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Control of oxidation and reduction in HfSiON/Si through N_2 exposure

Hiroyuki KAMADA*[1], Tatsuhiko TANIMURA[1], Satoshi TOYODA[1-3], Hiroshi KUMIGASHIRA[1-3], Masaharu OSHIMA[1-3], Guo Lin LIU[4], Ziyuan LIU[4], Kazuto IKEDA[4], and Takae SUKEGAWA[4]
[1]Department of Applied Chemistry, The University of Tokyo, Tokyo 113-8656, Japan
[2]Core Research for Evolutional Science and Technology, Japan Science and Technology Agency, Tokyo 102-0075, Japan
[3]Univ-of Tokyo Synchrotron Radiation Research Organization, 113-8656, Japan
[4]Semiconductor Technology Academic Research Center, Kanagawa 222-0033, Japan

Introduction

Further downscaling of complementary metal-oxide-semiconductor field effect transistors is severely limited by the thickness of SiO_2 dielectric films, which suffer from excess direct tunneling leakage currents. High dielectric constant (high-*k*) materials such as HfO_2, HfSiO, and HfSiON have been therefore used as gate dielectrics alternatives to conventional SiO_2. However, several problems need to be solved such as silicidation of HfO_2 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 HfO_2 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 N_2 or O_2 gas ambient. It should be noted that N_2 gas contains 0.2 ppm of O_2 as a residual impurity. Photoemission measurements were carried out 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 4*f* and Si 2*p* core levels were obtained from HfSiON film annealed under several conditions of N_2 or O_2 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 N_2 partial pressure (P_{N2}) of 10 and 760 Torr, respectively. However, no chemical reaction was detected for the sample annealed at P_{N2} 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 O_2 ambient. The thicknesses of Si oxide were evaluated using the peak-intensity ratio of Si-oxide to Si-substrate from Si 2*p* 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 P_{O2} is less than that in the N_2 ambient gas. Furthermore, upon annealing in N_2 gas, less partial pressure of O_2 is required for an appropriate annealing condition. This is probably because nitrogen molecules play an important role in retard of the reduction reaction [2].

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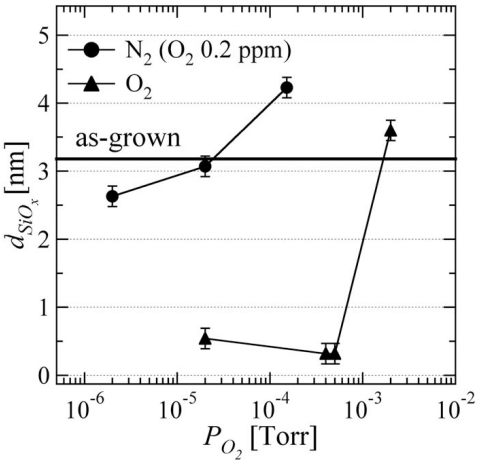

Fig. 1 SiO_2 equivalent thickness of dielectric films as a function of O_2 partial pressure (P_{O2}).

References

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* kamada@sr.t.u-tokyo.ac.jp