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Evaluation of Electronic Defect States at Poly-Si/HfO_2 interface by Photoelectron Yield Spectroscopy

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1. Introduction

The continuous scaling of CMOS devices to the sub-100nm technologies will force the implementation of a higher dielectric constant (high-k) gate dielectric as the alternative of conventional SiO_2 to achieve a required capacitive coupling between the gate and Si(100) below some limit on the gate leakage. Among various candidates for the high-k gate dielectric, Hf-based materials such as Hf oxides and their silicates and aluminates have attracted much attention because of their high dielectric constant, wide band gap and thermal stability[1]. On the other hand, serious problems of Fermi level pinning or flat-band voltage shift (ΔV_{FB}) in MOS devices with HfO_2 gate dielectric have been reported [2,3], and the formation of both donor-like and acceptor-like states at poly-Si/HfO_2 interface has been discussed based on the experimental result that the positive and negative ΔV_{FB} are observed for n^+poly gate and p^+poly gate MOSFETs, respectively. Therefore, direct evaluation of defect states at the poly-Si/HfO_2 interface is still a matter of research.

In this work, we have applied total photoelectron yield spectroscopy (PYS) [4] to quantify the defect states at and near the poly-Si/HfO_2 interface and demonstrated the change in interface state density and energy distribution from the PYS spectra that are taken at each process step.

2. Experimental

A 1.0nm-thick chemical oxide layer was formed on HF-last n-Si(100) with a donor concentration of ~$6\times10^{14}cm^{-3}$. 3.0nm-thick HfO_2 layer was formed in ambient O_2 at ~1×10^{-4}Pa by an electron beam evaporation method, and followed by O_2 anneal at 500ºC at 34Pa for 5min to densify the film. Subsequently, 5nm or 30nm-thick amorphous-Si films were deposited uniformly on HfO_2/SiO_2/Si(100) at 440ºC by low pressure chemical vapor deposition (LPCVD) using 10% Si_2H_6 diluted with He at 26.7Pa. The amorphous-Si films were crystallized at 600ºC in ambient H_2 at 53Pa for 15min as confirmed by surface sensitive Raman scattering measurements. At each process of sample preparation, chemical bonding features and energy distribution of electronic defect states were evaluated using x-ray photoelectron spectroscopy (XPS) and PYS, respectively.

3. Results and Discussion

For 5nm-thick amorphous Si deposited on HfO_2, no chemically-shifted Si signals due to oxidized states is detected as shown in Fig. 1. After poly-crystallization of the Si layer, small chemically-shifted Si2p signals are observable, indicating the formation of Si-O bonds within 2 monolayers at poly-Si/HfO_2 interface. Since there is no significant change in Hf4f spectrum before and after Si deposition and poly-crysatallization, no Hf-Si bonds was formed within detection limit of this XPS analysis as much as $10^{13}cm^{-2}$. These results obtained by XPS confirm the formation of compositionally abrupt poly-Si/HfO_2 interface. In addition, considering the fact that Hf4f spectra from the samples covered with a-Si and poly-Si are shifted by -0.8eV with alignment of Si2p substrate peak at 99.3eV, it is likely that a significant amount of electrons transfer from the top Si layer to HfO_2 layer. Figure 2 shows the PYS spectrum of 5nm-thick poly-Si/HfO_2/SiO_x/Si(100) together with that of HfO_2/SiO_x/Si(100). Since the photoemission of valence electrons from Si becomes significant for photons with energies higher than 5.15eV as seen in the PYS spectrum taken for H-terminated Si(100), which mainly consists of the photoemissions from the valence band and acceptors, observed high photoelectron yields of the samples with HfO_2/SiO_x and 5nm-thick poly-Si on it indicate

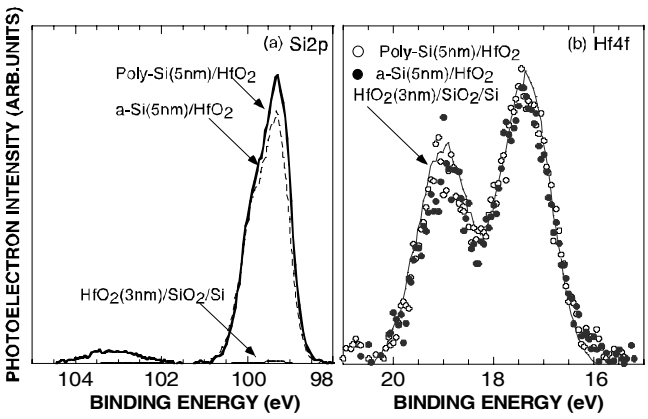

Fig.1 Si2p (a) and Hf4f (b) spectra taken from the samples before and after polycrystallization of a 5nm-thick Si film on HfO_2/SiO_x/Si(100). The photoelectron take-off angle was 90º. The biding energy was calibrated by the Si2p peak 99.3eV from the Si(100) substrate and the photoelectron intensity was normalized by the peak intensity of Hf4f signals.

that there exist significant amount of defects located at the energy region from the Si valence band edge toward the Si conduction band. Notice that, in the photon energy range of 4.7-5.1eV, the photoelectron yield obtained after 5nm-thick poly-Si formation becomes about one order of magnitude larger than that of $HfO_2/SiO_x/Si(100)$ in spite that the photoelectron yield is normalized by the yield for Si valence electrons in the photon energy region of 5.7-6.0eV. This result indicates abrupt increase in defect states density in the band gap. To verify whether the defects are originated from poly-Si film or poly-Si/HfO_2 interface, PYS spectra of 30nm-thick as-deposited amorphous Si film and after poly-crystallization in H_2 ambient were measured and compared with the PYS spectrum of 5nm-thick poly-Si/$HfO_2/SiO_x/Si(100)$ as shown in Fig.3. For 30nm-thick Si films. almost no change in the yield between before and after poly-crystallization is observable, which indicates no significant change in defects presumably because the annihilation of defects in amorphous network during H_2 annealing for poly-crystallization is canceled out by the generation of defect in poly-Si grain boundaries. Obviously, in the photon energy region of 4.9-5.4, 5nm-thick poly-Si/$HfO_2/SiO_x/Si$ shows higher yield than 30nm-thick Si. Considering the PYS spectra was also normalized with the yield for the Si valence band at the higher energy part, quite large amount of filled defect states are generated at and/or near the interfaces between poly-Si and HfO_2. From the first derivative of PYS spectra with respect to photon energy and taking into account of the contribution of Si valence electrons to the yield, the energy distribution of filled defect states was roughly estimated in real density as shown in Fig. 4. The result shows that, for the combination of poly-Si and HfO_2, filled defect states over $10^{13}cm^{-2}/eV$ are generated within 0.3eV from the Si valence band edge, which can not be interpreted in terms of the generation of Si-Hf bonds at the interface. Electron transfer from poly-Si into deeply localized traps in HfO_2 seems to be responsible for the observed high yield.

4. Conclusions

From PYS measurements for poly-Si, HfO_2 and poly-Si/HfO_2 systems, we confirmed that defect states of the order of $10^{13}cm^{-2}/eV$ are generated at and/or near the poly-Si/HfO_2 interface, which is not attributable to Si-Hf bonds but presumably to electron trapping at deeply localized states in HfO_2 from poly-Si.

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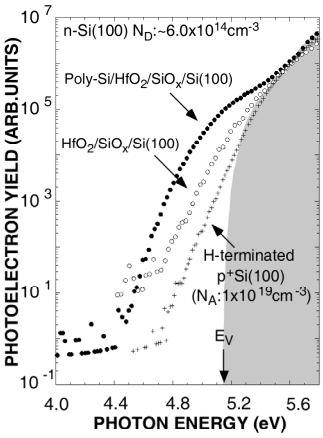

Fig.2 PYS spectra of poly-Si/HfO_2/SiO_x/Si(100), HfO_2/SiO_x/Si(100) and H-terminated p^+-Si(100). A gray region denotes the contribution of Si valence electrons to the photoelectron yield and the spectra were normalized by the yield in the photon energy region of 5.7-6.0eV.

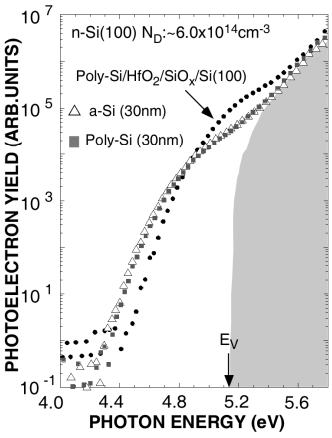

Fig.3 PYS spectra of 30nm-thick Si films before and after poly-crystallization by 600ºC in H_2 ambient. The sample surfaces were treated with a dilute HF solution to remove native oxide and to make a stable passivation with hydrogen.

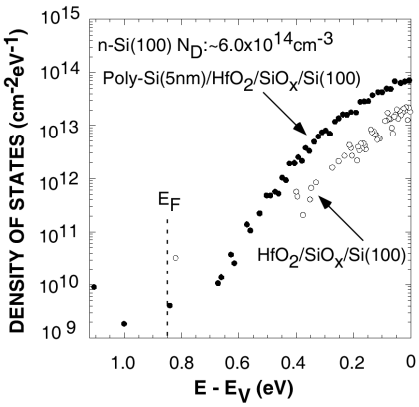

Fig. 4 Energy distribution of filled defect states before and after poly-Si formation on HfO_2/SiO_x/Si(100) evaluated from PYS spectra shown in Fig. 2.