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### Title
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### Journal
Applied Physics Letters, 89(24 July 2006)



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### Publication Date
2006

### DOI
10.1063/1.2240743

Peer reviewed



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# Detection and mobility of hafnium in $SiO_2$

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**Abstract**

High-angle annular dark-field imaging in scanning transmission electron microscopy and x-ray photoelectron spectroscopy were used to investigate thermal $SiO_2$ layers doped with Hf by ion-implantation. Hf was mobile under the focused electron beam in the as-implanted samples. After annealing for 5 min at 1200 °C, clusters of crystalline $HfO_2$ were observed that were a few nm in size and surrounded by residual Hf that had remained trapped in the $SiO_2$. Hf was not mobile under the electron beam in the annealed samples. Further annealing caused an expansion of the $SiO_2$ that was damaged by ion-implantation. Hf rearrangement was confined to the ion beam damaged regions of the $SiO_2$ layer. No diffusion of Hf into the undamaged $SiO_2$ was observed. The implications of the results for complementary metal-oxide-semiconductor transistors with $HfO_2$ gate dielectrics are discussed.

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$HfO_2$ films are under extensive investigation as a high-permittivity (*k*) gate dielectrics in Si complementary metal-oxide-semiconductor (CMOS) transistors [1]. In $HfO_2$ gate dielectric stacks, $SiO_2$-rich interfacial layers are often present at the interface with Si, either as a result of oxidizing growth or annealing conditions [2] or because they are intentionally grown as a nucleation layer before high-*k* deposition [3]. The chemistry of these interfacial layers and the nature of their interaction with the $HfO_2$ film are of great practical interest as they determine the electrical and dielectric properties of the gate stack. Initially intermixed $SiO_2/HfO_2$ interfaces may occur during deposition of the high-k oxide [4,5], but are expected to separate into $HfO_2$-rich and $SiO_2$-rich regions upon high-temperature annealing [6,7]. In the literature, a wide range of techniques have been employed to study the chemistry of interfacial layers in high-*k* stacks. However, only high-angle annular dark-field imaging (HAADF) in scanning transmission electron microscopy (STEM) is capable of atomic spatial resolution with (near) single atom sensitivity [8]. Recently Hf atoms or clusters have been imaged in $SiO_2$ by HAADF/STEM [9,10]. In this letter we apply HAADF/STEM to study $SiO_2$ layers doped with Hf by ion implantation. While Hf ion implantation is not used in conventional processing of high-*k* gate stacks the purpose of this study is to investigate the mechanisms and kinetics of demixing in $SiO_2$ containing precisely known amounts of Hf.

Hf was implanted into ~ 100 nm $SiO_2$ layers grown by thermal oxidation of (001) Si. The implantation was performed by a commercial vendor (Evans Analytical Group, Sunnyvale, California), using 25 keV Hf ions, resulting in an implantation depth of about 20 nm. The implantation doses were $1\times10^{13}$ Hf/cm$^2$ and $7.5\times10^{14}$ Hf/cm$^2$,

respectively. Samples were annealed in a rapid thermal annealing furnace in ultra-high purity (UHP) $N_2$ gas at 1200 °C for 5 min. The ramp-up time was 20 s and the samples took ~ 10 min to cool to room temperature. For selected samples, this anneal was repeated several times. Cross-section transmission electron microscopy (TEM) samples were prepared by polishing and ion-milling using Gatan's Precision Ion Polishing System (PIPS) with 3 – 3.5 kV Ar ions. Conventional high-resolution TEM (HRTEM) and HAADF/STEM were performed using a field-emission TEM operated at 300 kV (FEI Tecnai F30UT) with a $C_s$ ~ 0.52 mm and a resolution of better than 0.14 nm in HAADF/STEM [11]. The detector inner angle for HAADF imaging was ~ 68 mrad, which was large enough to avoid any strain contrast contributions [11]. X-ray photon electron spectroscopy (XPS) was carried out using a Kratos Axis Ultra XPS system. Binding energies were calibrated using the C 1s peak (285.0 eV).

Figure 1 shows a cross-section HAADF image of the as-implanted sample with $7.5\times10^{14}$ Hf/cm$^2$ (no anneal). The atomic number ($Z$) sensitive contrast of HAADF allowed for easy identification of the sample region that contained the implanted Hf ($Z_{Hf}$ = 72) because of its much greater brightness compared to $SiO_2$ ($Z_{Si}$ = 14 and $Z_O$ = 8). Estimated showed that in the projection along the electron probe about 13 Hf atoms/nm$^2$ were imaged the center of the implanted layer and 1-2 Hf atoms/nm$^2$ could still be detected in the tail of the implanted region in a TEM sample of 20 nm thickness. Hf atoms in the as-implanted sample were mobile under the electron beam and formed clusters upon prolonged exposure (see inset in Fig. 1).

No Hf could be detected in the sample with $10^{13}$ Hf/cm$^2$. This sample should only have ~ 0.2 Hf atoms/nm$^2$ near the maximum of a Gaussian distribution in a 20 nm thick

TEM sample. In amorphous materials, significant beam broadening was expected, which likely negatively affected the scattered intensity due to Hf atoms at greater depths in the sample, making detection of Hf atoms in this sample statistically difficult.

XPS Hf $4f$ edges showed that the as-implanted Hf was oxidized (Fig. 2). The Hf $4f_{7/2}$ binding energies for as-implanted and annealed samples were 17.2 eV and 17.3 eV respectively, with a splitting between the $4f_{7/2}$ and $4f_{5/2}$ peaks by 1.5 and 1.6 eV, respectively. These values were close to those reported for $HfO_2$ [12,13]. No shoulder in the Si 2*p* peak with annealing as would be indicative of a silicate [14] were detected, but Hf quantities may have been too small to detect such features.

The implanted Hf was immobile under the electron beam after high-temperature annealing at 1200 °C for 5 min (Fig. 3a). Annealing caused the formation of crystalline $HfO_2$ clusters (see insets) of ~ few nm in diameter. The lattice spacing and angles between planes in the clusters were consistent with monoclinic $HfO_2$ (see insets in Fig. 3). Precipitation of $HfO_2$ should have left the $SiO_2$ in the implanted region oxygen-deficient, but UHP $N_2$ may contain sufficient oxygen for re-oxidation [2]. The results were consistent with the strong driving force of $HfO_2$-$SiO_2$ mixtures to phase separate, as predicted by thermodynamic considerations [6]. In addition to clusters, residual bright contrast was visible in the regions between them. The contrast could have been due to residual Hf or defects resulting from ion-implantation, such as Si-Si clusters. However, most of the damage from ion-implantation in $SiO_2$ is believed to anneal out at temperatures below 1000 °C [15], and the intensity in these regions was similar to that in the as-implanted sample. Thus the contrast was interpreted as being due to small amounts of Hf that remained trapped in the $SiO_2$.

Subsequent annealing treatments (Fig. 3b) did not cause significant growth of the clusters or complete removal of residual Hf in the $SiO_2$. The Hf distribution was found to widen towards the surface with each annealing step, as can be seen from the HAADF intensity profiles in Fig. 4. The full width at half maxima of the Hf profiles were ~ 11 nm, ~ 16. 5 nm and ~ 18 nm in the as-implanted sample and after the first and subsequent (4 cycles) annealing steps, respectively. Hf did not diffuse into the undamaged $SiO_2$, i.e. towards the substrate side of the implanted region. After the longer anneal (4 cycles), the ion-damaged region expanded. This was not believed to be due to additional $SiO_2$ formation at the substrate interface (as this would have caused a shift of the Hf profile peak relative to the substrate), but rather an expansion of the implanted region due to reduction of density upon annealing and possibly some re-oxidation. Ion-implantation is known to cause densification of amorphous $SiO_2$ [16].

The results showed that Hf rearrangement (both under the electron beam and during annealing) occurred only in regions of the $SiO_2$ that were damaged by ion implantation. In the these regions, the mobility of Hf atoms was likely enabled by structural defects in the $SiO_2$ network [16]. Rearrangement of Hf was thus correlated with the annealing of atomic defects in $SiO_2$. Residual Hf that was not accommodated in the $HfO_2$ clusters before the structural damage annealed out remained trapped in the $SiO_2$, as further annealing did not cause large changes in the Hf distribution. This further confirmed that the diffusivity of Hf in undamaged $SiO_2$ is extremely low as expected given its high ionic charge [17]. Some residual Hf may also be expected in a metastable phase equilibrium [6]. Reports by others of Hf mobility [18] under an intense electron beam are therefore likely associated with electron beam damage.

With respect to interfacial layers in gate stacks the following conclusions could be made. If high-*k* deposition produces initial intermixing of layers then these may not completely demix upon annealing. This may explain reports of the detection of Hf in interfacial $SiO_2$ layers [9]. Note that the situation is likely different for amorphous "silicates" alloys synthesized at low temperatures from precursors, which are known to rapidly demix at high temperatures [7]. Phase separation in these materials may be facilitated by a relatively high concentration of impurities and pre-existing heterogeneity [19]. For interfaces between $HfO_2$ dielectrics and defect-free $SiO_2$ interfacial layers no interdiffusion is expected under annealing conditions typical for gate stack processing. Finally, $HfO_2$ nanocrystals embedded in $SiO_2$ obtained by the process described in this paper may be of interest for memory devices [20].

The authors thank Dr. Evgeni Gusev and IBM for providing the thermal $SiO_2$ wafers and the Semiconductor Research Corporation for support of this research. One author (S.S.) thanks Dr. Brendan Foran for valuable discussions and suggesting the Hf implantation experiments. The work made use of Facilities supported by the National Science Foundation (DMR 05-20415 and DMR 02-16466).

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## Figure Captions

**Figure 1**

Cross-section HAADF/STEM images showing implanted Hf in the sample with $7.5\times10^{14}$ $Hf/cm^2$. The insets show magnifications of the initial image (top) and an image recorded after ~ 35 min of exposure to a scanned electron beam, which caused clustering of the implanted Hf (bottom).

**Figure 2 (color online)**

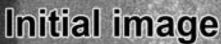
XPS 4*f* Hf and O 2*s* edges of the as-implanted and annealed $7.5\times10^{14}$ $Hf/cm^2$ samples, respectively.

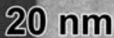
**Figure 3**

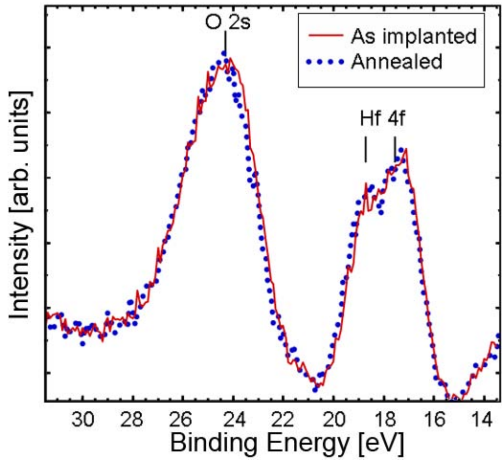
HAADF/STEM images of the sample with $7.5\times10^{14}$ $Hf/cm^2$ (a) after annealing at 1200 °C for 5 min and (b) after four annealing cycles each at 1200 °C for 5 min. The insets show HRTEM images of $HfO_2$ clusters along two different zone axes and a HAADF/STEM image, respectively.

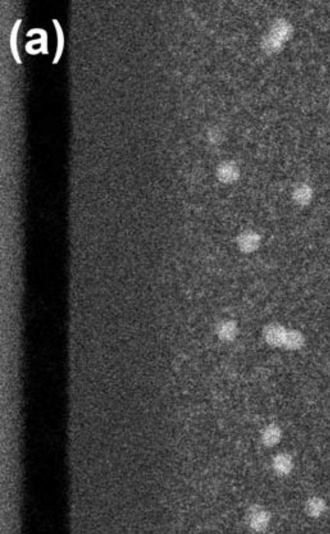
**Figure 4 (color online)**

HAADF image intensity profiles (integration width ~ 100 nm) across the $SiO_2$ film for three samples: as-implanted, annealed for 5 min at 1200 °C and after four annealing cycles (with each cycle for 5 min at 1200 °C). The Si is to the right (high intensity).

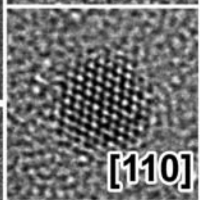

Initial image
After 35 min
$SiO_2$ Hf
$SiO_2$
Si

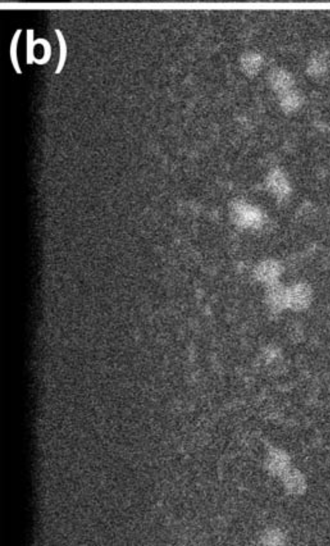

20 nm

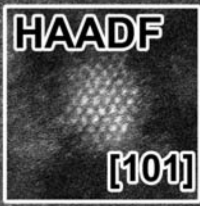

O 2s
As implanted
Annealed
Hf 4f
Intensity [arb. units]
30
28
26
24
22
20
18
16
14
Binding Energy [eV]


(a)

HRTEM
[101]


[110]


(b)
10 nm


HAADF
[101]

As-implanted
Annealed 1200°C, 5 min
Annealed 1200°C, 5 min, 4 cycles
Intensity [arb. units]
Distance [nm]
0
20
40
60
80