Deposition of MeOxNy (Me = Hf, Ti) thin films and its application to high-k dielectrics

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Various high-k materials have been studied as replacement for SiO_2 as a gate dielectric in MOS devices in recent years. However, many important characteristics have yet to be understood for high-k materials. Two candidates are HfO_xN_y and TiO_xN_y due to their reasonably high dielectric constant, low-leakage current, and a relative large band gap. A fundamental problem in their development, however, is crystallization after thermal treatment above 500 ℃, because grain interfaces which serve as leakage current path are formed. Poly-crystallization of thin film generates grain boundaries in thin dielectric film which acts as oxygen diffusion and leakage current path, resulting in high leakage current. Therefore, to remain amorphous state after thermal process is important to achieve the lower leakage current. Moreover, when a high-k metal oxide like HfO_2 is deposited on a Si substrate, an ultrathin low-k interfacial layer, either SiO_x or SiM_yO_x (where M is Hf) forms at the silicon interface. The interfacial layer grows either during the deposition of the high-k dielectric or during post-deposition anneals processes. Based on the previous results, we also realized that there were some arguments of TiO_xN_y crystal growth behavior, such as growth direction and structural property. Therefore, it is important to investigate both the crystallographic phase evolution and interfacial layer after annealing. Recently, it was reported that HfO_xN_y formed by incorporating N into HfO_2 could improve the thermal stability and electrical properties of these gate dielectric films.

In this study, we deposited the hafnium oxy-nitride (HfO_xN_y) and titanium oxy-nitride (TiO_xN_y) thin films because it shows significant reduction in leakage current density and superior thermal and electrical stability and it also exhibits the increase in crystallization temperature depending on the nitrogen concentration. HfO_xN_y thin films were synthesized in the temperature at 500 ℃ on p-type Si (100) substrates by plasma enhanced chemical vapor deposition (PECVD) method, using hafnium tert-butoxide as the hafnium oxide precursor. A mixture of NH_3 (60%) and N_2 (40%) in volume ratio was used as the reactive gas. In addition, we have also investigated the relationship between leakage currents and structures of the coating layers by the effects of composition and annealing temperature. We have also deposited TiO_xN_y thin films on Si(100) substrates at 500℃ using PECVD, and mainly investigated the structural and electrical properties of the oxy-nitride materials. Titanium iso-propoxide was used as precursor with different nitrogen flow rate to control oxygen and nitrogen contents in the films. The characteristics of film growth orientation and structure as well as morphology change behavior were also analyzed by XRD, TEM/TED, AFM, and SEM. Changes of chemical states of constituent elements in the deposited films were examined by XPS analysis. Deposition at higher nitrogen flow rate results in finer clusters with a nano-scale grain size and a slower growth rate. The obtained values of dielectric constant from HfO_xN_y and TiO_xN_y thin films were 15 and 10, respectively and the nitride layers highly decreased the leakage current density rather than oxide layers, resulting in improving thermal stability as well as electrical property.

KEY WORDS: HfO_xN_y and TiO_xN_y thin films, PECVD, high-k dielectrics, leakage current density, thermal stability, structural property

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