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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 detectors¹. 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.

p-type (boron-doped) SiGe structures were grown by rapid-thermal chemical vapor (RTCVD), in a system that has been described previously.⁵ The SiGe layers were Si, and a layer of graded Ge concentration was grown between the SiGe and the Si. Ir depositions were done by electron beam evaporation in a load-locked ultra-high vacuum. The wafers were RCA-cleaned, which slightly reduces the Si cap thickness and for in selecting the metal layer thickness. Before deposition, the Si surface was 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. For control, silicide/Si processed and deposited at the same time on boron doped Si substrates (10-15 ohm-cm) were processed with guard ring structures in the Si below the SiGe. Photocurrent measurements were made with a Perkin-Elmer single-pass photometer and a SiC globar at 1000 C as the infrared source. The input radiation was 139 Hz and the photocurrent measured by lock-in amplifier. Measurements were made at a temperature of 40 K or lower, and at various reverse bias voltages.

Experimental Results

The deposited Pt layer is thick enough to react with all the Si cap and some of the SiGe and Ir-SiGe reacted diodes had barrier heights of ~0.27 eV and ~0.31 eV, higher than typical values of 0.22 and 0.12 eV for the corresponding silicide/Pt-Si barrier heights are expected to vary widely depending on the detailed results of the Pt-SiGe reactions, for example, have been reported^{3,6} to result in Ge segregation and PtSi formation.

On the deposited Pt layer is not thick enough to consume the whole Si cap, the barrier height is raised, not lowered. We call such diodes Pt-SiGe reacted diodes. Figure 1 shows Fowler plots of PISi/Si/SiGe diodes of varying Ge content. The extrapolated barrier heights with increasing Ge concentration, or "effective", do not really correspond to an barrier height, but rather, are due to an yield because of the tunneling unconsumed Si layer. In the next equations for internal photoemission to take this into account.

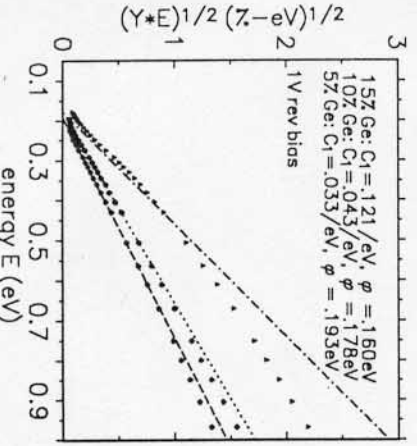


Figure 1: Fowler plots at 1V reverse bias, of PISi/Si/SiGe diodes of varying Ge content.

Reverse I-V characteristics for the PISi/Si/SiGe samples show leakage currents that are low for Schottky diodes on epitaxial Si, typically about 10⁻¹⁰ A/cm² at 1 volt reverse bias. Because the samples have no guard rings, these increase rapidly to about 10⁻² A/cm² 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 photocurrent 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 = C₁(hν - φ_s)²/hν, is obtained from Y = V_g²/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 hν above the sphere) and V_g 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_s 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 T_{avg}. We get

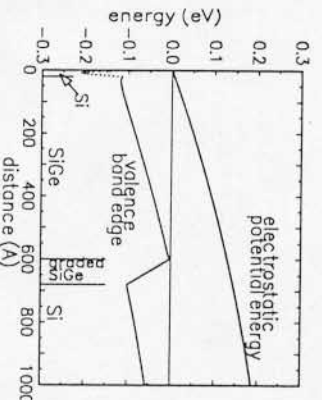


Figure 2: Calculated valence band-edge profile of a PISi/Si/SiGe/Si diode, showing both Si/SiGe interfaces.

$$Y = C_1(1 - T_{avg}) \frac{(h\nu - \phi_s)^2}{h\nu} + C_1 T_{avg} \frac{(h\nu - \phi_{sg})^2}{h\nu} \quad (1)$$

$$Y = C_1 T_{avg} \frac{(h\nu - \phi_{sg})^2}{h\nu} \quad \phi_s > h\nu > \phi_{sg} \quad (2)$$

where φ_s is the SBH with Si and φ_{sg} = φ_s - ΔE_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 T_{avg}. 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 T_{avg}. This value can be obtained from the data by first obtaining C₁T_{avg} 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 C₁(1 - T_{avg}), which is combined with C₁T_{avg} to give both C₁ and T_{avg}. An estimate of the Si barrier thickness d can be obtained from T_{avg}. If one approximates T_{avg} by the expression for tunneling through a rectangular barrier of height φ_s, T_{avg} = exp[-2d(2m(E_{av} - φ_s))^{1/2}/ħ], then the model predicts essentially a Si-like

rier for Si thicknesses of greater than 40 Å. The fitted values of τ_{ave} , C_1 , ϕ_b , and ϕ_{ng} are listed in Figure 3. For an E_{ave} halfway between ϕ_b and ϕ_{ng} , these values of τ_{ave} correspond to a Si barrier thickness of ~9-10 Å. The Si barrier thickness of ~9-10 Å is consistent with the deposited film thickness of ~10 Å. The Si barrier thickness of ~9-10 Å is consistent with the deposited film thickness of ~10 Å. The Si barrier thickness of ~9-10 Å is consistent with the deposited film thickness of ~10 Å.

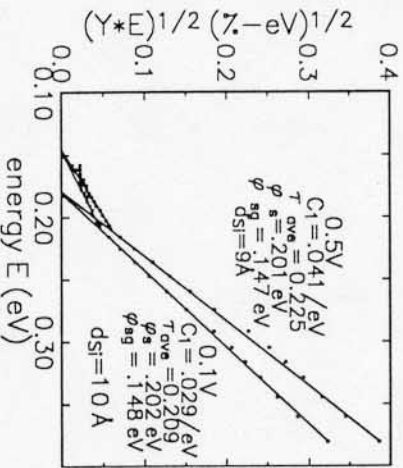


Figure 3: Magnified Fowler plot of a PtSi/Si/SiGe (13% Ge) diode.

the depletion region, the valence band-edge energy profile is calculated with little of the standard theory⁸. The electrostatic potential energy due to the space charge $\phi(x) = qN_A(W/V_{bi})z - z^2/2/\epsilon_s$, where the depletion width $W(V_{bi})$ depends on the built-in potential $V_{bi} = q\phi_{ng} - (E_c - E_v)$. For standard diodes, the valence band-edge energy is $E_v(z) = E_v(0) + q\phi_b$. For silicide/Si/SiGe/Si and silicide/SiGe/Si diodes, however, we have $E_v(z) = E_v(0) + q\phi_b(z)$, where $E_v(0)$ is the initial (non-equilibrium, flat-band) valence band profile in the metal-semiconductor junction. For a silicide/SiGe/Si diode, the built-in potential is given instead by $qV_{bi} = q\phi_{ng} + \Delta E_v - (E_c - E_v)$, where $q\phi_{ng}$ is the SiGe/Si band offset.

The calculated band-edge profile of Figure 2, the thickness and position of the graded SiGe/Si-substrate interface at zero bias does not extend to the "peak" at the SiGe/Si-substrate interface as determined by photoresponse measurements $\phi_{ng} = \phi_b - \Delta E_v$, so that the barrier height measured by photoresponse measurements is ϕ_{ng} . The SiGe/Si-substrate interface is determined by the silicide/Si/SiGe interface. The SiGe/Si-substrate interface is determined by the silicide/Si/SiGe interface. The SiGe/Si-substrate interface is determined by the silicide/Si/SiGe interface. The SiGe/Si-substrate interface is determined by the silicide/Si/SiGe interface.

possible in spite of the reduced quantum efficiency at low bias.

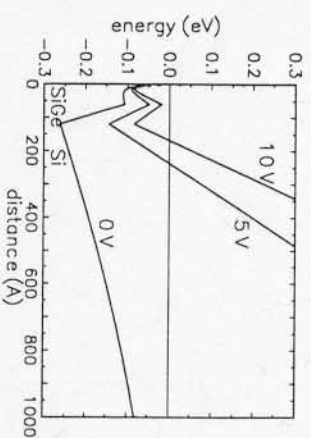


Figure 4: Calculated valence band-edge profile of a tunable silicide/SiGe/Si infrared detector at various bias voltages.

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 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 $\Delta\phi_{eff}(V, z_2) = qN_A z_2 (W(V) - W(V=0)) / \epsilon_s$, until the voltage where normal reverse-bias lowering of the Schottky barrier takes over.

Figure 6 shows the emission coefficients C_1 for the same samples, plotted to linearize the typical Schottky barrier dependence $C_1 \propto \exp(-z_m(V)/L)$, 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

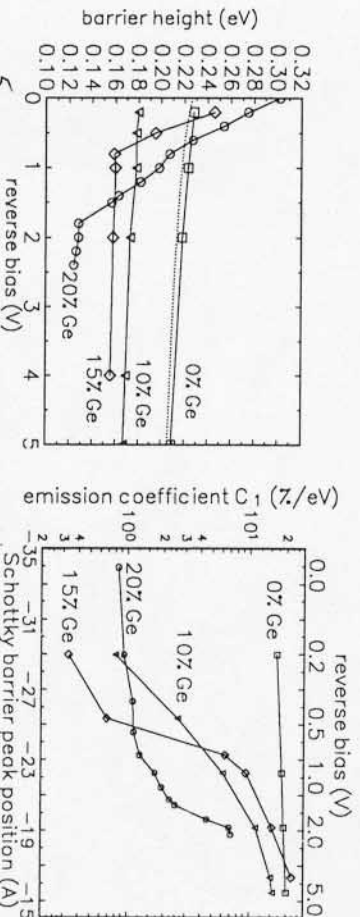


Figure 5: Schottky barrier heights at various bias voltages of a series of PtSi/Si/SiGe diodes of varying Ge content.

Figure 6: Emission coefficients C_1 at various bias voltages of a series of PtSi/Si/SiGe diodes of varying Ge concentration.

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

Conclusions

PSi/Si/SiGe diodes have effective Schottky barrier heights lower than PSi/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 unconsumed Si. This tunneling can account for the observed change in the slope of the Fowler plot at energies below the PSi barrier height. The barrier height obtained from this low-energy segment corresponds to the PSi 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 further in energy than the Schottky barrier height. Because the potential energy peak formed by 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.

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EFFECTS OF RAPID THERMAL ANNEALING ON W/Si_{1-x}Ge_x CONTACTS.

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ABSTRACT

Thermal reaction of W with Si_{1-x}Ge_x films epitaxially grown by Rapid Thermal Chemical Vapor Deposition was investigated in the temperature range 500°C - 1000°C. The samples were annealed either in a Rapid Thermal Annealing (RTA) system or in a conventional furnace, both in flowing nitrogen. The reaction products were investigated by Rutherford Backscattering Spectroscopy (RBS), Energy Dispersive Spectrometry (EDS) and X-ray diffraction (XRD). Sheet resistance measurements were also performed to follow the progress of the reaction. The reaction of W with Si_{0.67}Ge_{0.33} is similar to that of W with silicon. W reacts with silicon to form tetragonal WSi₂. The Ge-content in the silicide is lower than that of the deposited alloy. It is shown that an oxygen contamination occurs during conventional annealing and leads to the formation of non homogeneous Si_{1-x}Ge_x unreacted alloy below the silicide film. Rapid thermal annealing prevents this parasitic effect and the unreacted film remains homogeneous although a slight decrease in the Ge-content is observed. These results are correlated with Schottky barrier height measurements on p-Si_{0.83}Ge_{0.17} partially strained film. We observed an increase of the barrier height with increasing the temperature for annealing from 500°C to 1000°C. This trend may be explained either by strain relaxation or (and) Ge-content decrease in the unreacted alloy.

1-INTRODUCTION.

Si_{1-x}Ge_x/Si system is expected to play a major role in Si-based devices and has been extensively investigated. Astonishingly, little attention has been paid to metal/SiGe contact although the knowledge of metallizations to alloy is required for device applications. Recently the thermal reactions between transition metals^{2,3}, Pd³⁻⁶ and Pt⁴⁻⁷ have been examined and a few studies on the electrical properties³⁻⁵ of metal/Si_{1-x}Ge_x contact have been reported. Refractory metals such as tungsten have several characteristics that make them very attractive candidates for contact metallizations in VLSI circuits. The electrical properties and the thermal stability of W/Si_{1-x}Ge_x are consequently of great importance. In a previous work⁸, we have reported the electrical properties of W/p-Si_{1-x}Ge_x Schottky diodes. We clearly evidenced that the composition and the strain dependence of the Schottky barrier height on p-type follows the same trend than the band gap. The results were explained in terms of a pinning effect of the Fermi level relative to the