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Characterization of the interface between the Hf-based high-*k* thin film and the Si using spatially resolved electron energy-loss spectroscopy

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ABSTRACT

The interfacial structures of HfO_2 and HfAlO thin films on Si have been investigated using spatially resolved electron energy-loss spectroscopy. We have found that interfaces are not atomically sharp, and variation in the symmetry of the local atomic coordination lasts for a couple of monolayers for both the as-deposited HfO_2 and the HfAlO samples. Annealing of the HfO_2 film in the oxygen environment leads to the formation of a thick SiO_2/SiO_x stack layer in-between the original HfO_2 and the Si substrate. As a comparison, the interfacial stability is significantly improved by Al incorporation into the HfO_2 film (forming HfAlO), which effectively reduced/eliminated the interfacial silicon oxide formation during the oxygen annealing process. The mechanism of the high-*k* film/substrate stabilization by Al incorporation is discussed based on the experimental results.

1. Introduction

High-*k* materials have been widely studied as the gate dielectric to replace SiO_2 in the future complementary metal-oxide-semiconductor (CMOS) integrated circuit technology (Wilk et al., 2001; Wallace and Wilk, 2003). Among various candidates, HfO_2-based materials are considered to be the most promising ones due to their large dielectric constants, which ensure the improved device electrical performance at larger dielectric thickness compared to that of SiO_2. In 2007, using an undisclosed thick hafnium-based material as the gate dielectric, Intel released a 45 nm high-*k* silicon technology, in which reduced transistor leakage by more than 10 times over the current silicon dioxide technology was claimed, making the future of this family of materials more promising.

The major concern of using HfO_2 as the gate dielectric layer is its interfacial quality with the Si substrate, which determines the ultimate performance of the device (Robertson, 2004). Chemical reactions occurring at the film/substrate interface during the film growth and/or post-deposition treatment have been discussed in the literatures, in which two possible interfacial configurations have been suggested. Cho et al. (2002) have reported an interfacial layer of hafnium silicate was grown at an initial growth stage and changed into silicide layer when annealed at 700 °C under ultrahigh vacuum condition. Such a metallic silicide layer is highly undesirable as it would result in a large channel leakage between the source and drain. On the other hand, SiO_2 formation in-between the HfO_2 and the Si has also been observed both during deposition with high O partial pressure and after the post-deposition oxygen annealing process (Lu et al., 2006; Ferrari and Scarel, 2004). Although the oxidation mechanisms are still debated, the formed low-*k* SiO_2 layer will increase the overall equivalent oxide thickness (EOT) and degrade the device performance. Several strategies have been proposed to improve the interfacial stability of the high-*k* hafnium-based films on Si. For example, better stability against annealing at 1000 °C has been observed for HfO_2/SiO_xN_y film stack on Si (Bastos et al., 2002), in which direct incorporation of a third element (such Al, Si or N) in HfO_2 has also been attempted for this purpose (Visokay et al., 2002; Bae et al., 2003). Nevertheless, a detailed understanding on the interfacial structure of the HfO_2/Si, and the effect of a third element addition on the interfacial structure before and after the oxygen annealing remain unclear.

In this paper, we have carried out a systematic investigation on the interface between the HfO_2 film and the Si substrate before and after oxygen annealing. The effect of Al incorporation on the film/substrate interface has also been evaluated. In particular, we have employed electron energy-loss spectroscopy performed in a scanning transmission electron microscope (STEM) to acquire information on their local structure across the film/substrate interface. The subtle differences of the interfacial profiles obtained from these samples provide abundant information on their interface structural quality.

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2. Experimental

HfO_2-based thin films with thickness of about 20 nm were deposited by pulsed laser deposition (PLD) on p-type (1 0 0) Si substrates, using high-purity targets of HfO_2 and hafnium aluminate (Hf/Al ratio 1:1). The silicon substrate were treated by an HF etch before the thin film deposition, to leave the silicon surface terminated by hydrogen. The substrate temperature was maintained at 550 °C during the deposition, and the post-deposition annealing was performed in O_2 at 750 °C for 45 min.

The high resolution STEM images were taken using a high angle annular dark field (HAADF) detector in a STEM (Tecnai G2, FEG). The electron energy-loss spectroscopy (EELS) was performed in the STEM line scan mode, using a Gatan imaging filtering (GIF) system attached to the same microscope. The electron probe size was maintained at 0.3 nm during the line scan. After subtraction of the background with a power-law method, the energy-loss spectra were fitted using Gaussian multi-peak fitting.

3. Results and discussion

HAADF image taken at the as-deposited HfO_2 dielectric and the Si substrate shows a sharp interface—the Si crystalline fringes extends to the boundary of the bright/dark contrast (Fig. 1(a)). After oxygen annealing, an amorphous interfacial layer of $\sim$3 nm thickness is found to develop in-between the bright contrast (corresponding to the high-*k* film) and the crystalline fringes of Si (Fig. 1(b)). Similar to the interface between the as-deposited pure HfO_2 and Si, the one between the as-deposited HfAlO and the substrate appears to be sharp (Fig. 1(c)) as well. Although an amorphous interfacial layer also appears after the O_2 annealing of HfAlO (Fig. 1(d)), the thickness of such a layer has been reduced to $\trianglelefteq 1$ nm, being much smaller than that of the annealed HfO_2 on Si.

More detailed information on the interfacial structures of these samples are obtained from the O K-edge energy-loss spectra taken in the STEM line scan mode across the interface between the high-*k* films and the Si substrate. Fig. 2 shows such spectra recorded from the as-deposited HfO_2. The open circle markers on the HAADF image illustrate the positions of the electron probes, and

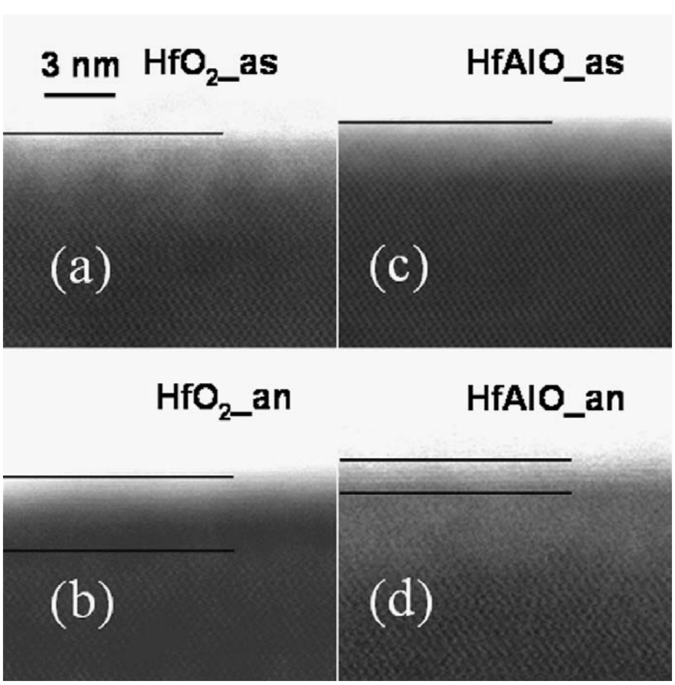

Fig. 1. HAADF image of the HfO_2 (HfAlO)/Si interface before and after annealing.

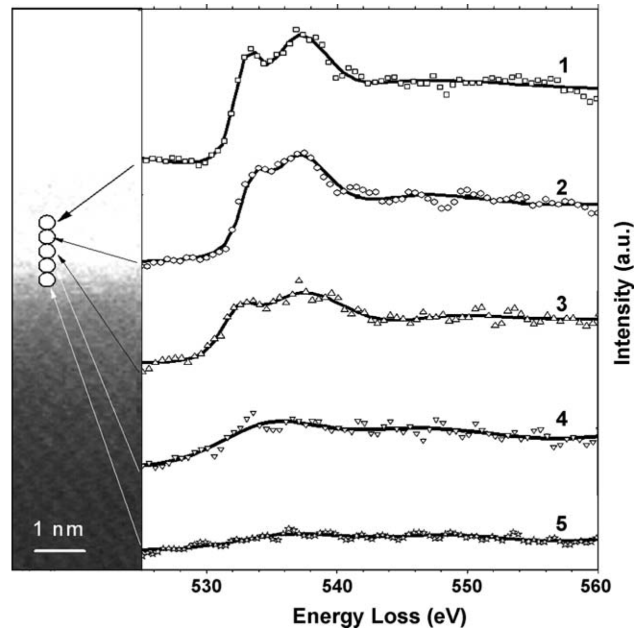

Fig. 2. O K-edge energy-loss spectra recorded across the as-deposited HfO_2/Si interface.

consequently from which location each spectrum was taken. Away from the HfO_2/Si interface, the oxygen K-edge gives a double-peak feature (line 1), which is slowly broadened as the electron probe approaches the interface (lines 2 and 3). A single broad peak is observed for the oxygen K-edge (line 4), which intensity rapidly falls off as the electron probe moves into the Si (line 5).

A significantly different interfacial profile (Fig. 3) has been observed for the oxygen K-edge recorded across the interface of the annealed HfO_2 thin film and the Si. The double-peak feature (lines 1 and 2) is still observed at regions away from the interface when bright contrast is observed in the corresponding HAADF image, although the relative intensity of the two peaks has changed

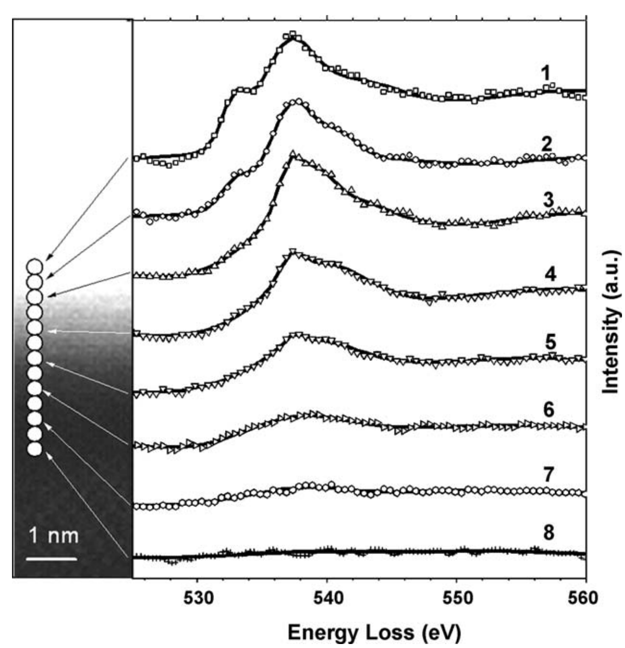

Fig. 3. O K-edge energy-loss spectra recorded across the HfO_2/Si interface after oxygen annealing.