Surface Science Letters

Effect of nitrogen incorporation and oxygen vacancy on electronic structure and the absence of a gap state in HfSiO films

Moon Hyung Jang a,1, Kwang Sik Jeong b, Kwun Bum Chung c, Jin Woo Lee d, Myeung Hee Lee e, Mann-Ho Cho a,b,∗

a Atomic-scale Surface Science Research Institute, Yonsei University, Seoul 120-749, Republic of Korea
b Institute of Physics and Applied Physics, Yonsei University, Seoul 120-749, Republic of Korea
c Department of Physics, Dankook University, Cheonan 330-714, Republic of Korea
d LG Innotek, 379, Gasoo-Dong, Osan, 447-705, Republic of Korea
e Department of Physics, Yonsei University, Wonju 220-710, Republic of Korea

A R T I C L E   I N F O

Article history:
Received 18 October 2011
Accepted 9 April 2012
Available online 20 April 2012

Keywords:
HfSiO
Ab-initio calculations
Medium energy ion scattering
Near-edge x-ray absorption fine structure
Reflection electron energy loss spectroscopy
Absence of gap state

A B S T R A C T

The effect of nitrogen (N) incorporation into HfSiO on the electronic structure and band alignment of HfSiO films was investigated. N depth profile data obtained by medium energy ion scattering (MEIS) showed that the concentration of N or the bonding or electronic state of N in the film was stable when the film was annealed at 950 °C, while the oxygen (O) in HfSiO films was present in dissociated form, as evidenced by the unoccupied electronic state of O. The valence band offsets of the HfSiO films were strongly affected by N incorporation due to the presence of N in a 2p state. Moreover, a reduction in the conduction band offset of a HfSiO film was confirmed after the film was annealed in an atmosphere of N2. The unoccupied state of the O vacancy is responsible for the change in the conduction band offset. The results of ab-initio calculations for the density of states (DOS) of HfSiO and HfSiON supercells were in agreement with the experimental results. The incorporation on N into HfSiO prevents the formation of a gap-state inside the band gap despite the fact that an O vacancy is generated in the film.

© 2012 Elsevier B.V. All rights reserved.

HfSiO has been investigated as a gate dielectric, in an attempt to improve the mobility at the interface and the structural stability of HfO2. However, a survey of the literature indicates that HfSiO films are separated into two phases comprised HfO2 and SiO2 at temperatures above 900 °C, due to the high chemical potential [1]. One possible solution for eliminating this phase separation problem is the nitridation of HfSiO, since it would reduce the difference in the chemical potential for eliminating this phase separation problem is the nitridation of HfSiO at 900 °C, due to the high chemical potential [1]. One possible solution for eliminating this phase separation problem is the nitridation of HfSiO, since it would reduce the difference in the chemical potential for eliminating this phase separation problem is the nitridation of HfSiO at 950 °C, while the oxygen (O) in HfSiO films was present in dissociated form, as evidenced by the unoccupied electronic state of O. The valence band offsets of the HfSiO films were strongly affected by N incorporation due to the presence of N in a 2p state. Moreover, a reduction in the conduction band offset of a HfSiO film was confirmed after the film was annealed in an atmosphere of N2. The unoccupied state of the O vacancy is responsible for the change in the conduction band offset. The results of ab-initio calculations for the density of states (DOS) of HfSiO and HfSiON supercells were in agreement with the experimental results. The incorporation on N into HfSiO prevents the formation of a gap-state inside the band gap despite the fact that an O vacancy is generated in the film.

The focus of this study was to clarify the origin of changes in the electronic state and the band gap (Eg) and the band offset of HfSiO using PNA conditions that are actually employed in the fabrication process [6]. HfSiO films were deposited on p-type Si (100) substrates in 10 Å-thick SiO2 layers by atomic layer deposition (ALD) at 300 °C. Nitridation and sequential post annealing treatments were performed to investigate the effect of N2 on the physical properties and the band alignment of HfSiO as follows: (1) Nitridation of the as-grown film was performed in a NH3 atmosphere for 60 s at 750 °C (RTN) (2). After the RTN process, the film was sequentially annealed in a N2 atmosphere for 30 s at 950 °C (RTN). The depth profile of the HfSiO films was determined by MEIS using a 100 keV proton beam in a double alignment geometry. Near edge x-ray absorption fine structure (NEXAFS) O/N K-edge spectra were obtained at the 7B1 beamline at the Pohang acceleration laboratory (PAL). N 1s core level and valence spectra were obtained by x-ray photoelectron spectroscopy (XPS). Reflection electron energy loss spectroscopy (REELS) spectra were obtained using a VG ESCALAB 210 apparatus with a primary energy of 1000 eV.

The ab-initio calculations were performed for the following systems: (1) HfSiO and (2) HfSiON without an O vacancy and (3) HfSiO and (4) HfSiON with O vacancies (neutral, positively charged and negatively charged vacancy: V0, V +, V 2+, V − and V2−) to confirm

* Corresponding author at: Institute of Physics and Applied Physics, Yonsei University, Seoul 120-749, Republic of Korea.
E-mail address: mh.cho@yonsei.ac.kr (M.-H. Cho).
1 Current address: Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA 19104, USA.

0039-6028/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.susc.2012.04.010
the effect of incorporated N and the O vacancies in the HfSiO and HfSiON films. It is important to determine the extent of the charged O vacancy because these defects affect the conduction process that occurs via electrons or holes [7]. The supercells contained 24, 48, 95 and 191 atoms in the cases of (1) Hf4Si4O16, (2) Hf8Si8O28N4, (3) Hf16Si16O63 and (4) Hf32Si32O111N16, respectively. In the cases of N incorporation, N is located substitutionally on O site. It was necessary to increase the size of the supercells to permit only one O vacancy to be generated in (3) and (4). Since these supercells have been verified in numerous previous studies, it would be very useful to analyze the experimental behavior of the HfSiO films using ab-initio calculations [8]. The total energy and the density of the states were calculated using the Vienna Ab-initio Simulation Package (VASP) [9]. To optimize the total energies and geometry using pseudopotentials, a plane-wave cutoff energy of 450 eV with the Perdew, Burke, Ernzerhof (PBE) exchange-correlation functional of the generalized gradient approximation (GGA) was used. The electronic states were calculated after geometrical optimization using the same PBE functional with a plane-wave cutoff energy of 500 eV. Three-dimensional atomistic visualizations were carried out using VESTA code [10].

Fig. 1 shows MEIS depth profiles determined by fitting the raw data. The raw data with the fitting results are shown in supplementary material (Fig. S1) [11]. The Hf to Si ratio was about 1.0 at the interfacial region, while it was about 1.3 at the surface region of an as-grown film. After the RTN process, as shown in Fig. 1(b), the total number of N atoms in the entire film appeared to be 25.9% of the total number of O atoms in an as-grown film. In the mean time, the total number of O atoms decreased by about 29.2% compared to that for an as-grown film, indicating that N readily substitutes for O in the film, in spite of the fact that there is a 3.3% difference between them. Previous reports showed that most of the N reacts with SiO2 in HfSiO, resulting in the formation of chemical bonds such as N=Si=Si and Si–O–N. The reaction process between N and SiO2 is based on exchange of O by randomized interaction (GGA) was used. The electronic states were calculated after geometrical optimization using the same PBE functional with a plane-wave cutoff energy of 500 eV. Three-dimensional atomistic visualizations were carried out using VESTA code [10].

Fig. 2. (a) K edge NEXAFS spectra of O in an as-grown film, an RTN film and an RTNA film. (b) N K edge NEXAFS spectra of RTN and RTNA films. (c) N 1s XPS core level spectra of RTN and RTNA films. Open circles denote the raw data and the solid line superimposed on the raw data represent the results for the convolution of the fitted components (lines).
bonding in nitrided SiO$_2$ structure is dissociated at the high annealing temperature. In Fig. 2(b), the peak shape and intensity of the K edge spectra of N for RTN and RTNA are almost the same, indicating that their electronic structure was not significantly altered by the RTNA process.

The XPS N 1s spectra (open circles) in Fig. 2(c) were deconvoluted with several N chemical states of N1 to N5. Except for the N1 and N5 lines, no significant changes in intensity were evident. Based on the peak position of N 1s for HfSiO$_3$N$_y$ (Hf–N=Si$_2$) and Si$_2$N$_4$ (N=Si$_2$) at 396.8 and 397.8 eV, respectively, the N1 line at about 397.3 eV is presumably due to a N component related to Si-rich HfSiO$_3$N$_y$ [12,13]. In addition, as discussed above, the concentration of N has a tendency to follow that of Si. Therefore, this core level state is estimated to be in a Si-rich HfSiO$_3$N$_y$ state. In spite of the N$_2$ annealing at a temperature of 950 °C, the N1 intensity of RTNA is similar to that of an RTN film. Combining these data with nitrogen MEIS profiles, it is obvious that the N in the film and interfacial region is stable, even after an RTNA process. According to previous reports, the N2 component at 398.3 eV can be attributed to the presence of SiO$_2$N states [12,16].

The evaluated values of $E_g$, $\Delta E_{\text{fi}}$, and the calculated conduction band offsets ($\Delta E_{\text{c}}$) are tabulated in Table 1, where $\Delta E_{\text{c}} = E_g - \Delta E_{\text{fi}} - \Delta E_{\text{p}}$. An important finding is that, after nitridation (RTN), the magnitude of the decrease in the value of $\Delta E_{\text{c}}$ is not as large as that of $\Delta E_{\text{fi}}$ [21]. However, the values for $\Delta E_{\text{fi}}$ for the RTNA film are decreased to 0.21 eV, compared to that for the RTN film. This decrement can be attributed to the O vacancy in HfSiO$_3$N$_y$ which is located adjacent to Hf and Si sites, because the energy state for the O vacancy is located below the conduction band. Thus, the change in $E_g$ after RTNA can be caused by the formation of an O vacancy as a defect state.

To investigate the role of N incorporation and O vacancies more precisely, ab-initio calculations were carried out. Fig. 4(a) shows the calculated total density of states (DOS) and $E_g$ for several HfSiO and HfSiON systems with and without an O vacancy. In the case of the HfSiO system, the value for $E_g$ is estimated to be 4.67 eV, which is lower than the experimentally determined value for the as-grown HfSiO film because the local density approximation (LDA) is underestimated. Hence, the discussion is confined to the exact value of $E_g$.

![Fig. 3. (a) REELS spectra of as-grown, RTN and RTNA films denoted with $E_g$ values. (b) XPS valence spectra as a function of the energy relative to VBM of Si for as-grown, RTN and RTNA films. Values of $\Delta E_{\text{fi}}$ are denoted with sample conditions.](image)

![Fig. 4. (a) REELS spectra of as-grown, RTN and RTNA films denoted with $E_g$ values. (b) XPS valence spectra as a function of the energy relative to VBM of Si for as-grown, RTN and RTNA films. Values of $\Delta E_{\text{fi}}$ are denoted with sample conditions.](image)

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>As-grown</th>
<th>RTN</th>
<th>RTNA</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_g$</td>
<td>5.34</td>
<td>4.36</td>
<td>4.16</td>
</tr>
<tr>
<td>$E_c$</td>
<td>2.25</td>
<td>1.41</td>
<td>1.42</td>
</tr>
<tr>
<td>$E_{\text{p}}$</td>
<td>1.97</td>
<td>1.83</td>
<td>1.62</td>
</tr>
</tbody>
</table>
value of $E_g$ is not affected by the charge in the O vacancy (neutral, positively charged and negatively charged), as shown in Fig. 4(a). In addition, the findings indicate that the origin of this change is from the conduction band of the system. The PDOS in the HfSiON system with a positively charged vacancy ($V^{2+}$) in Fig. 4(c) shows that the lowering of the conduction band offset is related mainly to Hf PDOS as discussed above. However, no evidence was found for the existence of defect states (O vacancy) within the band gap in the HfSiON system (Fig. S2 in Ref. [22]) while the HfSiO system with an O vacancy has a gap-state inside the band gap, as shown in Fig. 4(a). Xiong et al. reported on the formation of a VN$_2$ complex which consists of two N atoms and an O vacancy in the theoretical results for an N incorporated HfO$_2$ system [23]. The theoretical results also show that the gap-state is not generated because of the closed shell properties of the VN$_2$ complex. In the case of a HfSiON system with an O vacancy, as shown in Fig. 4(d) (HfSiON with $V^+$), the same situation holds. N atoms are paired next to the vacancy and the formed VN$_2$ complex, as indicated by the open red circles. Therefore, we propose that the absence of a gap-state in the HfSiON system with an O vacancy can be explained by the formation of a VN$_2$ complex. The absence of a gap state can minimize the electron trap inside the band gap which could subsequently affect the leakage current with Schottky emission.

In summary, the effects of N incorporation and an O vacancy on the electronic state of HfSiO films were investigated. The incorporation of N results in a reduction in $E_g$ and $\Delta E_v$ because N 2p states are main constituents of VBM. In addition, the most influential factor for determining the value for $\Delta E_c$ is the presence of O vacancies in the RTNA film because of the unoccupied Hf electronic state. The absence of a gap-state within the band gap originates from the VN$_2$ complex in a HfSiON system with an O vacancy.

Acknowledgment

This work was partially supported by the Joint Program for Samsung Electronics-Yonsei University and the IT R&D program of MKE/KEIT (10035320, “Development of novel 3D stacked devices and core materials for the next generation flash memory”). We gratefully acknowledge the technical advice of K. Chae, C. C. Hwang, and H.-N. Hwang at PAL on beamline 7B1.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.susc.2012.04.010.
References

[22] See supplementary material for the density of states for the HfSiO and HfSiON with or without vacancy.