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High-resolution RBS analysis of Si-dielectrics interfaces

Zhao Ming[1], Kaoru Nakajima[1], Motofumi Suzuki[1], Kenji Kimura[1],
Masashi Uematsu[2], Kazuyoshi Torii[3*], Satoshi Kamiyama[3], Yasuo Nara[3],
Heiji Watanabe[4], Kenji Shiraishi[5], Toyohiro Chikyow[6], Keisaku Yamada[7]

[1]Department of Micro Engineering, Kyoto University, Yoshida-honmachi, Sakyo, Kyoto 606-8501, Japan
[2]NTT Basic Research Laboratories, NTT Corporation, Atsugi 243-0198, Japan
[3]Semiconductor Leading Edge Technologies, Inc. 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan
[4]Department of Precision Science and Technology, Osaka University, Suita, Osaka 565-0871, Japan
[5]Institute of Physics, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8571, Japan
[6]National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan
[7]Nanotechnology Research Laboratories, Waseda University, Shinjyuku, Tokyo 62-0041, Japan

1. Introduction

In the future complementary metal-oxide-semiconductor (CMOS) devices, SiO_2 cannot be used for gate dielectric films because of its high leakage current. Alternative materials with a dielectric constant higher than SiO_2, such as HfO_2, have been extensively studied [1]. The interfaces between Si and these dielectric materials are not so good as compared to Si/SiO_2. For better device performance, characterization and precise control of the Si/dielectrics interface are of prime importance. In this talk, examples of the analysis of the Si-dielectrics interfaces using high-resolution Rutherford backscattering spectroscopy (HRBS) are presented with a particular emphasis placed on the interface reaction during thermal processing of HfO_2/SiO_2/Si stack structures.

2. Experimental

A HfO_2 film of ~3 nm thickness was grown by ALD after preparing a SiO_2 layer of 0.7 nm thickness on Si(001). The samples were annealed in an infrared furnace at 500 - 900°C in 0.1 Torr dry oxygen for 2 - 20 minutes. The sample was also annealed in $^{18}O_2$ ambient to investigate the diffusion behavior of oxygen. These samples were observed by HRBS using 400 keV He^+ ions as a probe. The details of the HRBS measurement were described elsewhere [2].

3. Results and discussion

Fig.1 shows examples of the HRBS energy spectra observed under [111] channeling condition before and after annealing. The solid line shows the spectrum of the as-grown sample. There are three peaks corresponding to Hf (at ~ 390 keV), Si in the SiO_2/Si interface region (at ~ 350 keV) and O (at ~ 330 keV). The thickness of the interfacial SiO_2 layer is estimated to be 0.7 nm from the spectrum.

The spectra observed after annealing at 900°C in O_2 are 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. In addition to these changes, a new peak appears around 361 keV, showing that a thin SiO_2 layer was formed. The origin of the surface SiO_2 layer was discussed elsewhere [3].

Figure 2 shows the thickness of the observed interfacial SiO_2 layer as a function of the annealing time. The initial growth rate of the interfacial SiO_2 layer is ~ 0.5 nm/min in the first 2 min, which is much faster than the reported oxidation rate (0.1 nm/min) for 0.7 nm SiO_2 atop Si at the same temperature and at higher O_2 pressure [4]. The growth rate becomes almost saturated at a thickness ~ 2 nm. This kind of initial enhancement and subsequent suppression of SiO_2 growth reminds one the oxidation of Si

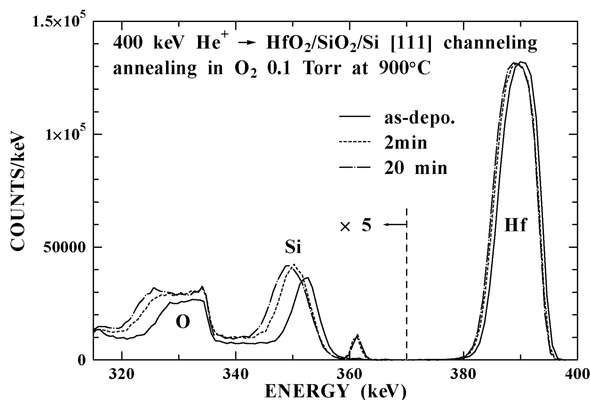

Fig. 1: HRBS spectra of HfO_2/SiO_2/Si.

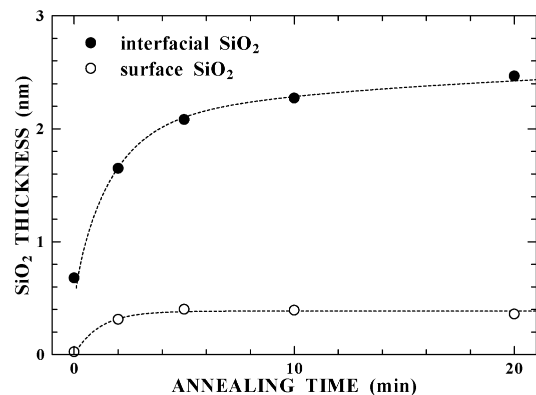

Fig. 2: Interface and surface SiO_2 thickness as a function of annealing time.

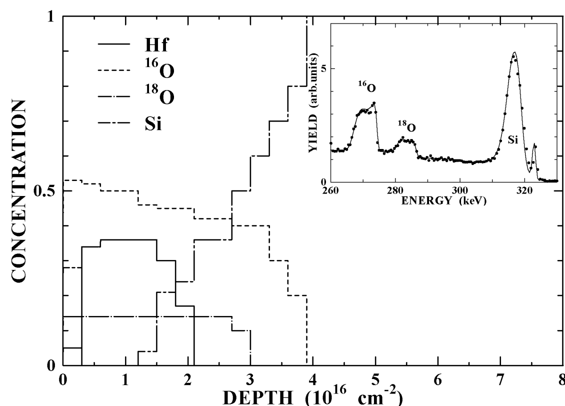

Fig. 3: Elemental depth profiles observed after annealing at 900°C in 0.1 Torr $^{18}O_2$ for 20 minutes.

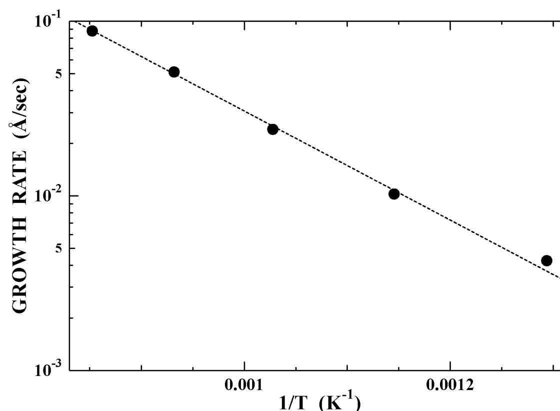

Fig. 4: Initial growth rate of the interfacial SiO_2 layer as a function of temperature.

by atomic oxygen [5 - 8].

In order to clarify the origin of the enhancement of SiO_2 growth rate, the behavior of oxygen during the annealing was observed using ^{18}O as a tracer. The inset of Fig. 3 shows observed HRBS spectrum of $HfO_2/SiO_2/Si(001)$ annealed at 900°C in 0.1 Torr $^{18}O_2$ for 20 minutes. The signal of ^{18}O can be observed separatly from ^{16}O signal. Figure 3 shows the depth profiles derived from the observed HRBS spectra. The flat profile of ^{18}O in HfO_2 demonstrates an extremely high diffusion coefficient of oxygen in HfO_2. This indicates that the oxygen diffusion in HfO_2 is not the rate limiting step in the interfacial layer growth.

More detailed inspection of ^{18}O profile reveals that ^{18}O exists only near the HfO_2/SiO_2 interface in the SiO_2 layer. This is quite different from the ^{18}O distribution in SiO_2/Si structure oxidized by $^{18}O_2$, which usually shows an accumulation of ^{18}O near the SiO_2/Si interface [9]. In that case, molecular oxygen is the dominant diffusing oxidant. If the dominant diffusing oxidant in HfO_2 is also the molecular oxygen, the accumulation of ^{18}O near the SiO_2/Si interface should be observed. The absence of the interface accumulation indicates that molecular oxygen is decomposed into atomic oxygen in HfO_2 and the atomic oxygen is the dominant diffusing oxidant.

There are two possible mechanisms of diffusion of atomic oxygen in oxides, the interstitial and exchange mechanisms [10]. In the interstitial mechanism, the interstitial oxygen atoms diffuse through empty space between the lattice sites. If this is the case, ^{18}O should accumulate in the SiO_2/Si interface region. On the other hand, the exchange mechanism involves the continuous replacement of a lattice site by the diffusing defect. This mechanism is characteristic of diffusion of anions in oxides such as MgO [11]. In this mechanism, incorporated ^{18}O atoms push the already existing ^{16}O toward SiO_2/Si interface. The present ^{18}O profile demonstrates that the exchange mechanism is a dominant mechanism both in the HfO_2 and SiO_2 layers.

Figure 4 shows Arrhenius plot of the initial growth rate of SiO_2 in the first 2-min. The activation energy is estimated to be ~0.6 eV. Because the diffusion process in HfO_2 is not the rate limiting process in the present case as was mentioned above, this activation energy should be related to the oxygen diffusion in SiO_2 and/or oxygen reaction with Si at SiO_2/Si. The obtained activation energy is comparable to the reported diffusion activation energy of O^- in SiO_2 (0.14 ~ 0.7 eV) [12, 13], confirming that the dominant diffusing oxygen species is not molecular oxygen but the atomic oxygen ion.

4. Conclusion

The diffusion mechanism of oxygen in HfO_2 was studied by HRBS using ^{18}O as a tracer. The observed ^{18}O profile indicates that molecular oxygen is decomposed into atomic oxygen and the atomic oxygen diffuses through HfO_2 via an exchange mechanism.

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*Present affiliation: Hitachi, Ltd.