Extended Abstracts of the 2007 International Conference on Solid State Devices and Materials, Tsukuba, 2007, pp. 838-839

A-7-1 (Invited)

Schottky Barrier and Stability of Metal/High-k Interfaces; Theoretical View

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1. Introduction

In recent downsizing Si-based devices, SiO_2 gate oxide and poly-Si metal gate are being replaced by high-k materials such as HfO_2 and pure metals, respectively. At these metal/high-k interfaces, the Schottky barriers (effective workfunctions of metals; WF) show unusual behaviors that have never been observed in our device history. When the metal/high-k interfaces are fabricated at low temperature below a few hundred ^oC, the WFs of p-metals such as Au increase, while those of n-metals such as Al decrease. These changes are entirely opposite to the predictions of the conventional charge-neutrality theory of Schottky barrier, which we believed to use as a guiding principle to design the WF. On the other hand, when the interfaces are exposed to high-temperature annealing, the WFs of n-metals keep the original low-temperature positions, while those of p-metals largely decrease and are fixed at a certain energy position, which phenomena is often called the Fermi-level pinning (FLP).

What occurs at metal/high-k interfaces? The purpose of this paper is to explain the mechanisms of unusual behaviors of the WF at these interfaces, reviewing recent relevant studies and showing our recent theoretical results. We are sure that the fundamental understanding of such behaviors will work as a new guiding principle and activate advanced designs of future devices.

2. Schottky Barrier at Metal/high-k Interface

A New Theory of Schottky Barrier

At most of metal/semiconductor interfaces, the Fermi energies of all metals tend to move toward the effective Fermi energies of semiconductors, ϕ_{CNL}. These ϕ_{CNL} are called the charge neutrality levels and are believed intrinsic to individual bulk semiconductors. However, at metal/high-k interfaces, the Fermi energies of p and n metals move toward opposite directions as shown in Fig. 1(a). To explain this unusual change, we developed a new general theory of Schottky barrier [1]. We first review this theory

Due to the large ionicity of high-k materials, the electronic states in metals (MIGS) are difficult to penetrate into high-k layers. This characteristic indicates that the interface electronic properties are quite sensitive to which atomic coupling is realized at the interface. By modeling such interface characters, we can obtain the generalized charge neutrality level ϕ^G_{CNL} as [2]

$$\phi^G_{CNL} = E_{VB} + E_G \frac{|t_{M\text{-}O}|^2 D_{unocc} D_{VB}}{|t_{M\text{-}O}|^2 D_{unocc} D_{VB} + |t_{M\text{-}Hf}|^2 D_{occ} D_{CB}}$$

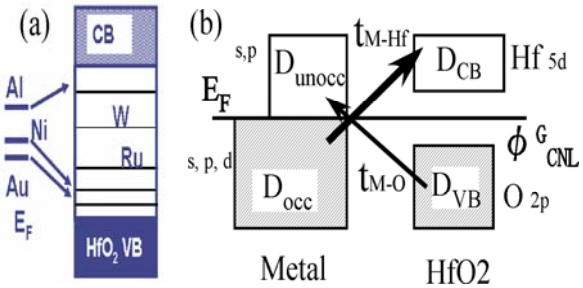

Fig.1 (a) Fermi-energy change at intrinsic metal/HfO_2 contact from vacuum position. (b) Hybridization model of a new generalized Schottky-barrier theory at metal/HfO_2 interfaces.

Here, $t_{M\text{-}O}$ and $t_{M\text{-}Hf}$ denote the interface atom couplings, i.e. electron transfer energies, between metal and O atoms and between metal and Hf atoms, respectively. E_{VB} and E_G are valence-band energy and band gap of HfO_2. Various D s are density of states shown in Fig. 1(b) [2]. This formula is the generalization of conventional theory, thus applying not only to conventional interfaces but also to high-k interfaces [2]. In case of p-metals such as Au, for example, the Au-Hf coupling manifests the interface due to large occupied density of states D_{occ} and thus the strong hybridization occurs between orbitals of Au and Hf as shown by bold arrow in Fig. 1(b). This theory predicts that such hybridization induces the charge transfer from Au to Hf, decreases the Fermi energy, and increases the WF of Au.

Correlation of Atom Coupling and WF at Interfaces

The new theory argues the importance of interface atom coupling, thus the theory being justified by studying the relation between the atom coupling and the WF value at the interface. Figure 2(a) shows the calculated Fermi energy positions of Al and Au by the first-principles theoretical method when monolayer metal atoms are located at various positions of HfO_2 interfaces. It is clearly recognized that Fermi-energy position depends on not only the metal kinds but also the metal-atom positions Especially, both Fermi energies of Al and Au are low when the metal atoms are located on Hf (position 1), while they become high when located over O (position 3). This common variation to both Al and Au clearly justifies our generalized ϕ^G_{CNL} theory.

By analyzing the charge distribution, we can check that such variation of Fermi energy occurs reflecting the charge transfer caused by the orbital hybridization at the interface. It should be noted that, though the electronegativity order is O>Au>Hf, the charge transfer occurs from Au to Hf and from O to Au. This is because Hf and O are not isolated

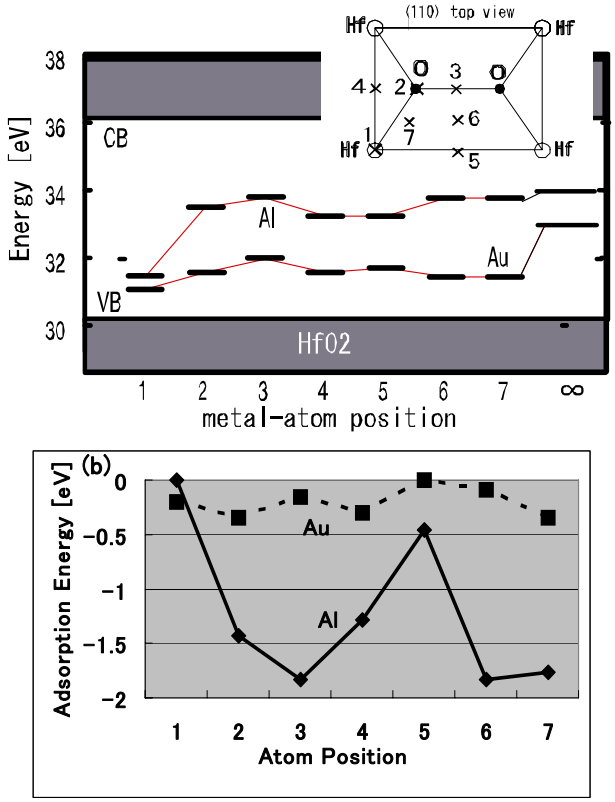

Fig.2 (a) Calculated Fermi-energy positions for Al and Au as a function of adsorption site on (110) HfO_2 surfaces. (b) Calculated adsorption energies of Al and Au atoms as a function of adsorption site. Adsorption sites are numbered in the inset of (a).

atoms but elements of HfO_2, thus existing as Hf^{4+} and O^{2-} ions and simply obtaining and supplying electron charge by the hybridization, respectively.

To judge what interface coupling is realized in real interfaces, we have to consider the stability of interface. Figure 2(b) shows the calculated formation energies of interfaces corresponding to various atom couplings shown in Fig. 2(a). In case of Al, the interface with Al-O coupling has much lower energy than that with Al-O. Thus the interface is made of Al-O and the Fermi energy tends to increases (WF decreases) by the charge transfer from O to Al. On the other hand, in case of Au, both Au-Hf and Au-O couplings have similar energies, which indicate the sensitivity and controllability of the p-metal WFs in the fabrication processes.

3. Fermi-Level Pinning at Metal/high-k Interface

An Oxygen Vacancy Theory of FLP

When the metal/high-k interfaces are exposed to high temperature processes, the FLP occurs only for the p-metal gate cases. Shiraishi et al constructed an oxygen-vacancy theory that the thermal annealing easily produces oxygen vacancies (V_O) in HfO_2 films and induces the FLP through the charge transfer from V_O to metals, as shown in Fig. 3(a) [3]. The rationality of such scenario has recently been examined by the beautiful experiment by Akasaka et al [4] and the precise calculations of V_O defects in HfO_2 by Broqvist and Pasquarello [5].

FLP at Au/HfO_2 Interfaces

To examine whether such charge transfer really occurs and to study the stability of V_O state, we artificially produce V_O in HfO_2 films and performed the first-principles calculations of metal/HfO_2 interfaces. Figure 3(b) shows the calculated WFs of Al and Au as a function of the V_O positions. The formation energy of V_O and the amount of charge transfer are also displayed. It is seen that the charge transfer is really induced and the FLP occurs in case of Au, not depending on the position of V_O. Moreover, the V_O is formed by consuming 2-4 eV energy. These results directly justify the oxygen-vacancy theory for major origins of FLP.

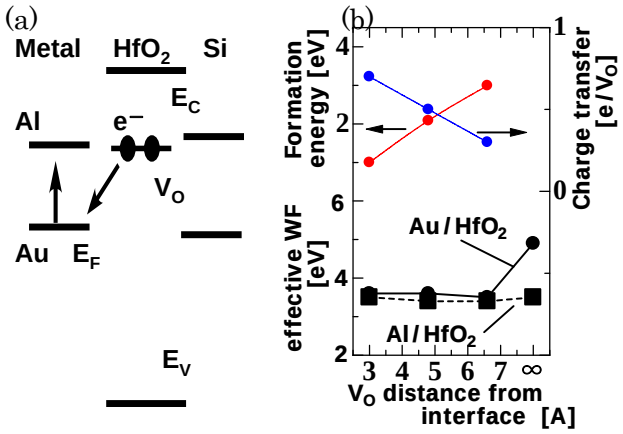

Fig.3 (a) Schematic picture of Fermi-level pinning of p-metals (Au) caused by the charge transfer from V_O to Au. (b) Calculated effective workfunctions of Al and Au when HfO_2 has oxygen vacancy at various positions. ∞ corresponds to no vacancy.

4. Conclusions

The origins of Schottky-barrier change at metal/high-k interfaces were explained from theoretical viewpoints. The unusual variation of intrinsic Schottky barriers is caused by the orbital hybridization at the interface, thus being a natural behavior rather than an anomalous behavior. On the other hand, the Fermi-level pinning is caused by the charge transfer from oxygen vacancy in HfO_2 to metal layers. We showed that the large ionicity of HfO_2 is the key to understand these changes of Schottky barriers.

Acknowledgements

The present work was performed by the High-k net collaboration [2], and supported by the Selete and the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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