*Electrochemical and Solid-State Letters*, **8** (2) G35-G37 (2005)
1099-0062/2004/8(2)/G35/3/$7.00 © The Electrochemical Society, Inc.

# $Si\text{-}SiO_2$ Interface Passivation Using Hydrogen and Deuterium Implantation

**T. Kundu and D. Misra**[z]

*Department of Electrical and Computer Engineering, New Jersey Institute of Technology, Newark, New Jersey 07102, USA*

Hydrogen/deuterium was implanted in ⟨100⟩ silicon to passivate dangling bonds at the $Si/SiO_2$ interface when a thin oxide is grown on implanted silicon substrate. It was observed that implantation energy and dose influence the interface passivation. Measured interface states at the $Si/SiO_2$ interface suggest an isotope effect where deuterium implanted devices yielded better interface passivation compared to that of hydrogen implanted devices. Diffusion of implanted hydrogen and deuterium to the interface is affected by the implantation damage.

© 2004 The Electrochemical Society. [DOI: 10.1149/1.1843752] All rights reserved.

Manuscript submitted July 20, 2004; revised manuscript received September 3, 2004. Available electronically December 14, 2004.

Recently deuterium has been used to passivate dangling bonds at the $Si/SiO_2$ interface[1] and $Si/HfO_2$ interface[2] after the hydrogen/deuterium (H/D) isotope effect was discovered.[3] Deuterium passivation brings significant improvement in hot-carrier lifetime in metal oxide semiconductor (MOS) transistors.[3,4] This is because hot carrier stimulated deuterium desorption and depassivation of the silicon dangling bonds that generates interface trap states is substantially reduced as compared to hydrogen desorption. Annealing in deuterium ambient is one of the methods used to incorporate deuterium at the $Si/SiO_2$ interface.[5-7] The challenge is to retain the implanted deuterium at the $Si/SiO_2$ interface until the CMOS fabrication process is completed. Alternate approaches like growing gate oxide in $D_2O$ ambient,[8] or incorporation of deuterium by pyrogenic oxidation[9] have yielded significant interface passivation because of higher deuterium retention.

Another approach is to incorporate deuterium by ion implantation. Harvey *et al.* have implanted deuterium to a partially completed device (before metalization) to incorporate deuterium at the $Si/SiO_2$ interface.[10,11] However, the impact of this was minimal and identical to deuterium annealing, as deuterium does not take part in oxide growth process. In addition, this process compromises the integrity of the gate oxide. In this work, we have used low energy ion implantation where hydrogen and deuterium were implanted in silicon substrate before the thin gate oxide is grown to incorporate hydrogen/deuterium at the $Si/SiO_2$ interface of a MOS device. Earlier work on deuterium implantation[12] and subsequent diffusion in single crystal silicon and in $Si/SiO_2$ system suggests that deuterium diffuses slowly in $SiO_2$ compared to crystalline silicon. Therefore, if gate oxide is grown after deuterium implantation strong interface passivation is possible. Deuterium implantation also provides a spatially uniform distribution of deuterium through out the channel. Preliminary work with low energy implant showed promising results.[13] Through electrical characterization this work demonstrated for the first time that an optimized implantation condition could effectively passivate the interface states due to deuterium retention at the interface. The measured interface states density $D_{it}$ in the order of $10^{10}$ $eV^{-1}$ $cm^{-2}$ confirms the passivation by deuterium as it is identical to a typical forming gas anneal. Hydrogen was implanted to explore the possible the isotope effect.

## Experimental

To optimize the implantation conditions for interface passivation various implanted energies starting from 15 keV to 35 keV with different implantation doses were used to implant deuterium into 5-inch p-type Si wafer with a resistivity 0.8-1.2 ohm-cm. Hydrogen was also implanted at 20 keV and 25 keV. Table I summarizes the implantation conditions. Stopping and range of ions in matter (SRIM) simulation was employed to obtain an estimated implantation depths for various implantation energies (Table II). Implantations were carried out at the Core Systems' specialty ion implanted services after wafers were cleaned and a 20 nm thick sacrificial oxide was deposited by steam oxidation. High-energy ($>50$ keV) deuterium implantation can possibly be hazardous as possible nuclear reactions may occur. It is important to know that the sacrificial oxide was used to prevent the direct exposure wafer surface to minimize damage. The wafer without any implantation was used as a control wafer. Following removal of sacrificial oxide dry oxidation was used to grow 6.5 nm of gate oxide at 800°C for 30 min with a flow rate of 750 sccm $N_2$ and 500 sccm $O_2$. 3000 Å of Al was immediately deposited to form MOS capacitors. The oxide thickness was measured using ellipsometer on 13 sites and less than 5% variation across the wafer was found. This was also compared to the thickness estimated from the electrical measurements (capacitance-voltage, CV, measurements), which yielded similar results. To ensure a good ohmic contact Al was also deposited at the back. A post metal annealing was carried out at 400°C for 20 min. Interface state density $D_{it}$ was estimated using HP 4284 using high-frequency (HF)/low-frequency (LF) CV measurement techniques across the band gap by measuring at least 10 devices per device type.[14]

## Results and Discussion

Passivation of dangling bonds at the $Si/SiO_2$ interface by implanted deuterium can be evaluated by estimating interface state density, $D_{it}$. Figure 1 shows the interface states for different implanted doses as a function of implanted energy. The solid line connecting the Dose 2 and Dose 3 data points serves as a visual guide and does not represent any functional dependence. It is clearly seen that the control device has the highest mid-gap $D_{it}$ of $1.5 \times 10^{11}$ $eV^{-1}$ $cm^{-2}$. Devices with implantation dose of $1 \times 10^{14}/cm^2$ (Dose 2) show the lowest values of $D_{it}$ at implantation energy of 20 and 25 keV to be 1.1 and 1.2 $\times$ $10^{10}$ $eV^{-1}$ $cm^{-2}$ respectively. For devices with implantation energies 15, 20, and 25 keV it is clear that Dose 2 has contributed to lower $D_{it}$ whereas Dose 3 ($1 \times 10^{15}/cm^2$) has increased $D_{it}$. For devices with implantation energies 30 and 35 keV, on the other hand, the interface states were lower for Dose 3 compared to Dose 2 even though the overall $D_{it}$ much higher compared to 20 and 25 keV. Dose 1 ($1 \times 10^{13}/cm^2$) was only used for 20 and 25 keV implantation energies where the devices show comparable results to that of Dose 2. Devices implanted at 15 keV with Dose 3 and devices implanted at 30 keV with Dose 2 showed a $D_{it}$ value similar to that of the control device indicating minimal or no interface passivation was achieved.

For devices implanted at 15 keV the implantation depth, obtained from SRIM simulation, was shallow (Table II) and it is possible that after implantation and during oxide growth the ions have out diffused showing similar results to that of a control case. The observed improvement in case of Dose 2 compared to Dose 3 is mainly be-

---

[z] E-mail: dmisra@njit.edu

**Table I. List of the hydrogen and deuterium implantation conditions.**

| | | Implantation matrix (16 Wafers) | | | | |
|---|---|---|---|---|---|---|
| | Dose implantation energy (keV) | $D_{\mathrm{dose1}}$ $1 \times 10^{13}/\mathrm{cm}^2$ | $D_{\mathrm{dose2}}$ $1 \times 10^{14}/\mathrm{cm}^2$ | $D_{\mathrm{dose3}}$ $1 \times 10^{15}/\mathrm{cm}^2$ | $\mathrm{H}_{\mathrm{dose2}}$ $1 \times 10^{14}/\mathrm{cm}^2$ | $\mathrm{H}_{\mathrm{dose3}}$ $1 \times 10^{15}/\mathrm{cm}^2$ |
| 1 Control wafer (no implantation) + | 15 | | x | x | | |
| | 20 | x | x | x | x | x |
| | 25 | x | x | x | x | x |
| | 30 | | x | x | | |
| | 35 | | x | x | | |

**Table II. The estimated depths at which concentration peak occurs was obtained form initial SRIM simulation results.**

| Implantation energy | 15 keV | 20 keV | 25 keV | 30 keV | 35 keV |
|---|---|---|---|---|---|
| Peak depth and straggle (deuterium) | 0.3084 μm and 8.52 nm | 0.3863 μm and 10.03 nm | 0.4587 μm and 11.2 nm | 0.5279 μm and 11.4 nm | 0.5918 μm and 12.9 nm |
| Peak depth and straggle (hydrogen) | | 0.2963 μm and 7.3 nm | 0.3866 μm and 8.42 nm | | |

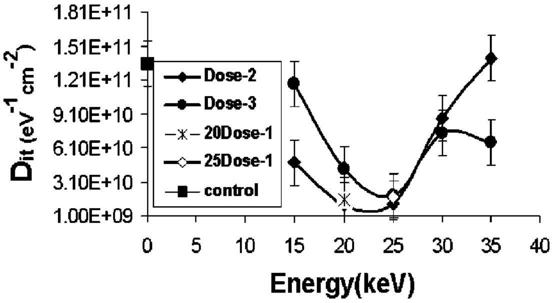

**Figure 1.** Interface state density $D_{\mathrm{it}}$ as a function of deuterium implantation energy at different doses indicates that an optimal interface passivation is possible in the range of 20-25 keV implantation energies with a dose of $1 \times 10^{14}/\mathrm{cm}^2$. The solid line connecting the Dose 2 and Dose 3 data points serves as a visual guide.

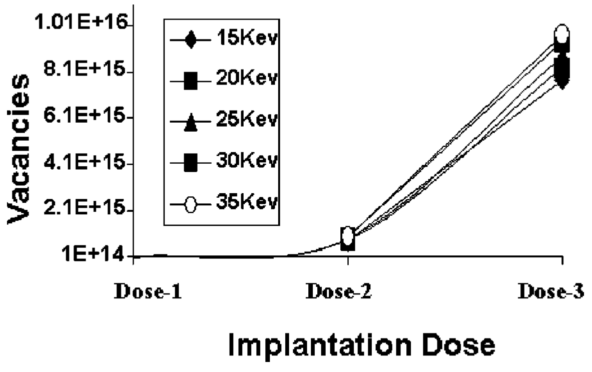

**Figure 2.** Vacancy concentration as a function of implanted dose for deuterium implantion at different energies shows that vacancy concentration increases rapidly from Dose 2 to Dose 3 compared to Dose 1 to Dose 2.

cause the implanted ions at Dose 3 created more number of Frenkel defects[15] compared to that of Dose 2 during implantation. During oxide growth the defect-assisted diffusion dominated the out diffusion of deuterium, implanted at a higher implanted dose.

Similar arguments are valid for 20 and 25 keV deuterium-implanted devices where Dose 2 has shown better $D_{\mathrm{it}}$ values compared to Dose 3. However, the thermal budget during oxide growth is such that optimal interface passivation was observed for devices with deuterium implanted at 20 keV with Dose 2. Because the vacancy creation during implantation significantly impacts the diffusion of H and D in silicon it can be seen from SRIM simulation (Fig. 2) that the vacancy creation during implantation increases rapidly with increase in dose. In the case of 30 and 35 keV implantation cases even though the implantation damage is relatively higher, deuterium has to travel a longer distance to reach at the interface. Because simultaneous annealing of defects during oxide growth is expected the peak deuterium concentration immediately after implantation will make a difference. We believe the higher peak concentration of deuterium and higher implantation straggle, as computed from SRIM simulation (not shown), for devices implanted 35 keV with Dose 3 has resulted in better $D_{\mathrm{it}}$ values.

As the identical behavior of interface passivation for 20 and 25 keV implanted devices was observed, the details of the passivation process was further evaluated and compared to that of hydrogen implantation for possible isotope effects. All experiments were performed with Dose 2 and Dose 3 for both the implantation energies for hydrogen and deuterium. The low frequency and high-frequency CV measurements for 20 keV-implanted devices were given in Fig. 3 for both hydrogen and deuterium implantation. The CV characteristic of the control sample is also plotted for reference. The CV characteristics suggest an identical passivation behavior in both the cases. The high-frequency CV characteristics show more flatband shift for deuterium and hydrogen implanted devices compared to control sample indicating possible hydrogen and deuterium incorporation into the oxide after the interface passivation.

The deuterium implanted devices for both implantation energies at 20 and 25 keV shows better results compared to their hydrogen-implanted counter parts. It is known that deuterium presence in the oxide reduces the bulk oxide charge.[16] During oxidation deuterium and hydrogen ions diffuse towards the interface and depending on the thermal budget some ions get into oxide leaving the majority of ions at the interface. This is expected as deuterium has a lower diffusivity in $\mathrm{SiO_2}$ compared to silicon.[12] It is also observed that for deuterium-implanted device D20-Dose-2 shows a larger bulk oxide charge ($5.04 \times 10^{-8}$ C/cm$^2$) but reduced interface states $D_{\mathrm{it}}$ ($1.1 \times 10^{10}$ eV$^{-1}$/cm$^2$) compared to D25-Dose-3 ($1.08 \times 10^{-8}$ C/cm$^2$ and $1.2 \times 10^{10}$ eV$^{-1}$/cm$^2$) (not shown). This further confirms that for D20-Dose-2 more deuterium atoms contribute to interface and less get into oxide where as in case of D25-Dose-2 more enter into oxide and less contribute to interface compared to D20-Dose-2.

By carefully comparing the interface state density $D_{\mathrm{it}}$ for both hydrogen and deuterium implantation (Fig. 4) it is noticed that interface states for both the cases are significantly lower compared to control devices. The average $D_{\mathrm{it}}$ values for deuterium-implanted devices are lower in case of Dose 2 for both the implantation energies

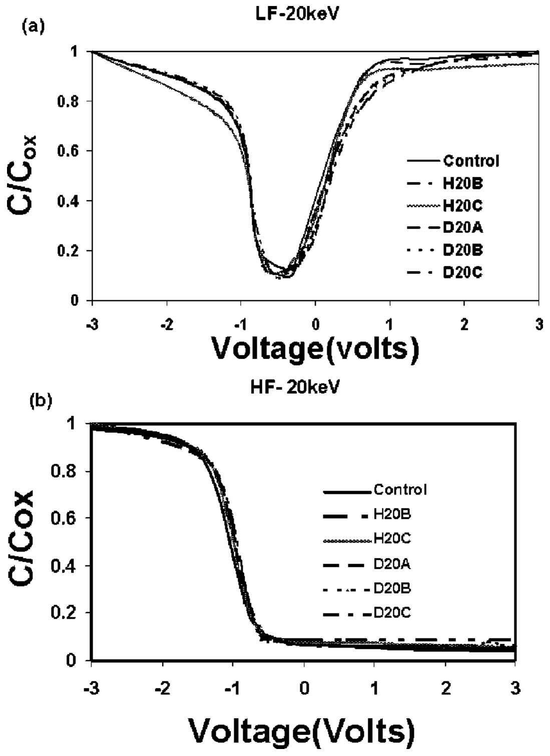

**Figure 3.** Low-frequency (20 Hz) (a) and high-frequency (1 MHz) (b) CV measurements of 20 keV implantation energy for different implantation doses along with control devices.

20 and 25 keV even though there is some overlapping was noticed. For 20 keV, Dose 2, hydrogen-implanted devices the lowest observed value of $D_{it}$ is $1.2 \times 10^{10}$ eV$^{-1}$ cm$^{-2}$ and for deuterium implanted devices it is $1.1 \times 10^{10}$ eV$^{-1}$ cm$^{-2}$. This behavior can be attributed to defect creation during implantation, implantation depth, and straggle and implanted ion concentration.

Hydrogen and deuterium are electronically equivalent as static electronic structure of S-H and S-D bonds are identical.[17] The difference in behavior can be attributed to dynamics of these bonds. As discussed earlier, implanted deuterium and hydrogen ions initially tend to diffuse to the defect sites mostly vacancies that were formed during implantation damage. If these ions initially passivate the bulk dangling bonds the mechanism of these ions diffusing to interface during oxidation (annealing) will be entirely different because of the isotope effect. Form the observed $D_{it}$ results we believe an isotope effect is present.

## Conclusions

We have investigated the impact of hydrogen/deuterium implantation on the possible passivation of silicon dangling bonds at the Si/SiO$_2$ interface when a thin oxide is grown on implanted silicon substrate. It was observed that implantation energy and implantation dose significantly influence the interface passivation. Electrical measurements of interface state density suggests that an isotope effect is present as the deuterium implanted devices yielded better interface passivation compared to that of hydrogen implanted devices. The optimized deuterium implantation condition was found to be implantation energy of 20 keV with a dose of $1 \times 10^{14}$ atoms/cm$^2$ to effectively passivate the interface. The passivation efficiency seems to depend on transient enhanced diffusion of implanted hydrogen or deuterium, which is significantly affected by the defects/vacancies created due to implantation damage.

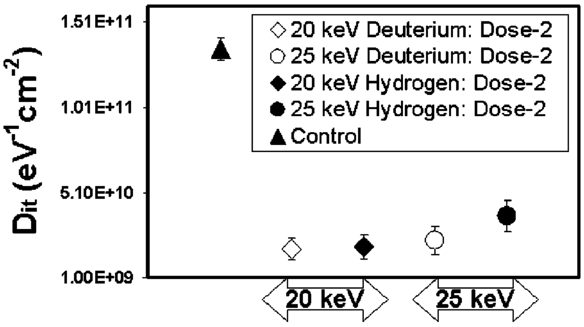

**Figure 4.** Comparison of lowest observed interface state densities between hydrogen and deuterium implanted devices at two different implantation energies and for Dose 2.

## Acknowledgment

This work was supported by a grant from National Science Foundation (award no. ECS-0140584).

*The New Jersey Institute of Technology assisted in meeting the publication costs of this article.*

## References

1. R. A. B. Devine, J.-L. Autran, W. L. Warren, K. L. Vanheusdan, and J.-C. Rostaing, *Appl. Phys. Lett.*, **70**, 2999 (1997).
2. H. H. Tseng, *Tech. Dig. - Int. Electron Devices Meet.*, **2003**, 83.
3. J. W. Lyding, *Proc. IEEE*, **85**, 589 (1997).
4. I. C. Kizilyalli, *IEEE Electron Device Lett.*, **19**, 444 (1998).
5. H. C. Mogul, L. Cong, R. M. Wallace, P. J. Chen, T. A. Rost, and K. Harvey, *Appl. Phys. Lett.*, **72**, 1721 (1998).
6. I. J. R. Baumvol, E. P. Gusev, F. C. Stedile, F. L. Freire, M. L. Green, and D. Brasen, *Appl. Phys. Lett.*, **72**, 450 (1998).
7. P. J. Chen and R. M. Wallace, *Appl. Phys. Lett.*, **73**, 3441 (1998).
8. H. Kim and H. Hwang, *Appl. Phys. Lett.*, **74**, 709 (1999).
9. Y. Mitani, H. Satake, H. Itoh, and A. Toriumi, *Tech. Dig. - Int. Electron Devices Meet.*, **2000**, 343.
10. T. A. Rost, and K. C. Harvey, U.S. Pat. US6221705 (2001).
11. K. C. Harvey, U.S. Pat. US6017806 (2000).
12. H. Park and C. R. Helms, *J. Electrochem. Soc.*, **139**, 7 (1992).
13. D. Misra and R. K. Jarwal, *J. Electrochem. Soc.*, **149**, G446 (2002).
14. E. H. Nicollian and J. R. Brews, *MOS Physics and Technology*, John Wiley & Sons, New York (1982).
15. J. Tatarkiewicz, *Physica B*, **170**, 383 (1991).
16. Y. Mitani, H. Satake, H. Itoh, and A. Toriumi, *Tech. Dig. - Int. Electron Devices Meet.*, **2000**, 343.
17. C. G. Van de Walle and B. R. Tuttle, *IEEE Trans. Electron Devices*, **47**, 1779 (2000).