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 (SiO2) 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 HfO2, 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 interlayer of Silicon oxide/nitrides between Si and HfO2 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 HfO2/SiO2/Si samples. These samples were further irradiated by 80 MeV Ni ions to study ion induced inter-diffusion of Hf and Si across HfO2/Si interface as a function of ion fluence.

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1. Introduction

Hafnium based high dielectric constant materials are critical for the state-of-the-art integrated circuit technology [1]. Silicon dioxide (SiO2) has been widely used as a successful gate dielectric material because of its excellent interface properties with Si in MOS devices. SiO2 has been used as a gate dielectric for few decades and kept 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 SiO2 on Si is about 100 A/cm2 [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 SiO2. Hence several high-k materials like Al2O3, HfO2, ZrO2, Y2O3, and La2O3 have been examined as replacement for SiO2 as gate oxide [5,6]. Among all these high-k materials, ZrO2 and HfO2 are found to be most suitable for this purpose [7]. These two materials have similar properties like high dielectric constant (κ ~ 25 for both) and similar band gaps (Eg (ZrO2) ~ 5.8 eV and Eg (HfO2) ~ 6.0 eV) and enticed attention to replace traditional SiO2 gate dielectric [8]. The enhanced thermal stability of HfO2 over ZrO2 on Si surface has led HfO2 as the leading material in the industry [9]. SiO2 has already been replaced by HfO2 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 HfO2 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 HfO2 [19]. Hence it...
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 HfO2/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 HfO2 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 HfO2 based devices for terrestrial/space applications. Here we present a study on ion beam characterization and modification HfO2/SiO2/Si samples.

2. Experimental

ALD grown HfO2 samples were obtained from SEMATECH, USA. The typical sample structure was “HfO2 (2.5 nm)/SiO2 (1 nm)/Si (substrate)”. This sample was cut into several pieces for irradiation studies. Irradiation details of these samples are given in Table 1.

Table 1
Sample structure and irradiation details.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ion and energy</th>
<th>Irradiation fluence (ions/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2A</td>
<td>–</td>
<td>Pristine</td>
</tr>
<tr>
<td>H2C</td>
<td>Ni, 80 MeV</td>
<td>5 x 10¹²</td>
</tr>
<tr>
<td>H2D</td>
<td>Ni, 80 MeV</td>
<td>5 x 10¹³</td>
</tr>
</tbody>
</table>

Room temperature SHI irradiation was performed in a high vacuum chamber (<10⁻⁸ mbar) at a constant beam current of one particle Ampere (~1 pA). The beam (1 mm in diameter) is uniformly scanned over 1 x 1 cm² 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 θ = 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 (111) axis of Si) to minimize background scattering from Si substrate and to analyze amorphous layers (SiO2/HfO2) 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 size for omega and two-theta circles. The storage ring, Helios 2, was running at 700 MeV, typically stored electron beam current size for omega and two-theta circles. The storage ring, Helios 2, was running at 700 MeV, typically stored electron beam current size for omega and two-theta circles. The storage ring, Helios 2, was running at 700 MeV, typically stored electron beam current size for omega and two-theta circles. The storage ring, Helios 2, was running at 700 MeV, typically stored electron beam current size for omega and two-theta circles. The storage ring, Helios 2, was running at 700 MeV, typically stored electron beam current size for omega and two-theta circles. The storage ring, Helios 2, was running at 700 MeV, typically stored electron beam current size for omega and two-theta circles. The storage ring, Helios 2, was running at 700 MeV, typically stored electron beam current size for omega and two-theta circles. The storage ring, Helios 2, was running at 700 MeV, typically stored electron beam current size for omega and two-theta circles. The storage ring, Helios 2, was running at 700 MeV, typically stored electron beam current size for omega and two-theta circles. The storage ring, Helios 2, was running at 700 MeV, typically stored electron beam current size for omega and two-theta circles. The storage ring, Helios 2, was running at 700 MeV, typically stored electron beam current size for omega and two-theta circles.

Fig. 1. Random and channeled HRBS spectra of pristine sample (H2A). Solid line shows the SIMNRA simulation of random HRBS spectrum.
layer on Si-surface. It is well known that SiO₂ is very much stable on Si surface. Hence this mixed layer might have formed either during or after the deposition of HfO₂ layer. Inter diffusion of Hf into SiO₂ and Si into HfO₂ at SiO₂/HfO₂ 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, SiO₂ is considered as an interlayer in HfO₂-based MOS technology [17,18]. Hence it is important to study the stability of SiO₂/HfO₂ interface over Si/HfO₂ interface. Further it is well known that SiO₂ is more susceptible over Si to swift heavy ion induced track formation. This prompted us to study the effect of SHI on SiO₂/HfO₂ interface although SHI induced mixing is not reported in Si/HfO₂ and SiO₂/HfO₂ systems.

80 MeV Ni ion irradiation induced inter-diffusion of Si and Hf across HfSiO/HfO₂ 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 \( \chi_{\text{min}} \) of about 15% is observed in the near surface channels of Si (1 1 1) aligned spectra of pristine (H2A) sample. The \( \chi_{\text{min}} \) 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 (\( \frac{Y_{\text{Hf}}}{\sigma_{\text{Hf}}}:\frac{Y_{\text{Si}}}{\sigma_{\text{Si}}}:\frac{Y_{\text{O}}}{\sigma_{\text{O}}} \)) 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 HfO₂ (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 fluence.
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/HfO2 interface. As mentioned earlier SiO2 is more susceptible to SHI induced track formation when compared to Si. Hence more prominent SHI induced intermixing effects are expected in HfSiO/HfO2, SiO2/HfO2 systems when compared to Si/HfO2 system. However an interlayer is essential for HfO2 based MOS devices because HfO2 itself is not thermally stable on Si surface. Hence it is important to study the irradiation effects on “interlayer/HfO2” interface. Present study provides useful information for understanding the effects of SHI on “interlayer/HfO2” interface.

4. Conclusion

HRBS, Channeling and XRR measurements of ALD grown HfO2/SiO2/Si samples are reported in this paper. These measurements suggest that the interlayer is a mixed Hf0.18Si0.82O1.5 (0.6 nm) layer instead of a pure SiO2 (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/HfO2 interface. It is important to note that the existence of interlayer (like SiO2) is essential for HfO2 based MOS devices because HfO2 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/HfO2” interface.

Acknowledgements

We would like to thank Prof. Leonard C. Feldman, Rutgers University for providing samples for this study and for his valuable suggestions. We thank IUAC, New Delhi for providing necessary experimental facilities and for necessary financial support through an UFR project. Thanks are due to IBA-2013 organizers, IAEA, DST-PURSE-UH and CSIR, India for financial support. NMB acknowledges the financial support from CFN, UH; UGC-DAE-CSIR Kalpakkam and UGC, India in the form of UGC-CSIR-JRF. APP thanks CSIR for Emeritus Scientist award.

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