

Si emission from the SiO₂/Si interface during the growth of SiO₂ in the HfO₂/SiO₂/Si structure

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(Received 4 November 2005; accepted 16 March 2006; published online 13 April 2006)

HfO₂/SiO₂/Si(001) structures were annealed in dry oxygen, and compositional depth profiles were measured by high-resolution Rutherford backscattering spectroscopy. Growth of the interfacial SiO₂ layer and simultaneous surface accumulation of Si were observed. The observed result indicates that silicon species are emitted from the SiO₂/Si interface to release the stress induced by oxidation as was predicted by recent theoretical studies. © 2006 American Institute of Physics.

[DOI: 10.1063/1.2195101]

The downscaling of Si devices has led to the need for fine control techniques to form oxide layer as thin as 1 nm. Therefore, an understanding of Si oxidation is strongly demanded by the industry as well as in materials science.¹ This is also the case even if SiO₂ is replaced by high-*k* materials in future Si devices. An ultrathin (sub nanometer) SiO₂ layer is intentionally grown on Si before the formation of the high-*k* film to get better device performance.² Thus, the understanding of Si oxidation is still an important issue.

The oxidation of relatively thick (>10 nm) films is well described by the so-called Deal-Grove model.³ The oxidation kinetics for very thin films, however, cannot be explained by the Deal-Grove model.⁴ The oxidation rate for thin films is much faster than that expected from a linear relationship predicted by the Deal-Grove model. The failure of the Deal-Grove model may be related to the large volume expansion upon oxidation. During oxidation of Si, oxidant diffuses through the disordered oxide network and reacts with silicon substrate at the SiO₂/Si interface.^{3,5–7} The volume of the increased oxide region is about twice larger than that of the decreased Si region. The volume expansion results in high stress on the interface between Si and SiO₂,^{8,9} which should be released when the oxidation proceeds. Recent theoretical studies predicted that Si species are emitted from the SiO₂/Si interface into the SiO₂ to reduce the stress.^{10,11} Most of the emitted Si species diffuse into and through the SiO₂. Depending on the SiO₂ layer thickness, emitted Si species accumulate at the surface as a new oxide layer (in case of thin films) or they are incorporated in the SiO₂ layer through oxidation (in case of thick films).¹² There are several experimental results consistent with this scenario.^{13,14} Nevertheless, there is no direct observation of the predicted Si emission so far.

In the present work, we use HfO₂/SiO₂/Si structures to observe the Si emission. It is known that the interfacial SiO₂ layer grows during the high-temperature thermal processing

of the high-*k*/SiO₂/Si structures in oxygen ambient.¹⁵ Here, we observe the behavior of Si atoms during the growth of the interfacial SiO₂ layer using high-resolution Rutherford backscattering spectroscopy (HRBS). A recent study on the thermal decomposition behavior of HfO₂/SiO₂/Si indicates that Si species can outdiffuse through a HfO₂ film.¹⁶ The emitted Si species from the SiO₂/Si interface, therefore, are expected to accumulate at the surface of the HfO₂ film. Thus, the emitted Si can be separately observed from the interfacial SiO₂ layer using HRBS.

A HfO₂ film of 4 nm thickness was grown by atomic layer deposition (ALD) using tetrakis(ethylmethylamino)hafnium (Hf[N(CH₃)(C₂H₅)₂]₄) with O₃ as an oxidant after preparing a SiO₂ layer of 0.7 nm thickness on Si(001).¹⁷ In order to prepare a high quality HfO₂ film, the sample was annealed in O₃ at 275 °C for 10 min after deposition. The samples thus prepared were annealed in an infrared furnace (MLLA 3000) at 500–900 °C in 0.1 Torr dry oxygen for 2–20 min. For comparison, the sample was annealed also in an ultrahigh vacuum chamber (base pressure 4 × 10^{−10} Torr) at 800 °C for 2 min.

These samples were observed by HRBS using 400 keV He⁺ ions as a probe. The details of the HRBS measurement were described elsewhere.¹⁸ In the present measurements, samples were aligned to a channeling configuration with the [111] axis parallel to the incident beam, reducing the substrate contribution to the signal. Energy spectra of He⁺ ions scattered at 50° were measured by a 90° sector magnetic spectrometer.

Figure 1 shows the observed HRBS energy spectra. The solid line shows the spectrum of the as-grown sample. There are three peaks in the spectrum. The large peak at ~390 keV corresponds to Hf in the HfO₂ layer. The peak at ~350 keV corresponds to Si in the SiO₂/Si interface region. This Si interface peak consists of contributions from the interfacial SiO₂ layer and the substrate Si atoms which can be seen by the channeling ions. The latter contribution mainly comes from the topmost Si atomic layer in the substrate Si (this is

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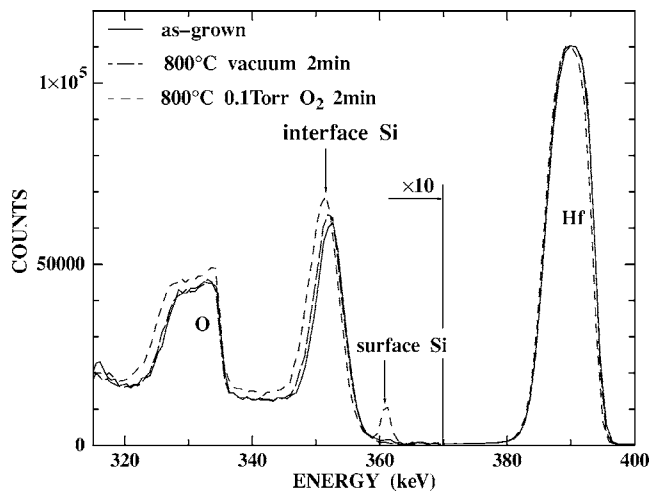


FIG. 1. HRBS energy spectra observed under [111] channeling conditions for the as-grown $\text{HfO}_2/\text{SiO}_2/\text{Si}(001)$ sample (solid line) and the sample annealed at 800 °C for 2 min in 0.1 Torr O_2 (short dashed line). The spectrum for the sample annealed at 800 °C for 2 min in vacuum is also shown for comparison (dashed line). The incident ion was 400 keV He^+ and the angle of incidence and the scattering angle were 54.74° and 50°, respectively.

essentially the same as the so-called surface peak in a usual channeling spectrum) and is almost independent of the thickness of the interfacial SiO_2 layer unless the SiO_2 layer is extremely thick. The increase of the Si interface peak yield is, therefore, attributed to the growth of the SiO_2 layer. The third peak seen at ~330 keV corresponds to O in both the HfO_2 and the interfacial SiO_2 layers. The thickness of the interfacial SiO_2 layer is estimated to be 0.7 nm from the observed result.

The spectrum of the sample annealed at 800 °C in O_2 (short dashed line in Fig. 1) is quite different from that of the as-grown sample. Both the Si peak as well as the O peak become wider after annealing, indicating the growth of the interfacial SiO_2 layer. The increase of the interfacial SiO_2 layer is estimated to be 0.6 nm from the observed Si peak. In contrast to the Si and the O peaks, the shape of the Hf peak does not change but a small shift (~0.3 keV) towards lower energies is observed. A similar shift was also observed for the leading edge of the Si interface peak. These shifts suggest the formation of an overlayer on the HfO_2 surface. In addition to these changes, a new peak appears around 361 keV, which corresponds to Si at the surface. The amount of the surface Si is estimated to be 3.3×10^{14} at./cm² (corresponding to a SiO_2 layer of 0.14 nm thickness). The energy shift of the Hf peak due to the formation of a 0.14 nm SiO_2 overlayer is calculated to be 0.27 keV. This is in good agreement with the observed energy shift, suggesting that SiO_2 overlayer of 0.14 nm thickness was formed on the HfO_2 layer. However, there could be an alternative explanation of the surface Si signal, i.e., pinholes might be formed in the HfO_2 film during oxidation.¹⁹ In order to eliminate this possibility, the surface of the sample was examined using atomic force microscopy (AFM) and scanning electron microscopy (SEM). No pinhole was observed, confirming the formation of SiO_2 overlayer on HfO_2 . In addition, there was also no signature of void formation at the oxide/silicon interface in the observed AFM and SEM images.

Figure 2 shows observed HRBS spectra of the samples annealed in 0.1 Torr O_2 for 2 min at various temperatures.

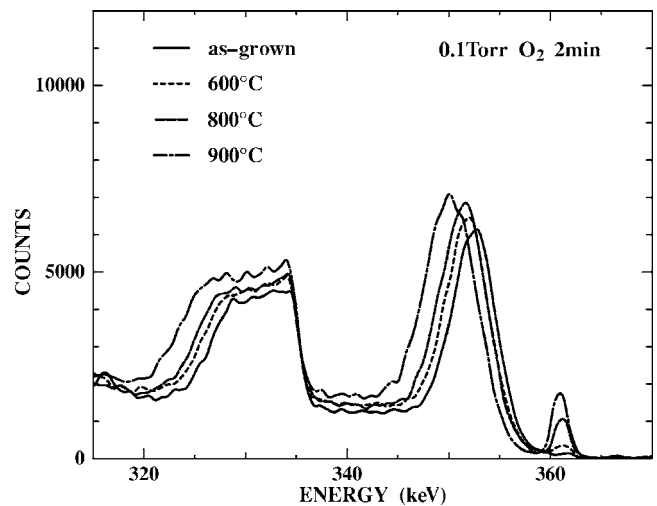


FIG. 2. HRBS energy spectra observed under [111] channeling conditions for as-grown $\text{HfO}_2/\text{SiO}_2/\text{Si}(001)$ sample (solid line) and samples annealed at various temperatures in 0.1 Torr O_2 for 2 min: 600 °C (short dashed line), 800 °C (dashed line), and 900 °C (dot-dashed line). The incident ion was 400 keV He^+ and the angle of incidence and the scattering angle were 54.74° and 50°, respectively.

Only the signals for Si and O are shown because the Hf peak did not change except for the small energy shift mentioned above. Widths of both Si and O peaks increase with increasing temperature, indicating that the thickness of the interfacial SiO_2 layer increases with annealing temperature. The yield of the surface Si also increases with increasing temperature, showing that there is a strong correlation between the growth of the interfacial SiO_2 layer and the SiO_2 overlayer. This strongly suggests that the origin of the surface Si is the Si emission from the SiO_2/Si interface during the growth of the interfacial SiO_2 layer. There are, of course, other possibilities, e.g., the heating itself may cause the surface accumulation of Si independent of the oxidation. In order to see if this is the case, the sample was annealed in vacuum at 800 °C for 2 min. The observed HRBS spectrum (a dashed line in Fig. 1) is very similar to the spectrum of the as-grown sample. Neither the surface Si peak nor the growth of the interfacial layer is seen. This clearly indicates that the observed surface Si is a result of the oxidation and is not a result of the heating itself.

Finally, we studied the annealing time dependence of the Si emission. The samples were annealed at 900 °C in 0.1 Torr oxygen for various annealing times. The increase of the Si areal density of the surface SiO_2 layer, ΔD_s , and that of the interfacial SiO_2 layer, ΔD_i , were measured and the results are shown as a function of the annealing time in Fig. 3. The ratio of the increase of the surface Si to that of the interface Si, $\Delta D_s/\Delta D_i$, is also shown to clear up their quantitative relation. The interfacial SiO_2 layer increases with increasing annealing time. This growth rate slows down when the annealing time exceeds 5 min. The surface Si also increases with annealing time but saturates after 5 min. The ratio, $\Delta D_s/\Delta D_i$, is about 0.3 at an annealing time of 2 min. This means that more than 23% ($=0.3/1.3$) of Si atoms are emitted from the SiO_2/Si interface during oxidation. This is in good agreement with the result of the first principles calculation, which showed that one Si atom is kicked out of the SiO_2/Si interface when every three Si atoms are oxidized.¹¹

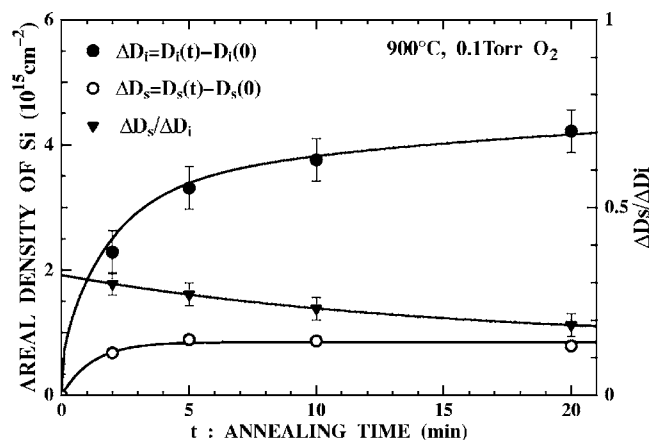


FIG. 3. The change of the Si areal density for the interfacial SiO₂ layer (●) and that for surface SiO₂ layer (○) for the samples after annealing at 900 °C in 0.1 Torr O₂. The ratio (▼) of the latter to the former is also shown.

The observed ratio, $\Delta D_s/\Delta D_i$, decreases with increasing annealing time, indicating that a part of emitted Si atoms is incorporated in the interfacial SiO₂ layer. After 5 min the surface Si does not increase while the interfacial SiO₂ layer still grows. This means that the emitted Si species are almost completely incorporated in the SiO₂ layer and cannot reach the surface when the thickness of the SiO₂ layer exceeds ~ 2 nm in the present conditions (900 °C in 0.1 Torr oxygen).

In conclusion, the growth of the interfacial SiO₂ layer and the simultaneous surface accumulation of Si were observed when HfO₂/SiO₂/Si was annealed in oxygen. A strong correlation was found between the growth of the interfacial SiO₂ layer and the Si surface accumulation. The observed result indicates that silicon species are emitted from the SiO₂/Si interface during the growth of the interfacial SiO₂ layer to release the stress which is induced by oxidation. The fraction of the emitted Si was estimated to be

more than 23%, which is consistent with the recent theoretical studies.

This work was supported in part by the Special Coordination Funds for Promoting Science and Technology from the Ministry of Education, Culture, Sports, Science, and Technology. This work was also supported by the Center of Excellence for Research and Education on Complex Function Mechanical System (COE program) of the Ministry of Education, Culture, Sports, Science, and Technology. The authors thank K. Shiraishi and H. Kageshima for fruitful discussions.

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