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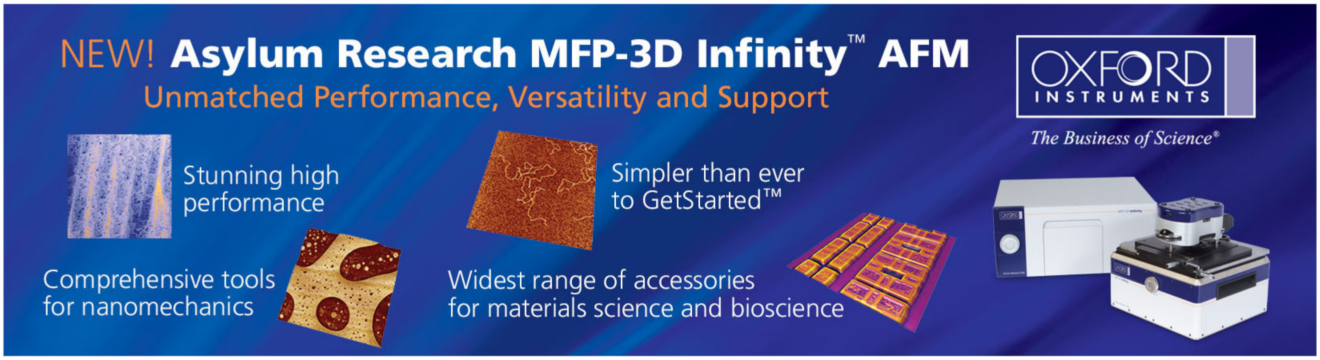

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Suppression of interfacial reaction for HfO_2 on silicon by pre-CF_4 plasma treatment

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In this letter, the effects of pre-CF_4 plasma treatment on Si for sputtered HfO_2 gate dielectrics are investigated. The significant fluorine was incorporated at the HfO_2/Si substrate interface for a sample with the CF_4 plasma pretreatment. The Hf silicide was suppressed and Hf–F bonding was observed for the CF_4 plasma pretreated sample. Compared with the as-deposited sample, the effective oxide thickness was much reduced for the pre-CF_4 plasma treated sample due to the elimination of the interfacial layer between HfO_2 and Si substrate. These improved characteristics of the HfO_2 gate dielectrics can be explained in terms of the fluorine atoms blocking oxygen diffusion through the HfO_2 film into the Si substrate. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2337002]

Hafnium oxide gate dielectrics are considered to be the most promising candidates to meet the future ultralarge-scale-integration (ULSI) technology.[1,2] However, it is still a big challenge to introduce the high-*k* materials into the complementary metal oxide semiconductor process, especially because of difficulties in controlling the film thickness. During the film growth and postprocessing, the formation of an interfacial layer (IL) is likely and limits the reduction of the effective oxide thickness (EOT).[3,4] The reasons for this unwanted layer are the presence of excess oxygen during the film growth that initially oxidizes the Si surface[5] and Si diffusion into the film producing a silicate layer.[6] Therefore, methods such as cosputtering of silicon and aluminum with hafnium to deposit hafnium silicate and aluminate dielectrics[7,8] and the use of nitric gas for chemical vapor deposition[9] or oxidizing sputtered metal nitride such as HfN to form hafnium oxynitride (HfON) films[10] are used to improve dielectric quality. However, the nitridation technique induces positive interface charges[11] leading to higher hysteresis and lower channel mobility. In this work, a CF_4 plasma pretreatment approach is proposed which improves the interface between the HfO_2 gate dielectric and the Si substrate. The transmission electron microscopy (TEM) and Fourier transform infrared (FTIR) spectroscopy were employed and it was found that the growth of the interfacial layer had been inhibited by fluorine passivation of the silicon surface for oxidation and by the blocking of oxygen diffusion into the silicon. It was also observed that the capacitance EOT was much decreased for the CF_4 plasma pretreated sample.

A standard RCA clean was performed on all samples in the beginning. Then, some samples were treated by CF_4 plasma for 1 min in a plasma enhanced chemical vapor deposition system. Further samples not subjected to the plasma treatment but otherwise identical were the as-deposited samples. In order to analyze the surface of the all samples, attenuated total reflection FTIR spectroscopy was used to inspect the variation of the native oxide formation on the silicon substrate. Then HfO_2 films with three different thicknesses of 5, 7, and 9 nm were deposited by reactive rf sputtering. Finally, a TaN metal gate of 50 nm was also deposited by rf sputtering and aluminum films of 300 nm were evaporated on both the top and bottom of the silicon wafer to form metal oxide semiconductor capacitors. High frequency (100 kHz) capacitance-voltage (*C-V*) characteristics were measured with an HP4284A analyzer. The physical thicknesses of HfO_2 thin film and the interfacial layer were measured with TEM. In addition, the fluorine distribution was obtained with the secondary ion mass spectroscopy (SIMS), and the Hf–O, Hf–Si, and Hf–F bondings were characterized by electron spectroscopy for chemical analysis (ESCA).

Figure 1 shows the SIMS analysis of the HfO_2 films with pre-CF_4 plasma treatment. It is apparent that fluorine atoms have accumulated mainly at the interface between the HfO_2 thin film and the silicon substrate after the CF_4 plasma pre-

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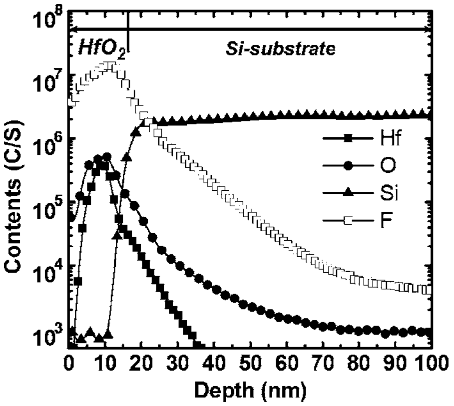

FIG. 1. SIMS depth profile of the HfO_2 gate dielectrics. The fluorine atoms accumulated mainly at the HfO_2/silicon substrate interface after CF_4 plasma pretreatment.

treatment. This observation indicated that fluorine atoms first are distributed at the surface of the silicon substrate after the CF_4 plasma pretreatment, and are then incorporated into the HfO_2 thin film during the hafnium dioxide deposition to form fluorinated HfO_2 gate dielectrics. In addition, these fluorine atoms also terminate the dangling bonds of silicon substrate and accumulate at the interfacial layer region.[12]

Figure 2 shows the Hf 4*f* ESCA spectra of as-deposited and CF_4 treated samples, respectively. A take-off angle (TOA) of 90° was used to measure the ESCA spectra. For the as-deposited sample, as shown in Fig. 2(a), two distinct peaks of the Hf–O bonding at 18.7 and 20.3 eV are clearly visible. In addition, Hf–Si bondings at 14.7 and 16.8 eV are also observed, meaning that Hf silicide was formed during the HfO_2 film deposition. Fortunately, this formation of Hf–Si bonding was effectively suppressed for the CF_4 plasma pretreated samples as shown in Fig. 2(b). This observation is a clear indication that the fluorine atoms accumulated at the Si/HfO_2 interface were responsible for the reduction of the amount of Si participating in Hf silicide formation.[13] From the inset of Fig. 2, we can see that the fluorine atoms were only incorporated into the HfO_2 thin film when CF_4 plasma pretreatment was employed. Furthermore, the intensity of the Hf 4*f* spectra of HfO_2 dielectrics after CF_4 plasma pretreatment was much larger although the original peak value at 20.3 eV was less distinct than for the as-deposited sample. This indicates that the Hf–F bonds were formed.[14] It is induced by the fluorine incorporation into the HfO_2 thin film after CF_4 plasma pretreatment, as shown in the SIMS profiles in Fig. 1 and the inset in Fig. 2.

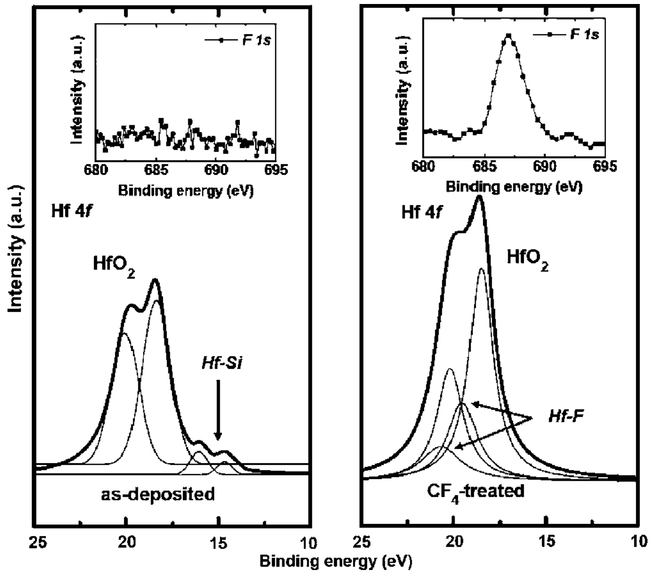

FIG. 2. Hf 4*f* ESCA spectra of (a) as-deposited sample and (b) CF_4 plasma treated sample. The inset figures are the fluorine 1*s* ESCA spectra. A take-off angle (TOA) of 90° was used to measure the ESCA spectra.

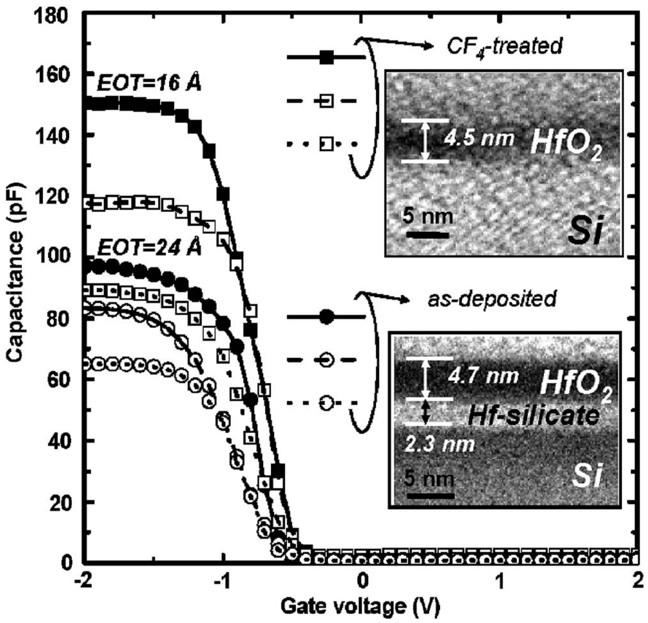

FIG. 3. *C-V* characteristics for the samples with and without CF_4 plasma pretreatment for various HfO_2 thin film thicknesses. The inset figures are the TEM images for the as-deposited and CF_4 plasma pretreated samples.

Figure 3 presents the capacitance-voltage (*C-V*) characteristics of HfO_2 gate dielectrics with and without the CF_4 plasma pretreatment. The EOTs of as-deposited samples were 2.4, 2.9, and 3.8 nm, respectively. As discussed before, for the sample without CF_4 plasma pretreatment, the sputtered HfO_2 thin films tended to have ILs at the HfO_2/Si interfaces that have relatively small dielectric constants[5,6] as shown in the inset TEM image [Fig. 3(b)]. The composition of the interfacial layer is believed to be hafnium silicate because the estimated dielectric constant of the interfacial layer is higher than that of SiO_2. After the CF_4 plasma pretreatment, the IL was effectively suppressed as shown in Fig. 3(a). As a result, the EOTs decreased from 3.8 to 2.9, 2.9 to 2.0, and 2.4 to 1.6 nm, respectively. Figure 4 shows the FTIR absorbance spectra of the Si wafer with and without CF_4 plasma treatment. The FTIR method employed in this work utilizes a high-index Ge hemisphere in intimate contact with the samples. As depicted in Fig. 4, there is a dominant band at 939 cm^{-1}, which is the GeO reference peak associated with the hemisphere. In addition, the broad features that appear at 1100 cm^{-1} are the characteristic bulk interstitial Si–O–Si vibrations. For the sample without CF_4 plasma treatment, one observes a strong and sharp band at 1221 cm^{-1} from the $Si-O_x$ surface layer on Si. The peak is very typical of the native oxide on silicon. After CF_4 plasma treatment, the native oxide band at 1221 cm^{-1} has disappeared and been replaced by a significantly weaker absorption band centered near 1180 cm^{-1} which is similar to that observed for amorphous SiO_2 films on Si.[15] It is believed that the reduction of native oxide regrowth on CF_4 plasma

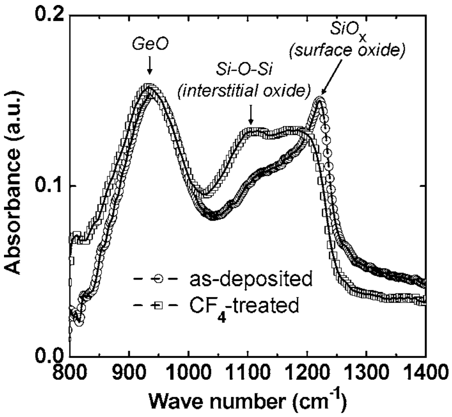

FIG. 4. FTIR spectra of the Si wafers with and without the CF_4 plasma treatment. Whereas the as-deposited sample showed a characteristic native oxide band at 1221 cm^{-1}, the CF_4 plasma treated sample did not. The latter sample had a broader weaker oxide feature at 1180 cm^{-1} indicating whatever Si–O_x material was present was more amorphous and with lower surface coverage than in the as-deposited sample.

treated Si substrates resulted from the fluorine passivation of the silicon surface. From these results, it seems reasonable that for the as-deposited sample, the excess oxidizing species such as oxygen radicals, ions, and molecules in the plasma diffuse into the silicon substrate and contribute to the interfacial layer growth. On the other hand, for the CF_4 plasma treated HfO_2 gate dielectrics, the growth of interfacial layer is inhibited by fluorine passivation of the Si substrate and the blocking of oxygen diffusion into the Si. This hypothesis is supported by both the TEM imaging and FTIR spectroscopy.

In summary, the characteristics of CF_4 plasma pretreated HfO_2 gate dielectrics were investigated. After the CF_4 plasma pretreatment, the fluorine atoms were distributed at the interface between the HfO_2 thin film and silicon substrate, effectively inhibiting the formation of an interfacial layer between the HfO_2 thin film and Si substrate. The fluorine passivation also plays a role in blocking oxygen diffusion into the Si, resulting in an EOT reduction for the HfO_2 gate dielectrics. The CF_4 plasma pretreatment technology can be used in device fabrication with high-*k* gate dielectrics for future ULSI applications.

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