Feasibility of Ultra-Thin Films for Gate Insulator by Limited Reaction Sputtering Process

IEICE TRANS. ELECTRON., VOL.E87–C, NO.2 FEBRUARY 2004

PAPER Special Section on Recent Progress in Oxide Thin Films by Sputtering

Feasibility of Ultra-Thin Films for Gate Insulator by Limited Reaction Sputtering Process

Kimihiro SASAKI[†a)], *Member*, **Kentaro KAWAI**[†], **Tatsuhiro HASU**[†], **Makoto YABUUCHI**[†], *Nonmembers*, *and* **Tomonobu HATA**[†], *Member*

SUMMARY A new sputtering technique named "*limited reaction sputtering*" is proposed and the feasibility toward an ultra-thin gate insulator is investigated. 5–10 nm thick ZrO_2 films were prepared on Si(100) substrates and analyzed by XPS, HR-RBS and RHEED. Significant Zr diffusion into the Si substrate and interface oxidation were not observed. An optimum film was obtained at growth temperature of 300°C, oxygen flow rate of 4.2% and 500°C-10 sec RTA. The equivalent oxide thickness of 2 nm was realized with leakage current of 10^{-7} A/cm^2 at 1.5 MV/cm.

key words: *reactive sputtering, gate insulator, ZrO_2, high-k*

1. Introduction

Down-scaling of ULSI devices has been aggressively progressing, in which lateral-scaling, typically the gate length, has been emphasized as a figure of the scaling. Recent years, however vertical-scaling of devices forces the gate oxide into a limitation as an insulator. Thus, an alternate gate insulator with a high dielectric constant and a low leakage current, so-called high-k material, is necessary in order to maintain the improvement of ULSI performances. There are many researches on the candidates of the gate insulator [1], in which physical and electrical properties are investigated in detail. However, the method on how to fabricate them has been hardly discussed. We consider that preparation method of the films ought to influence their properties.

In the conventional reactive sputtering technique using an oxide target or the oxide mode sputtering, high energy neutral oxygen atoms [2], which is strongly chemically reactive, are produced together with sputtered atoms. Si substrates exposed to the radiation are easily oxidized, resulting in growing a thick undesirable oxide. Moreover, the high energy particles are likely to cause an intermixing between a film and a substrate. Thus the sputtering technique is not regarded as an adequate way to prepare an ultra-thin gate oxide. On such the application of sputtering technique it is important to control the radiation effect, in which an atomic order precision is required.

Whereas, we have successfully prepared epitaxial Yttria-stabilized Zirconia thin films [3] and ultra-thin oxide films [4] with negligible Si oxidation layer by developing a new sputtering technique, named "*limited reaction sputtering*," in which the metal mode sputtering and oxidation processes are separated. In this paper we explain the concept of the technique and discuss the feasibility of the sputtering process on application to the ultra-thin gate oxide.

Manuscript received May 29, 2003.
Manuscript revised August 27, 2003.

[†]The authors are with the Faculty of Engineering/Graduate School of Natural Science and Technology, Kanazawa Univeristy, Kanazawa-shi, 920-8667 Japan.
a) E-mail: sasaki@ec.t.kanazawa-u.ac.jp

2. Principle of Limited Reaction Sputtering

A home made plasma-controlled DC magnetron sputtering apparatus is shown in Fig. 1. Ar and O_2 gases are introduced in the apparatus and a Zr metal disc is installed in a target chamber. In a conventional reactive sputtering process using a metal target, the target surface is exposed to a reactive ambient resulting in surface oxidation, in other words the oxide mode sputtering. Against that, for our apparatus the target is installed in a target chamber and capped by a plate with an aperture.

Carrying out sputtering under this condition some part of Zr atom sputtered from the target is deposited on the inside wall of the target chamber, on which only oxygen is gettered but Ar not. In other words, the spontaneous differential pumping is brought about. Thus, oxygen partial pressure decreases inside the target camber and the target is not oxidized [4]. As a result Zr metal atoms can continue to be sputtered and supplied to the substrate. On the other hand, the supplied Zr atoms react with the ambient oxygen, then a ZrO_2 film grows on the substrate. In short, the metal mode reactive sputtering is realized. Thus, we named this sputtering mechanism "*limited reaction sputtering*." Where, the significance to realize the process is that the target ma-

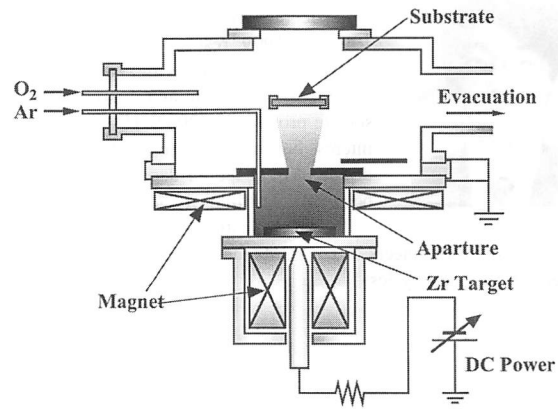


Fig. 1 Schematic diagram of sputtering apparatus used for the experiment.

Table 1 Parameters of apparatus and sputtering conditions.

Target-substrate distance	57mm
Sputtering DC power	80W
Gas pressure	10mTorr
Target	Zr 4N purity, ϕ 100mm
Film grwth rate	6nm/min
Background pressure	$\sim 5 \times 10^{-8}$Torr

terial must be strongly reactive with oxygen, thus has a fast pumping speed. For example, for Zr target sputtering an abrupt decrease of the film growth rate was observed while for the In-Sn alloy target to prepare ITO films [5] the film growth rate monotonically decreased suggesting that a weak gettering action. Thus an effective pumping speed is not anticipated for such a material.

An abrupt transition of sputtering condition from the metal mode to the oxide mode takes place when the oxygen flow rate exceeds a certain threshold value. Also the aperture size and the sputtering power are the other parameters influencing the threshold. As a matter of course, the parameters influence properties of the deposited film and the interface.

3. Details of Experiment

After chemically cleaned (conventional RCA cleaning) and followed by dipped in 5% diluted HF solution, n-type Si (100) wafer substrates with resistivity of 0.001–0.02 Ωcm were loaded into the sputtering chamber. The Si surface is in the hydrogen-terminated condition thus no native oxide. (Actually, epitaxial growth took place at substrate temperature of 600°C [3].) After 30 min pre-sputtering without oxygen to refresh target surface, 5–10 nm thick ZrO_2 films were deposited on the Si substrates with changing oxygen flow rate (determined as $O_2/(O_2+Ar)$) and substrate temperature. The sputtering gas pressure was kept by controlling a throttle. Sputtering parameters are listed in Table 1.

In nitrogen ambient 500°C-10 sec rapid thermal annealing (RTA) treatment to the samples was carried out by a lamp heating apparatus. Al dot electrodes with 300 μm in diameter were evaporated onto the ZrO_2 films and current-voltage and capacitance-voltage properties were measured. On the electric property evaluations the accumulation biasing condition was used.

Crystallinity of prepared films was characterized by reflection high-energy electron diffraction (RHEED). Chemical bonding structure of films and interface was evaluated by X-ray photoemission spectroscopy (XPS). The depth profile of the atomic composition was analyzed by high-resolution Rutherford back scattering (HR-RBS).

4. ZrO_2 Films and Interface Structure

The growth temperature is one of the most important process parameter. It is advisable to use an amorphous film

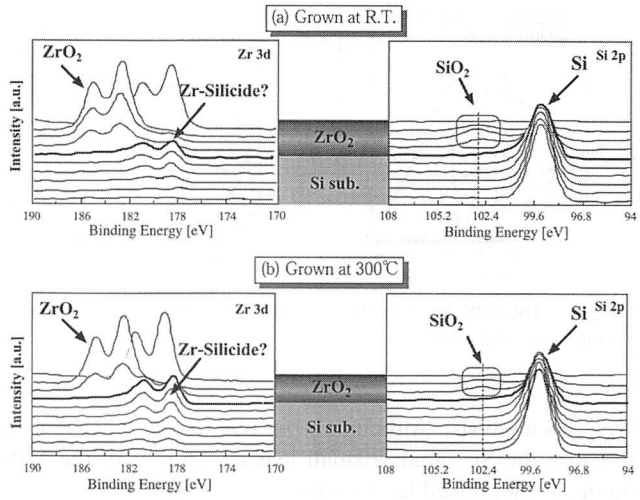


Fig. 2 XPS spectra of the 5 nm ZrO_2 films prepared at (a) room temperature and (b) 300°C.

rather than an imperfect crystalline one because crystalline defect and grain boundary often cause a leakage current. In order to get the prospect, RHEED observation was carried out. A obscure ring pattern suggesting poly-crystallization was observed for a ZrO_2 film prepared at 400°C but a hollow pattern for 300°C. Thus the growth temperature was set at 300°C which is the maximum temperature without causing crystallization and at room temperature (R.T.) as a reference. On film thickness, in order to make the resolution high 5 nm thick ZrO_2 films were prepared for XPS and HR-RBS analyses. In the XPS analysis, XPS measurement and an Ar ion etching were performed alternately. Change of the XPS spectrum along with depth direction are shown in Fig. 2.

First, paying attention to the Zr 3d peaks, it can be observed that oxide state changes to metal state abruptly especially for the R.T. film and Zr seems to diffuse into the Si substrate. However, if so, a mixture spectrum of oxide state and metal state would be observed somewhere in the spectra, because the escape depth of photoelectrons is a few nm while the film thickness is as thin as 5 nm. It may be possible to explain the abrupt change of the spectra by taking account of knock on phenomenon of Zr atoms into Si substrate during the Ar ion bombardment of the etching. On the contrary, for 300°C films a slight mixing spectrum is observed. Because of the elevated substrate temperature, Zr diffusion would take place. If so, it is a lethal drawback to apply to MISFETs. However, the Ar ion etching is not always performed uniformly so that the mixing spectrum is possible to appear. The diffusion observed will be discussed in more detail later using HR-RBS analysis. Anyway, significant difference between R.T. and 300°C is not observed on the oxide state Zr spectra.

Next, paying attention to Si 2p peaks metal state Si signal is observed through the spectra. Because there are two factors to cause this such as Si diffusion into the film and the comparable film thickness with the escape depth of photoelectron, it is difficult to make clear the origin only from

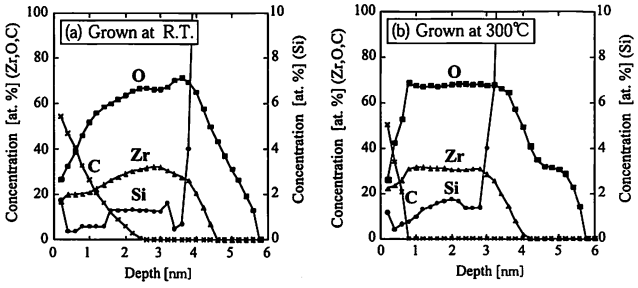


Fig. 3 HR-RBS depth profile of the ZrO_2 films prepared at (a) room temperature and (b) 300°C.

the XPS analysis. Although a pin hole is the other reason to cause the Si signal, a small leakage current of the MIS diode, as mentioned later, could reject the possibility.

On the other hand, oxide state Si signal is slightly observed and Si oxide seems to distribute around the middle of the film and appreciable Si surface oxidation is not observed. Comparing R.T. films with 300°C films, the intensity of the oxide Si signal is weak and shifts to lower binding energy side for 300°C film. These phenomena would be explained as follows. ZrO_2 has a larger heat of formation (−263 kcal/mol) than that of SiO_2 (−218 kcal/mol). Thus Zr absorbs oxygen and SiO_2 is reduced. Moreover the reduction is enhanced with elevating temperature. As a result, Si is oxidized more weakly at higher temperature.

For analyzing extreme thin films, a non-distractive technique is desired. In order to make clear the diffusion phenomenon of Zr into Si substrate as mentioned above, HR-RBS technique was employed to analyze the interface.

Figure 3 shows the HR-RBS depth profiles for (a) R.T. and (b) 300°C films. As can be seen in the figure, oxygen distributes over the whole region in which Zr distributes. Therefore, any diffusion of Zr into Si substrate is not detected with the HR-RBS analysis although its detection limit is an extent of a few %. The Zr diffusion as seen in XPS analysis is clearly decided to be due to the knock on effect by the Ar bombardment. Note that unlike Zr atom, oxygen dose not remain in Si. Oxygen atom is considered to volatilize before reacting with Si.

Observing Si distribution in the film the concentration increases around the middle of the film. Regarding the distribution as that of SiO_2, the tendency agrees with that observed in the XPS analysis although the reason is not clear.

Comparing the film structure, for 300°C film the film composition is revealed uniform through the film and stoichiometry is satisfied, while for R.T. film the film composition, thus the oxidation degree, is fluctuated.

5. Electric Properties of ZrO_2 Films

Identical ZrO_2 has 5 times larger dielectric constant than that of SiO_2. Aiming at the equivalent oxide thickness of 2 nm, 10 nm thick ZrO_2 films were prepared for investigating electric properties.

Figure 4 shows the relative dielectric constant of ZrO_2

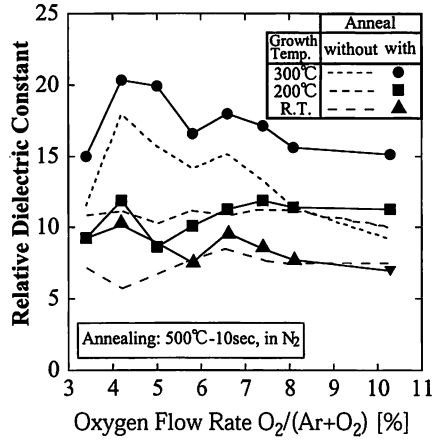


Fig. 4 Relative dielectric constant of 5 nm thick ZrO_2 films prepared with changing oxygen flow rate ($O_2/(O_2$ + Ar)). Dashed lines: before 500°C-10 sec RTA. Bold lines: after RTA.

films prepared with changing oxygen flow rate ($O_2/(O_2$ + Ar)). Results with and without RTA are shown by bold and broken lines, respectively. On discussing the obtained results, some competitive physical processes connecting the growth temperature should be considered. Namely, as increasing temperature the Si surface is likely to be oxidized, while the reduction power of Zr becomes stronger resulting in decreasing the interfacial oxide, also, film integrity is improved.

For the R.T. film with annealing, relative dielectric constants are as small as 7–10 and somewhat decrease with increasing the oxygen flow rate, while for 200°C film, it is slightly increasing although its dielectric constant is still small. According to the above hypothesis, these results are interpreted as follows. For the film growth at R.T., the reduction power by Zr is weak so that interfacial oxide grows resulting in decrease of the nominal dielectric constant. While for 200°C, it contributes to suppress interfacial oxide growth resulting in no decrease of dielectric constant. For 300°C film with annealing, a decreasing tendency of the relative dielectric constant appears again although its value is as large as 15–20. This result means that the interfacial oxide grows slightly, simultaneously, dielectric constant of the film become higher.

For R.T. and 200°C films the annealing effect is not revealed remarkably. This may be because the interfacial oxide predominates the apparent dielectric constant. On the other hand, for 300°C film except for the oxygen flow rate of 3.2%, growth of interfacial oxide is conjectured thinner so that the property of the film appears. As for 3.2%, dielectric constant of the film is considered small because of imperfect oxidation of Zr. Also the relative dielectric constants of 300°C films always appreciably increase with annealing. This may be because film was more strongly oxidized and densified.

The leakage current properties for oxygen flow rate are shown in Fig. 5, where the leakage current values are shown at the electric field of 1.5 MV/cm. It decreases with in-

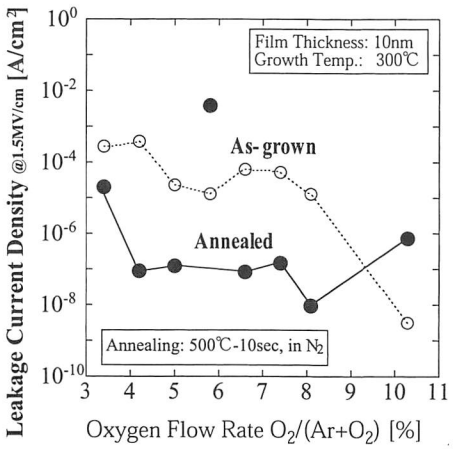


Fig. 5 Leakage current properties of 5 nm thick ZrO_2 films for oxygen flow rate. The values are shown at electric field of 1.5 MV/cm.

creasing oxygen flow rate. This tendency is explained by considering the decrease of dielectric constant as shown in Fig. 4. Namely, because of an interface SiO_2 growth, insulation performance is improved while dielectric constant decreases. By the way, the leakage current is observed to decrease as much as 2–3 decades by the annealing process. According to RHEED observations of RTA films, amorphous structure was still kept. A current leakage via grain boundary dose not occur. Consistently considering that the dielectric constant increased with the annealing, it is concluded that the film integrity was improved with suppressing growth of the interface SiO_2.

6. Conclusion

We have been investigating the practical use of the limited reaction sputtering process for the gate oxide fabrication. The critical issue of Zr diffusion into Si substrate was rejected. Also growth of an excess interfacial oxide decreasing nominal dielectric constant could be suppressed. Some optimum conditions were found as follows; substrate temperature of 300°C during film preparation, oxygen flow rate of 4.2% and 500°C-10 sec RTA. After the optimization a 10 nm thick ZrO_2 film with a relative dielectric constant of 20 and a leakage current as small as 10^{-7} A/cm^2 at 1.5 MV/cm was obtained. Although the equivalent oxide thickness of this film is as thick as 2 nm, considering the very small leakage current the film thickness affords to reduce, thus further thinner equivalent oxide thickness is feasible. In conclusion, the limited reaction sputtering is useful as a tool for the preparation of ultra-thin gate insulators.

Acknowledgement

This work was partly supported by Grant-in-Aid for General Scientific Research (Scientific Research (C) No.13650338) from the Ministry of Education, Science, Sports and Culture. The authors are grateful to Mr. K. Sasakawa at Kobelco Research Institute Inc., for the HR-RBS and XPS analysis.

References

[1] E.P. Gusev, D.A. Buchanan, E. Cartier, A. Kumar, D. DiMaria, S. Guha, A. Callegari, S. Zafar, P.C. Jamison, D.A. Neumayer, M. Copel, M.A. Gribelyuk, H. Okorn-Schmidt, C.D. Emic, P. Kozlowski, K. Chan, N. Bojarczuk, L.-A. Ragnarsson, P. Ronsheim, K. Rim, R.J. Fleming, A. Mocuta, and A. Ajmera, "Ultrathin high-K gate stacks for advanced CMOS devices," Tech. Dig. of 2001IEDM, pp.451–454, 2001.

[2] K. Tominaga, S. Iwamura, Y. Shintani, and O. Tada, "Energy analysis of high-energy neutral atoms in the sputtering of ZnO and $BaTiO_3$," Jpn. J. Appl. Phys., vol.21, no.5, pp.688–695, 1982.

[3] M. Nagashima, S. Nakano, K. Sasaki, and T. Hata, "Growth dependence of reactive sputtered Yttria-stabilized Zirconia on Si(100), (110),(111) substrates," Jpn. J. Appl. Phys., vol.38, part 2, no.1A/B, pp.L74–L77, 1999.

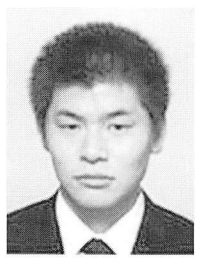
[4] K. Sasaki, T. Hasu, K. Sasaki, and T. Hata, "Limited reaction growth of YSZ (ZrO_2:Y_2O_3) thin films for gate insulator," Vacuum, vol.66, pp.403–408, 2002.

[5] T. Hata, S. Nakano, Y. Masuda, K. Sasaki, Y. Haneda, and K. Wasa, "Heteroepitaxial growth of YSZ films on Si(100) substrate by using new metallic mode of reactive sputtering," Vacuum, vol.51, no.4, pp.583–590, 1998.

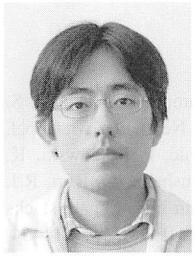
[6] Z. Alam, P.K. Saha, T. Hata, and K. Sasaki, "High-rate reactive deposition of indium oxide films on unheated substrate using ozone gas," Thin Solid Films, vol.352, pp.133–137, 1999.

Kimihiro Sasaki received B.S. and M.S. degrees from Miyazaki University in 1981 and 1983, respectively. He joined Tokyo Institute of Technology in 1983 and received Dr.Eng. degree in 1992. Since 1993, he has joined Dept. of Electrical & Electronic System Engineering in Kanazawa University. His research field is the physics of electron devices and their fabrication technologies.

Kentaro Kawai was received B.S. and M.S. degrees from Kanazawa University in 2001 and 2003, respectively. He has joined Chubu Electric Power Co., Inc. since 2003.



Tatsuhiro Hasu was received B.S. and M.S. degrees from Kanazawa University in 2000 and 2002, respectively. He has joined Seiko EPSON Corp. since 2002.



Makoto Yabuuchi was received B.S. degree from Kanazawa University in 2002. He is currently a master course student.

Tomonobu Hata was received B.S. degree from Kanazawa University in 1965 and M.S. and Dr.Eng. degrees from Tokyo Institute of Technology in 1969 and 1972, respectively. He has joined Kanazawa University since 1972. His research interests are the sputtering technology and thin films.