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BEAM INTERACTIONS WITH MATERIALS AND ATOMS

Ion beam studies of Hafnium based alternate high-k dielectric films deposited on silicon

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ABSTRACT

Hafnium based high dielectric constant materials are critical for the *state-of-the-art* integrated circuit technology. As the size of the transistor decreases, the thickness of the gate dielectric (SiO_2) should be reduced to maintain device capacitance at a desired level. This thickness reduction results in high OFF-state leakage current due to quantum tunneling. Recently alternate high-k materials, like HfO_2, have been introduced as gate dielectrics. However deposition of these high-k materials on Si wafers results in high concentration of interface defects due to their thermodynamic instability on Si. Introduction of thin inter layer of Silicon oxide/nitrides between Si and HfO_2 is expected to improve interface quality. Hence it is important to study the composition, thickness and intermixing effects to optimize the fabrication of Hafnium based Metal-Oxide-Semiconductor (MOS) devices. Here, we have performed High Resolution Rutherford Backscattering Spectrometry (HRBS) and X-ray Reflectivity (XRR) measurements to characterize $HfO_2/SiO_2/Si$ samples. These samples were further irradiated by 80 MeV Ni ions to study ion induced inter-diffusion of Hf and Si across HfO_2/Si interface as a function of ion fluence.

1. Introduction

Hafnium based high dielectric constant materials are critical for the *state-of-the-art* integrated circuit technology [1]. Silicon dioxide (SiO_2) has been used as a successful gate dielectric material because of its excellent interface properties with Si in MOS devices. SiO_2 has been used as a gate dielectric for few decades and kept the pace of Moore's law till the recent 65 nm technology generation [2]. As the size decreases, the thickness of oxide should be reduced to maintain device capacitance at a desired level. This reduction in thickness below a critical value, can result in high off-state leakage current due to direct tunneling. Typical leakage current due to quantum tunneling in 1 nm SiO_2 on Si is about 100 A/cm^2 [3,4]. High gate leakage current can damage the device performance and increase the standby power consumption. This direct tunneling through the gate dielectric imposes a fundamental limitation to further scaling with SiO_2. Hence several high-k materials like Al_2O_3, HfO_2, ZrO_2, Y_2O_3, and La_2O_3 have been examined as replacement for SiO_2 as gate oxide [5,6]. Among all these high-k materials, ZrO_2 and HfO_2 are found to be most suitable for this purpose [7]. These two materials have similar properties like high dielectric constant ($\kappa \sim 25$ for both) and similar band gaps (E_g (ZrO_2) $\sim$ 5.8 eV and E_g (HfO_2) $\sim$ 6.0 eV) and enticed attention to replace traditional SiO_2 gate dielectric [8]. The enhanced thermal stability of HfO_2 over ZrO_2 on Si surface has led HfO_2 as the leading material in the industry [9]. SiO_2 has already been replaced by HfO_2 in new generation MOSFETs [10]. However optimization of the synthesis of these materials is still under study [11–16]. Deposition of these high-k materials on Si wafers can result in high concentration of interface defects due to their thermodynamic instability on Si surface [6]. Introduction of thin interlayer of Silicon oxide/nitrides between Si and HfO_2 is expected to improve the interface quality, device reliability and performance [17,18]. Hence it is extremely important to investigate the quality, composition and thickness of this oxide and its inter-layers for fabricating reliable CMOS devices. It has also been reported that Hf silicates like HfSiO are attractive because of their high dielectric constant and enhanced thermal stability compared to HfO_2 [19]. Hence it

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is important to study the composition, thickness and intermixing effects to optimize the fabrication of Hafnium based MOS devices.

Swift Heavy Ion (SHI) irradiation plays a major role in synthesis, modifications and characterization of materials [20]. Interface engineering schemes using SHI irradiation have been extensively studied over the past few years to elucidate intermixing/diffusion issues [21]. Such studies are also useful for understanding the diffusion process of various elements across different interfaces. It is well-known that ion beam mixing has an important role in the formation of silicides in various systems like Fe/Si, Co/Si, Mo/Si, Mn/Si, Ti/Si, Zr/Si etc. [22]. To the best of our knowledge, there are no reports on SHI induced mixing of Hf/Si or HfO_2/Si interfaces although some reports exist on ion beam studies of Hf-based high-k dielectric materials [23,24]. It was shown that the increase in RF-power during sputter deposition of HfO_2 on Si substrate can lead to the formation of Hf-silicates [12,13]. Hafnium silicates belong to a new class of alternate high-k dielectric materials with tunable electrical and thermal properties [15,16,25,26]. Hence it is important to optimize the synthesis and to study ion beam mixing of this technologically important interface. Particularly, it is of great interest to understand defect creation and mixing at the interface due to ion irradiation and its impacts on the material properties and the device performance when we use HfO_2 based devices for terrestrial/space applications. Here we present a study on ion beam characterization and modification HfO_2/SiO_2/Si samples.

2. Experimental

ALD grown HfO_2 samples were obtained from SEMATECH, USA. The typical sample structure was "HfO_2 (2.5 nm)/SiO_2 (1 nm)/Si (substrate)". This sample was cut into several pieces for irradiation studies. Irradiation details of these samples are given in Table 1. Room temperature SHI irradiation was performed in a high vacuum chamber (<10^{-6} mbar) at a constant beam current of one particle nano Ampere (~1 pnA). The beam (of 1 mm in diameter) is uniformly scanned over 1×1 cm^2 area on samples using magnetic scanners to achieve uniform irradiation profiles. 80 MeV Ni ion irradiations were performed to ensure uniform electronic energy deposition throughout the dielectric stack.

HRBS/Channeling measurements were performed on all samples at National University of Singapore (NUS). HRBS measurements were performed utilizing an incident beam of 500 keV He^+ ions with scattering angle of $\theta = 65°$ and energy resolution of detector = 1.3 keV. Incident angle (α) and exit angle (β) were kept at 55° and 60° respectively. The beam was channeled in the substrate (along ⟨1 1 1⟩ axis of Si) to minimize background scattering from Silicon and to analyze amorphous layers (SiO_2/HfO_2) on Si surface. Further details about HRBS-measurement system can be found elsewhere [27,28]. HRBS spectra were analyzed using SIMNRA simulation software.

Samples were further investigated by high resolution X-ray specular reflectometry at grazing incidence angle in the X-ray demonstration and development (XDD) beam line at Singapore Synchrotron Light Source (SSLS). The diffractometer is the Huber 4-circle system 90,000-0216/0, with high-precision 0.0001° step size for omega and two-theta circles. The storage ring, Helios 2, was running at 700 MeV, typically stored electron beam current of 300 mA. X-ray beam was conditioned to select 8.048 keV in photon energy (Cu-K_α radiation equivalent) by a Si (1 1 1) channel-cut monochromator (CCM) and toroidal focusing mirror, blocked to be 0.90 mm high in vertical direction and 3.0 mm wide in horizontal direction by a slit system. Such set-up yielded X-ray beam with about 0.01° in vertical divergence. The detector slit was adjusted to be 1.00 mm high to ensure recording all reflected photons. The typical counting time was 5 s for every step and step size of two-theta was 0.02°. Diffuse scattering (background) of off-set scans were also measured at theta off-set angle of +0.20° in the range of above measurement. The pure reflectivity was obtained by subtracting the diffuse scattering from the raw data. The simulations were performed using M805 and LEPTOS 1.07 release 2004 (Bruker) simulation software. XRR measurements were also performed using Bruker D8 Advance diffractometer in with an incidence angle of 0.4°, using a Cu-K_α (1.5406 Å) source at University of Hyderabad, India.

Table 1
Sample structure and irradiation details.

Sample	Ion and energy	Irradiation fluence (ions/cm^2)
H2A	–	Pristine
H2C	Ni, 80 MeV	5×10^{12}
H2D	Ni, 80 MeV	5×10^{13}

3. Results and discussion

Random and channeled HRBS spectra of pristine sample (H2A) are shown in Fig. 1. Beam is channeled in the substrate along Si ⟨1 1 1⟩ direction to minimize background scattering from silicon. Prominent surface peaks corresponding to Si and O from amorphous layers on surface are observed due to a reduction of about 85% in the back scattering yield of Si (χ_{min} = ~15%) in ⟨1 1 1⟩ aligned spectrum. The elemental composition of the surface layer is estimated using the relative intensities of Hf, Si and O peaks (Y_{Hf}/σ_{Hf}:Y_{Si}/σ_{Si}:Y_O/σ_O) in channeled spectra. Counts estimated for 3 mono layers (ML) of Si (~2.04×10^{15} cm^{-2}) were subtracted from the total yield of Si to eliminate/minimize the contribution of Si-surface peak because the contribution of reconstructed Si-peak is expected to be from around 3 ML [29,30]. This analysis of pristine sample suggests the formation of a mixed $Hf_{0.18}Si_{0.33}O_{0.45}$ layer instead of pure SiO_2 and HfO_2 layers as intended. Random HRBS spectrum was analyzed using SIMNRA simulation software. The SIMNRA fit shown in Fig. 1 (solid line) further confirms the formation of a mixed $Hf_{0.18}Si_{0.32}O_{0.5}$ (0.6 nm) interlayer between Si-substrate and HfO_2 (1.8 nm) layer. Pure SiO_2 and HfO_2 layers are considered for analyzing the HR-XRR data shown in Fig. 2, where the interface roughness is attributed to mixing effects. Further XRR analysis also provides an estimate of surface roughness.

HRBS, Channeling and XRR results of pristine sample, summarized in Table 2, are comparable to each other and to nominal values within experimental limits. These measurements convincingly suggest the formation of a mixed HfSiO layer instead of a pure SiO_2

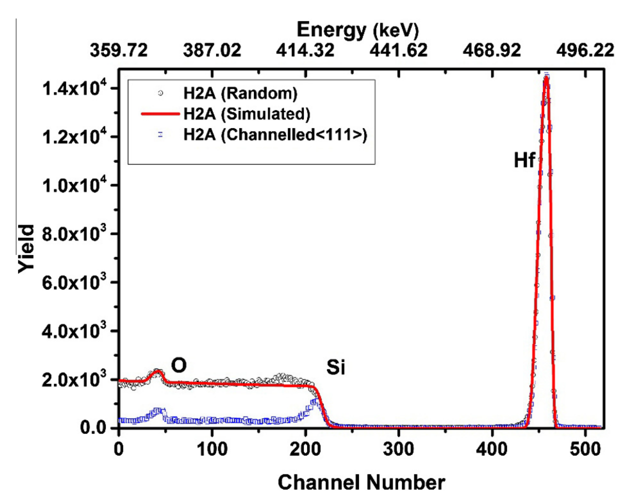

Fig. 1. Random and channeled HRBS spectra of pristine sample (H2A). Solid line represents the SIMNRA simulation of random HRBS spectrum.

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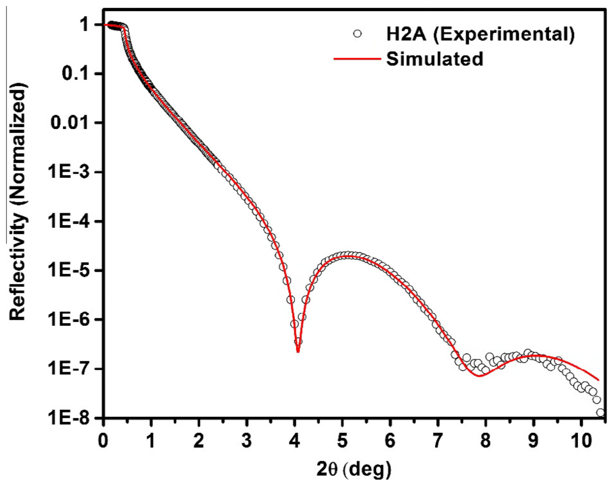

Fig. 2. HR-XRR spectra of pristine sample (H2A). Solid line represents the LEPTOS simulation of HR-XRR data.

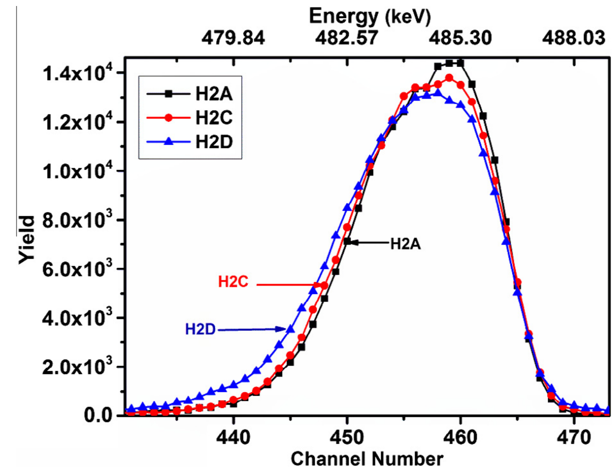

Fig. 3. (a) HRBS spectra (zoomed on Hf-peak) of irradiated and un-irradiated samples.

layer on Si-surface. It is well known that SiO_2 is very much stable on Si surface. Hence this mixed layer might have formed either during or after the deposition of HfO_2 layer. Inter diffusion of Hf into SiO_2 and Si into HfO_2 at SiO_2/HfO_2 interface is likely to be responsible for the observed mixed layer. This information is expected to be useful for understanding the kinetics of growth during atomic layer deposition.

As mentioned earlier, SiO_2 is considered as an interlayer in HfO_2-based MOS technology [17,18]. Hence it is important to study the stability of SiO_2/HfO_2 interface over Si/HfO_2 interface. Further it is well known that SiO_2 is more susceptible over Si to swift heavy ion induced track formation. This prompted us to study the effect of SHI on SiO_2/HfO_2 interface although SHI induced mixing is not reported in Si/HfO_2 and SiO_2/HfO_2 systems.

80 MeV Ni ion irradiation induced inter-diffusion of Si and Hf across $HfSiO/HfO_2$ interface is evident in the HRBS and XRR spectra shown in Fig 3. Fig. 3a shows the HRBS spectra (zoomed on Hf-peak) of irradiated and un-irradiated samples. The lower energy edge of this Hf-peak in H2D sample clearly confirms the diffusion of Hf into HfSiO interlayer. Similar effects are also observed in the XRR spectra, measured by Bruker D8 Advance diffractometer, shown in Fig. 3b.

Table 3 summarizes the results of HRBS/channeling analysis of irradiated and un-irradiated samples. As mentioned earlier, a χ_{min} of about 15% is observed in the near surface channels of Si ⟨1 1 1⟩ aligned spectra of pristine (H2A) sample. The χ_{min} in H2C and H2D is estimated to be 12% and 19% respectively. As mentioned earlier, the elemental composition of the surface layer is estimated using the relative intensities of Hf, Si and O peaks (Y_{Hf}/σ_{Hf}:Y_{Si}/σ_{Si}:Y_O/σ_o) in channeled spectra after subtracting the contribution of Si-surface peak. No considerable changes in the relative concentrations of various elements in mixed layers are noticed as a function of fluence. This is reasonable because this analysis assumes a single amorphous layer to start with. However, SIMNRA simulation of random spectrum suggests the existence of a pure HfO_2 (1.8 nm) layer on the surface of interlayer. Table 4 summarizes the results of SIMNRA analysis of HRBS spectra obtained from irradiated and un-irradiated samples. A systematic increase in the concentration of Si relative to that of Hf in interlayer is noticed as a function of

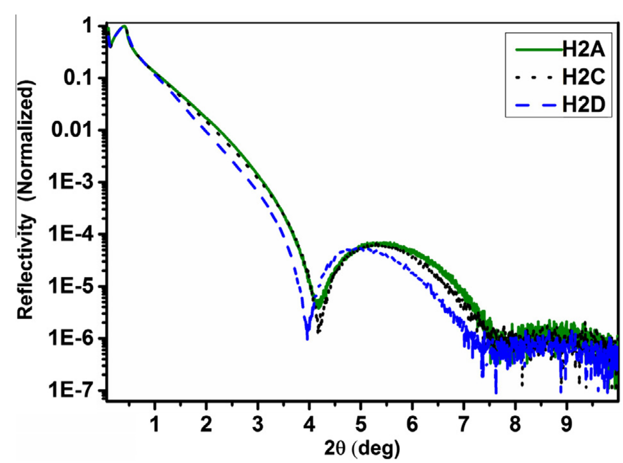

Fig. 3. (b) XRR spectra of irradiated and un-irradiated samples.

Table 3
HRBS/channeling analysis of irradiated and un-irradiated samples.

Sample	χ_{min} (%)	Hf:Si:O Y_{Hf}/σ_{Hf}:Y_{Si}/σ_{Si}:Y_O/σ_O (estimated from corresponding peaks in channelling spectra)*
H2A	15	0.182:0.328:0.451
H2C	12	0.177:0.326:0.449
H2D	19	0.183:0.314:0.469

* Counts estimated for 3 ML (mono layers) of Si (~2.04×10^{15} cm^{-2}) were subtracted from the total yield of Si to eliminate/minimize the contribution of Si-surface peak.

Table 2
Sample structure obtained from HRBS and HR-XRR.

Sample structure obtained from different methods				
Nominal values (as per growth)	HRBS	Channelling (from surface peaks)	HR-XRR	Roughness estimated by HR-XRR
HfO_2 (2.5 nm)	HfO_2 (~1.8 nm)	–	HfO_2 (2.37 ± 0.03 nm)	0.37 ± 0.05 nm (at surface)
SiO_2 (1 nm)	$Hf_{0.18}Si_{0.32}O_{0.5}$ (~0.6 nm)	$Hf_{0.18}Si_{0.33}O_{0.45}$	SiO_2 (1.8 ± 0.1 nm)	0.24 ± 0.03 nm (at interface)
Si (bulk)	Si (Bulk)	Si (Bulk)	Si (Bulk)	

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Table 4
SIMNRA analysis of HRBS spectra of irradiated and un-irradiated samples.

Sample	Layer I Hf:O (Surface)	Layer I thickness 10^{15} atoms/cm^2	Layer II Hf:Si:O	Layer II thickness 10^{15} atoms/cm^2
H2A	0.333:0.667	13	0.180:0.320:0.500	7
H2C	0.320:0.680	12	0.156:0.396:0.448	8
H2D	0.306:0.694	12	0.145:0.360:0.495	12

fluence. Similarly a systematic increase in the thickness of interlayer is also observed. These two observations together with XRR analysis confirm that SHI can induce intermixing across HfSiO/HfO_2 interface. As mentioned earlier SiO_2 is more susceptible to SHI induced track formation when compared to Si. Hence more prominent SHI induced intermixing effects are expected in HfSiO/HfO_2, SiO_2/HfO_2 systems when compared to Si/HfO_2 system. However an interlayer is essential for HfO_2 based MOS devices because HfO_2 itself is not thermally stable on Si surface. Hence it is important to study the irradiation effects on "interlayer/HfO_2" interface. Present study provides useful information for understanding the effects of SHI on "interlayer/HfO_2" interface.

4. Conclusion

HRBS, Channeling and XRR measurements of ALD grown HfO_2/SiO_2/Si samples are reported in this paper. These measurements suggest that the interlayer is a mixed $Hf_{0.18}Si_{0.32}O_{0.5}$ (0.6 nm) layer instead of a pure SiO_2 (1 nm) layer as intended. Further the effects of 80 MeV Ni ion irradiation on this interface have also been studied. A systematic increase in the concentration of Si relative to that of Hf, as a function of fluence is observed in the interlayer. The thickness of this interlayer is also found to increase with increase in fluence. These observations together with XRR analysis confirm that SHI can induce inter-diffusion of Hf and Si across HfSiO/HfO_2 interface. It is important to note that the existence of interlayer (like SiO_2) is essential for HfO_2 based MOS devices because HfO_2 is not thermally stable on Si surface. Present study yields useful information for elucidating the growth kinetics and ion assisted diffusion of various elements across this technologically important "interlayer/HfO_2" interface.

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