Materials Research Society Symposium D, Boston, MA, Nov. 29 - Dec. 3, 1993

SCHOTTKY BARRIER HEIGHTS OF Pt SILICIDES ON SiGe

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Abstract

Silicide/SiGe Schottky barriers are of importance for applications in infrared detectors and SiGe contacts, as well as for fundamental studies of metal-semiconductor interfaces. We have fabricated silicide/SiGe Schottky diodes by the reaction of evaporated Pt and Ir films on p-SiGe alloys with a thin Si capping layer. The onset of metal-SiGe reactions was controlled by the deposited metal thickness. The Schottky barrier heights were determined from internal photoemission. Pt-SiGe and Ir-SiGe reacted diodes have barrier heights that are higher than the corresponding silicide/p-Si diodes. PtSi/Si/SiGe diodes, on the other hand, have lower "barrier heights" that decrease with increasing Ge concentration. The smaller barrier heights in such silicide/Si/SiGe diodes are due to tunneling through the unconsumed Si layer. Equations are derived accounting for this tunneling contribution, and lead to an extracted "barrier height" that is the Si barrier height reduced by the Si/SiGe band offset. Highly bias-tunable barrier heights are obtained (e.g. 0.30 eV to 0.12 eV) by allowing the SiGe/Si band offset to extend higher in energy than the Schottky barrier, leading to a cut-off-wavelength-tunable silicide/SiGe/Si Schottky diode infrared detector.

Introduction

Silicide/$Si_{1-x}Ge_x$ diodes may have a lower barrier height than the corresponding silicide/Si diode because of the smaller bandgap of SiGe. This is the motivation for their possible use in extended range silicide infrared detectors[1]. 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.[2] 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.[3] 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.[4] 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. An approach that bypasses the problems of metal-SiGe reactions, 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.[4] Codeposition of metal and Si in stoichiometric ratio would be another method of avoiding complex metal-SiGe reactions.

In this paper, 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.

Mat. Res. Soc. Symp. Proc. Vol. 320. ©1994 Materials Research Society

Experimental Details

The p-type (boron-doped) SiGe structures were grown by rapid-thermal chemical vapor deposition (RTCVD), in a system that has been described previously.[5] The SiGe layers were capped with Si, and a layer of graded Ge concentration was grown between the SiGe and the Si. The Pt and Ir depositions were done by electron beam evaporation in a load-locked ultra-high vacuum system. The wafers were RCA-cleaned, 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 wafers were held at elevated temperatures during deposition and the silicides were formed by annealing in-situ for one hour. 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 ohm-cm). Some samples were processed with guard ring structures in the Si below the SiGe. 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.

Experimental Results

When the deposited Pt layer is thick enough to react with all the Si cap and some of the SiGe, we find that the barrier height is raised, not lowered. We call such diodes Pt-SiGe reacted diodes. Pt-SiGe and Ir-SiGe reacted diodes had barrier heights of ~0.27 eV 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. The barrier heights are expected to vary widely depending on the detailed results of the reaction. Pt-SiGe reactions, for example, have been reported[3,6] to result in Ge segregation and preferential PtSi formation.

When the deposited Pt layer is not thick enough to consume the whole Si cap, the Fowler plots extrapolate to a lower barrier height. Because some unconsumed Si remains, the interface is that of PtSi/Si, and the lower effective barrier height is due to tunneling through a potential energy barrier formed by the Si. For this reason we refer to such diodes as PtSi/Si/SiGe diodes. Figure 1 shows Fowler plots of PtSi/Si/SiGe diodes of varying Ge concentrations. The extrapolated barrier heights decrease with increasing Ge concentration. These linearly extrapolated, or "effective", barrier heights, do not really correspond to an actual barrier height, but rather, are due to an increase in the yield because of the tunneling through the unconsumed Si layer. In the next section, the equations for internal photoemission are extended to take this into account.

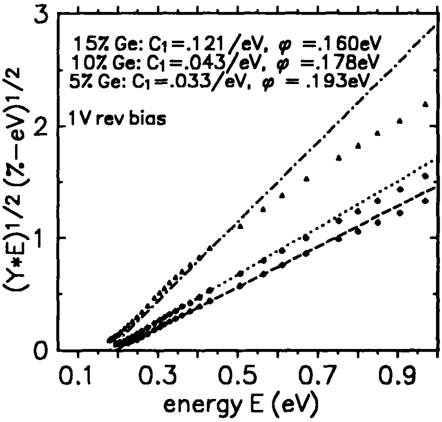

Figure 1: Fowler plots at 1V reverse bias, of PtSi/Si/SiGe diodes of varying Ge content.

Reverse I-V characteristics for the PtSi/Si/SiGe samples show leakage currents that are low for Schottky diodes on epitaxial Si, typically about 10^{-10} A/cm^2 at 1 volt reverse bias. Because the samples have no guard rings, these increase rapidly to about 10^{-2} A/cm^2 at about 10 volts bias. Control diodes made on substrate Si, however, could be biased much higher without breakdown. This may be due to the higher quality of the Si substrates or the higher doping of the epilayers, or a combination of both.

Internal photoemission with a tunneling barrier

Figure 2 is the valence band-edge depth profile of a silicide/Si/SiGe/Si diode, showing the thin potential barrier formed by the unconsumed Si. We briefly outline the derivation of equations for photoresponse in the presence of such a tunneling barrier. The internal quantum efficiency is the probability that a photoexcited carrier will be emitted over the Schottky barrier. The Cohen-Fowler equation for the internal quantum efficiency, $Y=C_1(h\upsilon-\phi)^2/h\upsilon$, is obtained from[7] $Y=V_c/V_s$, where V_s is the k-space volume of states into which carriers can be photoexcited from the Fermi sphere (a shell of width $h\nu$ above the sphere) and V_c is the k-space volume of states in V_s that satisfy the conditions for emission. In order to model the effects of a tunneling barrier, we therefore divide V_c into two regions, one for perpendicular energies above the Si barrier, and the other for perpendicular energies corresponding to tunneling through Si barrier. We then reduce the volume of this second region by an average tunneling probability τ_{ave}. We get

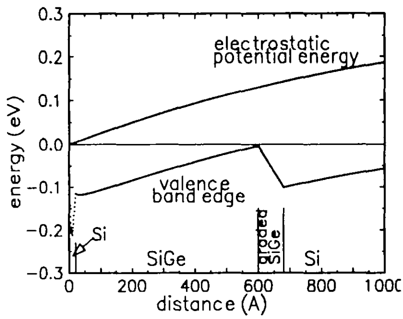

Figure 2: Calculated valence band-edge profile of a PtSi/Si/SiGe/Si diode, showing both Si/SiGe interfaces.

$$Y = C_1(1-\tau_{ave})\frac{(h\nu-\phi_s)^2}{h\nu} + C_1\tau_{ave}\frac{(h\nu-\phi_{sg})^2}{h\nu} \qquad h\nu > \phi_s \qquad (1)$$

$$Y = C_1\tau_{ave}\frac{(h\nu-\phi_{sg})^2}{h\nu} \qquad \phi_s > h\nu > \phi_{sg} \qquad (2)$$

where ϕ_s is the SBH with Si and $\phi_{sg} = \phi_s - \Delta E_v$ where ΔE_v is the valence band offset. Equation (2) 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_{ave}. Equations (1) and (2) result in a Fowler plot with a segment of reduced slope below ϕ_s, as shown in Figure 3. Only the slope of this low energy segment, and not its intercept, depends on the value of τ_{ave}. This value can be obtained from the data by first obtaining $C_1\tau_{ave}$ from the slope of the low energy segment, then subtracting the extrapolation of this segment from the high energy part. The slope of the reduced higher energy segment gives $C_1(1-\tau_{ave})$, which is combined with $C_1\tau_{ave}$ to give both C_1 and τ_{ave}. An estimate of the Si barrier thickness d can be obtained from τ_{ave}. If one approximates τ_{ave} by the expression for tunneling through a rectangular barrier of height ϕ_s, $\tau_{ave} = \exp[-2d(2m(E_{ave}-\phi_s))^{1/2}/\hbar]$, then the model predicts essentially a Si-like

Schottky barrier for Si thicknesses of greater than 40 Å. The fitted values of τ_{ave}, C_1, ϕ_s, and ϕ_{sg} are shown in Figure 3. For an E_{ave} halfway between ϕ_s and ϕ_{sg}, these values of τ_{ave} 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 ϕ_{sg} ~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.

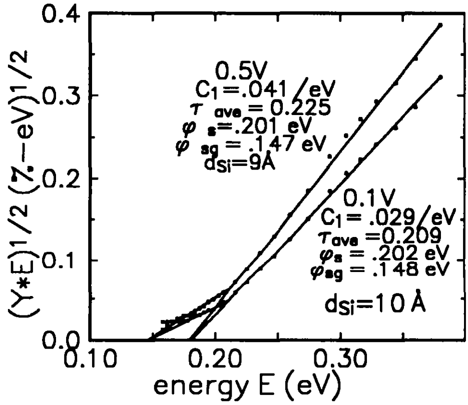

Figure 3: Magnified Fowler plot of a PtSi/Si/SiGe (13% Ge) diode.

Tunable-barrier-height PtSi/SiGe/Si diodes

In silicide/SiGe/Si Schottky diodes, the SiGe/Si-substrate band offset may act as an additional barrier to photoemitted carriers, depending on the SiGe thickness and grading. If the SiGe layers are thin enough to lie entirely in the depletion region, the valence band-edge energy profile is calculated with little modification of the standard theory[8]. The electrostatic potential energy due to the space charge region is $U(z,W)=q^2N_a(W(V_{bi})z-z^2/2)/\varepsilon_s$, where the depletion width $W(V_{bi})$ depends on the built in potential difference $qV_{bi}=q\phi_b-(E_v-E_F)$. For standard diodes, the valence band-edge energy is $E_v(z)=U(z)+q\phi_b$. For silicide/Si/SiGe/Si and silicide/SiGe/Si diodes, however, we have $E_v(z)=U(z)+E_v^{(i)}(z)$, where $E_v^{(i)}(z)$ is the initial (non-equilibrium, flat-band) valence band profile in the semiconductor structure, i.e., before any charge redistribution. For a silicide/SiGe/Si Schottky diode, the built in potential is given instead by $qV_{bi}=q\phi_{bsg}+\Delta E_v-(E_v-E_F)$, where $q\phi_{bsg}$ is the silicide/SiGe barrier height and ΔE_v is the SiGe/Si band offset.

In the calculated band-edge profile of Figure 2, the thickness and position of the graded layer are such that the "peak" at the SiGe/Si-substrate interface at zero bias does not extend higher than $\phi_{sg} = \phi_s-\Delta E_v$, so that the barrier height measured by photoresponse measurements are indeed those determined by the silicide/Si/SiGe interface. The SiGe/Si-substrate offset, however, can be designed to be extend higher in energy than the Schottky barrier, and then pulled down with reverse bias, forming a tunable barrier height Schottky diode detector. Figure 4 illustrates such a silicide/SiGe/Si tunable-barrier-height detector. The effective barrier height of such a structure is much more sensitive to reverse bias than normal Schottky diodes because the potential peak is much further into the semiconductor. For emission over the SiGe/Si peak occuring at low bias, the quantum efficiency (determined by the emission coefficent C_1) would be very much reduced because of scattering in the thicker semiconductor region before the peak position[9]. However, the C_1 coefficient should revert to its normal value at higher biases corresponding to emission over the Schottky barrier. Because uniformity, and not quantum efficiency, is the competitive advantage of silicide infrared detectors, applications may be possible in spite of the reduced quantum efficiency at low bias.

Figure 5 is a plot of the barrier heights of a series of PtSi/Si/SiGe/Si samples, measured by internal photoemission, as a function of reverse bias. The dotted curve is the theoretical reverse bias lowering for a typical PtSi/Si diode. The bias dependence of the barrier heights of the 0% and 10% Ge samples closely follow this curve. For the 15% and 20% samples, however, the barrier heights rapidly decrease with reverse bias, as expected for emission over the SiGe/Si interface. The barrier heights then level off to their normal bias dependence, which is expected at biases such that the SiGe/Si offset is pulled down below the Schottky barrier. The bias-sensitivity of the barrier height in such diode structures is determined by the thickness of the SiGe layer. If we denote the voltage-induced change in the effective barrier height by $\Delta\phi_{eff}(V,z_2)$, where z_2 is the distance from the metal-semiconductor interface to the SiGe/Si interface, then $\Delta\phi_{eff}(V,z_2)=qN_a z_2(W(V)-W(V=0))/\varepsilon_s$, until the voltage where normal reverse-bias lowering of the Schottky barrier takes over.

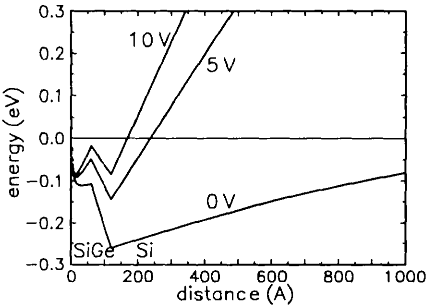

Figure 4: Calculated valence band-edge profile of a tunable silicide/SiGe/Si infrared detector at various bias voltages.

Figure 6 shows the emission coefficents C_1 for the same samples, plotted to linearize the typical Schottky dependence[9] $C_1 \propto \exp(-z_m(V)/L)$, where $z_m(V)$ is the bias-dependent position of the Schottky barrier maximum for 10^{16} cm^{-3} doping, and L is a scattering length in the semiconductor between the metal-semiconductor interface and the Schottky barrier maximum. The 0% and 10% samples have a linear dependence typical of Schottky emission, with slopes

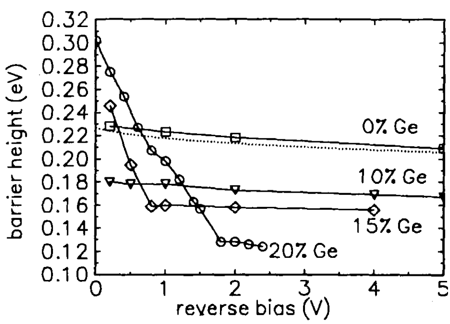

Figure 6: Schottky barrier heights at various bias voltages of a series of PtSi/Si/SiGe diodes of varying Ge content.

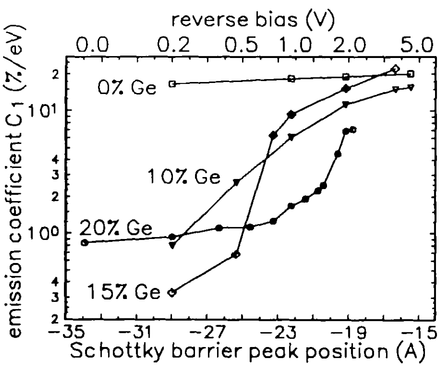

Figure 5: Emission coefficients C_1 at various bias voltages of a series of PtSi/Si/SiGe/Si diodes of varying Ge concentration.

corresponding to L = 90 Å and L = 5 Å, respectively. The difference in scattering lengths may be due to a combination of alloy scattering and defect scattering in the epitaxial material. The 15% and 20% samples, however, have nonlinear relationships with low values corresponding to the highly bias-variable barrier heights (for emission over the SiGe/Si interface), then a rapid rise to higher values corresponding to emission over the Schottky barrier.

Conclusions

PtSi/Si/SiGe diodes have effective Schottky barrier heights lower than PtSi/Si. The effective barrier heights decrease with increasing Ge concentration. The lowered barrier height obtained from the Fowler plot by standard linear extrapolation does not correspond to an actual barrier height, but is the result of the tunneling through the potential energy barrier formed by the unconsumed Si. This tunneling can account for the observed change in the slope of the Fowler plot at energies below the PtSi barrier height. The barrier height obtained from this low-energy segment corresponds to the PtSi barrier height reduced by the Si/SiGe band offset. If the SiGe layer is thin enough, depending on Ge concentration, the SiGe/Si band offset can extend higher in energy than the Schottky barrier height. Because the potential energy peak formed by this SiGe/Si offset is deeper into the semiconductor than the Schottky barrier, it is more bias dependent, resulting in a Schottky diode with a highly bias-tunable effective barrier height.

Acknowledgements

We would like to acknowledge the assistance of James Bockman, James Murrin, Darin Leahy, Alok Tripathi, the optical and electrical measurement work of Melanie Weeks, and the David Sarnoff Research Center for performing some of the Pt evaporation.

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