Schottky barrier heights of Pt and Ir silicides formed on Si/SiGe measured by internal photoemission

J. R. Jimenez
Electro-Optics Technology Center, Tufts University, Medford, Massachussetts 02155

X. Xiao[a] and J. C. Sturm
Electrical Engineering Department, Princeton University, Princeton, New Jersey 08544

P. W. Pellegrini and M. M. Weeks
Rome Laboratory, Hanscom Air Force Base, Massachussetts 01731

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Lowered-barrier-height silicide Schottky diodes are desirable for obtaining longer cutoff-wavelength Si-based infrared detectors. Silicide Schottky diodes have been fabricated by the reaction of evaporated Pt and Ir films on p-Si$_{1-x}$Ge$_x$ alloys with a thin Si capping layer. The onset of metal-SiGe reactions was controlled by the deposited metal thickness. Internal photoemission measurements were made and the barrier heights were obtained from these. Pt-SiGe and Ir-SiGe reacted diodes have barrier heights of ~0.27 and ~0.31 eV, respectively, higher than typical values of 0.22 and 0.12 eV for the corresponding silicide/p-Si diodes. Their emission constants are also lower and more voltage dependent than silicide/Si diodes. PtSi/Si/SiGe diodes, on the other hand, have lower barrier heights (~0.15 eV) than the PtSi/Si barrier height. The barrier height shifts in such silicide/Si/SiGe diodes are interpreted by accounting for tunneling through the unconsumed Si layer. This is done analytically using a simple model based on the Cohen, Vilms, and Archer (unpublished) modification to the Fowler equation, and leads to an extracted barrier height, that is, the Si barrier height reduced by the Si/SiGe band offset.

I. INTRODUCTION

Arrays of PtSi/Si Schottky diode detectors have excellent electro-optical characteristics for infrared imaging in the medium-wavelength infrared (MWIR) window (3–5 μm).[1] The detection mechanism is infrared absorption in the metal, followed by internal photoemission over the Schottky barrier into the semiconductor. Despite the low quantum efficiency of this detection process, focal plane arrays (FPAs) of PtSi/Si diodes produce exceptional infrared images because of the high uniformity of response from diode to diode. This, together with other advantages of Si such as mature processing technology and the ease and low cost of integration with Si two-dimensional multiplexers, has allowed silicide infrared detectors to compete favorably with older, more established infrared materials such as HgCdTe. There is, therefore, considerable impetus for extending the wavelength range of silicide/Si detectors into the long-wavelength infrared (LWIR) window (8–12 μm), where other materials still have an advantage, by reducing the Schottky barrier height (SBH) of ~0.22 eV for PtSi/p-Si and ~0.12 eV for IrSi/p-Si.[2,3]

Silicide/Si$_{1-x}$Ge$_x$ diodes may have a lower barrier height than the corresponding silicide/Si diode because of the smaller band gap of SiGe. The formation of abrupt, near-ideal silicide/SiGe interfaces, however, is not as simple as the formation of comparable silicide/Si interfaces, because of the more complex chemistry of metal-SiGe reactions. There is at present significant variation in the reported barrier heights of diodes formed by the reaction of metals into SiGe. Kanaya *et al.*[4] have reported barrier heights (from forward I-V) for Pt and Pd reacted into p-SiGe (of various Ge concentrations) that were lower than the corresponding silicide/Si barrier heights. However, Liou *et al.*[5] report that the barrier heights (from forward I-V) of Pt and Pd reacted into n-Si$_{0.80}$Ge$_{0.20}$ were both ~0.68 eV, while Xiao *et al.*[6] report a barrier height (from photoresponse) for Pd reacted into p-Si$_{0.80}$Ge$_{0.20}$ of ~0.7 eV, substantially higher than the Pd silicide/Si SBH. This situation calls for better reporting of differing preparation procedures and supplemental information on metal-SiGe reaction products. Pt-SiGe reactions, for example, have been reported[3,7] to result in Ge segregation and preferential PtSi formation and formation of PtSi and the segregation of Ge at the interface. Precise values of the barrier height would be expected to depend on the detailed results of such reactions. An approach that bypasses these problems completely, however, is to grow a thin Si capping layer on the SiGe, with which a metal film of suitable thickness would react. Using this method, Xiao *et al.* have formed Pd and Pt silicides on Si/SiGe with lowered barrier heights.[6]

In this article we report our results on the barrier heights of Schottky diodes formed by the reaction of Pt and Ir layers with a Si cap on SiGe. Diodes were also formed with metal-SiGe reactions by depositing more than enough metal to completely consume the Si cap.

II. EXPERIMENTAL DETAILS

The SiGe layers were grown by rapid-thermal chemical-vapor deposition (RTCVD) in a reactor described previously.[8] An intermediate layer, in which the Ge concentration was graded to zero, was grown between the SiGe film and the Si substrate. This eliminates the abrupt valence-band

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[a] Present address: Intel Corporation, MS RN3-21, 2200 Mission College Blvd., Santa Clara, CA 95052.

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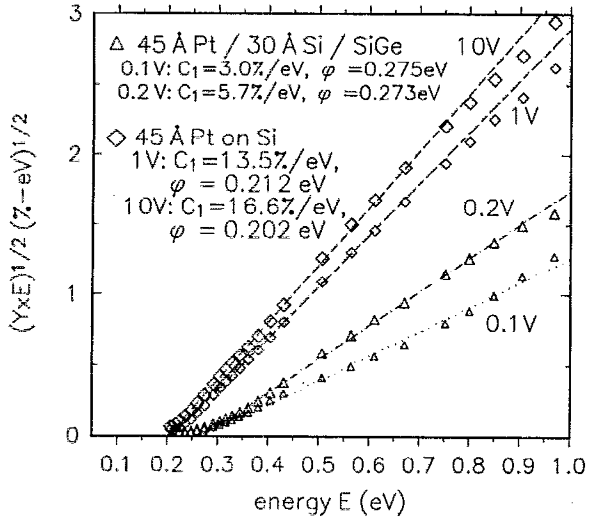

FIG. 1. Sample Fowler plots of diodes formed with Pt-$Si_{87}Ge_{13}$ reactions for two of the reverse-bias voltages used (0.1 and 0.2 V), shown with Fowler plots of the PtSi/Si control diodes processed at the same time. The barrier heights ϕ and emission coefficients C_1 are shown. The SiGe diodes were measured at lower reverse biases than the Si diodes because of their greater reverse leakage currents, but this difference in bias is not enough to account for the lower Pt-SiGe barrier heights through image-force lowering.

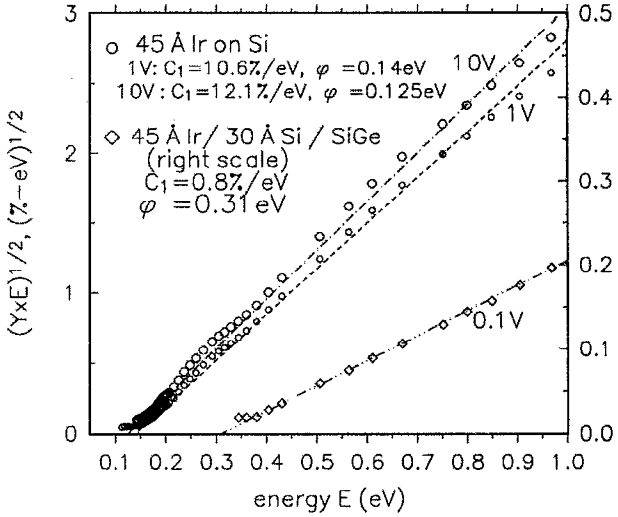

FIG. 2. Sample Fowler plot of diodes formed with Ir-$Si_{87}Ge_{13}$ reactions, shown with Fowler plots of the IrSi/Si control diodes processed at the same time. Note the difference in scale for the Ir-SiGe reacted diodes.

offset which would act as an additional barrier to emitted carriers. The graded layer was chosen to be in the diode's depletion region so that the upward grade of the valence band would be counteracted by the built-in field. The SiGe thicknesses are such that this upward grade does not extend higher in energy than the Schottky barrier height.[9] Samples used in this study had 13% Ge (500 Å) and 15% Ge (300 Å), on graded layers of 300 and 80 Å, and Si cap thicknesses of 30 and 40 Å, respectively. All the epilayers were doped p type (boron) from the residual doping in the reactor. The wafers were cleaned with standard wet chemical solutions, which slightly reduces the Si cap thickness and was accounted for in selecting the metal layer thickness. Before deposition, the Si surface was hydrogen terminated by dipping in aqueous HF solution. The Pt and Ir were deposited by electron-beam evaporation through a shadow mask in a load-locked ultrahigh-vacuum (UHV) chamber. The wafers were held at elevated temperatures during deposition and the silicides were formed by annealing *in situ* for 1 h. Pt diodes were formed at 350 °C while Ir diodes were formed at 550 °C. For control, silicide/Si diodes were processed and deposited at the same time on boron-doped Si substrates (10–15 Ω cm). Absolute photoresponse measurements were made with a Perkin–Elmer single-pass monochromator and a SiC globar at 1000 °C as the infrared source. The input radiation was chopped at 139 Hz and the photoresponse measured by lock-in amplifier. Measurements were made at a temperature of 40 K or lower, and at various reverse-bias voltages.

III. MEASUREMENTS

Figures 1 and 2 are the measured Fowler plots for the Pt-SiGe and Ir-SiGe reacted diodes and the control silicide/Si diodes, showing the barrier heights and the C_1 values. The control Si diodes and the SiGe diodes were processed at the same time. The barrier heights for both Pt and Ir reacted with SiGe alloys are higher than for the same metal reacted into Si. These trends are in disagreement with the results of Kanaya *et al.* but are consistent with the trend reported by Xiao *et al.* for Pd and the trend reported by Liou *et al.* for Pt. The image-force-induced lowering of the barrier height is present in both the Si and SiGe reacted diodes. The SiGe reacted diodes were measured at lower reverse biases than the Si diodes because of their greater reverse leakage currents; however, this difference is not enough to account for the higher barrier heights of the SiGe reacted diodes. The values of C_1 for the PtSi and IrSi control diodes are typical of those reported in the literature, but the C_1 values of the diodes with metal-SiGe reactions are substantially lower. Because C_1 depends on several scattering parameters, however, it is not possible to the determine at the present time the cause of the lowered C_1 uniquely. In Fig. 1 it can also be seen that there is a larger variation in C_1 with applied potential for diodes with Pt-SiGe reactions, compared to the control PtSi/Si diodes. It has been shown that the reverse-bias dependence of C_1 depends on the scattering length l_s in the semiconductor before the potential barrier maximum. The relationship has the form $C_1 \propto \exp(x_m/l_s)$, where x_m, the distance from the metal-semiconductor interface to the Schottky barrier maximum, is reverse-bias dependent.[10] Applying this to the reverse-bias measurements of C_1 yields scattering lengths of ~11 Å in the Pt-SiGe reacted diodes and ~43 Å in the PtSi/Si control diodes. This may indicate a greater amount of disorder and/or defects in the semiconductor side of the interface of the Pt-SiGe reacted diodes, which would be consistent with the studies reporting the segregation of Ge and the preferential formation of the PtSi phase in Pt-SiGe reactions.[3,5]

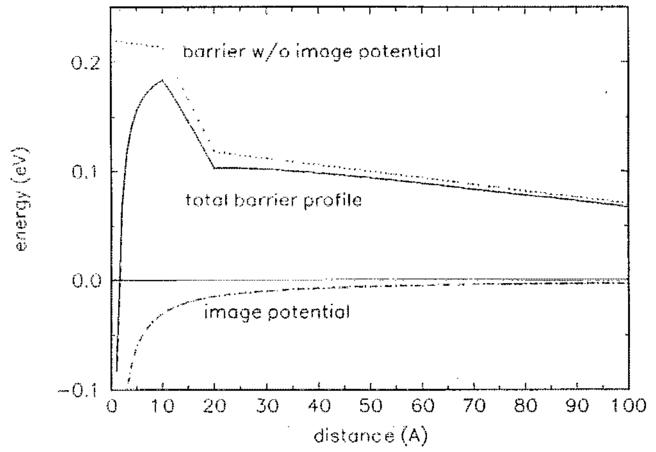

FIG. 3. Barrier profile of a Schottky diode on 10 Å Si, on SiGe, including the effects of the image-force lowering. On this length scale, the linear slope between Si and SiGe over 10 Å is a representation of the achievable interface abruptness with this growth technique. The profile is for 10^{16} cm^{-3} acceptor concentration, at a temperature of 40 K.

In forming silicide/SiGe diodes without metal-SiGe reactions, a drawback is the unconsumed Si that inevitably remains if metal-SiGe reactions are to be avoided. This Si layer would form a thin barrier that carriers would have to tunnel through (Fig. 3), reducing the quantum efficiency of the device. This barrier is not removed by the effects of the image force (also shown in Fig. 3), which normally lowers and shifts the barrier peak about 40 Å (depending on doping and reverse bias) into the semiconductor. Figure 4 is a measured Fowler plot of such a PtSi/Si/SiGe diode, shown with fitted barrier heights and emission constants C_1. The emission constants are of comparable value as, but much less voltage dependent than, those of the Pt-SiGe reacted diodes. This is consistent with the absence of disorder caused by Ge segregation in Pt-SiGe reactions. The barrier heights of ~0.18 eV are extrapolated in the usual manner. Although these barrier heights are already significantly lower than typical PtSi/Si diodes, they are more properly obtained by accounting for the effects of Si barrier. The Si barrier reduces the transmission probability for excited carriers with energy below the Si barrier height, so that one would expect the slope of the Fowler plot to be reduced at energies below the Si barrier height, leading to an even lower extrapolated cutoff. Xiao *et al.*[11] first modeled this effect, by modifying the Fowler theory of photoemission, obtaining a modified integral over the Fermi distribution that was then numerically evaluated. In this article, our treatment is based on a correction of the Fowler equation by Cohen, Vilms, and Archer,[12] and results in a simple, analytical form for the internal photoyield.

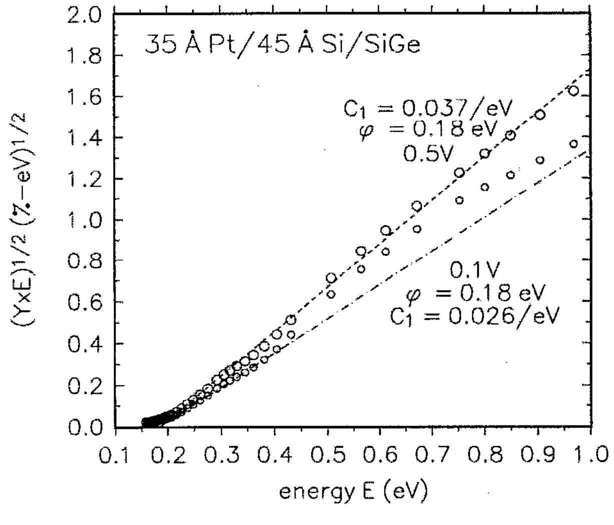

FIG. 4. Measured Fowler plots of PtSi/Si/Si$_{85}$Ge$_{15}$ diodes, formed with 35 Å Pt on 40 Å Si on SiGe, shown for two of the reverse-bias voltages used (0.1 and 0.5 V). The values of ϕ and C_1 are from linear fits without accounting for tunneling through the Si barrier.

IV. MODELING

Internal photoemission in Schottky diodes is usually described with Fowler theory,[13] in which the internal quantum efficiency Y (quantum efficiency per absorbed photon) is $Y \propto (h\nu - \phi)^2$, where ϕ is the Schottky barrier height and $h\nu$ is the photon energy. Cohen and co-workers[12] corrected this expression and showed that the internal quantum efficiency Y is more properly written as $Y = C_1(h\nu - \phi)^2/h\nu$, called the modified Fowler equation.[14] Plots of $\sqrt{Yh\nu}$ vs $h\nu$, called Fowler plots, are therefore linear with an energy axis intercept at the Schottky barrier height and a slope related to C_1. The Schottky emission coefficient C_1 depends in a complicated way on scattering lengths and mechanisms in the metal, such as hot-carrier–cold-carrier scattering, carrier-phonon scattering, and front-/back-wall scattering.[15]

The internal quantum efficiency is the probability that a photoexcited carrier will be emitted over the Schottky barrier. The modified Fowler equation is obtained by dividing the k-space volume of states that satisfy the conditions for emission (which has the shape of a cap), by the k-space volume of states into which carriers can be excited (a shell of width corresponding to $h\nu$).[16] We therefore divide the integration of the k-space volume into two regions, one for perpendicular energies above the Si barrier, and the other for perpendicular energies corresponding to tunneling through Si barrier. This is illustrated in Fig. 5. Thus, $Y = V_c/V_s$, where V_s is the volume of the shell of excited states, and V_c, the cap volume, is

$$V_c = \pi \int_{k(E_F+\phi_{sg})}^{k(E_F+\phi_s)} (k^2_{E_F+h\nu} - k_\perp^2)\,\tau(E)\,dk_\perp + \pi \int_{k(E_F+\phi_s)}^{k(E_F+h\nu)} (k^2_{E_F+h\nu} - k_\perp^2)\,dk_\perp, \quad h\nu > \phi_s, \tag{1}$$

$$V_c = \pi \int_{k(E_F+\phi_{sg})}^{k(E_F+h\nu)} (k^2_{E_F+h\nu} - k_\perp^2)\,\tau(E)\,dk_\perp, \quad \phi_s > h\nu > \phi_{sg}, \tag{2}$$

where $\tau(E)$ is the transmission probability through the Si barrier, ϕ_s is the SBH with Si, and $\phi_{sg} = \phi_s - \Delta E_v$ where ΔE_v is the valence-band offset. We have kept the assump-

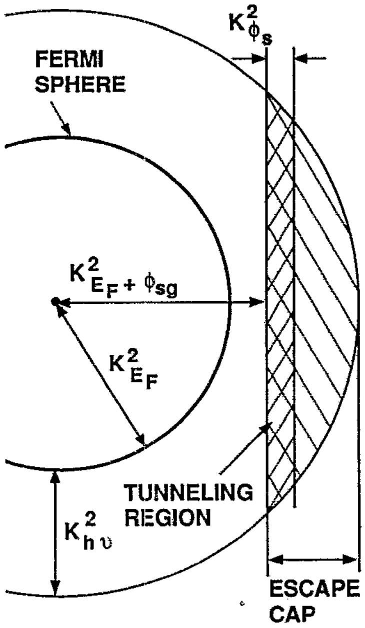

FIG. 5. Diagram in k space showing the escape cap and its two regions, corresponding to tunneling through the Si barrier, and emission over the Si barrier.

tions of the Fowler model so that $\tau=1$ above ϕ_s and $\tau=0$ below ϕ_{sg}. Calculations based on a simple barrier-and-step model indicate that the transmission coefficient through the Si barrier increases almost linearly with energy over the range of the Si barrier. If, as a first approximation, we neglect this energy dependence and use an average value τ_{avg} over the height of the Si barrier, then we obtain[17]

$$Y=C_1\frac{(h\nu-\phi_s)^2}{h\nu}+C_1\tau_{\text{avg}}\frac{(\phi_s-\phi_{sg})(2h\nu-\phi_s-\phi_{sg})}{h\nu},\quad h\nu>\phi_s, \tag{3}$$

$$Y=C_1\tau_{\text{avg}}\frac{(h\nu-\phi_{sg})^2}{h\nu},\quad \phi_s>h\nu>\phi_{sg}. \tag{4}$$

The first term in Eq. (3) is the normal equation for carriers emitted over the Si barrier height, and the second term is due to the fraction of excited carriers tunneling through the Si barrier. Equation (4) holds for photon energies such that all the emitted carriers tunnel through the Si barrier, and is of the same form as the modified Fowler equation, with the coefficient reduced by a factor of τ_{avg}. A plot of the expected behavior is shown in Fig. 6. Only the slope of the low energy part, and not the barrier height, depends on the value of τ_{avg}. This value can be obtained from the data by noting that Eq. (3) can be rearranged as

$$Y=C_1(1-\tau_{\text{avg}})\frac{(h\nu-\phi_s)^2}{h\nu}+C_1\tau_{\text{avg}}\frac{(h\nu-\phi_{sg})^2}{h\nu},\quad h\nu>\phi_s. \tag{5}$$

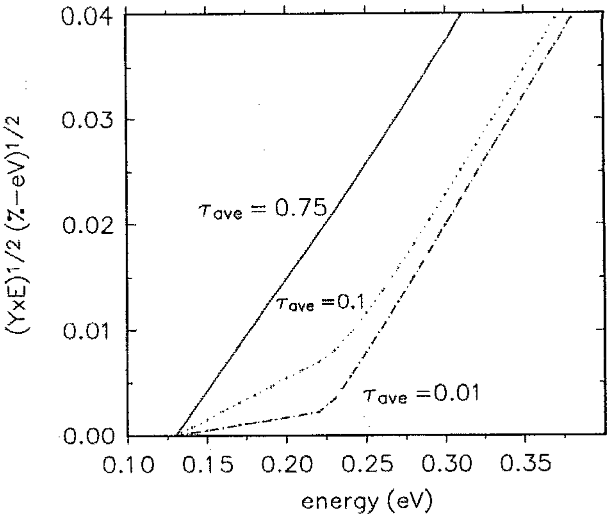

FIG. 6. Calculated Fowler plots of the yield predicted by the model accounting for tunneling through the Si barrier, for various average transmission probabilities. The calculations were made for $\phi_s=0.22$ eV, $\phi_{sg}=0.12$ eV, and $C_1=0.14$/eV.

Thus, after $C_1\tau_{\text{avg}}$ is obtained from the slope of the low-energy segment, the extrapolation of this segment can be subtracted from the high-energy part. The resulting slope gives $C_1(1-\tau_{\text{avg}})$, which is combined with $C_1\tau_{\text{avg}}$ to give both C_1 and τ_{avg}. An estimate of the Si barrier thickness d can be obtained from τ_{avg}. If one approximates τ_{avg} by the expression for tunneling through a rectangular barrier of height ϕ_s,

$$\tau_{\text{avg}}=\exp\{-2d[2m(E_{\text{avg}}-\phi_s)]^{1/2}/\hbar\},$$

then the model predicts essentially a Si-like Schottky barrier for Si thicknesses of greater than 40 Å. In this model, if it is easily seen that what is described as the "barrier height" for a silicide/Si/SiGe diode is just the silicide/Si barrier height reduced by the SiGe/Si band offset.

Figure 7 is a magnification of the low-energy part of Fig. 4, showing clearly the change in the slope of the Fowler plot. The data are fitted using the model described above, and values of τ_{avg}, C_1, ϕ_s, and ϕ_{sg} (shown in the figure) are obtained. For an E_{avg} halfway between ϕ_s and ϕ_{sg}, these values of τ_{avg} correspond to an estimated Si barrier thickness of ~9–10 Å, which is consistent with the deposited film thicknesses (Pt and Si), within their error limits. The low-energy segment extrapolates to $\phi_{sg}\sim 0.15$ eV, which is reasonably consistent with a valence-band offset of about 0.09 eV for 13% strained SiGe. Incorporating the energy dependence of τ would only result in some curvature of the low-energy segment, which is not discernible in the data. More extensive modeling is therefore not warranted.

V. SUMMARY

In summary, we have obtained lowered-barrier-height PtSi/Si/SiGe diodes useful for extending the cutoff wavelength of silicide Schottky barrier diodes. Diodes formed by reacting Pt and Ir into the SiGe layer had higher barrier

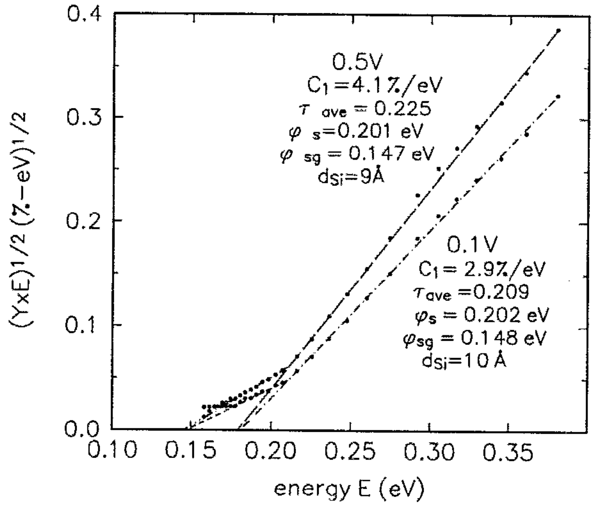

FIG. 7. Fowler plots of PtSi/Si/$Si_{85}Ge_{15}$ diodes, magnified to show clearly the low-energy segment, with fitted values for τ_{avg}, C_1, ϕ_s, ϕ_{sg}, and the Si barrier thickness d_{Si}.

heights than the corresponding silicide/Si diodes, a result in disagreement with some previous reports. The tunneling of carriers through the thin Si barrier in silicide/Si/SiGe diodes was modeled based on Cohen and co-workers' derivation of the modified Fowler equation. Tunneling, however, reduces the potential quantum efficiency of the device and could introduce spatial nonuniformities in the responsivity because of thickness variations in the unconsumed Si barrier after silicide formation. This, together with the sensitivity of the fabrication process to the relative accuracy of metal and Si thicknesses, suggests optimization by forming intimate silicide/SiGe diodes with simultaneous deposition of metal and Si.

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[16] Fowler's theory, on the other hand, is equivalent to taking Y to be proportional to the k-space volume of states that can emit, and neglecting the division by the k-space volume of states that carriers can be photoexcited into.

[17] The equations for Y are obtained by expanding the exact results of the integration to second order in $h\nu/E_F$ and ϕ/E_F in the numerator, and first order in the denominator.