A-9-3

First-principles studies on metal induced gap states (MIGS) at metal/high-k HfO$_2$ interfaces

T. Nakaoka[1], *K. Shiraishi[1,2], Y. Akasaka[3], T. Chikyow[2], K. Yamada[4,2], and Y. Nara[3]

(1) Graduate School of Pure and Applied Sciences, Univ. of Tsukuba, Tsukuba 305-8571, Japan
(2) National Institute for Materials Science, Tsukuba 305-0044, Japan
(3) Semiconductor Leading Edge Technology Inc., Tsukuba 305-8569, Japan
(4) Nanotechnology Research Laboratories, Waseda University, Tokyo 169-0041, Japan
Phone: +81-29-853-5911, Fax: +81-29-853-4492, Email: shiraishi@comas.frsc.tsukuba.ac.jp

1. Introduction

Hf-based high-k dielectrics such as HfO$_2$ and their related alloys are expected to become the alternative gate dielectric materials to ordinary SiO$_2$ in future LSIs [1]. In addition to the high-k dielectrics, the use of metal-gates is inevitable in the next generation ULSI devices to achieve much thinner EOT and to avoid Fermi level pinning that is observed in poly-Si gates. In this situation, work function values of various metal gate materials in contact with high-k Hf-based dielectrics have been intensively studied experimentally [2-6], and compared the experimental results with charge neutrality levels obtained by the theoretical calculations [7]. Although several metal work functions can be explained basically based on the charge neutral level theory [2-5], Koyama et al. recently reported the unusual work function behaviors of p-like metals that cannot be explained by the ordinary charge neutrality level theory [6]. They have found that Au and Pt work functions remarkably increase in contact with Hf-based dielectrics contrary to the prediction of the charge neutrality level theory.

In this study, we have performed the first-principles calculations, and the basic electronic structures of metal/high-k HfO$_2$ interfaces have been investigated. In particular, we have focused on the novel characteristics of metal induced gap states (MIGS) at metal/HfO$_2$ interfaces, and our theory has succeeded to reproduce the recently reported unusual behaviours of p-like metal work functions [6].

2. Models and Calculation Procedures

We modelled metals by simple jellium models in which plus ion is distributed uniformly. In the present study, we investigate HfO$_2$ (110) interfaces that are the neutral-charged faces. Our used models have super lattice structures and they consist of 24.9 Å jellium metal regions and 9 atomic layer thickness of HfO$_2$ regions. Our used electron density of jellium metal is the same as Al. For the distance between a jellium metal and a HfO$_2$ layer (d), we choose d=2.54 Å.

The calculations are performed by the first principles calculations within generalized gradient approximation (GGA) [8]. We adopted ultra-soft pseudo potential method [9,10], and pseudo wave functions are expanded by the plane wave basis set with kinetic energy cut-off value of 36 Ry. In the present calculations, the structural optimization has not been performed.

3. Results and Discussions

Figures 1(a)-(b) show the two typical MIGS obtained in the present calculations. It is noticeable that the penetration length of MIGS into HfO$_2$ is within 1~2 atomic layers. This reflects the large band gap of HfO$_2$. The characteristic feature of MIGS at jellium/HfO$_2$ interfaces is that MIGS has large amplitude at cation (Hf) atoms as well as anion (O) atoms; Figure 1(a) shows the typical example of MIGS that have large amplitude at O atoms, and Fig. 1(b) describes the MIGS with large amplitude at Hf atoms. These results indicate that metal wave functions can strongly hybridize with Hf 5d orbitals at metal/HfO$_2$ interfaces, although Hf^{4+} ion radius (0.8 Å) is much smaller than O^{2-} ion radius (1.4 Å).
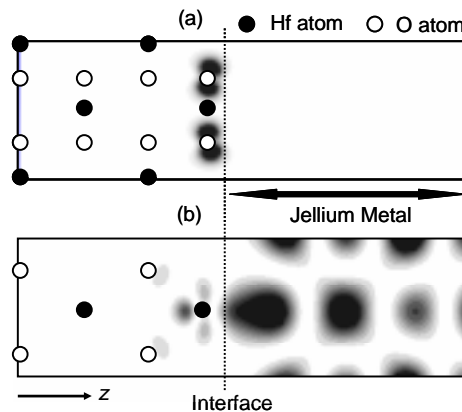

Fig.1: Contour plots of MIGS wave functions. (a) MIGS wave function that has large amplitude at O atoms. (b) MIGS wave function that has large amplitude at Hf atoms.

Large hybridization with Hf 5d orbitals can be explained as follows. In Fig.2, the atomic wave functions of Hf 5d and O 2p are shown. As described in this figure, empty Hf 5d orbital spreads over the outermost region. This delocalized feature of Hf 5d orbital is the cause of large hybridization with metal wave functions.

Next, we discuss the direction of the electron transfer across the interface. In Fig 3, we show the charge density difference averaged over the plane parallel to the
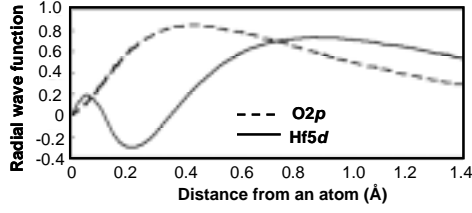
Fig.2: Atomic wave functions of Hf 5*d* and O 2*p*.

interface ($\Delta\rho$). $\Delta\rho$ is defined as follows.

$$\Delta\rho = \rho_{av} \text{ (metal/HfO}_2\text{)} - \rho_{av} \text{ (metal/vacuum)}$$
$$- \rho_{av} \text{ (vacuum/HfO}_2\text{)}.$$

As shown in Fig. 3, the electron transfer from metal region to HfO$_2$ region occurs. The direction of the electron transfer can be explained as follows. The hybridization of unoccupied states of a metal with O 2*p* orbitals results in the electron transfer from HfO$_2$ to a metal. On the other hand, the hybridization of occupied states of a metal with Hf 5*d* orbitals induces the electron transfer from a metal to HfO$_2$. Schematic illustration is given in Fig. 4. Therefore, the present results reflect to the fact that the metal-Hf 5*d* hybridization is larger than metal-O 2*p* hybridization. This electron transfer direction corresponds to the elevation of flat band voltages, and this is consistent with the recent experiments that reports unusual work function increases of Pt and Au in contact with Hf-based oxide [6].
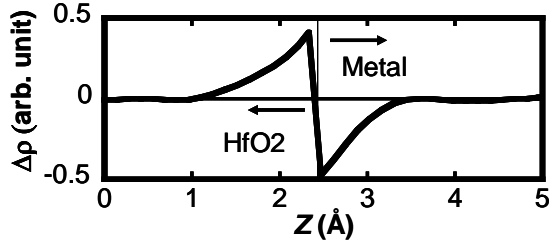

Fig.3: Calculated charge density difference averaged over the plane parallel to the interface as a function of z.

Since the present calculations are based on the simplified jellium model with ideal interface structures, careful investigation is necessary when we compare these results with real experiments. However, our results involve rich information that will shed light on the metal gate selection.
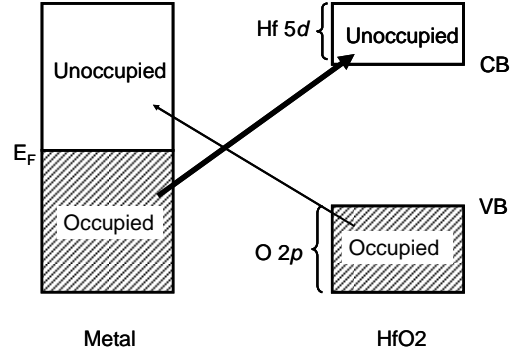

Fig.4: Schematic illustration of charge transfer direction induced by MIGS hybridization.

4. Conclusion

We have performed the first principles calculations of metal/high-*k* HfO$_2$ interfaces, and have clarified the characteristic features of MIGS. The MIGS have large amplitude at Hf atoms as well as O atoms, reflecting the delocalized properties of empty Hf 5*d* orbitals. Moreover, the strong metal-Hf 5*d* hybridization results in the electron transfer from a metal to HfO$_2$, consistent with the recently reported unusual behaviours of p-metal work functions.

References
[1] G. D. Wilk *et al.*, J. Appl. Phys. **89**, p.5243 (2001).
[2] S. B. Samavedam *et al.*, Tech. Dig. IEDM 2003, p.307.
[3] J. H. Lee *et al.*, Tech. Dig. IEDM 2003, p.323.
[4] Y-C Yeo *et al.*, IEEE Trans. EDL, **23**, p.342 (2002)
[5] Y. Akasaka *et al.*, Extend Abstract SSDM 2004, p.196.
[6] M. Koyama *et al.*, Tech. Dig. IEDM 2004, p.499.
[7] J. Robertson, J. Vac. Sci. Technol. B, **18,** p.1785 (2000).
[8] J.P. Perdew *et al.*, Phys. Rev. Lett. **77**, p.3865 (1996).
[9] J. Yamauchi *et al.*, Phys. Rev. B, **54**, p.5586 (1996).
[10] D. Vanderbilt, Phys. Rev. B **41**, p.7892 (1990).