

Experimental proof of direct correlation between hydrogen migrated to SiO₂/Si interface and MOSFET characteristics using high energy ¹⁵N²⁺ ion beam

Masamichi Suzuki¹, Riichiro Takaishi¹, Yusuke Higashi¹, Mitsuhiro Tomita¹, Yuichiro Mitani¹, Masuaki Matsumoto², and Katsuaki Fukutani²

¹ R&D Center, Toshiba Corporate

1, Komukai Toshiba-cho, Saiwai-Ku, Kawasaki 212-8582, Japan

Phone: +81-44-549-2075 E-mail: masamichi2.suzuki@toshiba.co.jp

² Institute of Industrial Science, University of Tokyo

4-6-1, Komaba, Meguro, Tokyo 153-8505, Japan

Abstract

High energy ¹⁵N²⁺ ion beam was used not only as NRA (Nuclear Reaction Analysis) for the estimation of hydrogen depth profile but also as the measure to migrate hydrogen to the SiO₂/Si interface. In the case of SiO₂ formed by wet oxidation (WO), the leakage current and interface trap density (Nit) were dramatically degraded after ion beam irradiation due to the depassivation of hydrogen in the bulk followed by hydrogen migration to the interface. As for SiO₂ formed by radical oxidation (RO), the significant hydrogen migration to the interface was not observed and the increased Nit value was almost the same as that of constant current stress case. The direct correlation between hydrogen at the interface and MOSFET degradation was successfully demonstrated.

1. Introduction

The scaling of CMOS transistors has been associated with an adverse effect of the reliability deterioration of gate dielectric. For instance, threshold voltage (V_{th}) shift caused by negative bias temperature instability (NBTI) have become obvious with the scaling [1]. The cause of this phenomenon has been considered to be hydrogen release followed by its diffusion [2]. On the other hand, it is revealed by first principle calculation that negatively charged hydrogen atoms in SiO₂/Si system migrate to the interface, resulting in the generation of dangling bonds at the interface through H₂O molecule desorption[3]. Although hydrogen has close relationship with MOSFET performance as mentioned above, accurate estimation of hydrogen depth profile is very difficult.

Resonant Nuclear Reaction Analysis (NRA) using ¹H (¹⁵N, α)¹²C reaction with the resonant energy of 6.5 MeV is one of effective method for the analysis of hydrogen profile because of its narrow resonant width (1.86 keV) [4,5]. However, when the ion exposures exceed a threshold of 3×10¹⁵/cm², the detachment of hydrogen atoms in SiO₂/Si system by energetic secondary electrons occur, resulting in migration of hydrogen to the SiO₂/Si interface [6]. In this paper, using this hydrogen redistribution behavior during NRA measurement, we demonstrate the direct correlation between hydrogen migrated to SiO₂/Si interface and MOSFET characteristics.

2. Experimental

Blanket samples with SiO₂(6 nm)/Si and nMOSFETs with Poly-Si(125 nm)/SiO₂(6 nm)/Si were fabricated, in which two kinds of SiO₂ were applied. One SiO₂ was fabricated by wet oxidation (WO); the other was fabricated by radical oxidation (RO). These SiO₂ were expected to contain different hydrogen concentration. Hydrogen depth profile of blanket samples were determined by NRA using ¹⁵N²⁺ ion beam (6.356~6.464 MeV).

Incident angle was 17° with respect to the sample surface. The same condition of ¹⁵N²⁺ ion beam except ion beam energy (6.528~6.674 MeV) was also irradiated to nMOSFETs for the estimation of impact of hydrogen migration to the interface on MOSFET performance. In our experiments, the ion exposures were designed to cause the hydrogen migration. The damage in SiO₂ such as a bond breakage stem from an atomic collision is considered to be negligible because nuclear stopping power in SiO₂ region is nearly zero at this energy. On the other hand, because the electron stopping power is dominant, the energetic secondary electrons are created by the ion beam irradiation, resulting in hydrogen migration. Therefore, the change of MOSFET performance is considered to be mainly due to the hydrogen migration. Fig.1 represents the evaluation concept of this study.

3. Results and Discussion

3.1 Hydrogen redistribution by high energy ¹⁵N²⁺ ion beam

Figs.2 show the hydrogen depth profile estimated by (a) High-resolution Elastic Recoil Detection Analysis (HERDA) and (b) NRA using each blanket sample. As expected, WO-SiO₂ contained higher concentration of hydrogen (Figs.2 (a)) and hydrogen migration to the interface by ion beam irradiation was observed characteristically in WO-SiO₂ (Fig.2 (b)).

3.2 Direct correlation between migrated hydrogen to the interface and MOSFET characteristics

Fig.3 shows gate current(I_g)-gate voltage(V_g) curves for two nMOSFETs *without* ion beam irradiation. Because they had the same SiO₂ thickness, the curves showed quite the same behavior dominated by Fowler–Nordheim (FN) tunnel current. Fig.4 shows the I_g-V_g curves *with and without* ion beam irradiation. I_g for nMOSFET with WO-SiO₂, in which hydrogen was supposed to migrate to the interface, dramatically increased with ion beam irradiation as compared with the case of RO-SiO₂. The dramatic increase in WO-SiO₂ is thought to be caused by the defects due to the depassivation of hydrogen in bulk stem from energetic secondary electrons generated with ion beam irradiation. Moreover, oxygen vacancies might be subsequently created by hydrogen condensation around the defects[7] due to depassivation of hydrogen, and the vacancies might also increase the I_g.

The interface trap density (Nit) was also strongly associated with the migrated hydrogen. While charge pumping curves (CP) for two nMOSFETs *without* ion beam irradiation are quite the same (Fig.5(a)) as is the case with I_g-V_g, the Nit for WO-SiO₂ case increased dramatically by ion beam irradiation (Fig.5(b)). Then, the conventional electrical stress (constant current stress) with the positive gate bias and ion beam irradiation were compared about Nit. The behaviors of Nit under constant current stress for both samples are almost the

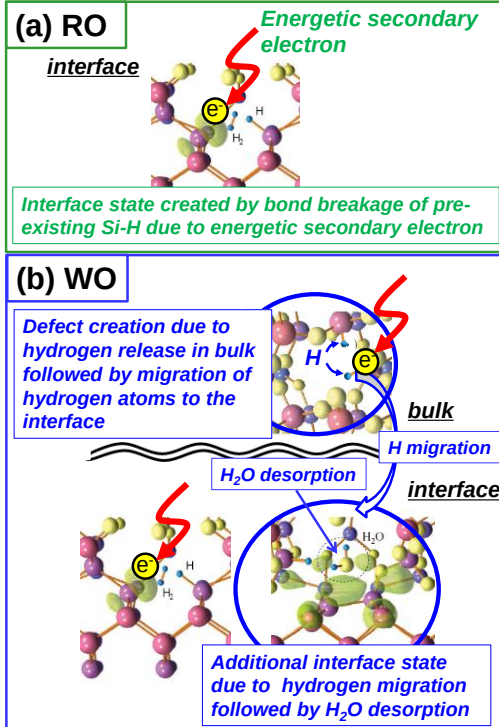
same and saturated at the lower Nit than that of WO-SiO₂ with ion beam irradiation as shown in Figs.6. We infer that, in the case of constant current stress, hydrogen has little to do with the Nit increase, because *negatively charged hydrogen* move away from SiO₂/Si interface under the stress condition with the *positive* gate bias[3]. The saturated Nit values in Figs.6 (b) are considered to depend on the number of pre-existing Si-H bonds at SiO₂/Si interface. The pre-existing Si-H bonds are broken by electron injection under constant current stress followed by formation of H₂ molecule[3], and Nit increases up to the saturated value. It should be noted that the saturated Nit value of RO-SiO₂ in figs.6(b) is equivalent to the value with ion beam irradiation shown in figs.6(a). These results can be explained as shown in Fig.7. Nit increase of RO-SiO₂ case in figs.6(a) is caused by breakages of pre-existing Si-H bonds due to energetic secondary electrons generated with ion beam irradiation as is the case of constant current stress, while the additional Nit increase occur in WO-SiO₂ case due to migration of hydrogen atoms from bulk to the interface followed by H₂O molecule desorption [3] with ion beam irradiation.

4. Conclusions

The direct correlation between hydrogen migrated to SiO₂/Si interface and MOSFET characteristics was demonstrated using high energy ¹⁵N²⁺ ion beam. It was experimentally proved that the degradations of Ig-Vg and Nit have a strong correlation with hydrogen migrated to the interface. We expect this evaluation method, which can control the amount of hydrogen migration to the interface, will be helpful for the resolution of hydrogen-associated MOSFET degradation.

Acknowledgements

The authors would like to thank I. Hirano, K. Kato, and A. Nishiyama for their helpful discussion.



Figs.7 Schematic of interface state formation for (a)RO-SiO₂ and (b)WO-SiO₂ with ion beam irradiation. Large balls represent Si atoms from red to blue according to the depth. Small blue and white balls represent H and O atoms, respectively. Yellow isosurfaces represent the electronic charges of the expelled electron and dangling bonds. These lattice models are cited from [3].

References

- [1] N. Kimizuka et al., Symp. VLSI Technology, pp73-74. (1999)73
- [2] S. Tsujikawa et al., IRPS, (2003)183
- [3] K. Kato, Phys. Rev. B 85(2012) 085307
- [4] M.A. Briere et al, IEEE Trans. Nucl. Sci. 37(1990)1658.
- [5] M. Wilde et al., J. Appl. Phys. 92(2002)4320.
- [6] Z. Liu et al., ECS Transactions, 35(4) (2011)55.
- [7] K. Kato, J. Appl. Phys. 113(2013) 133512

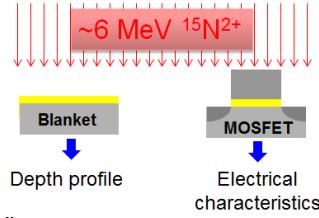
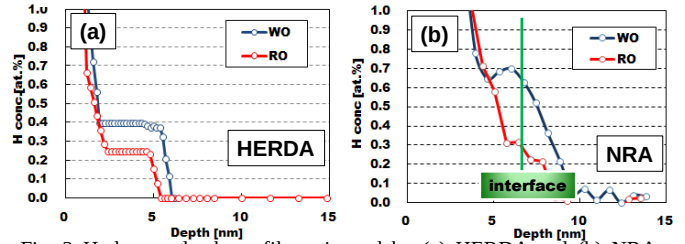


Fig.1 Schematic of evaluation concept of this study. ¹⁵N²⁺ ion beam with almost the same condition was irradiated to both blanket and nMOSFET samples. The beam energy for nMOSFET was set to be slightly high considering energy loss at Poly-Si layer region.



Figs.2 Hydrogen depth profile estimated by (a) HERDA and (b) NRA using blanket samples. Large signals at 0 nm in both figures are due to surface adsorbed species. During HERDA measurement, hydrogen migration is not observed, because the energy of the irradiated ion beam is relatively low (480 keV) and the spectra are constructed by summing up the data from various measurement points.

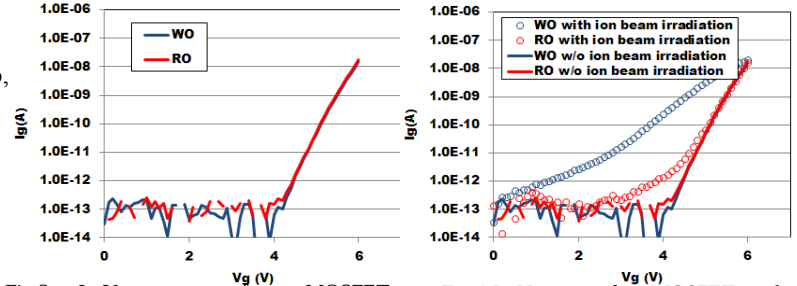


Fig.3 Ig-Vg curves for nMOSFETs (L/W=100 μm/100 μm) with WO-SiO₂ and RO-SiO₂ without ion beam irradiation.

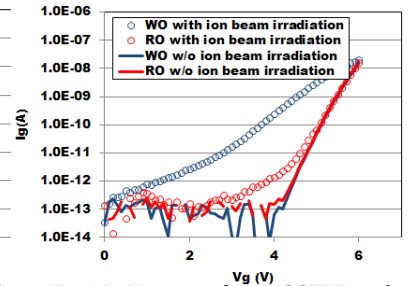


Fig.4 Ig-Vg curves for nMOSFETs with WO-SiO₂ and RO-SiO₂ with and without ion beam irradiation.

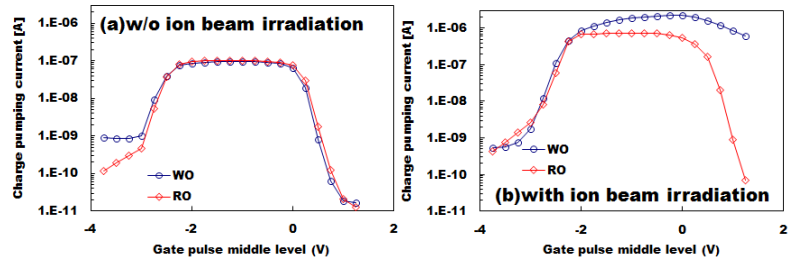
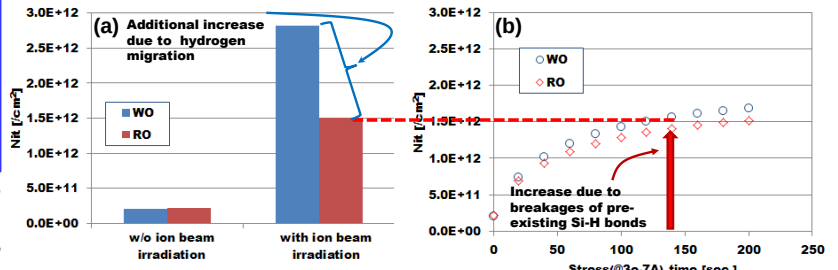


Fig.5 Charge pumping curves for nMOSFETs (L/W=50 μm/100 μm) with WO-SiO₂ and RO-SiO₂ (a) with and (b) without ion beam irradiation. The amplitude of the gate pulse was set to 3.5 V.



Figs.6 (a) Bar graph representing the change of Nit due to ion beam irradiation (hydrogen migration to the interface) and (b) dependence of Nit on duration of constant current (3X10⁻⁷ (A)) stress for nMOSFETs with WO-SiO₂ and RO-SiO₂.