High-k / substrate interface reaction by plasma assisted ALD and PVD
プラズマ支援 ALD 及び PVD での high-k 膜/基板界面反応

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Plasma assisted atomic layer deposition (PAALD) and Plasma enhanced physical vapor deposition (PEPVD) are the candidates of plasma utilized growth method for high-k dielectrics in micro- and nano-electronic applications. In PAALD, the atomically smooth HfO_2 film is grown on Si with TEMAH and O_2 ICP exposure although the interfacial SiO_2 thickness is increased with the ALD cycle. In PEPVD, the interface reaction of Hf metal with SiO_2 inhibits the increase although the film thickness and flatness is limited with the surface diffusion or film strain. The non-uniformity is suppressed with the small (10%) coverage of Ti over Hf metal.

1. Introduction

For reliable high-k gate dielectric film formation of high performance MOSFETs, Hafnium based oxides are commonly used currently. There are several issues on the high-k film such as leak current, uniformity, stabilities over annealing etc. The interfacial layer of SiO_2 needs to be controlled on its thickness due to the requirement of lower EOT (Equivalent oxide thickness) value. For the application of plasma generated reactants for the high-k growth process, PAALD and PEPVD are the candidates that can control the nano-thin film properties. The advantage of PAALD is the superior conformability and controllability of the thickness. In high-k PVD, the use of metal source enables the lower impurity of the film due to the absence of carbon atoms induced by CVD/ALD processes that use metalorganic precursors [1]. The merit is also applicable to the plasma enhanced process as well. The detailed surface chemistry of the nano-thin interfacial SiO_2 layer between the high-k material and Si substrate within PAALD and PEPVD is studied.

We clarify the kinetics using in-situ ultra high vacuum scanning probe microscope (UHV-SPM), XPS and SEM from the viewpoint of the nanoscale reactions of the high-k material and interfacial layer induced by the plasma exposure.

2. Experimental

The PEPVD growth chamber consists of the UHV-SPM (Omicron VT-AFM) with e-beam evaporator for Hf deposition and the inductive coupled plasma (ICP) chamber pumped with TMP/RP. The 10 turn N_2 ICP with 50 MHz excitation is separated from the UHV chamber by the gate valve. The Si(100) sample with SiO_2 (thick ~ 1.0 nm) is introduced from the ICP chamber and degassed in the UHV at 750 K. The sample is exposed to the Hf and Ti beam at room temperature. The total metal layer is equivalent to the HfO_2 film of 2.5 nm thick. Hf(Ti)SiON film is formed by the exposure of N_2 ICP (50W) for 30 min. The N_2 pressure is 30 mTorr and the distance of the coil end and the sample is 30 mm.

The PAALD chamber is equipped with the liquid MFC and evaporator for TEMAH supply with nitrogen buffer. O_2 ICP source is equivalent to the PEPVD and the pressure is 380 mTorr. The growth temperature is 150 ℃. The interval of the nitrogen flow between the TEMAH supply and O_2 ICP is 1 min.

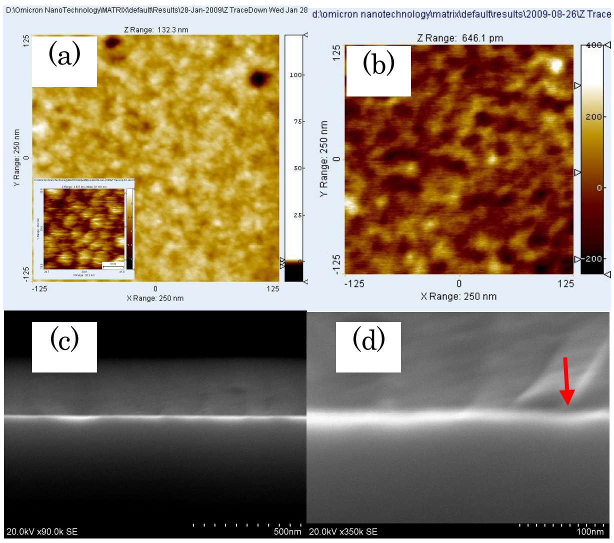

Fig.1. (a) AFM and (c,d) SEM image of HfSiON film by PEPVD with N_2 ICP exposure to Hf metal (2.5nm) on SiO_2/Si(100). (b) $Hf_{0.9}Ti_{0.1}SiON$ film grown by PEPVD.

3. Results and discussion

Figure 1 (a) shows the AFM image of PEPVD grown HfSiON film. The top surface has nano-scale roughness due to the initial Hf nano-particles (shown in inset) of 3-7 nm in diameter. The grown film has dispersed holes around 0.8 nm in depth. The cross-sectional SEM image of the film in Fig.1(d) shows that the holes are generated due to the fewer coverage of the Hf. Wider view in Fig.1(c) shows the film thickness varies with several hundred nm lateral period. Fig.1(b) shows the 10 % Ti coverage over Hf suppresses the hole generation. Film strain or surface diffusion can be the origin of the holes.

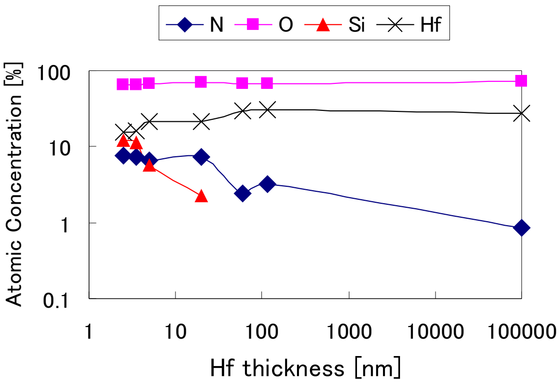

Fig.2. Atomic concentration change of HfSiON film grown by PEPVD for increased initial Hf thickness.

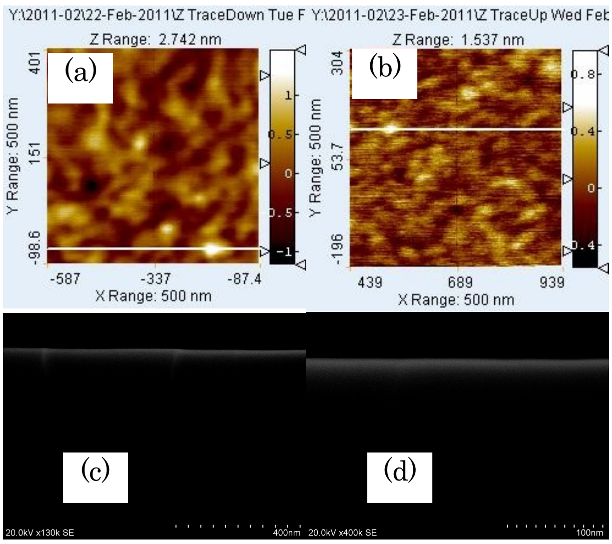

Fig.3. (a) AFM and (c,d) SEM image of HfO_2 film by PAALD on SiO_2/Si(100) with pure O_2 ICP. (b) Use of O_2(1%)/Ar(99%) ICP reduces surface roughness.

Figure 2 shows the atomic concentration change of the PEPVD grown HfSiON film for increased Hf thickness after 1 min. N_2 ICP exposure. The N atom incorporation into the film is enhanced with the decrease of the initial Hf metal thickness showing higher reactivity of Hf nano-particles which have higher surface to volume ratio. Si fraction in the film is increased with the N_2 ICP exposure time (not shown here) showing Si of SiO_2 layer diffuses to the Hf layer due to the plasma exposure. XPS spectrum shows the diffused Si react with N atoms as the plasma exposure time increases.

Figure 3 (a) shows the AFM image of the 20 cycle PAALD grown HfO_2 film. The surface is free from holes and the RMS roughness is 0.23nm. The cross-sectional SEM in Fig.3 (c) and (d) shows the film thickness is uniform from 10 nanometer to 1 micrometer range. Figure 3 (b) shows the HfO_2 film grown by PAALD with O_2(1%)/Ar(99%) ICP. The Ar dilution leads to the twice increase of metastable

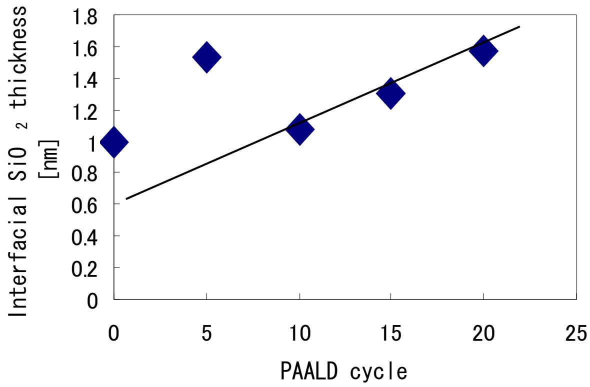

Fig. 4. Interfacial SiO_2 layer thickness with the PAALD cycle.

$O(^1D)$ atom density in the plasma [3] and three times increase of the flux to the surface [4]. The improved RMS roughness of 0.11 nm is due to the increased $O(^1D)$ flux which enhances the oxidation of TEMAH on the growing surface.

Figure 4 shows the the change of interfacial SiO_2 layer thickness for increased PAALD cycle. The PAALD cycle increase leads to the increase of the SiO_2 thickness due to the increase of the plasma exposure time. However, the trend of the increase shows that the SiO_2 thickness in the first growth stage is thinner than the initial SiO_2 thickness of the wafer. This implies the initial SiO_2 layer reacts with the chemisorbed TEMAH under O_2 ICP exposure.

In conclusion, interfacial reaction of the initial SiO_2 layer with the deposited high-k material under plasma exposure is examined for PEPVD and PAALD. In PEPVD, the interfacial reaction leads to the incorporation of Si into the high-k film layer. In PAALD, interfacial reaction leads to the decrease of the SiO_2 layer in first growth stage. Overall, the thickness uniformity of the PAALD grown film surpasses that of PEPVD, while PAALD have more carbon incorporation into the film.

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