[논 문] 한국재료학회지
Korean Journal of Materials Research
Vol. 4, No. 8 (1994)

Si기판 세정조건에 따른 산화막의 특성연구

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A study on characteristics of thin oxides depending on Si wafer cleaning conditions

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초 록 Gate oxide의 특성은 세정공정에서 사용된 last 세정용액에 큰 영향을 받는다. Standard RCA, HF-last, SCl-last, and HF-only 공정들은 gate oxidation하기 전 본 실험에서 행해진 세정공정들이다. 세정공정을 마친 Si기판들은 oxidation furnace에서 900℃로 thermal oxidation 공정을 거치게 된다. 100Å의 gate oxide를 성장시킨 후 lifetime detector, VPD AAS, SIMS, TEM, 그리고 AFM과 같은 분석장비를 이용하여 oxide의 특성을 평가했다. HF-last와 HF-only 공정에 의해 금속 불순물들이 매우 효과적으로 제거됐음을 알 수 있었다. Oxide의 표면 및 계면 형상은 AFM과 TEM 측정을 통하여 관찰하였다. 표면거칠기는 SCl 세정용액을 사용한 splits 실험에서 불균일함이 관찰되었고 HF-only 세정공정을 거친 시편의 표면 및 계면이 가장 smooth했다.

Abstract The characteristics of gate oxide significantly depend on the last chemical solution used in cleaning process. The standard RCA, HF-last, SC1-last, and HF-only processes are the pre-gate oxide cleaning processes utilized in this experiment. Cleaning process was followed by thermal oxidation in oxidation furnace at 900℃. A 100Å gate oxide was grown and characterized with using lifetime detector, VPD AAS, SIMS, TEM, and AFM. The results of HF-last and HF-only were shown to be very effective to remove the metallic impurities. And these two splits also showed long minority carrier lifetimes. The surface and interface morphologies of the oxide were examined with AFM and TEM. The rough surface morphologies were observed with the cleaning splits containing the SC1 solution. The smooth surface and interface was observed with the HF-only cleaning process.

Introduction

Si surface cleaning prior to the thin gate oxide growth becomes more critical as semiconductor processing technology moves towards deep submicron device structures[1~3]. The importance of cleaning process prior to gate oxidation is much more emphasized when the gate oxide thickness is reduced to less than 100Å[3~6]. The major factors affecting the oxide quality are particles and metallic impurities[7~10]. These contaminants are considered to degrade the oxide quality significantly. In 70's, RCA cleaning process was developed by W. Kern and is still a dominant process in semiconductor manufacturing process[11]. But in these days, the new concepts of Si wafer cleanings such as vapor phase cleaning[12~14] and H- or O-plasma cleaning[15~17] have been proposed by some other scientists. The vapor phase cleaning system is developed and now is applied to some processes such as contact, trench, and pre-silicide cleans. This vapor phase cleaning system, however, still has a problem to apply pre-gate oxide clean because of the unstable growth of the oxide. The plasma cleaning system is now under consideration to use contact, via hole and pre-gate cleans[18]. The important advantage of this plasma cleaning is the surface passivation to protect the Si wafer from the contamination. But wet chemical cleaning based on the RCA method is always a winner in actual device fabrication process.

In this experiment, we have utilized wet chemical cleanings based on the RCA methods before growing the gate oxide. This characteristics of gate oxide will be measured by using lifetime detector, VPDAAS(vapor phase deposition atomic absorption spectroscopy), SIMS(secondary ion mass spectroscopy), TEM (transmission electron microscopy), and AFM (atomic force microscopy).

Experimental

The Si substrates used in this study were Si (100)-oriented substrates(4"dia.) with resistivity of 10~20Ωcm(p-type, B-doped). The Si wafer cleaning prior to the gate oxidation was performed based on the standard RCA (piranha+SC1+dilute HF+SC2, B1), HF-last(piranha+SC1+dilute HF, B2), SC1-last (piranha+dilute HF+SC1, B3) and HF-only (piranha+dilute HF, B4). The cleaning splits above mentioned were classified as B1, B2, B3 and B4 in series. The SC1 and SC2 solutions are the mixtures of $NH_4OH+H_2O_2+H_2O$ and $HCl+H_2O_2+H_2O$, respectively. The piranha and dilute HF consist of $H_2SO_4+H_2O_2$, and HF $+H_2O$, separately. After wet cleaning Si substrates were collected and dried by the spin dryer. Precleaning was followed by thermal oxidation in oxidation furnace at 900℃. A 100 Å gate oxide was grown and characterized with using lifetime detector, VPD AAS, SIMS, TEM, and AFM.

Results and Discussion

The characteristics of the gate oxide are critically dependent on the Si substrate cleaning before the oxidation. In this study, we examined the metallic impurities and the surface and interface morphologies of the gate oxides. First we examine the chemical contents with VPDAAS. The results of metallic impurities in the oxides are listed in Table 1. It

Table 1. Amount of metallic impurities in SiO_2 measured by VPDAAS($10^{-10}/cm^2$)

elements	B1	B2	B3	B4
Al	145.9	14.7	1313.8	12.3
Fe	153.7	221.4	235.3	122.3
Cu	3.8	1.4	4.1	1.4

shows that the HF-last(B2) and HF-only(B4) cleanings exhibit the lower contents of metallic impurities than those of other cleaning splits which are B1 and B3. It means that the HF-last and HF-only cleaning are also effective to remove the metallic impurities. As far as metallic impurities are concerned, the SC2 cleaning solution which consists of $HCl+H_2O_2$ $+H_2O$ is standard procedure to eliminate the metallic contaminants[9,11]. In this experiments, however, metallic contaminants are thought to be removed and/or dissolved while etching the oxide with the dilute HF chemical solution. These data are well consistent with the minority carrier life time results which are shown in Table 2. The lifetimes of cleaning

Table 2. Dependence of minority carrier lifetimes on the Si wafer cleaning conditions.

split	average(μ sec)	deviation
B1	9.01	0.61
B2	44.22	3.02
B3	3.74	0.25
B4	45.12	2.19

splits of the B2 and the B4 exhibit longer than those of the B1 and the B3. According to the data of Table 1 and Table 2, the specimen with the high contents of metallic impurities exhibits a short minority carrier lifetime. The metallic impurities in Si device diffuse into the deep levels of the band gap of Si and act as the recombination centers for electrons and holes[9,19]. Therefore high contents of metallic impurities provide the many available sites for electrons and holes to recombine and shorten the minority carrier lifetimes significantly. The specimen of B3 shows the large amount of Al impurity. This Al contamination is reported frequently in alkaline environments such as SC1 which consists of NH_4OH, H_2O_2, and H_2O. In SC1, $Al(OH)_4^-$ complex is known to be soluble and not stable in H_2O_2. Therefore Al is contaminated in this SC1 step and this is the only possible explanation why Al is contaminated in the B3 split which is the SC1-last[20]. This Al contamination has been investigated with SIMS shown in Fig. 1. This

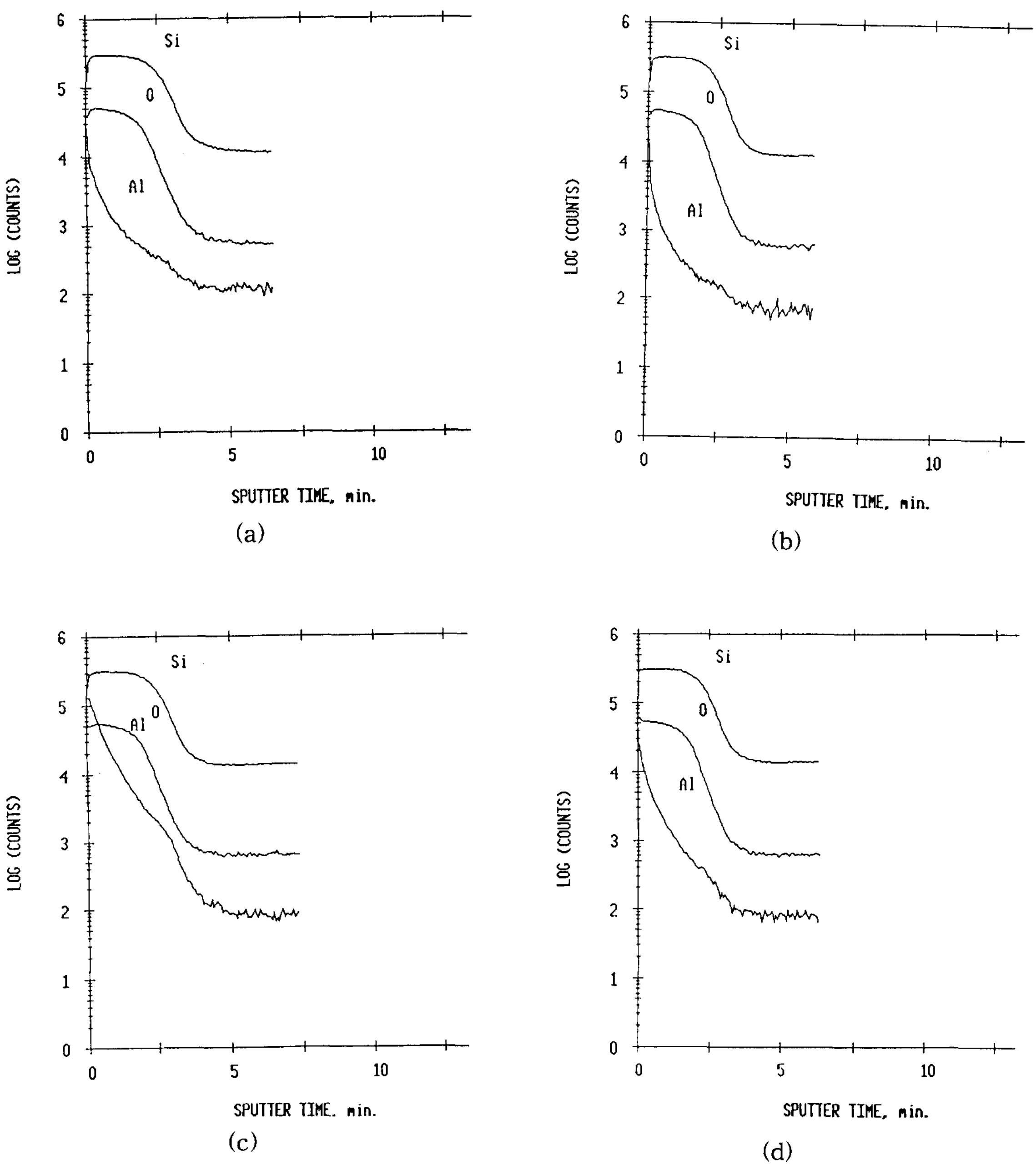


Fig. 1. SIMS depth profiles of specimens of a) B1, b) B2, c) B3, and d) B4.

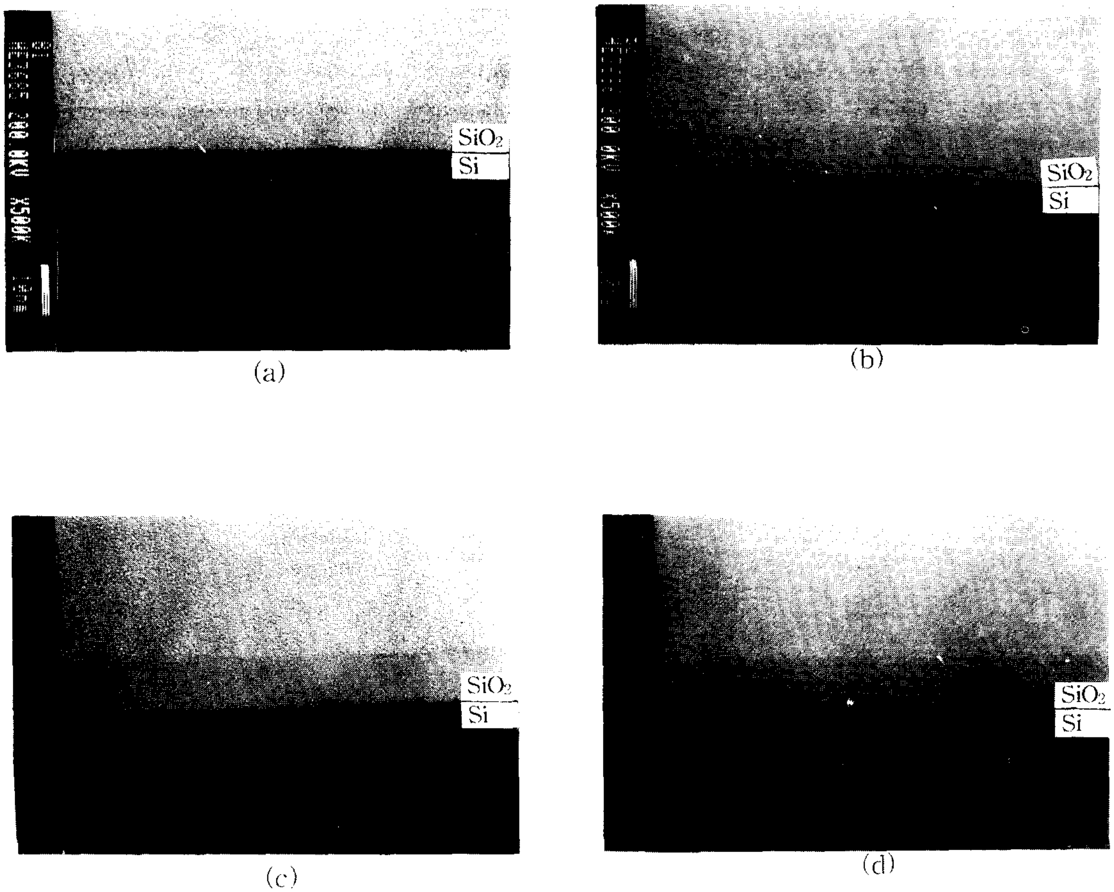
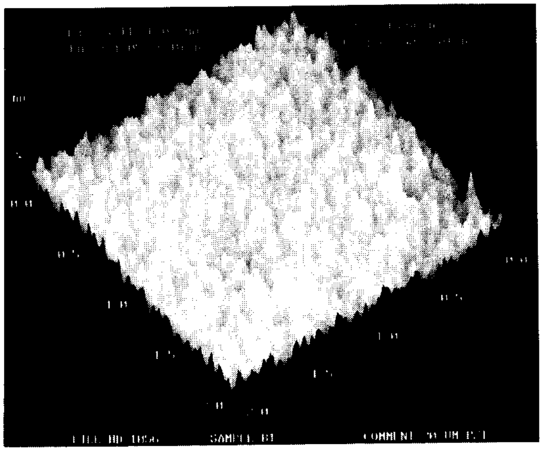
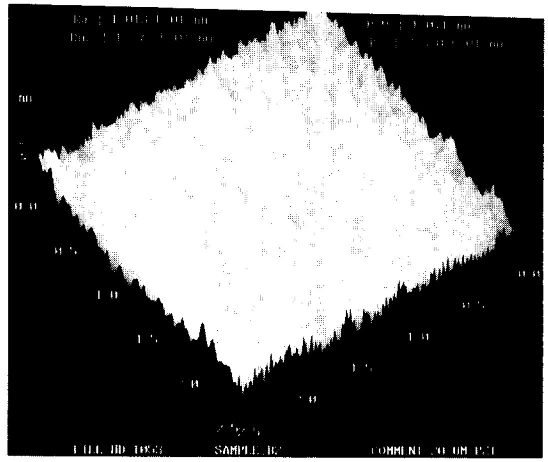


Fig. 2. Cross sectional TEM micrographs of SiO_2/Si interfaces of a) B1, b) B2, c) B3, and d) B4.

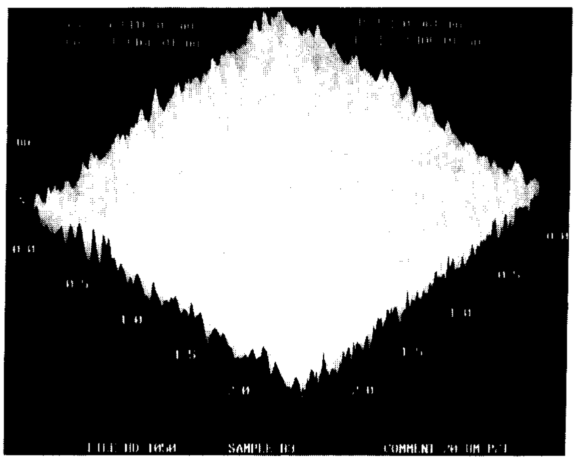
exhibits that the Al is located in SiO_2 layer. This also indicates the Al may degrade the oxide characteristics. It need to do further measurement of the electrical properties to identify. Fig. 2 and Fig. 3 are the surface and interface morphologies of SiO_2/Si measured by TEM and AFM. The interface morphologies of the specimens of SiO_2/Si indicate the relatively smooth interface. The B4 specimen among other specimens shows the better interface morphology. This means the HF-last cleaning does not degrade the interface characteristics of SiO_2/Si. However, the interface of SiO_2/Si observed by TEM is about 1500Å, which is short to generalize the whole specimen. The surface morphology of SiO_2 is believed to be same as the interface morphology of SiO_2/Si. Therefore we have utilized the AFM to verify the large area of the surface of SiO_2. The average scan area of AFM in this result is about $2\mu m \times 2\mu m$ which is very large compared to TEM. The surface morphologies of B1, B2, and B3 measured by AFM are quite different with that of B4. And Table 3 is the measured values of RMS(root - mean - square) roughnesses and peak-to-valley heights of these AFM data. The RMS roughness of B4 is about 0.9Å and the peak-to-valley is about 7 Å. The B1, B2, and B3 show the 1.1～1.3Å in RMS roughnesses and the 9～11Å in peak-to-valley heights. These data show the B4 split cleaning exhibits the much smoother surface morphologies compared to the those of B1, B2, and B3 cleaning splits. This result is also consistent with TEM micrographs. Here B4 split(HF-only cleaning) exhibits the better surface morphology. The reason why the B4 surface is different with others is believed to



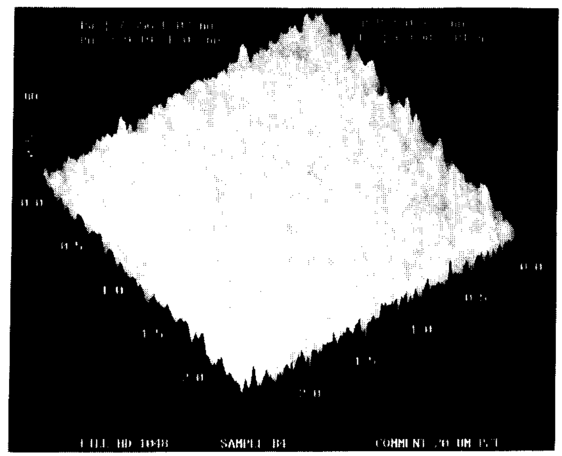
(a)



(b)



(c)



(d)

Fig. 3. Surface morphologies of SiO_2 of a) B1, b) B2, c) B3, and d) B4 measured by AFM.

Table 3. Measured RMS(root-mean-square) roughness and peak-to-valley values of SiO_2 surface by AFM(atomic force microscope).

split	RMS roughness(nm)	P-V(nm)
B1	1.053×10^{-1}	0.896
B2	1.272×10^{-1}	1.071
B3	1.146×10^{-1}	0.961
B4	0.919×10^{-1}	0.738

be related with SC1 cleaning solution. The cleaning splits of B1, B2, and B3 are cleaned with SC1 solution which is NH_4OH chemical in it. But the split of B4 does not consist of SC1 solution[21]. This result indicates the SC1 solution degrades the Si surface. In these experimental results, B4 split which is HF-only cleaning indicates the low metallic impurities and the smooth surface and interface morphologies.

Summary

The gate oxide properties have been examined with using lifetime detector, SIMS, VPDAAS, TEM, and AFM. It shows that the splits of B2(HF-last) and B4(HF-only) cleanings exhibit the small amount of metallic impurities. These results indicate that the HF-last and HF-only cleanings are also effective

to remove the metallic impurities. The split of B4 also exhibits relatively smooth surface and interface morphologies. However, the splits of B1, B2, and B3 which consist of SC1 solution show the degradation of the surface and interface morphologies. In this experiment we have examined the SC1 solution degrade the Si surface significantly.

In conclusion, the HF-only and HF-last cleanings exhibit the better characteristics in metallic impurities point of view compared to the B1 and B3. HF-only cleaning also shows much smoother surface and interface morphologies than those of HF-last cleaning.

Acknowledgements

This work was supported by the Ministry of Education(Semiconductor field) through grant ISRC-93-E-1103.

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