博士論文（要約）

Study on dipole layer formation and its origin at interfaces between two dielectric materials

（2つの誘電体の界面におけるダイポール層の形成とその起源に関する研究）

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Even though continuous scaling of transistors has benefited the semiconductor industry for the past a few decades, the dramatic increase of the static power due to the leakage has been an obstacle to further miniaturization of the devices. Therefore, high-k materials (materials with high dielectric constants) have been incorporated in gate stacks to reduce the leakage current while maintaining the same performance. However, since the year of 2007, it has been discovered that dipole layer formed at gate dielectric interfaces could shift the threshold voltage (V_{th}) of the transistors. Dielectric interface dipole layer induced V_{th} shift has been demonstrated at various interfaces, mostly at high-k/SiO_2 interfaces. Since the understanding on the effect of high-k material incorporation on V_{th} shift is essential in order to fabricate transistors with desirable V_{th}, the origin of dipole layer formation at dielectric interface, which is still incomplete, needs to be clarified. In this thesis, the purpose of this study is to gain a deeper understanding on the origin by conducting experiments and simulation on various dielectric interfaces in order to clarify the important factors that we should consider to design a gate stacks with desirable V_{fb} by changing the compositions or structures of the dielectrics.

In the first chapter, current process of understanding the origin of dipole layer formation at dielectric interfaces is introduced. Many models have been proposed which state that electronegativity, oxygen vacancy formation, dielectric contact induced gap states, and oxygen density are possible factors to cause charge separation at interface. Unfortunately, none of the proposed models is useful in explaining of both the directions and magnitudes of the dipole layers formed at general dielectric interfaces. However, the oxygen density difference model is a good starting point because it is reasonable in explaining the directions and magnitude of dipole layer formed at most reported high-k/SiO_2 interfaces. In addition, Molecular dynamics (MD) simulation which is an important method to reproduce dipole layer formation at a few high-k/SiO_2 interfaces and investigate the relationship between interfacial charge separation and ionic motion is introduced.

In the second chapter, the detailed experimental methods and simulation procedures is introduced.

In the third chapter, a possible contradiction with the oxygen density difference model which motivate us to study dipole layer formation at MgO/SiO_2 is introduced. The contradiction is possible negative V_{fb} shift by dipole at MgO/SiO_2 cannot be explained by the oxygen density difference model although it

is useful in explaining the directions and magnitudes of dipole layers formed at most reported high-k/SiO_2 interfaces. Therefore, we consider oxygen migration which is the only factor considered in the oxygen density difference model alone is not sufficient to explain the dipole layer formation at general high-k/SiO_2 interfaces. A missing factor that is not included in the oxygen density difference model should be clarified. So, understanding on the origin of the dipole layer formation at high-k oxide/SiO_2 interfaces have been discussed after investigation on the dipole magnitude variation at MgO/SiO_2 interfaces because observation of annealing temperature dependent dipole magnitude implies interface reaction as a different driving force rather oxygen density difference. Further, simulation has been performed to study the relation between atomic migration and charge separation at the interface, indicating that the effect of high-k cation migration should also be taken into account. A general understanding on the origin of dipole layer formation at high-k/SiO_2 interfaces is proposed.

In the fourth chapter, the opportunity of dipole layer formation at non-SiO_2 oxide interfaces is studied because it is suggested that dipole layer formation is an unique phenomenon at high-k/SiO_2 interfaces. Whether dipole layer formation can occur at non-SiO_2 oxide interfaces is still controversial. There is a report indicating no dipole layer formation at HfO_2/Al_2O_3 while an report shows weak dipole layer formation at Y_2O_3/Al_2O_3. Since cation effect is considered to induce a dipole layer at a reactive high-k/SiO_2 interface, as we will discuss in the third chapter. The cation effect at non-SiO_2 oxide is investigated in the example of MgO/Al_2O_3 which is a reactive system with high activation energy. MgO/Al_2O_3 interface is studied which showed a process dependent dipole direction and magnitude. Dipole-induced negative flatband voltage shift is observed after adding one layer of MgO on Al_2O_3/SiO_2/Si and annealing at 800° C. The negative dipole layer formation at MgO/Al_2O_3 is also confirmed by making MIM capacitors and by MD simulation. The MD simulation also indicates a cation effect in determining the negative dipole layer formation. The cation effect is possibly because of the ease to form a intermixed structure for MgO and Al_2O_3. In addition, dipole layer formation at HfO_2/Al_2O_3 has also been examined although there is evidence to indicate no dipole layer formation at HfO_2/Al_2O_3 which is possibly due to a different fabrication process. Our experimental results indicate a weak dipole layer formation at HfO_2/Al_2O_3 the direction of which can be explained by the oxygen density difference model. Therefore, we have demonstrated dipole layer formation at non-SiO_2 oxide interfaces in the examples of MgO/Al_2O_3 and HfO_2/Al_2O_3. The origin of dipole layer formation at non-SiO_2 oxide interfaces is

considered not different from that at high-k/SiO_2 interfaces. However, the driving force could be weak.

In the fifth chapter, to understand the origin of dipole layer formation at general interfaces of two dielectric materials, the effect of anion species at non-reactive dielectric interfaces is discussed. Dielectric interfaces with common cations are studied to avoid the complexity in distinguishing possible cation and anion effects. Experiments on Al_2O_3/AlF_xO_y interface is conducted. Possible dipole-induced flatband voltage shift which is affected by the F/O ratio of the AlF_xO_y layer is observed. MD simulation is also employed to examine the charge separation at Al_2O_3/AlF_3 interface. At this particular interface which has a same kind of cation but different kinds of anions, both anion density difference and valence differences are considered to drive the atomic migration originated charge separation.

Finally, the important factors determining the dipole layer formation at general dielectric interfaces have been proposed. The driving of dipole layer formation is simply discussed in the perspective of free energy minimization.