Extended Abstracts of the 2006 International Conference on Solid State Devices and Materials, Yokohama, 2006, pp. 222-223

J-2-4

The first principles calculations of Fermi level pinning in FUSI-PtSi/HfO_2/Si system induced by local distortion of HfO_2

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1. Introduction

The Fermi Level Pinning (FLP) phenomena [1] have been studied for the HfO_2 based high-k gate stack with p+poly-Si gate electrodes for CMOS device applications [1-3]. The FLP is the phenomenon that the Fermi level position of a gate electrode is shifted upward with respect to the position determined by the workfunction of the original material. The FLP phenomena have also been reported for the metal silicide gate electrodes such as PtSi or NiSi [4].

In this paper, we analyze the FLP of PtSi on HfO_2 using the concept of missing oxygen at the interface that is proposed originally for the p+poly-Si FLP [3] based on the first principles calculations. We construct a FUSI-PtSi/HfO_2/Si interface structural model and discuss the Fermi level position of the metal gate at Si substrate by changing oxygen density at the PtSi/HfO_2 interface.

2. Methodologies

Throughout this work, we used the Projector Augmented Plane Wave method with the local density functional theory corrected by the generalized gradient approximation [5-7]. The workfunction (WF) is obtained through the model as illustrated in Figs.1(a) and (b). The WF is determined by the difference between the potential energy at the vacuum region and the Fermi energy of the metal, where we incorporate the dipole corrections [8]. Theoretical values of WF obtained (averaged value of (100), (010) and (001) surfaces) are 4.91eV (Experimental value: 4.9eV) for PtSi and 4.67eV (Exp. 4.68eV) for NiSi. These values are in good agreements with experiments. The Si/HfO_2/FUSI-PtSi interface model structures are formed by using both monoclinic and B31 crystal structures for HfO_2 and mono-silicide PtSi, respectively. After forming the Si/HfO_2 interface, we place the PtSi layer with (010) crystal plane on top of the Si/HfO_2 layer. Our fully relaxed Si/HfO_2/PtSi structure is shown in Fig.1(c). There are two vacuums on the top and bottom of the structure, enabling us to obtain the material value of WF of the PtSi using the top vacuum, and the effective WF of PtSi in relation to the Si substrate using the bottom vacuum.

3. Results and Discussion

First of all, we briefly explain the electronic structures of Si/HfO_2/PtSi with ideal interface structures. In Fig.2, the Local Density of States (LDOS) for the layers specified by (A) to (E) in Fig.1(c), are shown. Figures 2(A) and (C) clearly show the bulk-like LDOS of Si and HfO_2, respectively. There is no extra gap state for the regions from A to C in Fig.1(c). In the region (E), the LDOS shows a metallic character as PtSi is metallic. At the top of the HfO_2 (D) the LDOS shows the metallic character due to the invasion of the metallic wavefunction into the insulator region. This character is a result of the so called metal-induced gap states (MIGS) proposed by Heine [9]. It should be noted that the Fermi energy of the PtSi layer is located at the top of the valence band of the Si substrate. In this ideal interface, the FLP does not exist contrary to the prediction based on a jellium model [10].

According to our proposed concept of missing oxygen at the interface [3], we relaxed the whole Si/HfO_2/PtSi system after removing oxygen atoms at the HfO_2/PtSi interface by 50% and 100%, and calculated the LDOS of Si layer at A in Fig.1(c). In Figs. 3(a), (b) and (c), we show the relaxed structures near the upper interface with 0%, 50% and 100% oxygen missing, and the corresponding LDOS of Si layer in Figs.3(d), (e) and (f). The origin of the energy axis is chosen as the Fermi energy of the PtSi layer. These figures show that the top of Si valence bands moves downward as the oxygen density at the HfO_2/PtSi interface decreases. The Fermi energy shift is estimated to be 0.0, 0.20 and 0.34 eV for 0%, 50% and 100% missing of oxygen at the upper interface. The origin of the FLP is attributed to the appearance of the dipole moment at the interfaces of HfO_2/PtSi

As shown in Fig.3, the oxygen removal leads to the bond formation between the metal layer and the Hf atoms. Nabatame et al. [4] pointed out that the presence of Si-Hf bonding is essential for the FLP. In order to check this view we calculate the same system by changing the Si concentration at the PtSi interface with 100% oxygen missing. Correspondingly, we changed the Pt concentrations from 75% to 100 % at the interface, where 100% Pt means Pt sheet layer at the HfO_2/PtSi interface and we denote such layer as Pt/PtSi. In Fig. 4(a), WF of the PtSi at the top or the bottom layer is plotted as functions of the Pt concentration at the interface. The bulk WF of the PtSi at the top layer does not change at all, whereas the WF at the bottom layer increases as the Pt concentration at the interface increases. The FLP shift ΔWF (=WF_{top}-WF_{bottom}) tends to

vanish as Si-Hf bonds disappear. In Fig.4(b) we plot the one dimensional charge transfer between PtSi and HfO_2 by projecting out the lateral direction. There appears a dipole in Pt/PtSi layer which compensates WF of Pt/PtSi.

To analyze the origin of the FLP, we decomposed the Si/HfO_2/PtSi into two components of HfO_2/PtSi and PtSi, and calculated each WF, separately and finally obtained ΔWF contribution due to the charge flow between them for ideal case as schematically shown in Fig.5(a). In Fig. 5(b), the contribution of films and the charge transfer are shown for the ideal, 100% oxygen missing, and Pt/PtSi structure. The electric charge always flows from the HfO_2 layer into the PtSi layer. In the ideal interface case, the charge flows are the largest among the three cases. The ΔWF becomes largest for 100% oxygen missing case; in which the main contribution to the FLP is not the charge flow but the Si/HfO_2 film dipole itself. This means that the presence of Si-Hf bonding changes the local structure of HfO_2 near the interface as shown in Fig.5(c) and (d) and induces a dipole moment into HfO_2 film and causes the FLP. In the case of Pt/PtSi, the Pt-Hf bonding also creates the 4-fold-site oxygen near the interface and changes the dipole of the HfO_2.

4. Conclusion

Using first principles calculations, we attributed the FLP at the HfO_2/PtSi interface to the missing of oxygen at the interface. The missing of oxygen creates Si-Hf bonding and changes the local structure of HfO_2 film near interface. This local distortion of HfO_2 contributes mainly to the FLP of PtSi/HfO_2.

Acknowledgements

The author (M.I) would like to thank Profs. Masataka Hirose and Jürgen Hafner for their encouragements and discussions. The present work was supported by NEDO.

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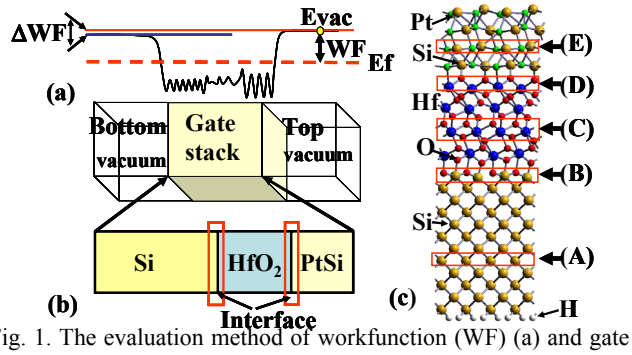

Fig. 1. The evaluation method of workfunction (WF) (a) and gate stack structure (b). Evac refers to the potential energy at vacuum, and WF is the difference between Evac and Ef. The relaxed structure for 12ML-Si/4ML-HfO_2/4ML-PtSi with ideal interfaces is illustrated in (c).

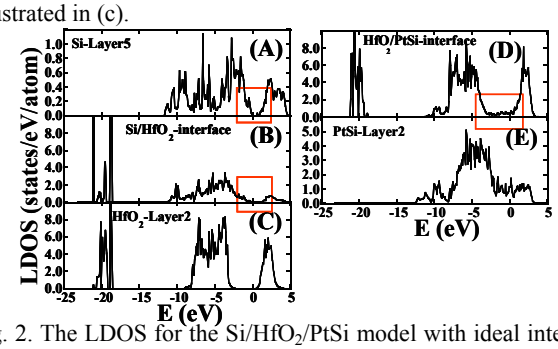

Fig. 2. The LDOS for the Si/HfO_2/PtSi model with ideal interface model are shown in (A) to (E) corresponding to the layers specified in Fig.1(c). The origin is chosen as the Fermi energy of PtSi.

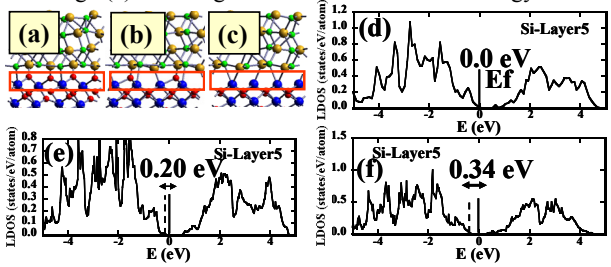

Fig. 3. The atomic structures between HfO_2 and PtSi with 0 %, 50% and 100 % oxygen missing ratios at the interface are shown in (a), (b) and (c), respectively. The corresponding LDOS of the 5th layer of the Si substrate are shown in (d) to (f) respectively.

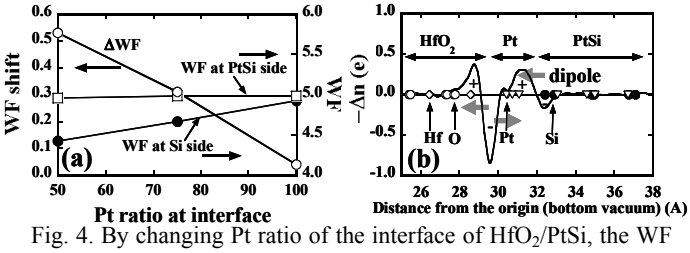

Fig. 4. By changing Pt ratio of the interface of HfO_2/PtSi, the WF are plotted in (a). The WF at PtSi and Si side are plotted by squares and solid circles. The bulk WF of PtSi never changes its physical values, whereas the effective WF decreases as the Pt content at the interface increases. The open circles indicate the Fermi energy shift ΔWF. In (b), the charge transfer at Si/HfO2 and Pt/PtSi interfaces. Also a charge density oscillation appears at the Pt/PtSi layer. Induced dipoles are shown in (b) by grey arrows.

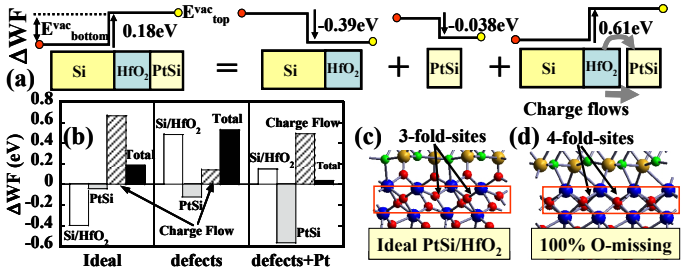

Fig. 5. The ΔWF value is divided into 3 components, contributions from the Si/HfO_2, the PtSi film and the charge flow among the Si/HfO_2 and the PtSi interface for ideal interface, (a) and is summarized in (b). The black column indicates the total sum. In (c) and (d), the structures of HfO_2 in contact to PtSi are shown. Oxygen atoms with 3-fold-sites in (c) change their coordination number and take the 4-fold-sites in (d) due to the Si-Hf bondings.