Effects of the Contents of Hydrochloric Gas on the Electrical Properties of the RTO/RTN Dual Dielectric Films

(HCl 첨가에 의한 RTO/RTN 이중 절연박막의 전기적 특성 변화)

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要 約

독립적인 nitridation step이 포함된 급속 열처리 공정을 이용하여 125-180 Å 두께의 이중 절연박막을 단결정 실리콘 상에 형성하였다. HCl가스의 첨가량과 공정시간의 변화에 따른 박막 특성의 변화를 고찰하였고, 이에 따른 박막의 전기적 특성을 관찰하였다. HCl 가스의 첨가에 의해 초기의 산화막 두께의 성장은 현저하게 나타났으나, nitridation 후의 박막두께의 변화는 10 Å 이하로 매우 저조하였다. 이중 절연박막의 항복전압은 HCl 가스의 첨가량에 비례하여 점차 증가하였고, 절연강도는 furnace나 독립적인 nitridation step이 포함되지 않은 급속 열처리 공정으로 형성한 같은 두께의 박막에 비해 높은 것으로 분석되었다.

Abstract

The dual dielectric films have been grown on single-crystalline silicon substrates with the thickness ranging from 125Å to 180Å at various gas and temperature conditions by using rapid thermal process that included independent nitridation step. The film characteristics and their dependence on the contents of the hydrochloric gas and the processing time have been studied. By the addition of the hydrochloric gas, the initial oxide thickness was significantly changed, but after sequential nitridation processes the thickness of the films was nevertheless a little bit varied within 10Å. All the samples of the dual dielectric films show the increased breakdown voltages in proportion to the additive contents of the hydrochloric gas and also show the higher breakdown strengths than the thermal oxide and nitrided oxide films grown by the conventional furnance process or the rapid thermal nitridation process that was composed of the dependent nitridation cycles.

I. Introduction

As the devices are scaled down to the submicron range, reliable thin dielectric films are required to fabricate high performance MOS devices (1-3). These films should have ultrathin (< 100 Å) and uniform thickness, high breakdown field, sharp breakdown distribution, clean interface and low defect density. However, thin thermal dielectric films grown by the furnace techniques appear to have several limitations such as the poor yield and reliability. As the result of

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technological and reliability problems, there have been demands for ultrathin dielectric films with higher quality to replace the conventional thermal dielectric films.

It has been recently proposed that the dielectric films produced by the rapid thermal process that was well known as a simple and easy thickness control process minimize these problems and improve their properties (4-7). Especially, it was found that nitride and nitrided oxide films possessed excellent characteristics as the diffusion barrier against dopants and other impurities, and enhanced the radiation resistance of oxide-silicon interfaces and the dielectric strength (8-15).

In this study, we obtained various dielectric films by the rapid thermal process that included independent two-steps of the sequential pre-annealing and oxidation process, and independent three-steps of the sequential pre-annealing, oxidation and nitridation process. Especially, the contents of the hydrochloric gas in the pure oxygen ambient were changed for the chlorine-based mobile ion gettering process. Then, the MIS (Metal Insulator Semiconductor) structures were fabricated for evaluating the electrical characteristics of the dielectric films.

We verified subsequently the effects of the independnet RTN (Rapid Thermal Nitridation) process step and the effects of the contents of the hydrochrolic gas on the electrical properties of the dual dielectric films that composed of the silicon oxide as the first layer and the nitrided oxide as the second layer.

And, these results were also compared with the characteristics of the dielectric films obtained by the furnance technique and the rapid thermal process that included a dependent RTN process step.

II. Experiment

All the experiments were carried out on < 100 >-oriented 4 inch, p-type silicon wafers with a resistivity of 6-9 ohm-cm. Fig. 1 shows the process sequence of the test sample fabrication. The wafers were cleaned with the aqueous solution of HF to remove the native oxide and rinsed with the deionized water. The growing processes of the thin dielectric films were sequentially carried out in the same process chamber of the Heatpulse 2146 (AG Associates) rapid thermal process system. Fig. 2 and 3 show the time-temperature profiles of these sequential processes and the 13 control steps of the gas species, respectively. The first pre-anneal step, 850°C for 30 sec, was introduced to stabilize the temperature of the process chamber.

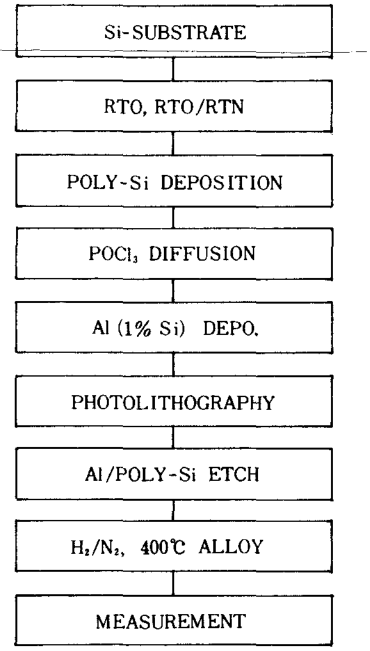

Fig.1. Process sequence of the test sample fabrication.

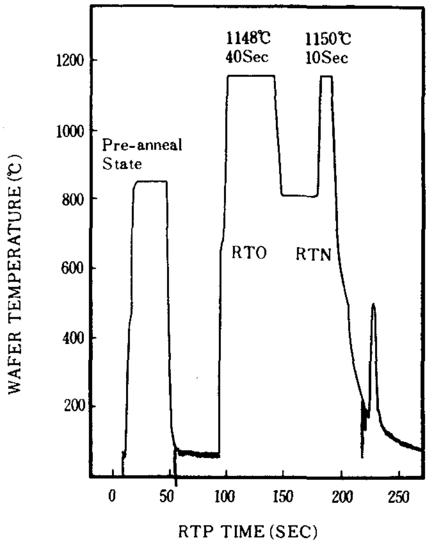

Fig.2. Typical time-temperature profiles of the sequential three-steps RTO/RTN process.

STEP	RTO			STEP	RTN		
	PROCESS	GAS	FLOW RATE		PROCESS	GAS	FLOW RATE
1	DELAY (15sec)	Ar	10	7	STEADY (800℃, 10sec)	Ar	4
2	DELAY (10sec)	O_2	10	8	STEADY (800℃, 20sec)	NH_3	4
3	DELAY (5 sec)	O_2	5	9	RAMP-UP (165℃/sec)	NH_3	1.5
4	RAMP-UP (200℃/sec)	O_2	1.5	10	STEADY (1150℃)	NH_3	1.5
5	STEADY (1148℃)	O_2	1.5	11	DELAY (5sec)	Ar	2
6	RAMP-DOWN (155℃/sec)	Ar	2	12	DELAY (5sec)	Ar	5
				13	DELAY (15sec)	Ar	10

Fig.3. Sequential 13 control steps of the process gas species (liter/minute).

The second oxidation step was performed for the growth of the oxide film at 1148°C for 40 sec in the ambient of pure oxygen, and the mixture of hydrochloric gas and oxygen, respectively. The contents of the hydrochloric gas in the pure oxygen ambient were changed from 0 to 8%.

After the completion of the steady-state of an oxide growth step, an intermediate step, 800°C for 30 sec, was introduced for the complete exchange of the ambient gas from the oxygen to the ammonia. That is, argon gas was firstly introduced into the process chamber at the end of the steady-state of RTO (Rapid Thermal Oxidation) process step and continued for 10 sec at the steady-state of the intermediate step for the complete evacuation of the oxygen gas. The ammonia gas was next introduced for 20 sec.

After the intermediate step, RTO oxide films were subsequently nitrided by the third nitridation step in dry ammonia ambient at atmospheric pressure, 1150°C for 10 sec and 120 sec, respectively. After the nitridation step, the ammonia gas was shut off and then the argon gas was introduced into the process chamber for its purging.

In the next place, MIS devices were fabricated with these dielectric films by the following process procedures. The polysilicon layer was deposited at 625°C and followed by the phosphorus doping from $POCl_3$ source, and the aluminium film was sputter-deposited. After the lithography process, the aluminium and the polysilicon layers were patterned with wet chemical and plasma etching for the formation of gates and metal contacts, respectively.

The capacitors received a final heat treatment at 400°C for 30 minutes in the forming gas (N_2 / 4% H_2) to enhance the ohmic contact and to reduce the interface state density. The area of the defined capacitors was 320 x 320um^2.

Ⅲ. Results and Discussions

1. Film thickness and refractive index

The thickness and the refractive indexes of dielectric films were measured with a Gaertner L116K automatic ellipsometer. The thickness uniformity of dielectric films was better than 2% in within-a-wafer and 1% in wafer-to-wafer. The effective thickness variation of the dielectric films was plotted in Fig. 4 as a function of the hydrochloric gas contents in oxygen gas and the RTN times. As shown in Fig. 4, the significant enhancement of the silicon oxidation rates with increasing the mixing ratio of the hydrochloric gas was observed. These results were believed to be due to the chlorine-based mobile ion gettering (16).

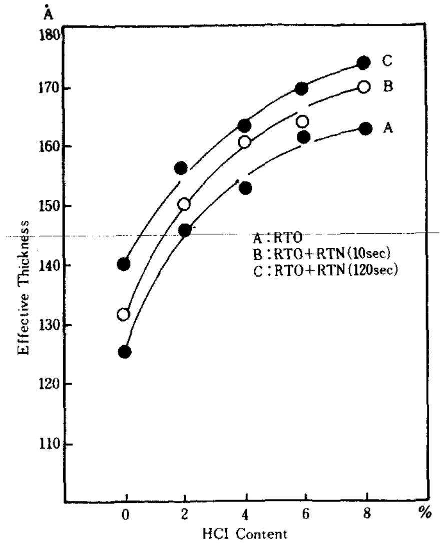

Fig.4. Effective thickness of the dielectric films as a function of the additive contents of hydrochloric gas.

But, after nitridation process for the formation of the dual dielectric films the effective thickness of the films were nevertheless slightly changed within 10Å. Above results show that the initial oxide thickness was significantly changed by the addition of the hydrochloric gas, but after sequential nitridation process the thickness of the dielectric films was not significantly changed.

In Fig. 5, we have plotted the effective refractive indexes of the dielectric films as a function of the additive contents of hydrochloric gas in oxygen gas and the RTN times. The effective refractive index of the dielectric film formed by RTO was 1.43. And, after the nitridation of this film, the refractive index increased with RTN process time, that is, 1.45 for 10 sec and 1.65 for 120 sec. The RI values increased monotonously for the RTO films, and these ones increased rapidly after nitridation process. These results show that the mobile ion gettering which were caused by the addition of chlorine atoms increased the initial oxide thickness, and also changed the RI values. And, the rapid increment of the RI values after nitridation process seems to be associated with the formation of the nitrided oxide films which possess higher RI values and with the slight change of the initial oxide thickness.

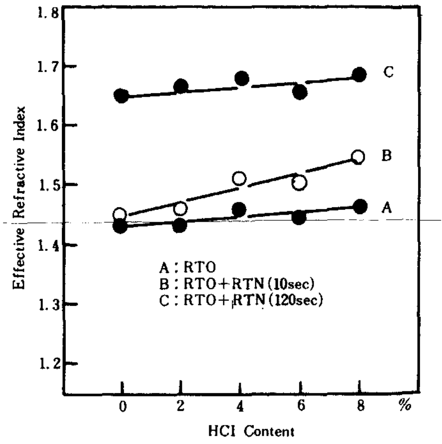

Fig.5. Effective refractive index of the dielectric films as a function of the additive contents of hydrochloric gas.

The samples nitridized for 120 sec showed the significant increment of RI values than the ones nitridized for 10 sec. It seems that the samples nitridized for 10 sec form the nitrided oxide layer on the surface of the oxide film, and consequently increase RI values. On the other hand, 120-sec-nitridized samples formed the nitrided oxide layers on the surface of the oxide and at the interface of the oxide-silicon by the diffusion of the nitridant species to the interface layer, and resultantly increased RI values more abruptly.

2. *Current-Voltage Characteristics*

The leakage current and the breakdown field measured were more than 100 samples for each condition with a ramped voltage source method on the 4145A Semiconductor Parametric Analyzer. Fig. 6 and 7 show the current-voltage characteristics of the MIS capacitors before and after nitridation (10 sec) process. All the samples of the dual dielectric films show the increase of dielectric breakdown voltages after nitridation process. Especially, the breakdown voltages of the dual dielectric films formed from RTO oxide films that hydrochloric gas were added constantly increased in proportion to the additive contents of the hydrochloric gas.

The 2%-added samples showed the increase of 5% of average breakdown voltages compared with

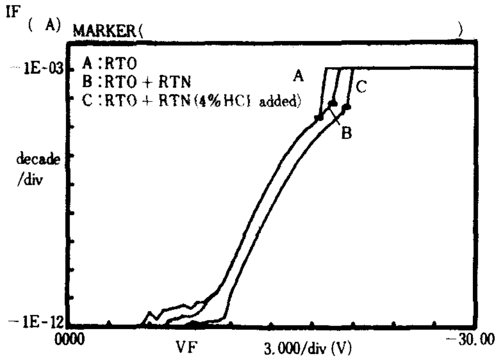

Fig.6. A typical current-voltage characteristics of the MIS capacitors (Effective thickness -A:125Å, B:133Å, C:160Å).

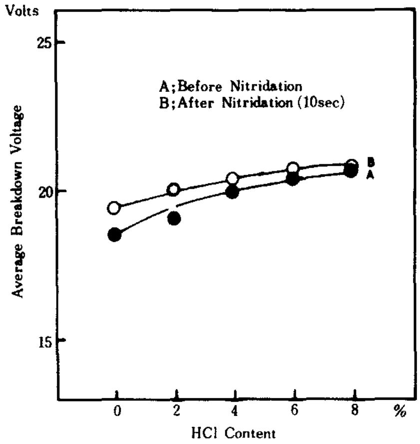

Fig.7. Average breakdown voltages of the dielectric films as a function of the additive contents of hydrochloric gas.

the RTO oxide samples, and the increase of 11% compared with the RTO oxide samples that hydrochloric gas were not added. But, the samples that the hydrochloric gases of respective 4% and 8% were added show lower increasing rate than the 2%-added samples. This results well agree with the phenomenon that the growth rate of the film saturates with the increase of contents of hydrochloric gas. And the results show that nitrided oxide films formed by RTN process increased the dielectric strength of the dual dielectric films, and as a result increased breakdown voltages.

Fig. 8 shows the dielectric breakdown distribution of the MIS capacitors which composed of dual dielectric films. The dual dielectric films also show the higher breakdown strengths than those of the thermal oxide and nitrided oxide films with the same effective thickness produced by the conventional furnace process (average breakdown voltage ; 13.2MV/cm, Ref. 4) or the rapid thermal nitridation process that composed of the dependent nitridation cycles (average breakdown voltage ; 12.8MV/cm, Ref. 15). It seems that these results were induced by the independent nitridation cycles that increased nitridant species of the thermal nitride-gas interface and enhanced a reaction with the silicon surface due to the complete exchange of the process gas in the quartz chamber.

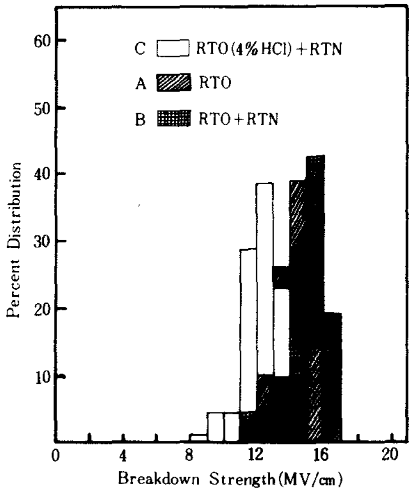

Fig.8. A typical dielectric breakdown distribution of the MIS capacitors (Average breakdown strength-A:12.20MV/cm, B:14.17MV/cm, C:15.09MV/cm).

However, the average breakdown strength decreased from 15MV/cm to 12MV/cm with the increase of contents of the hydrochloric gas, as a result of the increment of the initial oxide thickness. Above results show that the effects of the thickness variation and the quality of the initial oxide (RTO oxide) film by the addition of the hydrochloric gas could be neglected on the very short-time (about 10 sec) nitridation process, and formed nitrided oxide film on the surface of the RTO oxide with the same thickness. As the results it is concluded that the enhancement of the dielectric breakdown strength is dominantly influenced by the increase of the thickness induced by the addition of the hydrochloric gas than by the nitrided oxide layer grown with the ~~short-time nitridation process.~~

But, in the case of the samples which were subjected to the nitridation process for 120 sec, the breakdown phenomena were not observed within the above current-voltage measuring range. These results can be confirmed in the facts that the short-time (order of seconds) nitridation process nitridizes only the surface of the oxide film to the extent of a few tens of Å, and the longer nitridation process (order of minutes) increases the concentration of the nitrogen in the bulk of the oxide and leads to a full oxynitride structure. These nitridized layers showed the higher dielectric strength and affected the current conduction in the dielectrics.

3. Capacitance-Voltage Characteristics

Fig. 9 shows the high-frequency (1MHz) C-V characteristics of the MIS capacitors. There were no hysteresis and shift which were caused by the carrier trapping on C-V curve during measurement. The enhancement of the accumulation capacitance can be explained by increased dielectric constants of RTN films as well as the change in layer thickness. In the nitridation of silicon dioxide films, the dielectric constant increased by the addition of the hydrochloric gas, for example from 4.0 to 4.54 in the not-added samples, and to 5.06 in the 4%-added samples.

And, after nitridation process, the curves shift monotonously toward negative voltages, however the maximum capacitance value ~~decreased with the increase of the contents of~~ hydrochloric gas. It seems that this increase in flat band voltage (Vfb) about to 0.05 volts for the dual dielectric films is mainly induced by the fixed positive charges without the significant changes in the fast interface state density. The evaluated value of the fixed insulator charge density from C-V measurement was typically within the range of 1.0E11 charges/cm^2.

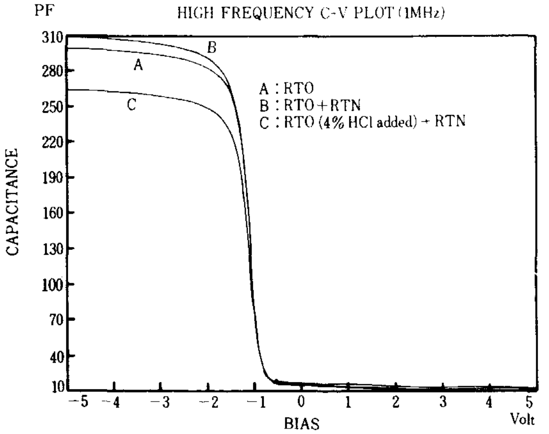

Fig.9. A typical high frequency (1MHz) capacitance-voltage characteristics of the MIS capacitors.

IV. Conclusion

We have obtained dual dielectric films that have more enhanced electrical properties by rapid thermal process. By increasing the additive contents of hydrochloric gas, oxidation rates were changed, which affected the current conduction in the dielectrics, but the nitridation rates were slightly changed.

The breakdown voltages of the dual dielectric films constantly increased in proportion to the additive contents of the hydrochloric gas. However, the average breakdown strength decreased with the increase of the contents of hydrochloric gas as a result of the increment of the initial oxide thickness. For the short-time nitridation process, the enhancement of dielectric breakdown strengths is mainly attributed to the increase of the film thickness, which is induced by the addition of hydrochloric gases than by the nitrided oxide layer grown with the nitridation process.

The present experimental results show that the suggested three-steps rapid thermal process including the independent nitridation cycle seems to be a simple and effective method to obtain dual dielectric films that have more enhanced electrical properties, and it is almost free from the instability which is caused by carrier trapping.

Conclusionally, it is believed that the dual dielectric films obtained by the three-steps rapid thermal process method can be utilized as an good alternate of thin oxide films by the conventional furnace system.

References

[1] Y.P. Han, "Ultra-thin gate-oxide characteristics and MOS/VLSI scaling implications," *IEEE International Electron Devices Meeting 82*, pp. 98-102, 1982.

[2] D.A. Baglee, "A review of recent developments in thin gate dielectrics for very large scale integration," *J. Vac. Sci. Technol.* A 4(3), pp. 1002-1004, May/June 1986.

[3] D.A. Baglee, "Characteristics & Reliability of 100Å oxides," *IEEE/IRPS*, pp. 152-155, 1984.

[4] J. Nulman, "Rapid thermal processing of thin gate dielectrics. Oxidation of silicon," *IEEE Electron Device Letters*, vol. EDL-6, no. 5, May 1985.

[5] J. Nulman, "Electrical characteristics of thin gate implanted MOS channels grown by rapid thermal processing," *IEEE International Electron Devices Meeting 85*, pp. 376-379, 1985.

[6] S.T. Ang, "Rapid thermal oxidation of silicon," *J. Electrochem.* Soc., 133(11), pp. 2361-2362, Nov. 1986.

[7] J. Nulman, "Ultrathin gate dielectrics on 150mm Si wafers via rapid thermal processing," *J. Vac. Sci. Technol.* A 4(3), pp. 1005-1008, May/June 1986.

[8] T. Ito, "Advantages of thermal nitride and nitroxide gate films in VLSI process," *IEEE Transactions on Electron Device*, vol. ED-29, no. 4, April 1982.

[9] M.M. Moselehi, "Thermal nitridation of Si and SiO_2 for VLSI," *IEEE J. Solid-State Circuit*, vol. SC-20, no. 1, Feb. 1985.

[10] M.M. Moslehi, "Compositional studies of thermally nitrided silicon dioxide (Nitroxide)," *J. Electrochem. Soc.*, 132(9), pp. 2189-2197, Sep 1985.

[11] M.M. Moslehi, "Rapid thermal nitridation of SiO_2 for nitroxide thin dielectrics," *Appl. Phys. Lett.* 47(10), pp. 1113-1115, Nov. 1985

[12] T. Ito, "Effect of thermally nitrided SiO_2 (Nitroxide) on MOS characteristics," *J. Electrochem. Soc.*, 129(1), pp. 184-188, Jan. 1982.

[13] T. Ito, "Direct thermal nitridation of silicon dioxide films in anhydrous ammonia gas," *J. Electrochem. Soc.*, 127(9), pp. 2053-2057, Sep. 1980.

[14] H.R. Grinolds, "Nitrided-oxides for thin gate dielectrics in MOS devices," *IEEE International Electron Devices Meeting 82*, pp. 42-45, 1982.

[15] J. Nulman, "Electrical and structural characteristics of thin nitrided gate oxides prepared by thermal nitridation," *IEEE International Electron Devices Meeting 84*, pp. 169-172, 1984.

[16] B.R. Singh, "Oxidation of silicon in the presence of chlorine and chlorine compounds," *J. Electrochem.* Soc., 125(3), pp. 453-461, March 1978. *

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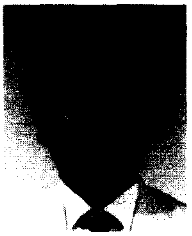

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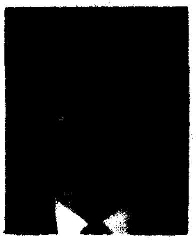

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