacitance vs. voltage was carried out with a Boonton r.f. bridge Type 75A at a frequency of 1 MHz. Extrapolation of a plot of $1/C^2$ vs. voltage to the voltage axis yielded the diffusion voltage $(\phi_{B0}-\phi_{Fn}-kT/q)$ from which the zero-field barrier height ϕ_{B0} was deduced knowing N_D.

As the diodes were not provided with guard rings, measurement of the current–voltage characteristic was restricted to forward bias, in which region the contribution of edge leakage currents was generally negligible. The characteristics log (current) vs. voltage were obtained directly on an x–y plotter using a Keithley logarithmic microammeter type 413.A. Extrapolation of the linear region of the curve to zero voltage yielded the saturation current from which the effective barrier height ϕ_B at zero-applied voltage was obtained.*

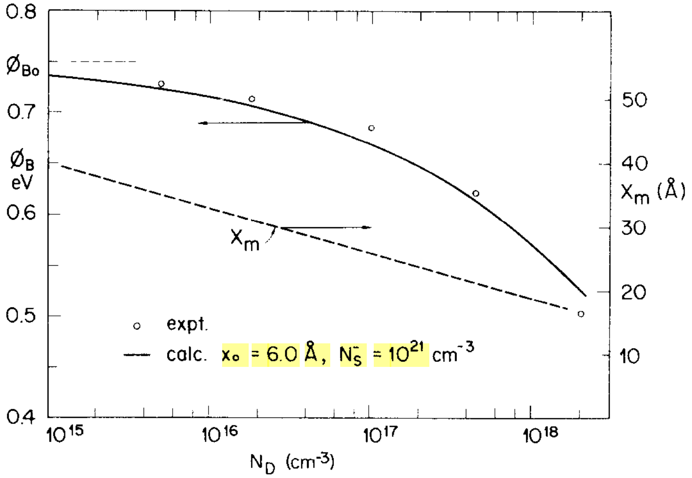

Fig. 2. Measured effective barrier heights of Pd-silicide Schottky diodes vs. doping concentration. The full curve is calculated from the model of Section 2 with $N_s^- = 10^{21}$ cm^{-3} and $x_0 = 6$ Å.

4. RESULTS

The second and third columns of Table 1 show the measured barrier heights ϕ_{B0} and ϕ_B, respectively, for five different doping concentrations. The figures represent average values for several diodes on one or more wafers. For the latter measurement, diodes showing excessive leakage currents, as evidenced by a non-linear log (current) vs. voltage characteristic or high n-value, were excluded.

The figures for ϕ_{B0} show that it is independent of doping within the accuracy of measurement, justifying the assumption made in Section 2. In contrast, the zero-voltage barrier heights decrease with increasing doping, and at a greater rate than may be accounted for by the image force lowering, $\Delta\phi_s$. This latter quantity, calculated from relation (2) with $V=0$ and relation (10), is shown in the fourth column. Clearly $(\phi_B+\Delta\phi_s)$ is less than ϕ_{B0} at the three higher doping concentrations.

Inclusion of the negative charge model to account for the additional barrier lowering removes the discrepancy rather well, as shown in Fig. 2. However, since exact theoretical values of the two parameters N_s^- and x_0 in this model are not known, an empirical approach was used in which the effective barrier height ϕ_B was calculated as a function of doping for a range of values of N_s^- and x_0 using a computer to evaluate equations (2)–(5).

The full line of Fig. 2 is the curve giving the best fit with experiment, the corresponding values of N_s^- and x_0 being 10^{21} cm^{-3} and 6·0 Å, respectively. The latter value is very close to that (5 Å) used by the authors of Ref. [7] for n-GnAs:Al diodes. On the other hand, the total negative charge $(N_s^- x_0)$ of 6×10^{13} cm^{-2} is lower than that predicted by Heine, by about a factor of 5. In this

*See Appendix.

Table 1. *Barrier heights of Pd-silicide diodes for five values of n-type doping concentration*

Doping cm^{-3}	ϕ_{B0} $(C\text{-}V)$	ϕ_B $(J\text{-}V)$	$\Delta\phi_s$	n Expt.	n Calc.
5×10^{15}		0·72(7)	0·019	1·02	1·02
$1{\cdot}8\times 10^{16}$	0·75	0·712	0·027	1·04	1·03
1×10^{17}	0·73	0·68(5)	0·041	1·04	1·05
$4{\cdot}5\times 10^{17}$		0·62	0·059	1·13	1·07
2×10^{18}	0·74	0·50	0·089	1·35	1·13

connection it should be noted that the results are not very sensitive to the chosen value of N_s^-. For example, increasing N_s^- to 10^{22} cm^{-3} and reducing x_0 to 4·0 Å yields results almost identical to that shown, with the exception of a faster decrease in ϕ_B at the highest doping.

It must be pointed out however that the experimental point at the highest doping of 2×10^{18} cm^{-3} should be below the curve, because of the considerable contribution to the forward current by tunneling[11]. Since the barrier heights were calculated on the assumption of thermionic emission only, the additional tunnel current leads to an estimated barrier height lower than the true value.

From this consideration therefore the former values of N_s^- and x_0 should be more realistic, although clearly N_s^- and hence the total surface charge cannot be exactly determined.

Figure 2 also shows, as a dashed line, x_m, the value of x at which the barrier height reaches its maximum. It is considerably greater than x_0, justifying the third assumption in Section 2 and in addition is great enough to allow the usual considerations governing the validity of the image force correction (10) [7].

As pointed out by Parker *et al.* [7] and indicated here by (6), the barrier lowering due to the negative charge is well approximated by

$$\Delta\phi = -\epsilon_m x_m.$$

This relation has also been used by the authors of Ref. [9] to estimate x_m for a variety of metal-silicide Schottky diodes, having a doping concentration in the region of $(3{\cdot}5\text{–}5{\cdot}5)\times 10^{15}$ cm^{-3}. The value of $x_m = 36$ Å at $N_D = 4\times 10^{15}$ cm^{-3} (shown in Fig. 2) is rather close to their values of 35 and 30 Å for rhenium and platinum, respectively.

Finally, the forward-current n-values, calculated from (9) are included in the last column of Table 1 for comparison with the experimental figures. The agreement is generally good except at the highest doping where tunneling, as mentioned earlier, plays a significant role in the current transport.

5. CONCLUSIONS

The flat-band barrier height of Pd-silicide Schottky diodes has been found to be $0{\cdot}75\pm 0{\cdot}01$ eV from capacitance–voltage and current–voltage measurements. In the doping range $10^{16} < N_D < 10^{18}$ cm^{-3} the effective barrier height for current conduction at zero voltage exhibits an electric-field dependence which is well described by the surface-state theory of Heine [6]. The experimental value for the 'extinction depth'of these states in the semiconductor is found to be within 4–6 Å for Pd-silicide. A total negative surface-state charge of 6×10^{13} cm^{-2} or greater is estimated, although further work is needed in order to define this figure more precisely.

Pd-silicide Schottky diodes show excellent forward current–voltage characteristics in the doping range $10^{15}-5\times 10^{17}$ cm^{-3}. Because of the intimate metal–semiconductor contact brought about by the silicide formation, the diodes should have good long-term stability.

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APPENDIX

The saturation current and n-value of a Schottky diode

Assuming thermionic emission over the barrier, the relationship between current density and applied voltage is

$$J = A^*T^2 \exp\left[\frac{-q}{kT}(\phi_{B0} - \Delta\phi_s)\right]\left\{\exp\left(\frac{qV}{kT}\right) - 1\right\} \quad (A.1)$$

in which T is the absolute temperature, V the applied voltage and $\Delta\phi_s$ the image force barrier lowering, given, in the text, by substituting equation (2) in (3) and (3) in (10). The constant, A^*, is the Richardson constant, modified by the effective mass of electrons in the semiconductor and including two small corrections for optical-phonon scattering and for quantum-mechanical reflection and tunneling. In the present work the vacuum value of 120 A/cm^2 was used throughout, since it has been shown for Si that A^* varies only slightly over a wide range of electric field, having a mean value of 112 A/cm^2[9]. Negligible error in the barrier height is therefore introduced by taking the former figure.

Equation (A.1) may be written in the form

$$J = J_s\left\{\exp\left(\frac{qV}{nkT}\right) - 1\right\} \quad (A.2)$$

for the forward direction of current flow, with J_s defined by

$$J_s = A^*T^2 \exp\left(\frac{-q\phi_B}{kT}\right). \quad (A.3)$$

The saturation current J_s therefore defines the effective barrier height at zero-applied voltage, whatever the mechanism responsible for barrier lowering.

Variation of the effective barrier height with electric field is described by inclusion of the numerical 'constant' n. At a forward voltage V of greater than about $3kT/q$ the slope of the log (J) vs. forward voltage characteristic is easily seen from (A.2) to be

$$\mathrm{d}[\ln(J)]/\mathrm{d}V = \frac{q}{nkT}. \quad (A.4)$$

Note added in proof

The image-force term given by equation (10) is derived on the basis of no additional barrier-lowering effects and is therefore only accurate when the image force alone defines the distance separating the potential maximum and the semiconductor–metal interface. An exact procedure for including the image-force correction is to add the image potential term $(-q/16\pi\epsilon_s x_m)$ to the right-hand side of equation (5) and its derivative with respect to x, $(q/16\pi\epsilon_s x_m^2)$, to the right-hand side of equation (4). With this alteration the total barrier lowering is governed solely by the parameter x_m and the term involving $\Delta\phi_s$ is removed from equations (9) and (11).

A revised calculation incorporating this modification yields the following values for the experimental results of Fig. 2: $x_0 = 8$ Å and $x_m = 54$ Å at $N_D = 4 \times 10^{15}$ cm^{-3} decreasing to 25 Å at $N_D = 2 \times 10^{18}$ cm^{-3}.

It is believed that this procedure is also applicable to the reverse current measurements reported in Ref. [8].