2C/2002S2002

Chemistry and Band Offsets of HfO_2 Thin Films for ULSI Gate Insulators

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Introduction

High-k dielectric materials have attracted much attention since physically thicker dielectric films are strongly required to create a very thin equivalent oxide thickness for sub 0.1 μm ULSI devices. Although various metal oxides with high dielectric constants have been proposed, HfO_2 has been regarded as one of the most promising candidates among them because of its high dielectric constant, high resistivity, and high thermal stability. So far many spectroscopic studies[1] have been done on the interfacial chemistry including silicate formation and band offsets for the HfO_2/Si system using photoelectron spectroscopy. The precise information about chemical states and band offsets, however, for the complicated HfO_2/silicate/Si system where the silicate interlayer formation is hardly prevented has not been obtained mainly due to insufficient energy resolution of X-ray photoelectron spectroscopy. In this study, therefore, the interfacial chemistry and band offsets of HfO_2 films grown on Si(100) substrates have been investigated using high resolution angle-resolved photoelectron spectroscopy.

Experimental

HfO_2 films with 4.4 nm and 7.5 nm thicknesses were grown by reactive sputtering of Hf metal with the oxygen ambient on p-Si(100) substrates. The thicknesses of HfO_2 films were measured by cross-sectional transmission electron microscope (TEM) and the compositions of the films were determined by energy dispersive x-ray (EDX) analysis. To determine the CET (capacitance equivalent thickness), C-V characteristics were measured. High-resolution synchrotron radiation photoelectron spectroscopy (SRPES) was performed with a Gammadata-Scienta SES100 electron analyzer with photon energies ranging from 330 eV to 800 eV at an undulator beamline 2C of the Photon Factory in KEK.

Results and discussion

A cross-sectional TEM image of the 4.4 nm HfO_2 film grown on Si(100) revealed a double layer structure with a 1.6 nm-thick upper layer and a 2.8 nm-thick lower layer, probably a $Hf_{1-x}Si_xO_2$ layer. C-V characteristics revealed that the CET for the 4.4 nm film was 2.6 nm. Figures 1(a) and (b) show Hf 4*f* photoelectron spectra from the $HfO_2/Hf_{1-x}Si_xO_2$/Si(100) samples with the oxide thicknesses of 4.4 nm and 7.5 nm, respectively. On the contrary, the Hf 4*f* spectrum from the 7.5 nm thick sample which has a very thin $Hf_{1-x}Si_xO_2$ interlayer with only 0.5 nm thickness is well fitted with only one component of Hf 4*f*, as shown in Fig. 2(b). It is also found that there is no Hf-silicide component at the interface. The similar chemical shift features were observed for O 1*s* spectrum. The O 1*s* spectrum can be well fitted with three chemical states, namely HfO_2, $Hf_{1-x}Si_xO_2$ at 1.3 eV shift and the unknown component at 2.5 eV shift.

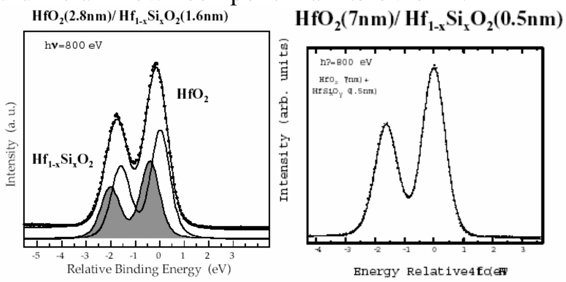

Fig. 1. Hf 4*f* photoelectron spectra from $Hf_{1-x}Si_xO_2$/Si (4.4 nm and 7.5 nm thick).

Next, we attempted to directly determine valence band offsets. The valence band maximum (VBM) was determined by extrapolating the valence band of Si. Since the measured valence band is composed of valence bands of HfO_2, $Hf_{1-x}Si_xO_2$ and Si, it is quite difficult to directly determine band offsets. In order to subtract the contribution from the Si substrate, we measured the valence band of a clean Si substrate. From these subtracted spectra, it is possible to determine valence band offsets to be 3.0 eV and 3.8 eV for HfO_2/Si and $Hf_{1-x}Si_xO_2$/Si, respectively.[2] In order to determine the band alignment, O 1*s* energy loss spectra were also measured. The extrapolated values from the O 1*s* energy loss spectra for the 4.4 nm and 7.5 nm films are 5.2 eV which can be regarded as the band gap of HfO_2. The band gap of 5.2 eV for HfO_2 and the valence band offset of 3.0 eV for HfO_2/Si lead to the conduction band offset for HfO_2/Si to be 1.1 eV, which is slightly smaller than 1.5 eV reported by Robertson. [3]

In conclusion, the interfacial chemistry and band offsets of HfO_2 films grown on Si are investigated using high resolution angle-resolved photoelectron spectroscopy, and are well correlated with interfacial structures revealed by cross-sectional TEM and C-V measurements.

This work was supported by STARC.

References

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