



Shifting Schottky barrier heights with ultra-thin dielectric layers

L. Lin^a, J. Robertson^{a,*}, S.J. Clark^b

^aEngineering Dept., Cambridge University, Cambridge CB2 1PZ, UK

^bPhysics Dept., Durham University, Durham, UK

ARTICLE INFO

Article history:

Received 24 February 2011

Received in revised form 16 March 2011

Accepted 23 March 2011

Available online 6 April 2011

Keywords:

Schottky barrier

Germanium

Calculation

Metal induced gap states

Insulator

Nanowires

Contact resistance

ABSTRACT

Ultra-thin (~ 1 nm) layers of dielectrics such as Al_2O_3 or SiN_x inserted between the metal and the semiconductor can be used experimentally to shift the Schottky barrier height (SBH) of various semiconductors to reduce their contact resistance. This property is particularly valuable for n-Ge with a normally high n-type SBH or for nanowires. The mechanism is often described as Fermi level de-pinning. We show how the mechanism consists of two parts, Fermi level de-pinning plus an interfacial dipole layer. The preferred dielectrics can be chosen in terms of their band offsets.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

The Schottky barrier height (SBH) is the important factor controlling the contact resistance of metal electrodes to doped semiconductors. If the SBH is very asymmetric in the semiconductor band gap, it can have a serious negative effect when the semiconductor is doped in the polarity with the large SBH. The situation in Si is not too bad, as the SBH lies 1/3 way up the band gap. However, in Ge, the SBH is very close to the valence band (VB), so that n-type SBHs are large [1–3].

Connelly et al. [4,5] noticed that inserting a thin dielectric layer could shift the SBH of a metal on Si. The important case came when Nishimura et al. [6], and Kobayashi et al. [7,8] used the idea for Ge. In Ge, the metal Fermi level of a Schottky barrier is pinned very close to the valence band, making a large SBH and a large contact resistance for n-Ge. This was improved by inserting a dielectric layer (Fig. 1). The effect was confirmed by others and also used on III–V semiconductor contacts [9–13]. It is also useful for contacts to nanowires.

The standard explanation [4,6,7] for this effect is that the Fermi level is pinned at a SB by the semiconductor's metal induced gap states (MIGS) [14–16]. On inserting the dielectric layer, the MIGS now decay inside dielectric layer, reducing their density of states, and so this removes the pinning. However, closer inspection of the data in Figs. 2 and 3 show that two effects are occurring, the unpinning, as above, and also a vertical shift of the SBH [7].

The degree of pinning at a Schottky barrier is given by the slope of the SBHs vs metal work function [14].

$$\phi_n = \phi_0 + S(\phi_M - \phi_0) \quad (1)$$

Here, ϕ_n is the measured n-type SBH, ϕ_0 corresponds to a reference energy level in the semiconductor band gap, ϕ_M is the metal work function, and S is a dimensionless Schottky barrier pinning factor. $S \sim 0$ corresponds to strong pinning, and $S = 1$ corresponds to no pinning (as expected for say a metal on SiO_2).

The underlying point is that MIGS and Eq. (1) is a simplified model of Schottky barrier pinning. ϕ_0 the reference energy is given by the charge neutrality level (CNL) in MIGS theory [14]. The CNL is a property of the bulk host band structure, and is fixed for that semiconductor. This is the limitation of the MIGS model. In practice, additional interface dipoles can shift ϕ_0 away from the CNL [17–20]. This dipole can arise because of a polar face on the semiconductor side [20,21]. This is known to be a large effect for example at the metal:HfO₂ interface [22]. Or it can arise from a change of interface structure, for example the difference between the A and B structures of the (1 1 1)NiSi₂:Si interface with 6-fold and 5-fold bonded Ni sites [19,23]. It is these factors which must be considered here.

2. Method

We have studied the cause of the vertical shift by calculating the barrier heights for epitaxial interfaces between metals (such as Ni) and Si, with two sub cells of cubic fluorite HfO₂ inserted be-

* Corresponding author. Tel.: +44 1223 748331; fax: +44 1223 332662.

E-mail address: jr@eng.cam.ac.uk (J. Robertson).

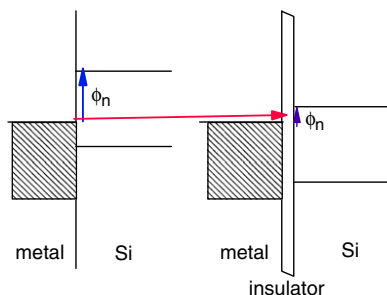


Fig. 1. Large n-type SBH for Ge. Insertion of thin insulator layer shifts n-type SBH to be small.

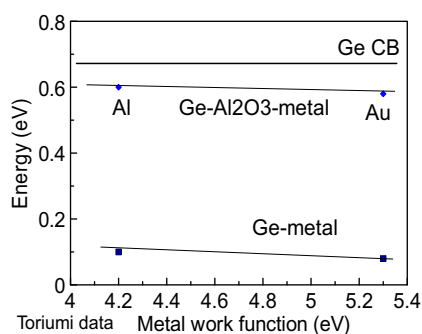


Fig. 2. Experimental SBH data for metals on Ge, with and without insulator layers, from [6].

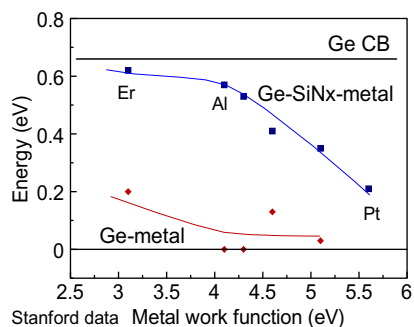


Fig. 3. Experimental SBH data for metals on Ge, with and without insulator layers, from [7].

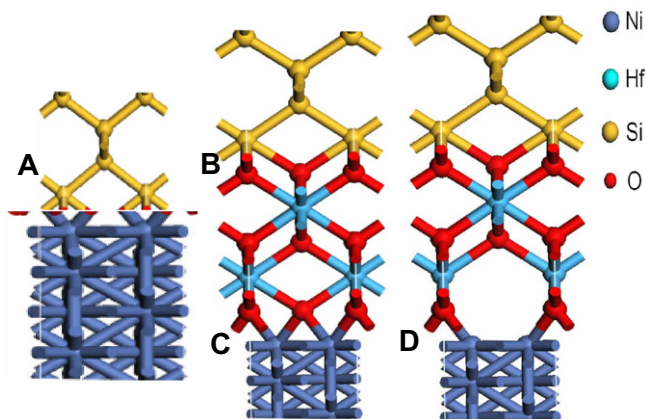


Fig. 4. Atomic bonding a Ni:Si Schottky barrier (A), Si:HfO₂ interface (B,) and either polar 2 oxygens(C) or non-polar 1 oxygen (D) Ni:HfO₂ interfaces.

tween the metal and Si as in Fig. 4. Cubic HfO₂ is chosen as the model insulator as it has a high symmetry and is fairly well lattice matched to Si and Ni. Si is chosen as the semiconductor instead of Ge for ease of calculations, because of its large band gap. The interfaces between HfO₂ and Si or Ni can have either 2 or 1 oxides per cell, corresponding to polar and non-polar interfaces C and D, respectively [21,23,24], as shown in Fig. 4. The supercell is symmetric, with two Ni:Si or Ni:oxide interfaces, no vacuum layer, and so no net electrical fields across the cell.

The calculations were carried out using the plane wave pseudo-potential code CASTEP to relax geometries and give the electronic structure. The cells contain six layers of metal and 10 layers of Si, two layers of HfO₂ and no vacuum. The supercell is symmetric, with no vacuum layer, and so no net electrical fields across the cell.

The electron exchange correlation energy is represented by the generalized gradient approximation (GGA). This is used for structure minimization. This uses ultra-soft pseudopotentials, a 400 eV cutoff and a $6 \times 6 \times 1$ k point mesh.

However, the GGA under-estimates the band gap, which can be a problem, because sometimes the interfacial dipole can result in the Si conduction band being above the HfO₂ conduction band, due to the GGA under-estimate of the band gap of HfO₂. Thus, we can add a shift to the valence band offset from the GW calculations [25]. We also used the screened exchange (sX) approximation in some cases [25]. This part of the calculation uses norm-conserving pseudopotentials and a 780 eV cutoff energy. However, this sX is not always successful for interface calculations, for two reasons. First it requires smaller supercells, due to its higher cost. Second, the screening depends on the local valence electron density, which of course varies within the cell from the metal to Si, and varies between the metals. The band gap is a sensitive function of the screening, but this can be controlled by the metal. Thus, sX results are used only as indicators.

The band line ups are derived from the local density of states in the bulk Si and metal regions, and not from reference potentials. These two methods give equivalent results.

3. Results

We calculated the band offsets of the various interfaces and interface combinations. The interface between HfO₂ and metals is known to be unpinned, but there is a large 0.8 eV offset between the polar and non-polar case [22], as shown in Fig. 5. The band offset between Si and HfO₂ interface also depends on the termination [24]. This is the source of the offset in barrier height.

The likely terminations present in practice will depend on the interfacial energy of the different terminations, and thus on the oxygen affinity of the Si and the metal. Si has a high oxygen affinity, and so the Si:HfO₂ interface is likely to be always O-rich (two

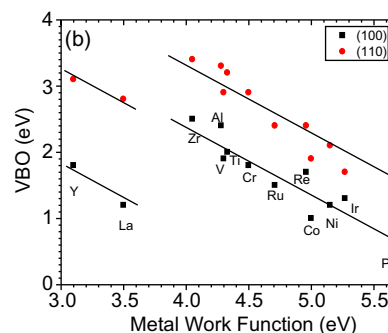


Fig. 5. Calculated valence band offsets of metal:HfO₂ interfaces, for polar (1 0 0) and non-polar(1 1 0) interfaces, from [22].

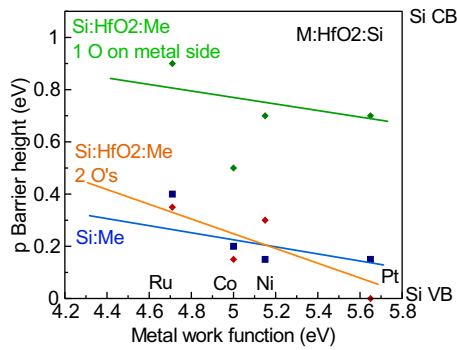


Fig. 6. Shift in effective Schottky barrier heights for the configurations in Fig. 4.

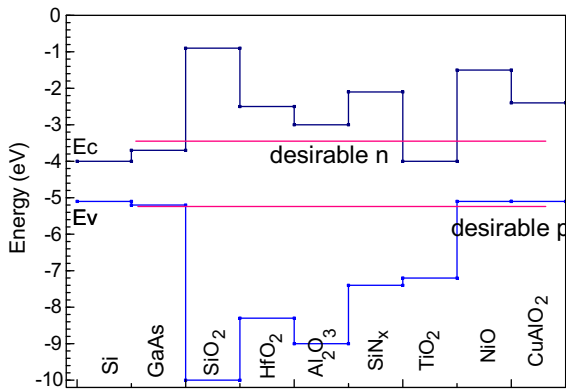


Fig. 7. Band alignments between Si, GaAs and various oxides and nitrides, showing that TiO₂ or SrTiO₃ are desirable for n-type insertion, and NiO or oxides like CuAlO₂ are desirable for p-type insertion. The data for Al₂O₃ is for the low density phase as formed by ALD, with 6.5 eV band gap.

oxygen per cell). On the other hand, for more electropositive metals like Ni with less strong bonding to oxygen, the interface is likely to be more oxygen-poor and non-polar. This leads to the combination shown in Fig. 4D. This interface is indeed found to have a roughly 0.5 eV shift in the overall SBHs compared to the Si:Ni interface shown in Fig. 6. This confirms that the important shift in SBH caused by the dielectric layers is due to the introduction of a dipole layer. The proof of this effect is that if there are the same number of oxygens on both interfaces (e.g. two Os), then the barrier height is roughly the same as for the direct Si:metal interface. This is indeed found for the case of Fig. 4B and C as seen in Fig. 6.

This confirms our proposal in the introduction that the SBH shift effect actually consists of two parts, the dipole shift and the MIGS unpinning.

4. Discussion

Coss et al. [27,28] argue that simply inserting a dielectric layer as in the Connolly method can only shift the SBH in an n-type direction. They proposed using the interface dipoles between SiO₂ and Al₂O₃ or La₂O₃ to allow shifting in either direction [28] from the local dipoles [29]. This is basically the same method, and is examined in detail by Lin and Robertson [29].

Roy et al. [30] have analyzed the contact resistance as a function of dielectric thickness and dielectric band gap for this mechanism

in a simplified tunneling model. They noted that the contact resistance for most dielectrics is still too high. They found that the lowest resistance for TiO₂ because it has a low conduction band offset to Si, as seen in Fig. 7 [31,32]. This means that one should avoid the Coss mechanism, as the relevant insulators Al₂O₃ or La₂O₃ have too large a band offset. So while they do provide the n- or p-type shift, they will not lower the contact resistance sufficiently due to their large band gap/tunnel barrier height.

Which dielectric should be used for shifting in a p-type direction? This should have a low valence band offset against Si (or semiconductor involved). The relevant choices are NiO or CuAlO₂, as can be seen from the band diagram in Fig. 7 assembled from data in Ref. [33].

5. Conclusion

The mechanism behind the shifting of Schottky barrier heights is described and predictions for suitable dielectrics are given for n- and p-type shifters.

References

- [1] A. Dimoulas, P. Tsipas, A. Sotiropoulos, E.K. Evangelou, Appl. Phys. Lett. 89 (2006) 252110.
- [2] A. Dimoulas, P. Tsipas, Microelectron. Eng. 86 (2009) 1577.
- [3] A. Toriumi, T. Tabata, C.H. Lee, T. Nishimura, K. Kita, K. Nagashio, Microelectron. Eng. 86 (2009) 1576.
- [4] D. Connolly, C. Faulkner, P.A. Clifton, D.E. Grupp, Appl. Phys. Lett. 88 (2006) 012105.
- [5] D. Connolly, IEEE Nanotechnol. 3 (2004) 98.
- [6] T. Nishimura, K. Kita, A. Toriumi, Appl. Phys. Exp. 1 (2008) 051406.
- [7] M. Kobayashi, A. Kinoshita, K. Saraswat, H.S.P. Wong, Y. Nishi, Technol. Digest VLSI (2008) 54.
- [8] M. Kobayashi, A. Kinoshita, K. Saraswat, H.S.P. Wong, Y. Nishi, J. Appl. Phys. 105 (2009) 0236702.
- [9] R.R. Lietsen, S. Degroot, M. Kuijck, G. Borghs, Appl. Phys. Lett. 92 (2008) 022106.
- [10] Y. Zhou, M. Ogawa, X. Han, K.L. Wang, Appl. Phys. Lett. 93 (2008) 202105.
- [11] Y. Zhou, W. Han, Y. Wang, F. Xiu, J. Zou, R.K. Kawakami, K.L. Wang, Appl. Phys. Lett. 94 (2009) 242104.
- [12] K. Yamane, K. Hamaya, Y. Ando, Y. Enomoto, K. Yamamoto, T. Sadoh, M. Miyao, Appl. Phys. Lett. 96 (2010) 162104.
- [13] J. Hu, K.C. Saraswat, H.S.P. Wong, J. Appl. Phys. 107 (2010) 063712.
- [14] W. Mönch, Phys. Rev. Lett. 58 (1987) 1260.
- [15] J. Tersoff, Phys. Rev. Lett. 52 (1984) 465.
- [16] J. Robertson, J. Vac. Sci. Technol. B 18 (2000) 1785.
- [17] J. Robertson, L. Lin, Tech. Digest IEDM (2009).
- [18] R.T. Tung, Phys. Rev. Lett. 84 (2000) 6078.
- [19] R.T. Tung, Phys. Rev. B 64 (2001) 205310.
- [20] M. Peressi, S. Baroni, R. Resta, A. Baldereschi, Phys. Rev. B 43 (1997) 7347.
- [21] A. Klein, presented at European Materials Research Society meeting, Warsaw, September 2010.
- [22] K. Tse, J. Robertson, Phys. Rev. Lett. 99 (2007) 086805.
- [23] G.P. Das, P. Blochl, O.K. Andersen, N.E. Christensen, O. Gunnarsson, Phys. Rev. Lett. 63 (1989) 1168.
- [24] P.W. Peacock, J. Robertson, Phys. Rev. Lett. 92 (2004) 057601.
- [25] V. Fiorentini, G. Guller, Phys. Rev. Lett. 89 (2002).
- [26] B.E. Coss, W.Y. Loh, R.M. Wallace, J. Kim, P. Majhi, R. Jammy, Appl. Phys. Lett. 95 (2010) 222150.
- [27] B.E. Coss et al., Tech. Digest IEDM (2010).
- [28] L. Lin, J. Robertson, Appl. Phys. Lett. 95 (2009) 012906; J. Appl. Phys. (2011), accepted for publication.
- [29] A.M. Roy, J. Lin, K.C. Saraswat, IEEE ED Lett. 31 (2010) 1077.
- [30] J. Robertson, Rep. Prog. Phys. 69 (2006).
- [31] J. Robertson, B. Falabretti, J. Appl. Phys. 100 (2006) 014111.
- [32] S.J. Clark, J. Robertson, Phys. Rev. B 83 (2011) 075205.

Further reading

- [26] S.J. Clark, J. Robertson, Phys. Rev. B 82 (2010) 085208.