On Oxidation Kinetics and Electrical Quality of Gate Oxide Grown in H_2O or D_2O Ambient

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Abstract— **In recent literature, a controversy has arisen over the question whether deuterium improves the stability of the MOS gate dielectric. This work presents a wide range of growth rate data of H_2O and D_2O gate oxides in an ultra-diluted ambient. A considerable and constant difference in oxidation rate is found between the two species. Although literature suggests a correlation between growth rate and dielectric quality, the degradation measurements on MOS capacitors with 8.5 nm gate oxides grown at 950 ˚C at low partial pressure show only a very weak difference between the isotopes. It appears that the difference in oxidation rate does not affect the gate oxide quality, and high quality grown gate oxides do not appear to benefit from the deuterium isotope effect.**

Keywords— **Deuterium, Hydrogen, Oxide growth, Oxide integrity**

I. INTRODUCTION

Hydrogen is used for passivating dangling bonds in CMOS. Since scanning tunnelling microscope experiments [1] showed that deuterium is harder to desorb from a silicon surface than hydrogen, there is a growing interest to replace hydrogen during some stage in the CMOS processing with deuterium to improve device stability. This may affect hot carrier degradation, charge to breakdown and stress induced leakage current.

Several authors [2-5] showed that replacement of hydrogen with deuterium to passivate interface states at the Si-SiO$_2$ interface reduces hot carrier degradation in MOS transistors. There is no consensus on the influence of deuterium incorporation into the CMOS processing on gate oxide integrity, i.e. charge to breakdown (Q_{bd}) and stress induced leakage current (SILC).

For instance, Hwang and co-workers [6-8] incorporate deuterium into their MOS capacitors by growing the gate oxide using D_2O. They report an improvement in SILC and Q_{bd} characteristics. Also Mitani et al. [9,10] use pyrogenic oxidation with D_2 and O_2 to grow the gate oxide. They confirm the improvement in SILC characteristics.

On the other hand, Wu et al. [11] processed CMOS test devices, which underwent a H_2 or D_2 anneal after the forming gas anneal. The deuterium-annealed sample did not show improved SILC or Q_{bd} characteristics. Esseni et al. [12] use either hydrogen or deuterium during the forming gas anneal. Their measurements of SILC after channel hot electron stress do not show an improvement if deuterium is incorporated.

Comparing the different reports, it appears that for deuterium to be beneficial for the gate oxide quality, it has to be incorporated in an early stage of processing, i.e. during the gate oxide growth. This raises the question if there is a difference in oxidation kinetics of silicon if hydrogen is replaced by deuterium leading to an improvement in oxide integrity. Indeed, both Mitani et al. and Hwang and co-workers briefly report a difference in oxidation rate. However, they do not link this difference to the improvement in oxide quality they measure. In this paper, additional data is obtained on the oxidation kinetics of silicon in a H_2O or D_2O ambient. The observed difference in oxidation rate is compared to the degradation characteristics as measured on processed test devices.

II. EXPERIMENTAL SETUP

A. Oxidation experiments

A thin (1-60 nm) layer of silicon oxide was grown on 4 inch <100> silicon wafers with a boron concentration of approximately $6 \cdot 10^{14} cm^{-3}$. Prior to oxidation the wafers were cleaned and dipped in a 1% HF solution until the wafer surface was hydrophobic.

The oxidation was performed in a horizontal furnace. Dry nitrogen gas flows at a rate of 4 l/min through a small tank containing either H_2O or D_2O (figure 1). The temperature of the tank determines the water vapour pressure of the outcoming wet nitrogen gas. For H_2O the

tank temperature is set at 17.5 ˚C and for D_2O at 20 ˚C. These temperatures correspond to a saturated vapour pressure of 0.02 Atm for both precursors [4]. The mass loss of the tank during oxidation was measured to be able to calculate the vapour pressure of the gas entering the furnace.

Oxidation time and temperature were varied from 0 to 960 min and from 750 ˚C to 950 ˚C. The resulting oxide thickness was measured with an ellipsometer.
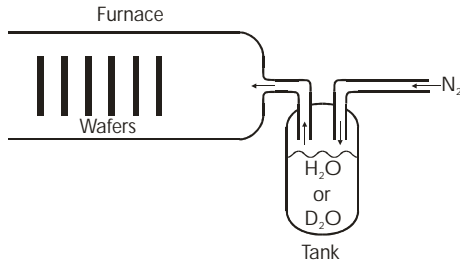

Figure 1:   The oxidation system.

B.   Device fabrication

MOS capacitors were fabricated to measure the oxide quality. First, a 300 nm field oxide was grown on a number of wafers. Active areas were etched in this field oxide and a gate oxide was grown using H_2O or D_2O as a precursor at 950 ˚C. The resulting gate oxide thickness as measured with an ellipsometer was 8.5 nm for both precursors. 300 nm poly silicon was deposited at 610 ˚C, followed by an arsenic implantation ($3 \cdot 10^{15}$ cm^{-2} 100 keV) and an implantation anneal of 30 min at 900 ˚C. MOS gates were then formed by wet etching of the poly. For good electrical contact, both the gates and the back of the wafer were provided with a 1 μm thick aluminium layer.

C-V and *I-V* curves were measured on these devices as a function of injected charge. The devices were stressed under gate injection conditions with a stress current of 100 mA/cm^2.
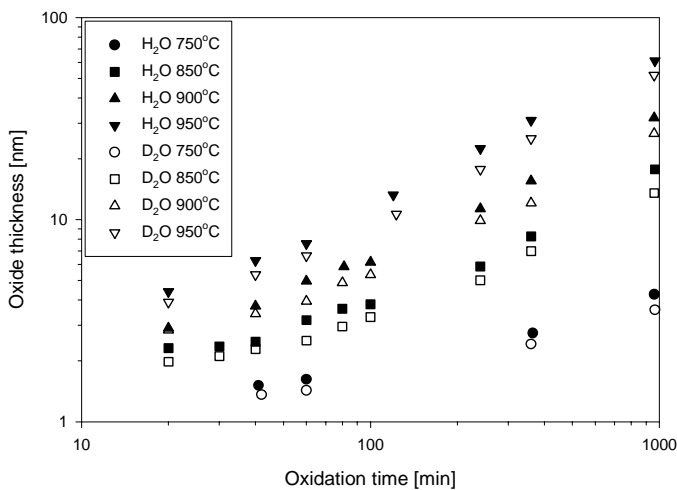

Figure 2:   Oxide thickness (measured by ellipsometer) as a function of oxidation time, temperature and precursor.

III.   OXIDATION KINETICS

A.   Oxidation rate

The measured oxide thickness, (figure 2), indicates that, for the same oxidation time and temperature, the oxide grown in a H_2O ambient is considerably thicker than the oxide grown in a D_2O ambient.

The difference between the oxide thickness for H_2O grown samples and D_2O samples appears to be a constant factor, independent of time and temperature. Figure 3 confirms this. The average ratio is:

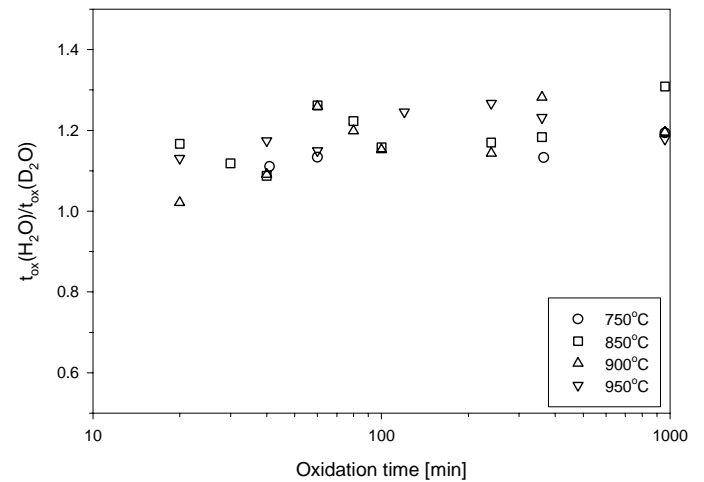$$\frac{t_{ox,H_2O}(t,T)}{t_{ox,D_2O}(t,T)} = 1.18 \pm 0.07$$

Figure 3:   Ratio of oxide thickness for H_2O oxidation and for D_2O oxidation as a function of oxidation time and temperature.

The observed difference in oxidation rate is not an artefact of the experimental setup. To verify this, the mass loss of the tank was measured during oxidation to be able to estimate the partial pressure of the precursors in the furnace.

The mass loss is converted to the amount of precursor that was used during oxidation (figure 4). There is a small difference between the amount of precursor introduced in the furnace for H_2O and for D_2O. The slope of the linear regression lines is 1.21 mmol/min for H_2O and 1.16 mmol/min for D_2O. Taking into account the nitrogen flow of 4 l/min, the precursor partial pressure is calculated to be $7 \cdot 10^{-3}$ Atm.

The difference of 4% in partial pressure for H_2O and D_2O is not enough to explain the 18% difference in oxide thickness. Typically, the pressure dependence of oxide growth is expressed by a power law [13]:

$$t_{ox} \sim P^n \qquad \text{with } 0.5 < n < 1$$

Using this equation, for a partial pressure difference of 4%, at most 4% difference in oxide thickness can be

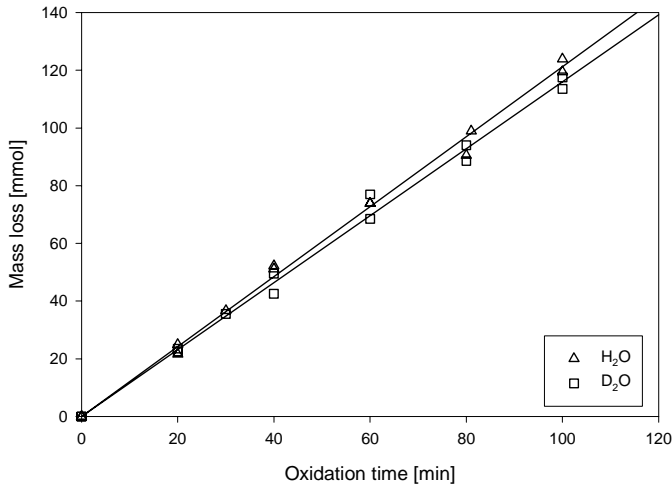expected. The 18% difference must therefore largely be attributed to an isotope effect.

Figure 4: **Amount of precursor introduced in the furnace as a function of oxidation time.**

B. Oxidation mechanism

If the observed difference in oxidation rate is not due to a difference in partial pressure, it must arise from the oxidation mechanism. To investigate this, the Arrhenius plot of the oxide thickness is presented in figure 5.

Two observations can be drawn from the Arrhenius plot. Firstly, the lines for the H_2O and D_2O grown oxides are almost parallel. This indicates a similar activation energy. Secondly, for both precursors, the slope of the lines is dependent on oxidation time and temperature. It appears that the shorter the oxidation time, the smaller is the activation energy and the lower the oxidation temperature, the smaller is the activation energy.
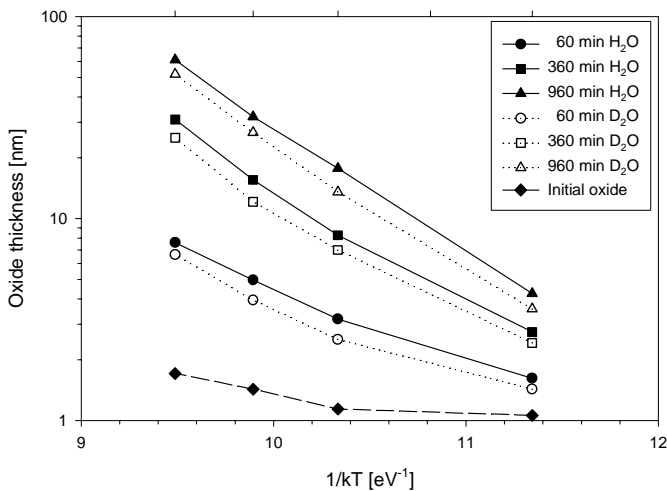

Figure 5: **Arrhenius plot of oxide thickness as function of oxidation time and precursor.**

Shorter oxidation times and lower oxidation temperatures result in thinner oxides. Therefore, it appears that the activation energy decreases with decreasing oxide thickness.

Figure 6 illustrates the two observations. Firstly, the activation energies for H_2O and D_2O grown samples are similar. Secondly, the activation energy depends on the oxide thickness. As the oxide is growing, the oxidation mechanism is changing.
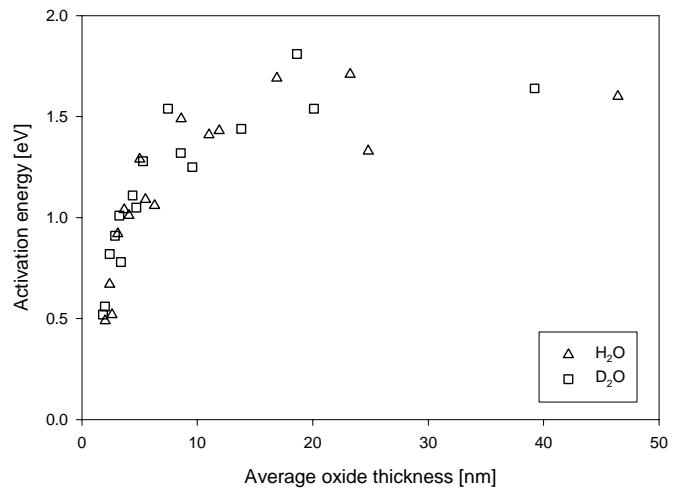

Figure 6: **Extracted activation energy for oxide growth as a function of average oxide thickness and precursor. The activation energy is extracted from every pair of adjacent measurement points in figure 2 for the same oxidation time, but different oxidation temperatures.**

However, native oxide formation cannot be neglected for the thinner oxides (< 10 nm). When the wafers go into the furnace, some clean room air (containing oxygen) is transported along into the furnace, which gives rise to an initial oxide grown during the ramp-up of temperature. This initial oxide is 1.06 to 1.71 nm thick for an oxidation temperature of 750 °C to 950 °C, as illustrated in figure 5.

This initial oxide influences the measured oxide thickness as a function of time. If the initial oxide had not been present before the actual oxidation process had started, the final oxide would have been thinner. For thick oxides, the influence is small, but for thin oxides, the influence can be substantial. In reality, the activation energy for thin oxides will be higher.

Yet, one may indeed expect a changing activation energy for small oxide thickness. In the beginning of oxidation, the precursor meets a bare silicon wafer surface. The precursor will somehow stick to the surface and dissociate. After the first monolayer has grown, the precursors will not directly react with a silicon surface, but a silicon surface with a monolayer of oxide. This will affect the sticking probability and dissociation rate of the precursor. It is to be expected that for the first few monolayers, the sticking probability and dissociation rate will keep changing. For thicker oxide layers, the bulk silicon will not have an influence anymore on at least the sticking probability.

The difference in oxidation rate between H_2O and D_2O oxides can be caused by a small difference in activation energy. As indicated above and illustrated in figure 6, the activation energies for H_2O and D_2O grown oxides are similar, but the extraction of the activation energy is sensitive to small errors in the oxide thickness. A difference of 15 to 17 meV in activation energy suffices to give a change of 1.18 at 750 °C to 950 °C. Unfortunately the data do not allow such a precise determination of the activation energy. It can be argued that the difference in oxidation rate in a H_2O and a D_2O ambient is caused by a small difference in activation energy. This difference in activation energy may arise from a difference in diffusion or energy required for dissociation.

IV. DEVICE CHARACTERISATION

A. Experimental results

The impact of deuterium saturated dangling bonds to MOS devices was studied. Quasi-static *C-V* measurements were done as a function of injected charge under FN-stressing. The general trend, as indicated in the inset of figure 7, shows that for increasing injected charge, the minimum increases and the valley of the graph is broadening. This translates to an increase in the number of interface states.

This trend is observed for both H_2O and D_2O grown samples. Figure 7 shows a small but distinct difference between the H_2O and D_2O grown samples. The generation rate of interface states under FN-stressing is slightly lower for the D_2O grown gate oxides.
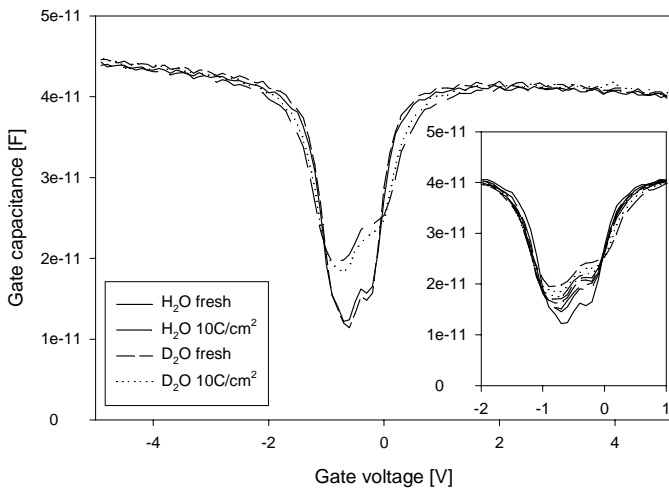

Figure 7: Comparison of *C-V* curves of H_2O and D_2O grown gate oxide before and after FN-stressing at –100 mA/cm² until 10 C/cm². The inset shows the general trend of device degradation during stressing for the H_2O grown gate oxide. The same trend is observed for D_2O.

Figure 8 shows the average of the measured stress induced leakage current of several devices. There is a large spread on the measured data and this is reflected in the large error bars. D_2O is only slightly better on average than H_2O, but the error bars almost completely overlap. Both precursors result in similar SILC behaviour.
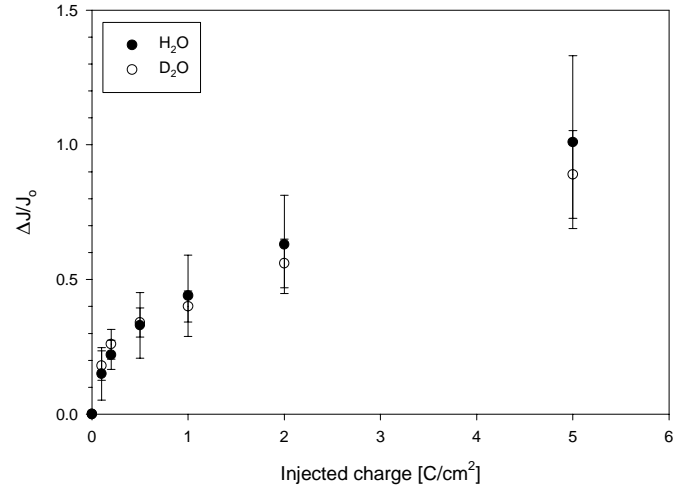

Figure 8: Ratio of stress induced leakage current and virgin current as a function of injected charge. Devices are stressed at –100 mA/cm². The current is measured at –6.5 V.

B. Discussion

Hwang and co-workers report a larger difference in *C-V* curves than shown in this work. Similar Hwang and co-workers and Mitani et al. indicate that for their samples SILC is reduced if the gate oxide is grown using D_2O. Both Hwang and co-workers and Mitani et al. grow their oxides at a high partial pressure at 850 °C. Furthermore, their oxides are 6.5 and 7.7 nm thick. The gate oxide investigated in this work is thicker, which automatically results in less SILC, so it will be harder to detect a difference. The partial pressure used in this work is much lower, which results in a lower oxidation rate, giving the oxide more time to relax. Furthermore, it results in less incorporation of hydrogen or deuterium. The higher oxidation temperature will additionally enhance the desorption of hydrogen and deuterium from the oxide bulk during the oxide growth, resulting in less incorporation of hydrogen or deuterium in the oxide.

The higher oxidation temperature and lower partial pressure give the growing oxide more thermal energy and time to relax and form the optimum structure. The oxide used in this work is a better quality oxide, with fewer defects to mask with hydrogen or deuterium. It appears that a high quality grown oxide does not benefit from a deuterium isotope effect. The difference in growth rate for the H_2O and D_2O grown oxides does not seem to have an effect on the degradation characteristics.

V. Conclusions

Oxide growth is slower in D_2O ambient than in H_2O ambient. The ratio of oxide thickness is constant and independent of time and temperature. The activation energy for H_2O and D_2O grown oxides are similar, but a small difference in the range of meV can explain the difference in growth rate. For thin oxides, two oxidation regimes are observed.

Device results show only marginal improvement of degradation characteristics. Similar experiments in literature see a larger difference. It appears that a high quality grown oxide does not benefit from the deuterium isotope effect.

Acknowledgement

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