Control of Schottky barrier heights by inserting thin dielectric layers

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The insertion of ultra-thin dielectric layers to lower n-type Schottky barrier heights is shown to partly involve the creation of a net interfacial dipole as well as unpinning of the Fermi level by suppression of metal-induced gap states. The existence of a net dipole requires a lack of cancellation of dipoles at the two interfaces. This requires a different metal(Ge)-O bond density at the two interfaces, in general requiring differing oxygen chemical potentials. This would need the inserted dielectric to be a diffusion barrier, not just able to create dipoles, favoring the use of Al_2O_3-based or nitrided dielectrics. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4764521]

Ge and III-V semiconductors are of great interest as high mobility channel materials for fully scaled CMOS. However, Ge and some III-Vs have a high source/drain contact resistance due to a large n-type Schottky barrier height (SBH). It has been found that the insertion of an ultra-thin (1–2 nm) layer of an insulator such as GeN_x or some oxides will lower the n-type SBH and thereby lower this contact resistance.[1–9] However, the exact mechanism of this effect is not fully understood. Part of the effect is the suppression of the metal induced gap states (MIGS), which pin the Fermi energy E_F at the direct metal-semiconductor interface.[1] But in other cases, the data are not compatible with a simple unpinning model, and there appears to be a global shift of the metal pinning energy to energies higher in the semiconductor's band gap. The mechanism behind this second effect is not really understood. We show here how this shift can arise from interface dipoles on each side of the insulator film, which would normally cancel out, but in this case do not because of a difference in oxygen (or nitrogen) ion density at the two interfaces. In a related situation, ultra-thin dielectric layers can be added between a ferromagnetic electrode and a semiconductor to act as a tunnel barrier to provide the correct impedance for spin polarised injection currents.[10–12] Thus, for both applications, it is interesting to understand complex contacts in more detail.

We first analyze the experimental data to show that there are two effects. Fig. 1(a) shows the SBH of various metals in direct contact with Ge. In this case, the slope of the SBH energy versus metal work function, the Schottky barrier pinning factor S, is very small, $S \sim 0$, indicating that there is a strong pinning. Fig. 1(a) also shows the SBH of metals on Ge when a thin GeN_x layer has been inserted, from data of Lieten et al.[5,6] S has now risen to $S \sim 0.32$, which is similar to metals that are deposited directly onto GeN_x. However, there has also been a small ~ 0.2 eV upward shift of the data points in Fig. 1(a), compared to a dashed line passing through the charge neutrality energy of Ge (at the valence band edge or 4.8 eV below the vacuum[13]). This indicates that there is mainly unpinning in this system,[5] but there is also a second effect. Similar data were found by Kobayashi et al.[3,4]

On the other hand, if the inserted layer is an oxide, there is a different response. Fig. 1(b) shows that if a Al_2O_3 layer is inserted between Ge and the metals, there is a general large upward shift of the SBH values, but slope is still quite

small.[2] This is because the pinning energy has been forced against the Ge conduction band edge.

The MIGS model[14–17] is the simplest model of unpinning. In this, the SBH ϕ_n varies with the metal work function ϕ_M as

$$\phi_n = \phi_0 + S(\phi_M - \phi_0),$$

where ϕ_0 is a reference energy, the charge neutrality level (CNL). The CNL is a property of the bulk semiconductor band structure, and its energy is fixed. It gives pinning at the
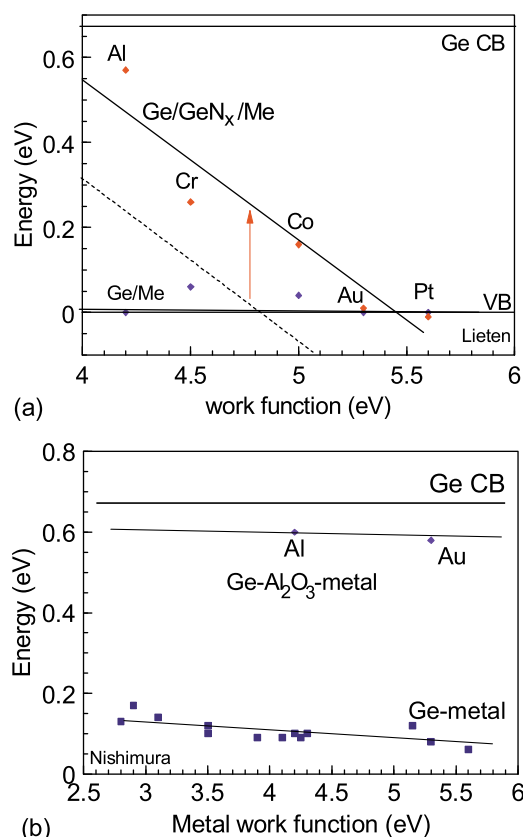

FIG. 1. (a) Barrier heights of metals on Ge with and without inserting thin GeN_x layer.[5,6] The dashed line indicates the expected barrier heights in the absence of a dipole, that is passing through the CNL energy of Ge. The dashed line is the expected trend of SBHs for inserted GeN_x without dipole layer effects, passing through the Ge CNL. (b) Barrier heights for metals on Ge with and without inserting thin Al_2O_3 layer.[2]
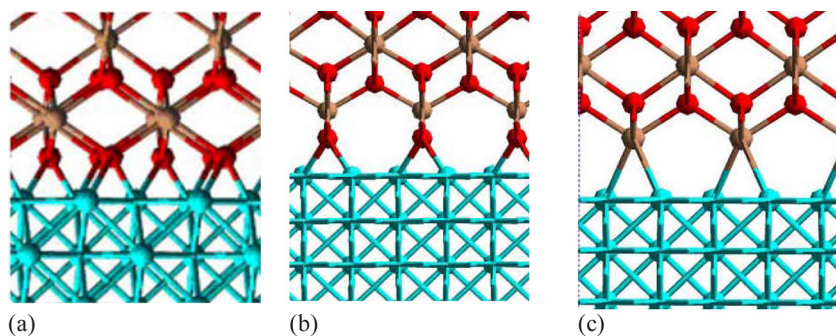
FIG. 2. Atomic images of O-rich, non-polar, and Hf-rich interfaces of metals on HfO_2.

same energy as at a non-polar interface. If the reference energy in the data shifts, as in Figs. 1(a) and 1(b), this indicates the presence of an interfacial dipole layer at one or both of the interfaces.[18–20] This effect is beyond the simple MIGS model. The question is how do these dipole layers arise?

We have studied the origin of these dipole layers by calculating the barrier heights for epitaxial supercell models of metal-insulator-semiconductor (MIS) structures, consisting of two atomic layers of cubic HfO_2 inserted between a metal and the Si. Cubic HfO_2 is chosen as the model insulator because it has a high symmetry and because it is approximately lattice-matched to both Si and Ni (the Si lattice is rotated by 45°). Si is chosen as the semiconductor rather than Ge because it has a larger band gap which eases the calculations (especially in view of the under-estimate of the band gap in the local density approximation). The calculations are carried out using the plane-wave pseudopotential code CASTEP to relax atomic geometries and give the electronic structure. The supercell contains six layers of metal, 2 layers of HfO_2, 10 layers of Si, and no vacuum. The supercell is symmetric so there is no overall electric field across the cell. The electron exchange-correlation energy is represented by the generalized gradient approximation (GGA). We use ultra-soft pseudopotentials with a cutoff energy of 400 eV and a $6 \times 6 \times 1$ k point mesh. We also study single supercells containing just metal-HfO_2 and Si-HfO_2 interfaces.

The interfaces between the metal and HfO_2 and between the Si and HfO_2 can have either 0, 1, or 2 oxygens per surface Hf of the HfO_2, that is Hf-rich, non-polar, or O-rich interfaces,[21,22] as shown in Figs. 2(a)–2(c). For the O-rich and non-polar Ni:HfO_2 interfaces, the interfacial oxygen is 4-fold coordinated. For the equivalent case of Si:HfO_2 interfaces, the interfacial oxygens are 4- or 2-fold coordinated, whereas at the Hf-rich interface, the interfacial Hf is 6-fold coordinated.[23]

Now, the three types of interface have very different band offsets, which arise because of the presence of interfacial dipole layers. The band offsets have been previously calculated for the O-rich and non-polar interfaces of HfO_2 with metals[21,22] and also for the case of Si:HfO_2,[23] as shown in Fig. 3. A GW correction of 1.23 eV is added to the valence band offset (VBO) to correct for the band gap error in GGA, following Fiorentini and Gulleri.[24] The O-rich interfaces have a VBO of about 0.7 eV less than the non-polar interface.[20] Similarly, the O-rich Si:HfO_2 interface has a smaller VBO than the non-polar Si:HfO_2 interface.

We have also calculated the formation energy for the different interfaces as a function of the O chemical potential, μ_O. A value of $\mu_O = 0$ corresponds to atmospheric pressure O_2,

whereas a low O chemical potential corresponds to an equilibrium between an oxide and a metal; for example, the Hf/HfO_2 equilibrium lies at $\mu_O = -5.8$ eV. We find that the most stable interface (with lowest formation energy) changes from an O-rich interface at high μ_O to non-polar interface at moderate μ_O and then to an Hf-rich interface at low μ_O. A compilation of formation diagrams for Ni, Mn, Si, and Ti overlayers on HfO_2 is shown in Fig. 4(a). The slope of the interface energy vs. O chemical potential in Fig. 4(a) equals the interface stoichiometry, $+1$ for metal-rich, 0 for non-polar, and -1 for O-rich interfaces, as will be used in Fig. 4(d).

We find that the cross-over chemical potential at which the Hf-rich interface and O-rich interfaces have equal stability varies with the electronegativity of the overlying metal. In fact, this energy correlates most closely with the formation energy of the bulk metal oxide per O atom,[25] as shown in Fig. 4(b). This is somewhat to be expected, as the relative stability of the interface M-O or M-Hf bonds will vary with that of the bulk M-O bonds (M = metal). It is interesting that the Si-HfO_2 interface also fits on this plot, despite Si being a semiconductor not a metal.

Now, the interface dipole per unit area is, therefore, proportional to the density of M-O or Si-O bonds per Hf across each interface. If the two interfaces on opposite sides of the inserted oxide have the same number of M-O bonds, then the dipoles at each interface will oppose each other and tend to cancel, Fig. 4(c). An explicit calculation of this using our supercell model confirms this effect.
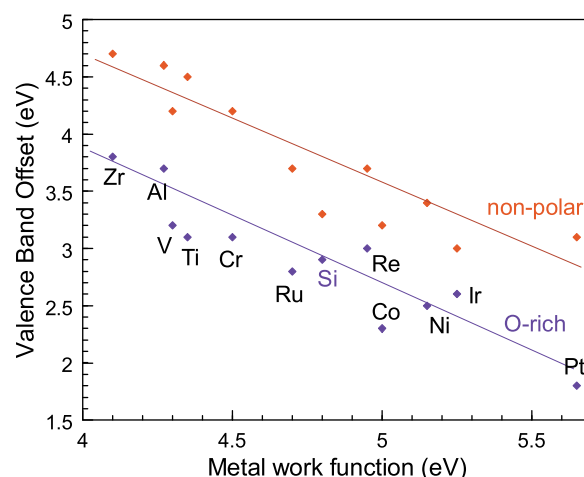

FIG. 3. Calculated valence band offsets for O-rich (polar and non-polar metal – HfO_2 interfaces. Including a GW correction to correct for the GGA band gap error. Note the 0.7 eV offset between the two types of interface due to an interface dipole at the polar interfaces.
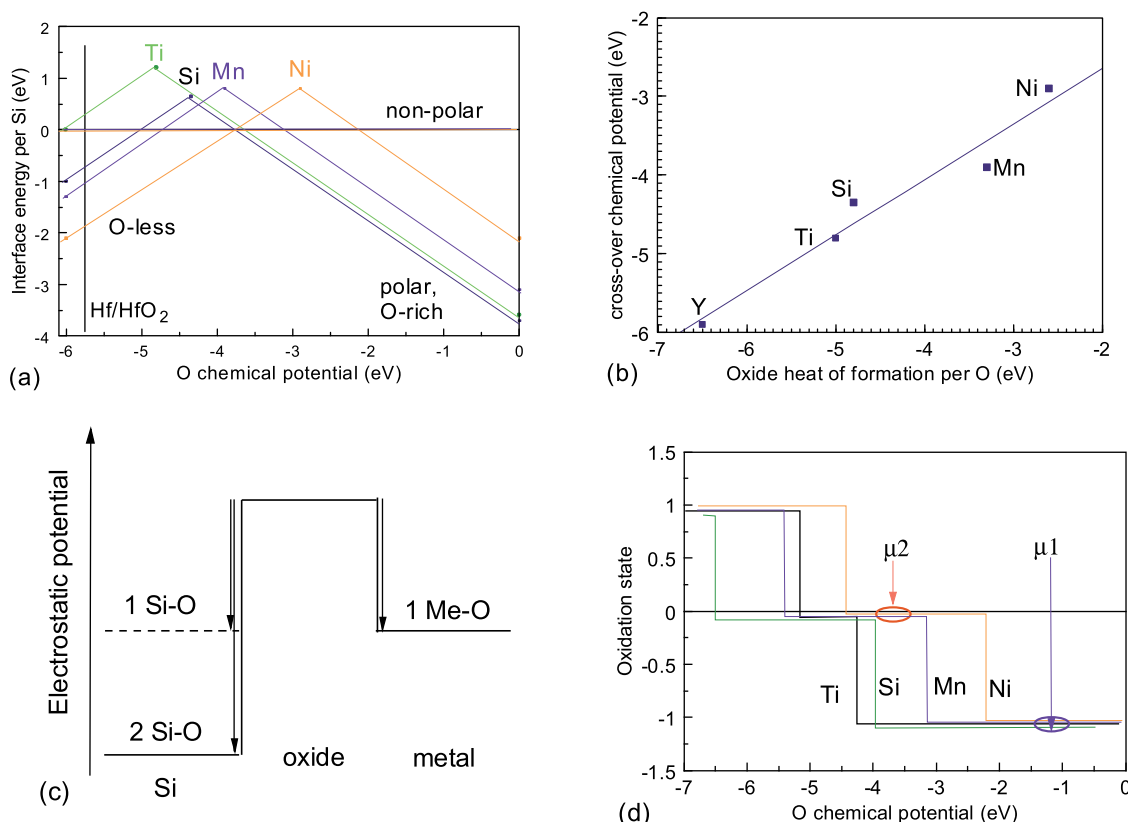
FIG. 4. (a) Interfacial energy vs O chemical potential, of various metals on HfO$_2$. (b) Cross-over chemical potential between stable O-rich and metal-rich interfaces, vs. the bulk metal oxide formation energy per O atom, after Ref. 25. (c) Schematic of effect of interface dipole layers on the band alignments and the effect of dipole cancellations. (d) Oxidation state of the interface given as the slope of interfacial energy vs. O chemical potential in (a). The interface dipole is proportional to the slope. Showing the need for different chemical potential to give no cancellation.

The density of M-O or Si-O interfacial bonds per interface unit cell is just the slope of the interface energy vs. chemical potential, μ_O, in Fig. 4(a), which we plot in Fig. 4(d) for the various metals or Si on HfO$_2$. This means that in general, the dipoles on each interface do not cancel, Fig. 4(c).

It is clear that there will be a net dipole across the MIS structure if the density of M-O bonds on the metal:HfO$_2$ interface differs from that of Si-O bonds on the bottom Si:HfO$_2$ interface. This depends on both the μ_O values at each interface and the oxygen affinity of the metal and the Si. The Si:HfO$_2$ interface will tend to have be O-rich with two Si-O bonds per cell because SiO$_2$ is very stable (formation energy of 4.8 eV per O atom). On the other hand, many metals such as Ni are less electronegative and could have a non-polar interface with a single Ni-O bond per unit cell.

However, this is not necessarily the case for more electropositive metals such as Al, Ti, Zr, or Hf itself. These would need a very low μ_O value to form the non-polar interfaces that would be needed for a net dipole. Nevertheless, a high μ_O value could exist at the Si-HfO$_2$ interface because the HfO$_2$ is deposited in an O-rich ambient, whereas a low μ_O value could exist for the upper metal:HfO$_2$ interface, because the metal is deposited in a metal-rich, O-poor ambient. So at deposition, the correct conditions exist to produce the differing μ_O values at the two interfaces and a net interfacial dipole for a range of metals as overlayers. But would this μ_O difference survive post-deposition annealing? A 2–3 eV chemical potential difference, like a 2 V voltage difference over a 1–2 nm thick film, is large. If the inserted insulator was HfO$_2$, then it might not survive because of the relative easy diffusion of O vacancies in HfO$_2$ above 450 °C (as seen in threshold voltage shifts[26] now known to be due to O vacancy diffusion). There may also be relatively easy diffusion of O or Ti through TiO$_2$. On the other hand, Al$_2$O$_3$, GeN$_x$, SiN$_x$, or a nitrided oxide are all good diffusion barriers and would form stable insertion layers, which could maintain a stable net dipole. The dipole is larger for the case of an oxide than a nitride, because M-O bonds are much more polar than metal-N bonds.

The question of atomic diffusion must be balanced with that of tunneling resistance. It has been noted that TiO$_2$ and ZnO are useful insertion dielectrics for n-type barriers because their small conduction band offsets[27] would allow easier tunneling and thus a lower series resistance.[8,28–30] This is true. The barrier for Al$_2$O$_3$ is larger, but not as high as originally cited[16] because the amorphous phase has a smaller band gap.[31] A way to reduce diffusion might be to use the mixed ion effect, such as in a TiAlO$_x$ alloy which would retain the low conduction band offset of TiO$_2$ and the diffusion barrier property of AlO$_x$. Another possible combination might be a nitrided TiO$_2$ where atomic diffusion is reduced by adding nitrogen, but this would need to be tested.

The present dipole mechanism relying on different oxygen stoichiometries or O ion densities at each interface is somewhat related to that of Kita and Toriumi,[32] but there the interface is between two dielectrics.[33]

In summary, the insertion of an ultra-thin dielectric layer to shift Schottky barrier heights in favor of n-type conduction

occurs because it causes a net interfacial dipole layer as well as an unpinning of the metal Fermi level due to suppression of MIGS. The existence of a net dipole requires a lack of cancellation of the dipoles at the two interfaces, which requires a different O-ion density at each interface. This requires in general maintaining a different O chemical potential at each interface. This is possible during deposition, but it requires that the inserted dielectric is also a diffusion barrier to maintain this factor. This favors the use of dielectrics containing Al_2O_3 or nitrogen to inhibit diffusion as well as those with a low conduction band offset.

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