Schottky Barriers of Rare-earth Transition-metal Intermetallics on Silicon

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Abstract. The ferromagnetic transition metals Fe, Co and Ni have high work functions (4.5 - 5.0 eV) and they invariably form Schottky barriers on Si, often detrimental to efficient spin injection and detection at the interfaces. The rare earths have lower work functions (2.5 - 3.2 eV) but they order magnetically below room temperature. We therefore investigate a series of 12 rare earth metals and alloys of Gd, Ce or Y with Fe or Co, which are evaporated onto (001) Si wafers. The lowest thermionic emission barrier height is found for CeCo₅ (48 meV), much less than those found for the 3d ferromagnets or their silicides (∼ 500 meV). Y is found to form an ohmic contact after a diffusion anneal at 1300 K. Further alloy additions are needed to lower the barrier height below 25 meV; a target for room temperature operation with significantly increased reverse bias current.

Efficient spin injection into semiconductors has been a prime objective of spin electronics for two decades. Recent work [1], promises reasonable efficiency of spin injection into the standard semiconductors via a low-work-function metal/insulator/semiconductor tunnel junctions, which is essentially a Schottky barrier (SB) contact. Very low barrier heights below 0.1 eV have been reported in the system Pt/Er/Si [2]. As a number of standard hard-ferromagnetic alloys are based on Pt (for example CoPt), a properly designed CoPt/Er/Si junction may be a candidate for spin injection into silicon, although quite different barrier heights are estimated by photoemission [3]. Very low and even ‘negative’ SB heights have been reported and heatedly debated in the Ti/Si system [4]. A review of early work on rare-earth overlayers on silicon is available [5]. Unlike Si, GaAs diodes (and most other compound semiconductors) have barrier heights well in excess of 0.5 eV, even with metals with very small work functions like Ga [6], due to the predominant role of the intrinsic surface states in determining of the barrier height [7].

The work functions of 3d metals lie in the range 3.4 - 5.2 eV [8]. Therefore, all 3d metals should create SBs on silicon when the interface index \( \varsigma \sim 1 \). The rare earth metals have work functions that are about 2 eV lower, but they order magnetically below room temperature. Intermetallics of rare earths and transition metals offer a compromise between ordering temperature and small work function. The latter could potentially have several positive effects: increased reverse bias current - important for all electrical injection/detection structures with low bias operation; transport dominated by ‘cooler’ electrons (closer to the Fermi level in the metallic ferromagnet) with higher spin polarisation; and diminished depletion layer width in the semiconductor with its associated spin-independent series resistance. In this work, their evaporated junctions with silicon are studied experimentally.

Commercial, moderately n-doped with phosphorous (with an activation energy \( E_d = 0.042(1) \) eV), \(<100>\) Si wafers (\( n \sim 5 \cdot 10^{17} \) cm\(^{-3}\)) are used as semiconductor substrates. All wafers...
are cleaned in boiling acetone, boiling methanol and 20 MΩ deionised water. Standard semiconductor grade etching solution NH₄OH:HF:H₂O is used for removing the surface oxide. The wafers are then washed in deionised water, dried in a stream of dry N₂ and immediately introduced into the vacuum chamber for deposition.

Deposition is done by thermal evaporation at 10⁻⁷ mBar (and rates ~ 0.1 nm/s) from sources of at least 4N purity. Metal alloy are prepared by in-vacuum arc-melting. Metal layer thickness is 30 nm. Thick Ag contact pads are evaporated for the external contacts on the metallic side. Shadow masking is used to define an active area of 1 cm². Ohmic back contacts are prepared by direct soldering with In metal at 400 K and rapid anneal at temperatures below 800 K (the process is stopped as soon as the In contacts to the Ag contact pads have melted, or ≈ 430 K on the junction side of the diodes). During this process, the metal side of the junctions is cooled by a jet of high-purity Ar gas, in order to avoid oxidation and diffusion of metal atoms across the interface, however thin silicide layer formation, during either junction or back contact formation, cannot be ruled out. Characterisation of the rare-earth-3d metal/Si junctions has been carried out using the 4-wire DC source-meters and a closed cycle refrigerator, that permits data acquisition in the interval 12 - 400 K. Non-inductive wiring and passive filtering is used in order to minimise electromagnetic interference with the refrigerator.

Information is obtained from the analysis of the temperature dependences of the I-V characteristics of the devices, which represent a 2D-surface in I-V-T space. An example is shown on figure 1. The measurement of a dense set of data points allows for numerical 2D β-spline interpolation and the extraction of arbitrary cuts through parameter space, in particular, \( I(T) \big|_{V=\text{const}} \) and \( V(T) \big|_{I=\text{const}} \). Those can be used for fitting and diode parameter extraction.

![Figure 1](image1.png)

**Figure 1.** I - V - T characteristic of a GdCo₂/Si junction. The color-scale span is: [-0.02, 0.2] mA.

Parameter extraction for real diodes, can be complicated by the fact that often the finite applied bias voltage \( V_a \) and temperature dependence of series resistance \( R_s \) must be corrected for. The analysis can be based on the modified diode model:

\[
I = S A'^{**} T^2 \exp\left(-q\phi_b/kT\right) \left\{ \exp[q (V_a - I R^* \exp(E_d/kT)) / kT] - 1 \right\}, \tag{1}
\]

where \( I \) is the total current, \( S \) is the junction area, \( A'^{*} \) is the effective Richardson constant, \( T \) is the absolute temperature, \( q \) is the elementary electronic charge, \( \phi_b \) is the SB height, \( k \) is Boltzmann’s constant, \( E_d \) is the offset of the dopant level with respect to the conduction band in the semiconductor and \( R^* \) is the saturation resistance of the semiconductor base¹.

¹ Activation of carriers in the semiconductor base (the neutral region of the semiconductor) is neglected, thus limiting the applicability of the model to low temperatures, for which \( kT \ll E_b \).

![Figure 2](image2.png)

**Figure 2.** Low bias ln \( I - 1/T \) characteristic of a GdCo₂/Si junction, via a cut at 0.2 V. Two different activation energies are clearly distinguishable.
Only thermionic emission and series resistance have been taken into account. This model is only applicable at temperatures for which the thermionic emission is the dominant process or $kT \gg E_{00}$, but not too high so that a large recombination current component can develop, or $kT \lesssim E_g/2$. Explicit solution for $\phi_b$ can be readily obtained from equation 1 in the form:

$$\phi_b = kT/q \{-\ln I + \ln (SA^*) + 2\ln T + \ln [\exp q (V_a - IR^* \exp (E_d/kT)/kT) - 1]\}. \quad (2)$$

The dominant term is $-\ln I$, so that if a plot of $-\ln I (1/T)$ is created the slope is, to a large extent, determined by $q\phi_b/k$. The remaining terms introduce further corrections, provided $R^*$, $E_d$ and the effective value of $S$ are known from independent investigations.

Results on all measured junctions are presented in table 1. While useful, this information is not free from artefacts. The main disadvantage of the simple model 2 is neglect of the recombination current $I_r$, which leads to an underestimate of the SB height. As $I_r$ has a different activation energy (normally about $E_g/2$), it should generally appear as a different slope in the activation plots at high temperature, as compared with the low-temperature limit. For recombination across the main gap in the semiconductor $E_g$, this leads to a temperature dependence of the form:

$$E_g = 2kT \{-\ln I + \ln I_r + \ln [\exp (V_a - IR^* \exp (E_d/kT)/kT) - 1]\}. \quad (3)$$

Thus it is clear, that the slope of the dependence $-\ln I (1/T)$ should be close to $E_g/2k$ at high enough temperature $T \gg E_g/2k$. More generally, the recombination activation energy $E_r$ lies in the range $E_d \lesssim E_r \lesssim E_g/2$. The above relations result in a ‘two-exponent model’ for the thermal activation of non-ideal SB.

An example of a junction where there are clearly two very different activation energies is shown on figure 2. The higher of the two, 0.641(2) eV is in excellent agreement with the fundamental gap of Si of $E_g/2 \approx 0.64$ eV. The lower of the two, 0.192(3) eV, corresponds to the effective barrier height for thermionic emission of electrons from Si into GdCo2. Though common, it is not obligatory, that the recombination process would be distinguishable on a thermal activation plot. In some junctions, a single process dominates in the whole experimentally accessible temperature range. Such behaviour is demonstrated by a Gd$_5$Si$_4$/Si diode on figure 3 with a

\begin{figure}[h]
\centering
\includegraphics[width=0.45\textwidth]{fig3.png}
\caption{Low bias $\ln I - 1/T$ characteristic of a Gd$_5$Si$_4$/Si junction, via a cut at 0.1 V. Only one activation energy is clearly distinguishable.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.45\textwidth]{fig4.png}
\caption{Low bias $\ln I - 1/T$ characteristic of a Ce$_2$Co$_7$/Si junction, via a cut at 0.2 V. The higher activation energy of 0.469(2) eV does not correspond to $E_g/2$.}
\end{figure}

$E_{00}$ is the voltage activation energy scale for tunnelling through the Si,

$E_g$ is the fundamental energy gap in the semiconductor base.

The details of recombination and current conversion at the interface are represented by constants $I_r$ and $E_r$. 

\footnote{\textnormal{2}} $E_{00}$ is the voltage activation energy scale for tunnelling through the Si.

\footnote{\textnormal{3}} $E_g$ is the fundamental energy gap in the semiconductor base.

\footnote{\textnormal{4}} The details of recombination and current conversion at the interface are represented by constants $I_r$ and $E_r$. 

\footnote{\textnormal{5}} $E_{00}$ is the voltage activation energy scale for tunnelling through the Si.
The last two columns in table 1 give a summary of the barrier heights and recombination activation energies of the diodes. The lowest effective thermionic emission barrier heights of ferromagnetic metal on Si(001) are exhibited by CeF$_2$Co$_{17}$/Si. There are very similar metal alloys, forming very different SBs, both in terms of barrier height $\phi_h$ and recombination energy $E_r$, as in the example of GdFe$_2$ and GdFe$_3$, where the first diode has $\phi_h = 0.195(2)$ V and $E_r = 0.429(1)$ eV, and the latter has $\phi_h = 0.097(2)$ V and $E_r = 0.227(1)$ V.

### Table 1. Minimal activation barrier heights $\phi_{\text{min}}$, total resistances $R$ at ± 0.1 V, actual barrier heights $\phi_h$ and recombination energies $E_r$, for Si Schottky diodes with active area of 1 cm$^2$. $\phi_{\text{ann}}$ denotes an annealed sample.

| Metal    | $\phi_{\text{min}}$ (V) | $R_{-0.1V}$ ($\Omega$) | $R_{+0.1V}$ ($\Omega$) | $\phi_h$ (V) | $E_r$ (eV) |
|----------|--------------------------|-------------------------|-------------------------|---------------|-------------|
| GdCo$_2$ | 0.42                     | 14250                   | 1617                    | 0.192(3)      | 0.641(2)    |
| Gd$_5$Si$_4$ | 0.19                   | 29640                   | 19250                   | 0.526(1)      | -           |
| GdFe$_3$ | 0.17                     | 22330                   | 22270                   | 0.097(6)      | 0.227(1)    |
| GdFe$_2$ | 0.26                     | 1307                    | 659.3                   | 0.195(2)      | 0.429(1)    |
| Gd$_2$Co$_7$ | 0.20                   | 9474                    | 4850                    | 0.435(1)      | -           |
| GdCo$_5$ | 0.20                     | 7838                    | 4868                    | 0.096(2)      | 0.376(3)    |
| Gd        | 0.38                     | 3.39·10$^6$             | 1.75·10$^6$             | 0.489(2)      | -           |
| Gd$_{\text{ann}}$ | 0.01          | 4613                    | 399.8                   | 0.435(1)      | -           |
| Ce$_5$Co$_{19}$ | 0.23              | 79680                   | 56380                   | 0.048(3)      | 0.503(6)    |
| CeCo$_5$  | 0.25                     | 7546                    | 4684                    | 0.536(1)      | -           |
| CeFe$_2$  | 0.76                     | 1145                    | 768.41                   | 0.215(1)      | 0.469(2)    |
| Ce$_2$Co$_{17}$ | 0.38            | 7478                    | 3237                    | 0.220(1)      | -           |
| Y         | 0.14                     | 248.8                   | 50.5                    | 0.091(2)      | 0.181(1)    |
| Y$_{\text{ann}}$ | 0.03            | 11.0                    | 10.9                    | -             | -           |
| Fe        | 0.26                     | 4756                    | 2645                    | -             | -           |
| Co        | 0.36                     | 16339                   | 2775                    | -             | -           |
| Ni        | 0.45                     | 5531                    | 3189                    | -             | -           |

The last two columns in table 1 give a summary of the barrier heights and recombination activation energies of the diodes. The lowest effective thermionic emission barrier heights of ferromagnetic metal on Si(001) are exhibited by Ce$_5$Co$_{19}$ (0.048 eV), GdCo$_5$ (0.097 eV) and GdFe$_3$ (0.097 eV), are significantly lower than their 3d-metal and silicide counterparts (about 0.5 eV). The barrier height deduced for Gd of about 0.4 eV agrees well with the one reported [9]. Also, Y is found to form ohmic contact to Si, but only after annealing at 1300 K. Unfortunately, this method of creating an ohmic junction is likely to lead to excessive impurity spin-scattering in the diffused region, which may lead to poor overall injection efficiency. Further work on rare-earth intermetallic alloys and their interfaces to silicon is necessary if a low barrier (low voltage operation) spin-transparent SB injectors/detectors are to be achieved.

### References

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