博士論文（要約）

Study of dopant-induced ferroelectric phase evolution in thin HfO_2 films

（ドーパントによって誘起された強誘電体相 HfO_2 薄膜に関する研究）

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There has been much interest recently in ferroelectric HfO_2 owing to its promising application in ferroelectric related devices, such as ferroelectric memories, ferroelectric field-effect transistors (FeFETs), and negative capacitance FETs (NCFETs). Before achieving these applications, a deeper understanding of the ferroelectric phase stabilization in HfO_2 is urgently needed. Up to now, although ferroelectric HfO_2 has been reported by incorporating various cation dopants (e.g., Si, Y, Al, Zr, Gd, and La), the role of dopants is still not well understood. For example, several fundamental questions, such as what the differences and similarities are between different dopants, and whether the anion doping could trigger the ferroelectricity in HfO_2, are remaining. Therefore, in this work, I paid attention to above concerns by investigating both cation and anion modulation effects on HfO_2 ferroelectricity as well as the thickness dependent ferroelectricity.

Firstly, the dopant-induced HfO_2 ferroelectric transition has been systematically investigated by using various cation dopants (e.g., Sc, Y, Nb, Si, Ge, and Zr) in Chapter 3. Both differences and similarities were discussed between these cation dopants by focusing on two key factors, the dopant ionic size and valence state. Then, I clarified the specific and non-specific effects of the cation modulation on HfO_2 ferroelectricity. It is found that the doping concentration sensitivities on HfO_2 ferroelectric transition are quantitatively different (the specific effect), while the maximum switchable polarization values (P_{SW}) are almost same for all dopants (the non-specific effect).

Secondly, I investigated the anion modulation effect on HfO_2 ferroelectricity and demonstrated that N incorporation could drive the ferroelectricity in HfO_2 films for the first time in Chapter 4. Compared with the cation doping, the HfO_2 ferroelectric transition is more sensitive to the N doping, which is believed due to two effects in N-doped HfO_2 films, the oxygen vacancy formation, and directional N bonding. Moreover, it is surprising to find out that the ferroelectric transition in N-doped HfO_2 film also follows the universal pathway, which has been observed in cation-doped HfO_2 films. On the basis of these findings, it is inferred that the dopant species independent phase transition route is related to the kinetic process of the $T-O-M$ phase transition, in which the metastable ferroelectric O phase formation might significantly reduce the nucleation energy of the M phase. Although both cation and anion dopants can trigger the $T-M$ phase transition, the strain condition and grain size seem to be kept same due to the same film thickness and fabrication processes. Therefore, it is quite understandable to observe a universal ferroelectric phase evolution pathway in doped HfO_2 films.

Moreover, the dopant dependent coercive field (E_c) in ferroelectric HfO_2 has been discussed in Chapter 4 as well. The E_c value is reduced with the doping concentration increase for all dopants (N, Sc, Y, Ge, and Si), which might result from the enhanced effective local field due to the formation of the high-*k* HfO_2 (the *T/C* phases). And it is also noticed that Y-, Sc- and N-doped HfO_2 films present a higher E_c than that of Si- and Ge-doped HfO_2 films. In the polarization pinning model, the high E_c possibly related to the positively charged oxygen vacancy formation, which could pin the ferroelectric dipole, and thus enhance the ferroelectric switching barrier and coercive field.

Besides the dopant effects, the stabilization of the ferroelectric phase in HfO_2 might be affected by other factors, such as the grain size and substrate strain. Thus, I studied the thickness dependent ferroelectricity in doped HfO_2 films in Chapter 5. It is found that P_{SW} is dramatically decreased with the film thickness increase (from 20 to 250 nm), which could not be well explained by the grain size effect. I suspected that the decrease of P_{SW} might be related to the phase transition kinetics or the depolarization field induced by the paraelectric layer. On the other hand, E_c presents a weak thickness dependence in ferroelectric HfO_2, which might be due to the restricted ferroelectric domain growth as the existence of the paraelectric phases.

Finally, I discussed the ferroelectric HfO_2 from the engineering viewpoint in Chapter 6. One critical drawback of ferroelectric HfO_2 is the large E_c, which enhances the operation voltage as well as the risk of dielectric breakdown. Also, the low-*k* interface layer (e.g., SiO_2) formation can cause a reliability issue. Thus, I proposed to use the high-*k* oxide semiconductor as the channel layer. Then, two kinds of HfO_2 based ferroelectric field-effect transistors were fabricated and presented good performances.