Extended Abstracts of the 2004 International Conference on Solid State Devices and Materials, Tokyo, 2004, pp. 786-787

C-9-1

Difference between O_2 and N_2 Annealing Effects on CVD-SiO_2 Film Quality Studied by the Time-Dependent OCP Measurement

Koji Kita, Kentaro Kyuno and Akira Toriumi

Department of Materials Science, School of Engineering, The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
Phone / Fax : +81-3-5841-7161 E-mail: kita@adam.t.u-tokyo.ac.jp

1. Introduction

The open-circuit potential (OCP) is a potential difference between two electrodes facing across a electrolyte without a current flow. Since the OCP measurement can sensitively characterize the surface of the electrode, it has been successfully applied for the study of the chemically oxidized Si surfaces [1,2] and the interfaces between high-k and Si [3]. We have reported that the bulk properties of dielectric films can be analyzed by the time-dependent OCP measurement (t-OCP) during the etching of the films [4].

In this study, we applied the t-OCP measurement to CVD- and thermal-SiO_2 films, in order to investigate whether the quality of CVD-SiO_2 film can approach to that of thermal-SiO_2 by a thermal treatment. This will provide an important information regarding to how far the thermal annealing can improve the properties of deposited films for gate dielectrics, including high-k films.

2. Experimental

Three kinds of SiO_2 films were grown on HF-last (100) Si substrates; (I) a 11.8 nm-thick SiO_2 film deposited by thermal CVD method using tetraethoxysilane (TEOS) at 650°C, (II) a 10.2 nm-thick thermal SiO_2 film grown at 750°C, and (III) a stacked film consisting of the CVD film on the thermal oxide. Both layers of sample (III) were prepared by the same conditions as sample (I) and (II), respectively. The OCP measurements were applied to those films before and after annealing at 800 - 1000°C in O_2 or N_2 ambient in order to understand the effects of thermal treatment on the film quality.

The t-OCP measurements were performed in 0.2 wt.% HF solution with a bare Si as the reference electrode, which was confirmed to show a stable potential of -0.23V against Ag/AgCl standard electrode. The voltage between the back contact of Si and the reference electrode was measured continuously. The details of the t-OCP measurement have been reported elsewhere [4,5].

3. Results and Discussion

The t-OCP for the thermal-SiO_2 (sample II) is shown in **Fig.1**. It consists of three stages. In the early stage, the OCP does not reach a steady-state, however, it shows a straight line clearly in the middle stage, corresponding to a steady-state etching [4]. In the final stage, the OCP shows a sudden drop followed by a gradual recovery, representing the end-point of the etching.

Figure 2 compares the t-OCPs for the three films before annealing. The CVD-SiO_2 film (sample I) is clearly distinguishable from thermal-SiO_2 (sample II) by the shape of the t-OCPs. The t-OCP of CVD-SiO_2 film does not show a straight line because the etching of the film finishes before establishing a steady-state. In the case of CVD-/ thermal-SiO_2 stacked film (sample III), the t-OCP seems to be a series of two curves, the one is for the CVD-SiO_2 and the other is for the thermal-SiO_2. It means that the depth-profile of SiO_2 films composed of several layers with different properties can be analyzed with the t-OCP.

Next, the CVD-SiO_2 films were annealed in O_2 and N_2 ambient and were investigated by the t-OCP measurement. **Fig.3 (a)** shows the change of the t-OCP for CVD-SiO_2 film by annealing in O_2 ambient at 1000°C. Since the shape of the t-OCP is approaching to that for the thermal-SiO_2 (shown in Fig.1), the CVD-SiO_2 film quality is considered to be improved significantly, to the level equal to the thermal-SiO_2. On the other hand, the t-OCP does not show

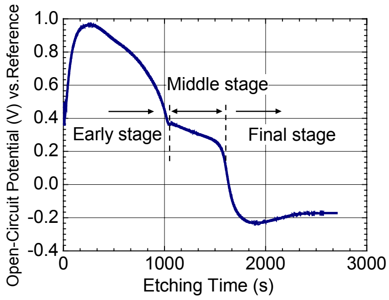

Fig.1 The t-OCP of thermal-SiO_2 measured in 0.2wt.% HF solution. It consists of three stages. In the early stage, the OCP does not reach a steady-state, however, it shows a straight line clearly in the middle stage, corresponding to a steady-state etching. In the final stage, the OCP shows a sudden drop followed by a gradual recovery, representing the end-point of the etching.

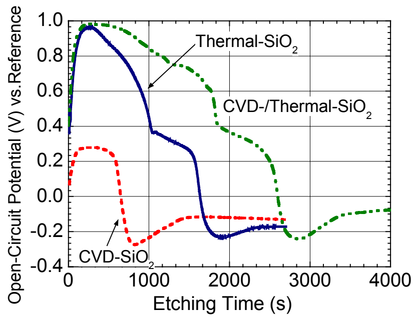

Fig.2 The t-OCPs for three films without annealing; CVD-SiO_2 (broken line), thermal-SiO_2 (solid line), and CVD-/thermal-SiO_2 stacked film (dot and dashed line), measured in 0.2wt.% HF solution. The t-OCP for CVD-SiO_2 film shows no straight line since the etching ends before the steady-state is established. The t-OCP for CVD-/thermal-SiO_2 stacked film seems to be the combination of the curve for CVD-SiO_2 with that for thermal-SiO_2 in series.

a straight line after N_2 annealing as shown in **Fig.3 (b)**, and is different from that of thermal-SiO_2. Thus it is concluded that the O_2 annealing at 1000°C improves the quality of CVD-SiO_2 films significantly, but the N_2 annealing does not. This difference suggests the importance of the reaction with O_2 during the thermal treatment for the quality improvement of the CVD-SiO_2 film. Actually the difference of the density between the CVD-SiO_2 films annealed in O_2 and N_2 was observed by a grazing incident x-ray reflectivity measurement, as shown in **Fig.4**.

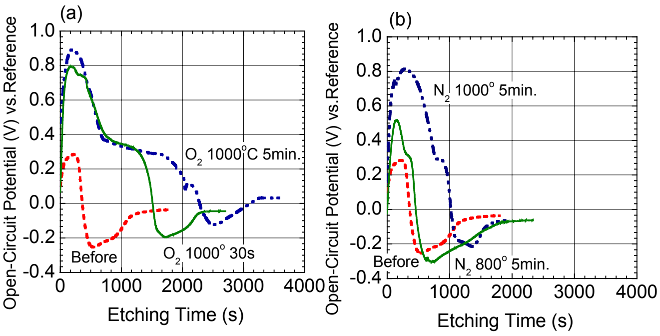

Fig.3 The t-OCP curves for CVD-SiO_2 films before and after annealing in (a) O_2 and (b) N_2. The film properties are considered to become similar to that of thermal oxide by O_2 annealing since the shape of t-OCP profiles is identical to the thermal oxide shown in Fig.2. The length of the straight line extends as the interface oxidation proceeds by longer annealing. However, after N_2 annealing, the t-OCP does not show a straight line.

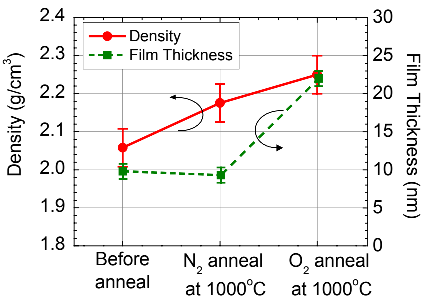

Fig.4 Change of the density and thickness of the CVD-SiO_2 films by annealing in O_2 and N_2 at 1000°C, evaluated by a grazing incident x-ray reflectivity (GIXR) measurement. The film annealed in O_2 showed higher density than that annealed in N_2.

Finally, we investigated the annealing effects on the CVD-SiO_2/thermal-SiO_2 stacked film (sample III). From the results shown in Fig. 3, it is expected that the CVD- and thermal-SiO_2 films will become undistinguishable after O_2 annealing due to the quality improvement of CVD-SiO_2 film. Actually, the t-OCP of the stacked film after O_2 annealing as shown in **Fig. 5** suggests that the film consists of a uniform layer, and the shape of the t-OCP approaches to that of a thick thermal-SiO_2 film. On the contrary, the existence of an interface was detected as a step of the t-OCP in the case of N_2 annealing. The step is understandable as the transition of the etching surface from one to the other layer in the case of HfO_2/SiO_2 stacked film[5]. However, since our stack consists of only SiO_2, the sudden drop in the t-OCP does not come from the dielectric properties difference between the two layers, but it might be attributable to the fixed charges left at the interface by

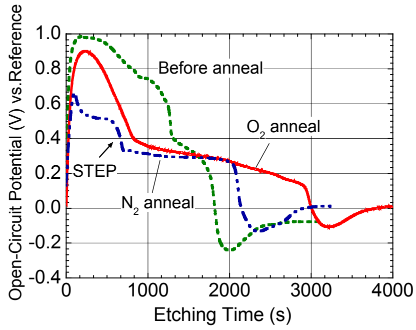

Fig.5 The t-OCPs for CVD-/thermal-SiO_2 stacked films before (dotted line) and after annealing in O_2 (solid line) and N_2 (dot and dashed line) at 1000ºC for 5min. The shape of the t-OCP after O_2 annealing indicates that the two layers are undistinguishable by t-OCP. On the contrary, the t-OCP for N_2 annealed film shows a step in the middle stage, which suggests that the interface still remains.

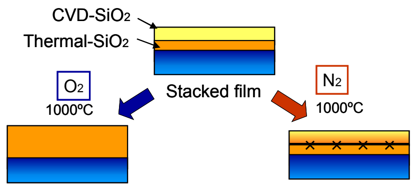

Fig.6. Schematic of the effect of O_2 and N_2 annealing on the CVD-/thermal-oxide stacked film, indicated by t-OCP measurements. Two layers cannot be distinguished after O_2 annealing, whereas the interface remains after N_2 annealing. The fixed charges at the interface might contribute to the step in t-OCP for N_2 annealed sample.

annealing. The annealing effect on the CVD-/thermal-SiO_2 interface is schematically depicted in **Fig.6**.

4. Conclusions

The quality of CVD-SiO_2 films is significantly improved by O_2 annealing at 1000°C since the t-OCP of the film becomes undistinguishable from that of the thermal-SiO_2, however, such improvement cannot be attained by N_2 annealing. In addition, the t-OCP profile indicates that the CVD-/thermal-SiO_2 interface disappears by annealing in O_2 but remains after annealing in N_2. These trends will be applicable to other deposited oxide films, including high-k dielectrics.

Acknowledgements

This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology in Japan, and NEDO/MIRAI project. The authors are grateful to H. Satake for providing SiO_2 films.

References

[1] H. F. Okorn-Schmidt, *IBM J. Res. Develop.* **43**, 351 (1999).
[2] V. Bertagna, R. Erre, F. Rouelle, E. Levy, S. Petitdidier, and M. Chemla, *Solid State Electrochem.* **5**, 306 (2001).
[3] H.F.Okorn-Schmidt *et al.*, *Proc. 4th Physics and Chemistry of SiO2 and the Si-SiO2 Interface 2000-2*, 505 (2000).
[4] K. Kita, M. Sasagawa, K. Kyuno and A. Toriumi, *Jpn. J. Appl. Phys.* Pt.2, **42,** L631 (2003).
[5] K.Kita, M.Sasagawa, K.Kyuno and A.Toriumi, *AIP Conf. Proceedings* **550**, 166 (2003).