High-k Gate Dielectrics and Devices Topical Conference Room Hall A-C - Session DI-TuP

Poster Session

DI-TuP1 Investigation of Initial Growth Stage of HfO@sub 2@ Films on Si (100) Grown by Atomic-layer Deposition using In-situ Medium Energy Ion Scattering, ***H.S. Chang***, *H. Hwang,* Kwangju Institute of Science and Technology (KJIST), South Korea*; M.-H. Cho, Y.J. Cho, K.J. Kim, D.W. Moon,* Korean Research Institute of Standards and Science (KRISS), South Korea

The initial growth stage of HfO@sub 2@ films on p-type Si(100) grown by atomic-layer deposition (ALD) was investigated using in-situ medium energy ion scattering (MEIS). The interaction between adsorbed HfCl@sub 4@ molecules and Si substrate was examined in relation to the film thickness, substrate temperatures, and surface states of the Si substrates. Interfacial reaction between Hf and Si at the initial growth stage was occurred and significantly depended on the surface state of the Si. The hafnium silicate with an amorphous structure was grown on the oxidized Si substrate at an initial growth stage. In particular, the interfacial layer thickness and the stoichiometry of the layer were depended on the surface state of Si substrate. As thickness of the film increased, the silicate formation was gradually changed into HfO@sub 2@ state. The physical analysis of the films with XPS and TEM also supported the interfacial reactions. Based on the interfacial interaction at the initial growth stage, we suggested the model for the interaction between Hf and Si at the initial growth stage in relation to the atomic size, bonding characteristics, and formation energy. This study will be helpful to understand the interfacial reactions at the initial growth stage and to control the reactions for the application of high-k dielectrics.

DI-TuP2 Effects of Annealing Temperature on the Characteristics of HfO@sub 2@/HfSi@sub x@O@sub y@ High-k Gate Oxides, ***H.-D. Kim***, *Y. Roh, D. Jung, N.-E. Lee,* Sungkyunkwan University, Korea

Several candidates for the future high-k gate oxides have been extensively studied by many research groups to overcome the problems such as large leakage current caused by the direct tunneling through extremely thin SiO@sub 2@. Recently, we reported that simple oxidation of sputtered Hf films on Si produces HfO@sub 2@/HfSi@sub x@O@sub y@ high-k oxides with excellent properties. We argued that the effective k of HfO@sub 2@/HfSi@sub x@O@sub y@ film may be controlled by changing the thickness ratio between HfO@sub 2@ and HfSi@sub x@O@sub y@. In this work, we further investigated the characteristics of HfO@sub 2@/HfSi@sub x@O@sub y@ high-k gate oxides to clarify the roles of annealing process. The 1.5 nm Hf film was directly deposited on Si substrate by sputtering at plasma power of 50 W for 4 min. Oxidation was performed at 500 °C for 60 min, followed by annealing at 500-900 °C in furnace under N@sub 2@ ambient. Pd gate metal was thermally evaporated on the HfO@sub 2@ film. Using the physical and electrical measurement techniques, we confirmed that the oxidation of the thin Hf films on Si results in the HfO@sub 2@/HfSi@sub x@O@sub y@ stack layer with the excellent electrical properties; negligible hysteresis, excellent EOT value (1.2 nm) and low leakage current (~2 X 10@super -3@ A/cm@super 2@ at 1.5 V after compensating V@sub fb@). Furthermore, we found that the level of leakage current decreases as annealing temperature increases. However, over 500 °C, annealing deteriorates the EOT value; e.g., 1.2 and 1.7 nm EOT values were obtained from 500 and 900 °C samples, respectively. We speculate that both thickness increase of HfO@sub 2@/HfSi@sub x@O@sub y@ films and the formation of additional SiO@sub 2@ layer between HfSi@sub x@O@sub y@ and Si cause these phenomena. We therefore suggest that annealing temperature must be carefully controlled to maintain the excellent characteristics of HfO@sub 2@/HfSi@sub x@O@sub y@ high-k gate oxides.

DI-TuP3 Thermal Stability of Al- and Zr- doped HfO@sub 2@ Thin Films by DC Magnetron Sputtering, ***Y.E. Hong***, *Y.S. Kim, D.H. Ko, D.W. Lee,* Yonsei University, South Korea*; J.-H. Ku,* Samsung Electronics, South Korea

Currently, high-k materials are under consideration as replacements for SiO@sub 2@ because physically thick film with high dielectric constant is possible solution for reducing leakage current. Among some metal oxides such as Al@sub 2@O@sub 3@, ZrO@sub 2@, and HfO@sub 2@, particularly HfO@sub 2@ exhibits excellent material properties such as high permittivity of up to 30, energy gap of 5.6eV and thermal stability in contact with silicon. However, after post-deposition annealing above 400°C, as-deposited amorphous HfO@sub 2@ crystallizes which may induce grain boundary leakage current. In addition, annealing in an oxygen rich ambient leads to fast diffusion of oxygen through the HfO@sub 2@, resulting in the growth of uncontrollable interfacial layer between HfO@sub 2@ and silicon substrate. In this study, we investigated comparatively the thermal stability properties of HfO@sub 2@ based films with Al- and Zr-doping. HfO@sub 2@ was prepared by sputtering Hf target in a mixture of oxygen and argon at room temperature. Al- and Zr-doping is achieved by co-sputtering using Al and Zr target. And the compositions of the doped films were controlled by target power. After the formation of the films, annealing at 500~900°C for 5min by furnace in N@sub 2@ ambient was followed. The compositions and the chemical states of the oxide films were confirmed by RBS and XPS. The crystallization temperature of the HfO@sub 2@ film which has 10% Al was 900°C. However, most of the Zr-doped HfO@sub 2@ films were crystallized from as deposited condition. As an annealing temperature increases, HRTEM analyses of the all doped films show the increased interfacial layer thickness, and the interfacial layer of the Zr-doped HfO@sub 2@ films is thicker than the Al-doped. The increased CET and leakage current values through CV/IV measurements and dielectric constant difference between Al- and Hf-doped HfO@sub 2@ films will be presented and discussed.

DI-TuP5 NH@sub 3@ Nitridation Effect on HfO@sub 2@-Al@sub 2@O@sub 3@ Films in the MOS Capacitor, ***C. Lee***, *J. Choi, M. Cho, C.S. Hwang, H.J. Kim,* Seoul National University, Korea

High-k gate dielectrics, such as HfO@sub 2@ and Al@sub 2@O@sub 3@, have been investigated as an alternative to SiO@sub 2@ for low power device due to high dielectric constant, thermodynamic compatibility of the interface with Si substrate, and a relatively large band gap. We investigated the nitrogen diffusion behavior and electrical characteristics, especially flat band voltage (V@sub fb@) shift and V@sub fb@ hysteresis by NH@sub 3@ nitridation of the MOS capacitors. The nitrided MOS capacitors include the various high-k gate dielectric stacks such as Pt gate/HfO@sub 2@/p-type Si, Pt gate/HfO@sub 2@-Al@sub 2@O@sub 3@/p-type Si, and Pt gate/capping Al@sub 2@O@sub 3@-HfO@sub 2@-Al@sub 2@O@sub 3@/p-type Si. HfO@sub 2@ and Al@sub 2@O@sub 3@ films were deposited on p-type epitaxial Si (100) wafers with a resistivity of 1 @ohm@cm by atomic layer deposition (ALD) technique using HfCl@sub 4@, Al(CH@sub 3@)@sub 3@ and H@sub 2@O at 300°C after RCA SC1 and HF cleaning. Post deposition annealing (PDA) of the samples was performed with rapid thermal annealing (RTA) at 700°C, 800°C, and 900°C in NH@sub 3@ for 30 seconds. Post-metallization annealing (PMA) of Pt-top electrodes was performed at 400°C for 30 min. under a 5% H@sub 2@ + 95% N@sub 2@ atmosphere. V@sub fb@ shifted negatively with increasing nitridation temperature, but it moved positively with increasing Al@sub 2@O@sub 3@ thickness. HfO@sub 2@-Al@sub 2@O@sub 3@ film showed excellent V@sub fb@ shift and hysteresis characteristics when it was post-metallization annealed in NH@sub 3@ at 800°C for 30 seconds. NH@sub 3@ nitridation effect on Pt gate/HfO@sub 2@-Al@sub 2@O@sub 3@/p-type Si MOS capacitors with increasing PDA temperature was analyzed by electrical evaluation, Auger Electron Spectroscopy (AES), atomic force microscopy (AFM) and high-resolution transmission electron microscopy (HRTEM).

DI-TuP6 Structural and Electrical Characterization of Aluminum Oxynitride Thin Films Obtained by RF-Sputtering, ***J.J. Araiza***, UAZ, Mexico*; M.A. Aguilar,* CICATA-IPN, Mexico, Spain*; C. Falcony, M. Jergel,* CINVESTAV-IPN, Mexico

The structural and electrical characteristics of aluminum oxynitride thin films deposited on silicon substrates by rf-sputtering are reported. The properties of the films were studied as a function of the deposition parameters, such as substrate temperature, RF sputtering power and the relative amount of argon and nitrogen gases introduced to the chamber. The films were characterized by atomic force microscopy, transmission and scanning electron microscopy, X ray diffraction, Infrared and Uv-vis spectroscopy and ellipsometry. Metal-Oxide-Semiconductors structures were also fabricated with the films deposited. Films with characteristics close to aluminum oxide and aluminum nitride were obtained, depending on the deposition parameters. It was found that the films can withstand electric fields up to 4.5 MV/cm, without observing destructive breakdown, with dielectric constants up to 8.7. In addition, the as deposited films present a surface roughness lower than 1.6 nm, refractive indexes from 1.5 to 2.0 and deposition rates up to 7.0 nm/min.

DI-TuP7 Plasma and Thermal Etching of High-k Materials for ALD Chamber Cleaning, *B. Ji,* ***D. Wu****, R.M. Pearlstein, S.A. Motika, E.J. Karwacki, M.J. Plishka,* Air Products and Chemicals, Inc.

High dielectric constant (high-k) materials such as Al@sub 2@O@sub 3@, HfO@sub 2@, and ZrO@sub 2@ are deposited onto semiconductor wafer surfaces by atomic layer deposition (ALD) in integrated circuits manufacturing. High-k ALD reactors must undergo periodic chamber cleaning to remove deposition residues from the internal surfaces of the reactor in order to maintain production yield. Due to their high chemical inertness and extremely low volatility, etching and cleaning high-k deposition residues has been technically challenging. By combining thermochemical calculations and experimental screening, we have identified BCl@sub 3@ as the most effective reagent for removing high-k materials from ALD chambers. We will report both plasma and thermal etching of Al@sub 2@O@sub 3@, HfO@sub 2@, and ZrO@sub 2@ using BCl@sub 3@. We will discuss the chemical mechanism of BCl@sub 3@-metal oxide reaction, and the influence of various process parameters on high-k materials etch rate.

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