

# Oxidation Enhancement Characteristics of $\text{SrTi}_x\text{Mg}_{1-x}\text{O}_{3-\delta}$ Catalyst for Low Temperature Gate Oxide Formation

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## Abstract

Following our successful results on low temperature oxidation of 4H-SiC, this work investigates oxidation characteristic of catalytic thermal oxidation using the perovskite oxide,  $\text{SrTi}_x\text{Mg}_{1-x}\text{O}_{3-\delta}$ , as catalyst. Si is used as oxidation target and is set beside the catalyst in a furnace tube. Enhanced oxidation is clearly observed in the temperature range 650-850°C. The diffusion length of oxygen atoms generated by the catalyst is found to be tens of mm. Chemical analysis and electrical characterization indicates that Si is free from contamination of the catalyst material.

## 1. Introduction

In the previous reports [1, 2], we showed that thermal oxidation rate of 4H-SiC was significantly enhanced by using functional oxide  $\text{SrTi}_x\text{Mg}_{1-x}\text{O}_{3-\delta}$  as the catalyst. It has been shown to be able to form an oxide film at the surface of Si-face 4H-SiC at temperatures as low as 850°C at which no practical growth of oxide is observed without the catalyst. Low temperature thermal oxidation will contribute not only to reduce energy for device production but also to form oxide under reduced thermal dissociation of the bulk. The oxidation enhancement has been observed also in oxidation of Si [3].

The enhancement of thermal oxidation is owing to oxygen atoms generated by the functional oxide. Fig. 1 shows the lattice structure of  $\text{SrTi}_x\text{Mg}_{1-x}\text{O}_{3-\delta}$ . In the lattice of the oxide material, the oxygen adsorption sites are formed as oxygen vacancies by replacing  $\text{Ti}^{4+}$  with  $\text{Mg}^{2+}$  in the  $\text{SrTiO}_3$  perovskite structure. When  $\text{O}_2$  molecules are introduced into  $\text{SrTi}_x\text{Mg}_{1-x}\text{O}_{3-\delta}$ , an oxygen atom occupies the oxygen vacancy as an  $\text{O}^-$  ion that is a metastable state. Therefore, it is desorbed from the adsorption site as an oxygen atom. Desorption of oxygen atoms was confirmed by using thermal desorption analysis [1, 3].

In the previous studies, however, the catalyst was placed in the part above the wafer 1 mm apart. If it is possible to place the catalyst further remotely of the wafer, this new oxidation enhancement method will become of practical use. In this study, we evaluate diffusion length of oxygen atoms under the thermal oxidation condition from oxidation characteristics of Si. Electrical characterization is also performed to examine contamination during oxidation.

## 2. Experimental methods

The experimental setup used in this study is schematically illustrated in Fig. 2, where the catalyst  $\text{SrTi}_{0.5}\text{Mg}_{0.5}\text{O}_{3-\delta}$  and a Si-wafer test piece were set in a quartz tube of an electric furnace. The catalyst whose weight was 0.25 g was put in the area of about 20 mm x 20 mm on a Si wafer. A Si wafer cut in the size of 15 mm x 50 mm was put aside of the catalyst. The distance between the catalyst and the Si wafer was 5 mm.

The Si wafer was n-type (100) face Si with the resistivity of 1~10  $\Omega\text{cm}$ . The oxidation was performed for 3h at 600~850°C with  $\text{O}_2$  flow of 1.5 L/min. Oxide thickness distribution on the Si wafer was measured by a spectroscopic ellipsometer.

## 3. Results and Discussion

Fig. 3 shows  $\text{SiO}_2$  thickness on the Si chip as a function of the distance from the catalyst. Results obtained from oxidation at 650, 750, and 850°C were plotted. Results obtained without catalyst at 850°C were also plotted (white circle) in the figure. We find that oxide thickness increases as position comes close to the catalyst in the distance range between 5 mm and 15-30 mm, while the oxide thickness is almost uniform beyond this distance range. The oxide thickness in the uniform thickness region agrees with the thickness formed without catalyst. Therefore, the results indicate that oxidation is enhanced by the presence of the oxide catalyst.

Assuming that the enhanced oxidation is owing to generation of oxygen atoms and that oxygen atoms transported by thermal diffusion, we carried out fitting the experimental data points with the Gaussian distribution,

$$t_{ox} = a * \exp\left(-\frac{x^2}{L^2}\right) + b, \quad (1)$$

where  $t_{ox}$  is the oxide thickness,  $a$  is the constant coefficient related to the concentration of O atoms,  $x$  is the distance from the catalyst,  $L$  is the diffusion length of O atoms,  $b$  is the thickness of oxide grown by the conventional dry oxidation. Fitted curves are shown in Fig. 3 by the dashed lines. The diffusion lengths extracted from these results are 19.2, 13.7, and 10.9 mm for oxidation at 850, 750, and 650 °C, respectively. These values are reasonably agrees with the values measured by using the laser induced fluorescence of oxygen atoms generated with a Pt catalyst under atmospheric pressure [4].

Fig. 4 shows Arrhenius plots of the linear rate constant,  $B/A$ , of the Deal-Grove model. The plots were made for the oxide thickness obtained at the distances 5 mm and 40 mm from the catalyst. We can clearly see that the activation energy of the linear rate constant is reduced by the presence of the catalyst.

Fig. 5 plots the activation energies of the linear rate constant as a function of the distance from the catalyst. The activation energy is reduced by about 0.2 eV from 1.2 eV as the position comes close to the catalyst.

Concerning contamination, chemical analysis with electron probe micro analysis did not indicate any traces of contaminants from the catalyst on the Si surface. In order to confirm this point, C-V measurements for MOS capacitors were carried out. Fig. 6 shows C-V curves of the sample

oxidized at 650°C. The C-V curve at the distance of 10 mm, i.e. a MOS capacitor in the enhanced oxidation region, is almost as same as that at the distance of 40 mm. No significant difference in breakdown voltages was observed between the two diodes. Thus, the enhanced oxidation does not degrade the electrical quality of the SiO<sub>2</sub> layer.

#### 4. Conclusions

The use of SrTi<sub>x</sub>Mg<sub>1-x</sub>O<sub>3-δ</sub> catalyst enhances the rate of thermal oxidation. Oxygen atoms generated by the catalyst and are transported by thermal diffusion as was revealed by the good agreement between experimental data and the theoretical model. The diffusion length of oxygen atoms is evaluated to be a few tens of mm in oxygen molecule ambient under the atmospheric pressure. No contaminant on the Si wafer was observed in both chemical analysis and electrical characterization.

In conclusion, the catalytic oxidation can be developed for use in practical low-temperature oxidation of semiconductors such as 4H-SiC and Si including poly-Si.

#### Acknowledgements

This work is supported in part by KAKENHI (No. 16K14258) from Japan Society for the Promotion of Science.

#### References

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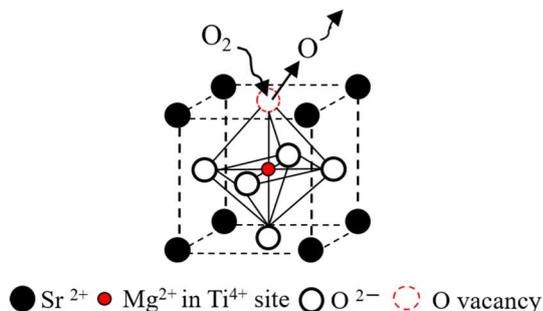


Fig. 1. Lattice structure of the SrTi<sub>x</sub>Mg<sub>1-x</sub>O<sub>3-δ</sub>.

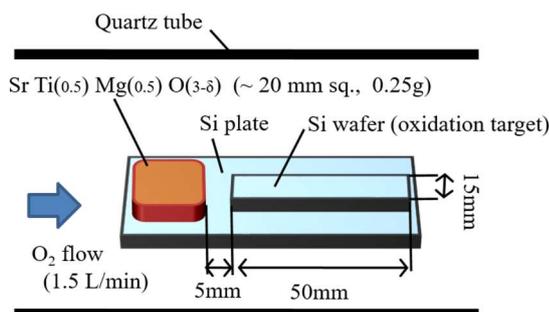


Fig. 2. Schematic of experiment setup.

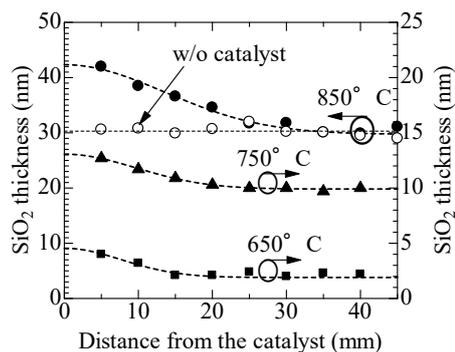


Fig. 3. Variation with distance from the catalyst of SiO<sub>2</sub> thickness grown at the surface of the Si wafer. SiO<sub>2</sub> thickness distribution of a Si wafer oxidized without the catalyst was also plotted.

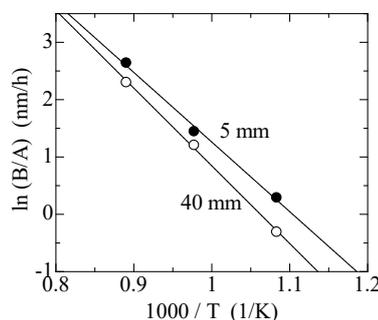


Fig. 4. Arrhenius plots of the linear rate constant,  $B/A$ , of the Deal-Grove model obtained at the positions 5 mm and 40 mm from the catalyst.

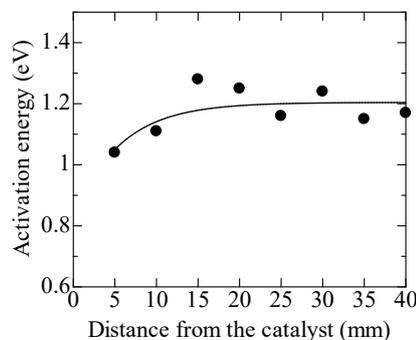


Fig. 5. Activation energy of the linear rate constant as a function of the distance from the catalyst.

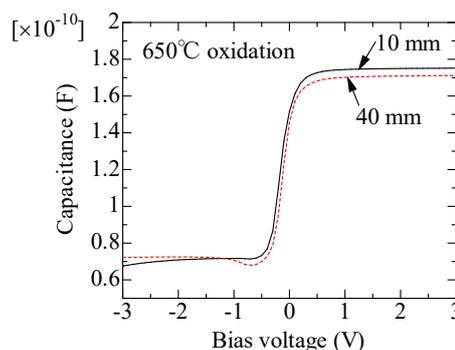


Fig. 6. MOS C-V characteristics of the SiO<sub>2</sub> layer grown at 650°C.