Control of oxidation and reduction in HfSiON/Si through N₂ exposure

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Introduction

Further downscaling of complementary metal-oxide-semiconductor field effect transistors is severely limited by the thickness of SiO₂ dielectric films, which suffer from excess direct tunneling leakage currents. High dielectric constant (high-k) materials such as HfO₂, HfSiO, and HfSiON have therefore been used as gate dielectrics alternatives to conventional SiO₂. However, several problems need to be solved such as silicidation of HfO₂ and oxidation of Si substrate in high-temperature annealing processes for dopant activation. These reactions can lead to degradation in the dielectric properties of high-k materials; Hf-silicidation due to a reduction of HfO₂ causes an increase of leakage current, while Si oxidation results in an increase of EOT (equivalent oxide thickness). It is reported that dielectric films are reduced or oxidized depending on the oxygen partial pressure of ambient gas [1]. Thus, it is necessary to explore proper conditions where these reactions are suppressed and elucidate the mechanism of suppression to improve the high dielectric properties. In this study, we have investigated thermal stability of HfSiON/Si gate stack structures upon annealing under a controlled ambient condition, by means of photoemission spectroscopy.

Experimental

HfSiON (N=20 %) films were deposited on clean p-type Si (001) substrates by atomic layer deposition. The physical thickness of these dielectric films was estimated to be 2 nm from ellipsometry measurements. Each sample was annealed at 1050 °C for 1 min in N₂ or O₂ gas ambient. It should be noted that N₂ gas contains 0.2 ppm of O₂ as a residual impurity. Photoemission measurements were performed at the undulator beam line BL-2C of the Photon Factory in High-Energy Accelerator Research Organization (KEK).

Results and Discussion

The photoemission spectra of Hf 4f and Si 2p core levels were obtained from HfSiON film annealed under several conditions of N₂ or O₂ ambient pressure. By analyzing chemical bonding states of these elements, it was found that the reduction of Hf-oxide component and the oxidation of Si substrate occurred for the sample annealed at N₂ partial pressure (P₁) of 10 and 760 Torr, respectively. However, no chemical reaction was detected for the sample annealed at P₂ of 100 Torr. Thus we have found that the annealing condition is most suitable for suppressing both the oxidation and reduction reactions effectively.

Next, we investigate the dependence on ambient gas species. Photoemission measurements were performed after annealing HfSiON/Si in O₂ ambient. The thicknesses of Si oxide were evaluated using the peak-intensity ratio of Si-oxide to Si-substrate from Si 2p spectra. The result was shown in Fig. 1. A straight line at around 3.2 nm denotes the thickness of the as-grown sample. As can be seen in Fig. 1, the thickness variation with changing P₂ is less than that in the N₂ ambient gas. Furthermore, upon annealing in N₂ gas, less partial pressure of O₂ is required for an appropriate annealing condition. This is probably because nitrogen molecules play an important role in retard of the reduction reaction [2].

The authors would like to thank Selete Inc. for providing high-k samples.

References


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