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Defect Fermi level pinning models for HfO_2 : p-metal gates

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1. Introduction

The implementation of high K oxides with metal gate electrodes has been more difficult due to the 'Fermi level pinning' problem, the difficulty of controlling the effective work function of gate electrode across the Si band gap energy. The effect is largest for p-metals, where the oxidative state of the gate electrode, annealing temperature and EOT roll-off are important [1,2]. Engineering solutions to the pinning problem have been found, but the physical origins of these effects are unsettled. The most likely cause is an extrinsic mechanism due to defects in the oxide. We give a detailed analysis of various vacancy mechanisms including the vacancy model of Akasaka and Shiraishi [3].

2. Results

We have recently showed theoretically that the intrinsic variation of barrier height at HfO_2-metal interfaces with the metal vacuum work function is unpinned [4]. The slope factor is S ~ 1, and the barrier height depends strongly on interface stoichiometry [4]. Thus an intrinsic pinning mechanism is not responsible.

A more likely mechanism is extrinsic band bending due to O vacancies, a metal variation of the Shiraishi pinning model of poly-Si gates [5]. The formation energy of neutral O vacancy in HfO_2 is large, 6.38 eV with respect to the O_2 molecule. Thus, few neutral vacancies are expected normally, so the mechanism is not so obvious. However, the vacancy formation energy varies with oxide Fermi energy, and decreases rapidly for E_F below ~3.9 eV w.r.t the oxide valence band edge, as the vacancy is now doubly positively charged, V^{2+}, Fig. 1. The slope is 2.

$$\Delta G_1 = G_0(n) - q.E_F. \qquad (1)$$

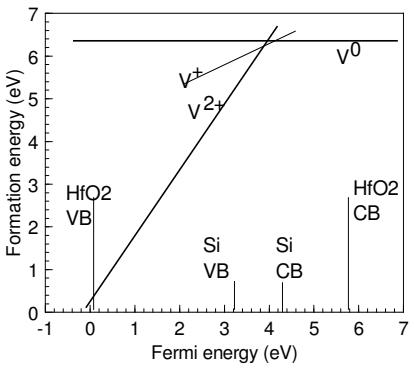

Fig 1. Formation energy of O vacancy in HfO_2, vs. Fermi energy in HfO_2 referred to oxide valence band edge

This effect is directly equivalent to the transfer of 2 electrons to the Fermi level of the metal gate, as in Fig. 2. Nevertheless, the vacancy formation energy never decreases enough in Fig. 1 for relevant E_F values to form many vacancies.

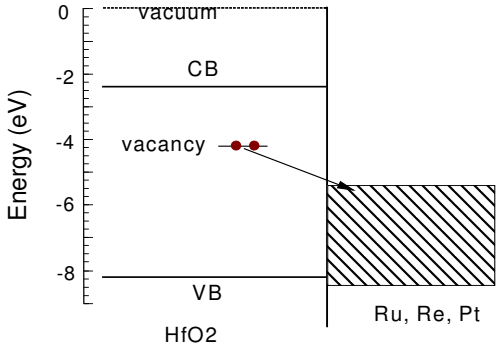

Fig. 2. Equivalent model. Vacancy formed in HfO_2 and its electrons transfer to Fermi level of a metal electrode. Energies referred to vacuum level.

We can also transfer the O arising from the vacancy into the gate metal, to form an MO_n unit. This gains the free energy of MO_n. The overall reaction is

$$O_O + (1/n)M = V_O^{2+} + (1/n)MO_n + 2e^- \qquad (2)$$

We have calculated this reaction energy for various metals, using experimental values of the oxide free energy (Fig. 3).

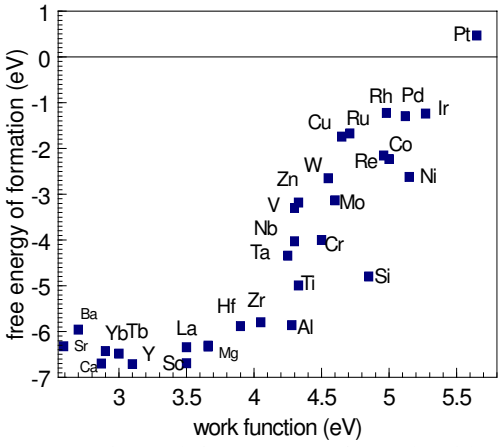

Fig. 3. Experimental free energy of metal oxides per O atom, plotted against work functions of the parent metal.

The vacancy concentration is [V] = n_0.exp (- ΔG/kT) where T ~ 1000^0C. We find that ΔG is never small enough to give a sufficiently large vacancy concentration.

Sufficient vacancy concentrations only result from a modified mechanism of Akasaka, Shiraishi, et al [3]. The O reacts with Si from the underlying channel to form SiO_2, Fig. 4. The net reaction is

$$O_O + Si = V_O^{2+} + ½\ SiO_2 + 2e^- \quad (3)$$

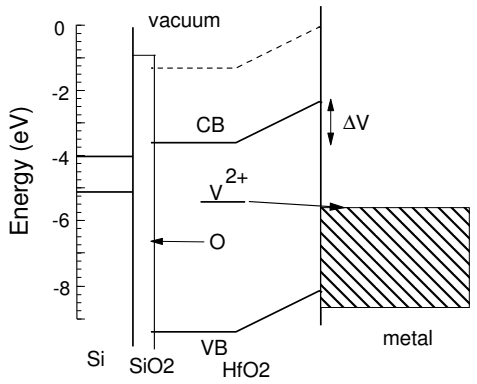

Fig. 4. Schematic band diagram of band bending due to layer of positively charged vacancies, reducing the energy between V^{2+} level and metal Fermi level.

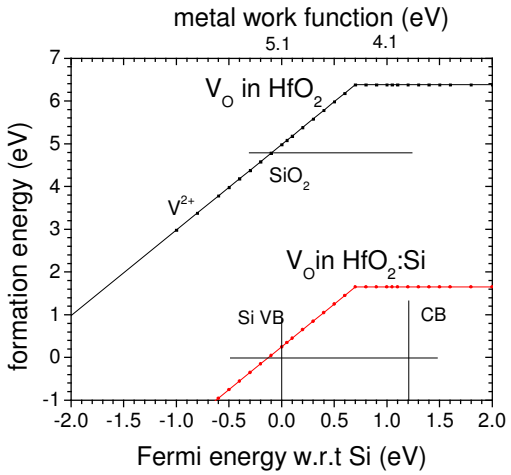

Fig. 5. Formation energy of O vacancy in HfO_2 on Si layer, vs E_F, with formation of SiO_2

The free energy of SiO_2 is 4.73 eV per O, and this is a substantial energy gain in eqn (2), and it reduces ΔG by this amount. This allows reaction (3) to be *exothermic* when E_F falls –0.05 eV below the Si valence band edge, ie for work functiona of above 5.15 eV (Fig 5). Thus, HfO_2 can *oxidise* Si for high WFs, contrary to the usual situation. The positively charged vacancies then cause a band bending of ΔV in the HfO_2 layer, as in Fig. 4 and [2]. This opposes the reaction energy (2).

$$\Delta G' = \Delta G_1 - q\ (E_F - \Delta V)$$

The vacancy concentration can be calculated numerically, and it is found to be large enough to account for Fermi level pinning of p-metals. We find that the effective work function becomes pinned at about the Si VB edge for our values, Fig. 6. The precise value of the pinning energy depends on the defect level and other factors such as the attraction of the charged defect for its image charge, neglected in the initial models.

The need for O diffusion through the SiO_2 interface layer accounts for both the observed temperature dependence [2] and that it only occurs at small EOT, the 'Vt roll-off' effect [1].

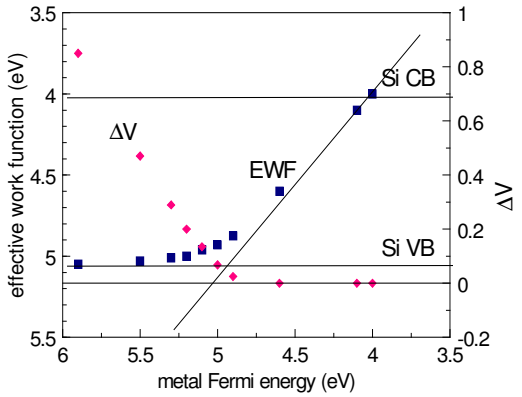

Fig. 6. Calculated metal effective work function vs. metal vacuum work function from model of Fig. 4.

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References

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