On Oxidation of Silicon in Ultra-Diluted H_2O and D_2O Ambient

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INTRODUCTION

Gate oxide fabrication of MOS devices demands the growth of high quality silicon oxide layers of only a few nanometers for present devices. These layers have to be grown in a well controlled manner, assuring good thickness control and uniformity. The growth is carried out in either a dry or wet ambient, where the electrical quality of wet oxides has been shown to exceed that of dry oxides [1-3]. Moreover, recent studies [4-5] indicate that replacement of hydrogen with deuterium, that is the use of heavy water instead of water, can further enhance the electrical quality of thin oxides. To assure reasonable oxidation times and therefore good process control, thin wet oxides have to be grown at either low temperature or reduced water vapour pressure.

Little experimental data is available on the growth of thin wet oxides and even less on the growth of thin deuterated wet oxides. Therefore, this work presents, for the first time, a wide range of growth rate data of H_2O and D_2O thin oxides in an ultra-diluted ambient at different temperatures.

EXPERIMENTAL SETUP

A thin (0-60 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 dipped in a 1% HF solution until the wafer surface was hydrophobic. The oxidation was performed in a horizontal furnace. Nitrogen flowed at a rate of 4L/min through a small tank taking up H_2O or D_2O vapour and carried the precursor into the furnace.

To exclude the influence of H_2O/D_2O pressure on the oxidation kinetics, the temperature of the small tank was set at 17.5°C for H_2O and at 20°C for D_2O. These temperatures correspond to a saturated vapour pressure of 0.02Atm for both precursors [6]. The actual vapour pressure of the outcoming wet nitrogen gas was estimated by measuring the mass loss of the tank during the oxidation. 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.

RESULTS AND DISCUSSION

The measured oxide thickness, (figure 1), 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 2 confirms this. The average ratio is:

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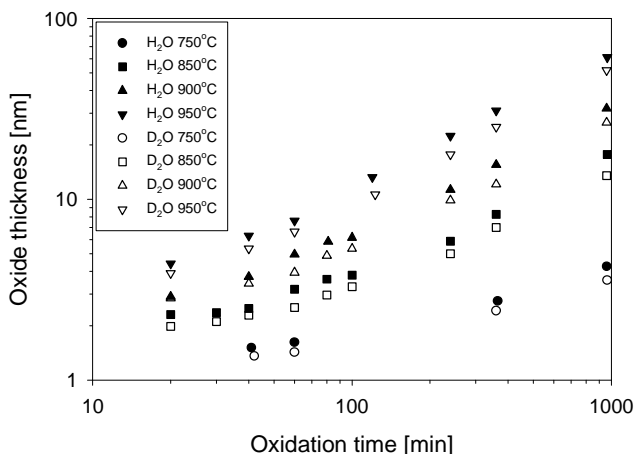

Figure 1: Oxide thickness (measured by ellipsometer) as a function of oxidation time for different oxidation temperatures and oxidation ambients.
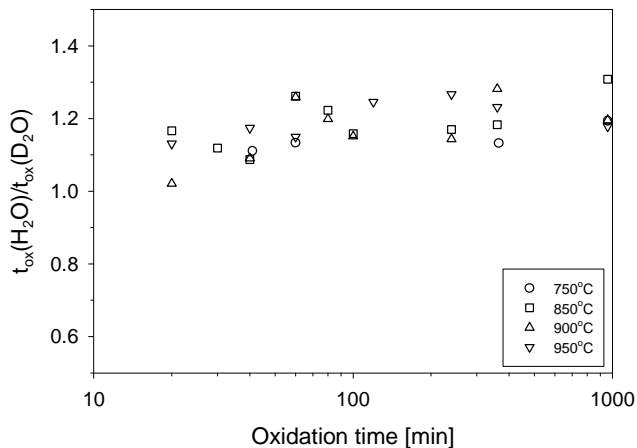

Figure 2: Ratio of oxide thickness for H_2O oxidation and for D_2O oxidation as a function of oxidation time for different oxidation temperatures.

The observed difference in oxidation rate is not an artefact of the experimental setup. The mass loss is converted to the amount of precursor that was used during oxidation (figure 3). 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.

To obtain further insight in the oxidation process, the activation energy for the oxide thickness is calculated for different thicknesses. The result is shown in figure 4. Two observations can be made from this graph. Firstly, the activation energy for H_2O and D_2O grown oxides is similar. Secondly, the activation energy is changing going from ultra-thin oxides to thin oxides. This indicates a change in oxidation mechanism.

However, two reservations have to be made. Firstly, the extraction of the activation energy is sensitive to small errors in the oxide thickness. A difference of 15-17 meV in activation energy suffices to give a change of 18% in oxidation rate in the temperature range of 750-950 ºC. Unfortunately the data do not allow such a precise determination of the activation energy. Secondly, during temperature ramp-up before oxidation, some initial oxide is grown due to some clean room air transported into the furnace together with the wafers. This initial oxide thickness 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. This implies that the activation energy for ultra-thin oxides will be higher than presented in figure 4.

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. 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. Still the silicon bulk will influence the oxidation process. This influence will decrease with increasing oxide thickness. For thicker oxide layers, the bulk silicon will not have an influence anymore. The existence of the two regimes can clearly be expected from the fact that native oxide growth automatically stops after a certain oxide thickness.

CONCLUSIONS

A wide range of growth data for thin H_2O and D_2O silicon oxides has been obtained. 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.

[1]   I.-W. Wu et al., *Journal of the Electrochemical Society*, Volume 136, pages 1638-1645, 1989.

[2]   G. Ghidini et al., *Solid-State Electronics*, Volume 41, pages 975-979, 1997.

[3]   W.-J. Cho et al., *Japanese Journal of Applied Physics*, Volume 38, pages 12-16, 1999.

[4]   H. Kim and H. Hwang, *Applied Physics Letters*, Volume 74, pages 709-710, 1999.

[5]   Y. Mitani et al., *IEEE Transactions on Electron Devices*, Volume 49, pages 1192-1197, 2002.

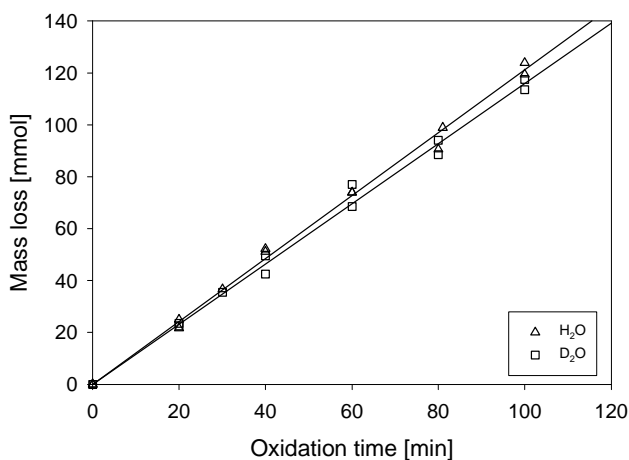[6]   CRC Handbook of Chemistry and Physics, 73rd Edition, CRC Press Inc., 1992, ISBN 0-8493-0566-7.

Figure 3: Amount of precursor introduced into the furnace as a function of oxidation time.
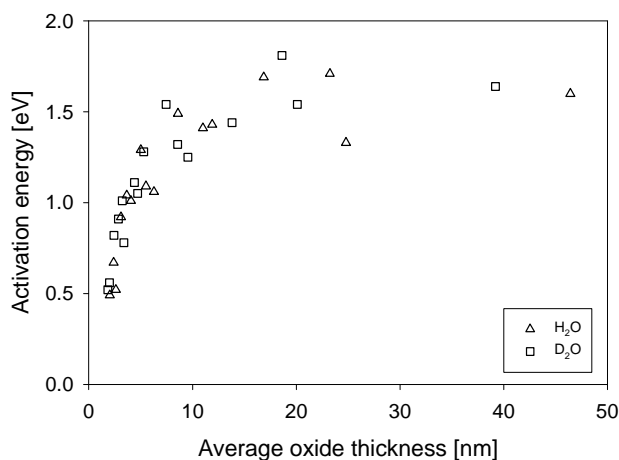

Figure 4: Extracted activation energy for oxide growth as a function of average oxide thickness for H_2O and D_2O ambient. The activation energy is extracted from every pair of adjacent measurement points in figure 1 for the same oxidation time, but different oxidation temperatures.