습식 산화한 LPCVD Silicon Nitride층의 물리적, 전기적 특성

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Physical and Electrical Characteristics of Wet-Oxidized LPCVD Silicon Nitride Films

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초   록 실리콘 질화막을 습식 산화하여 제작한 산화막/질화막 복합층과 이 박막의 산화막을 식각하여 제작한 oxynitride 박막의 물리적, 전기적 특성을 기술하였다. 900℃에서 산화시간이 증가함에 따라 산화막/질화막의 경우에는 축전용량은 급격히 감소하였으나 절연 파괴전장은 증가하였다. Oxynitride 박막은 축전용량과 절연파괴 전장이 모두 증가하였다. Oxynitride 박막의 경우 축전 용량의 증가와 절연 파괴 전장이 증가하였는데 이는 유효 누께 감소와 박막의 양질화에 기인하였다. 또한, 산화 시간의 증가에 따라 oxynitride 박막의 TDDB특성과 초기 불량율도 향상되었다. 결론적으로 oxynitride 박막은 dynamic 기억소자의 유전체 박막으로 사용하기에 적합하였다.

Abstract The physical and electrical characteristics of sub-10nm thick capacitor dielectrics formed by wet oxidation of silicon nitride(oxide/nitride composite) and by removing the top oxide of oxidized silicon nitride(oxynitride) are described. For the capacitors with an oxide/nitride composite layer, the capacitance decreases sharply, but the breakdown field increases with an increase in the wet oxidation time at 900℃. For the capacitors with oxynitride layers, the values of both the capacitance and the breakdown field increase with increasing wet oxidation time. The reduction of effective thickness and the improved quality of oxynitride film are responsible for the improved capacitance and increased breakdown fields, respectively. In addition, intrinsic TDDB characteristics and early breakdown failure rate of oxynitride film are improved with increasing oxidation time. Consequently, the oxynitride film is suitable for dynamic memories as a thin dielectric film.

I. Introduction

In ultra large scale integration(ULSI) devices such as dynamic random access memories (DRAMs), the capacitor dielectric film has been scaled downed to thicknesses less than 10nm. When the SiO_2 thickness is further reduced to 10nm to increase capacitance of the capacitor, it exhibits serious deficiencies, such as high leakage current and low breakdown voltage[1].

Thermally nitrided oxides with greater atomic density and higher dielectric constant have been reported to show many advantages[2]. The properties of oxynitride films created by thermal nitridation of SiO_2 have been reported [3, 4]. Some investigators [5-7] however, showed that the thermally nitrided films have a large number of electron traps which make them undesirable for use in devices. It is reported that an additional oxidation of the nitrided oxide results in the reduction of electron traps [8, 9] and capacitors with oxide/nitride/oxide composite (ONO) structure are used in DRAM devices. However, Little study has been done on the physical and electrical characteristics of the silicon oxynitride itself formed by removing the top oxide of wet oxidized silicon nitride film pre-

pared by low pressure chemical vapor deposition (LPCVD) method.

Thus, the present research was directed toward finding out the stress time dependence of leakage current and time-dependent dielectric breakdown(TDDB) behaviour of silicon oxynitride film and to develop capacitors that can be used in 64Mbit DRAM and beyond. In this paper we also present the dielectric properties of oxide/nitride composite created by wet oxidation of LPCVD silicon nitride on polycrystalline silicon(polysilicon) and of oxynitride produced by etching out of the top oxide of the oxide/nitride composite.

Ⅱ. Experimental Procedure

The capacitors used in this study were metal-insulator-metal(MIM) structure with heavily doped n-type polysilicon layers between the metal and the insulating dielectric layer. After field oxide isolation using standard local oxidation of silicon(LOCOS), bottom polysilicon layer with thickness of $0.25\mu m$ was deposited by LPCVD at $560°C$ using SiH_4 gas. The polysilicon was As-doped by ion implantation. Then silicon nitride layers with thickness of 8nm were deposited at $750°C$ with $0.15Torr(\sim 20Pa)$ flowing SiH_2Cl_2 and NH_3 gases. The silicon wafers with nitride layers were then oxidized at $900°C$ for 7.5 to 150min by the wet oxidation method. Finally, $0.3\mu m$ top polysilicon layers were deposited on the ON structure by LPCVD at $625°C$ flowing SiH_4 gas and were phosphorus-doped at $900°C$ using $POCl_3$ as a dopant source, to make the top electrode to the dielectric films. In some cases, the silicon oxide layers on the silicon nitride were removed by chemical etching with a solution of 1HF and $49H_2O$ before the formation of the top polysilicon electrode to investigate the effect of wet oxidation on the physical and electrical properties of silicon nitride itself.

The thicknesses of the top silicon oxide and the silicon nitride layers were measured using an ellipsometer with a He-Ne laser. The

dielctric constants of the specimens were determined from the measured values of capacitance and thickness. In some cases, the effective thickness of the dielectric layers in terms of the dielectric constant of $SiO_2(3.9)$ was also determined from the capacitor with an area of $2.74 \times 10^{-3}cm^2$ using a HP 4275A LCR meter at 10kHz and zero voltage. The thickness of the film was also measured using cross-sectional transmission electron microscope(X-TEM).

The time zero dielectric breakdown voltage was measured by taking current-voltage(I - V) curves with a HP 4145B semiconductor parameter analyzer. The breakdown voltage was defined as the gate voltage at a current density of $10\mu A/cm^2$. For the investigation of the change of I - V characteristic during charge injection, the leakage current was measured under constant field stress of 9MV/cm for 200sec. The TDDB characteristics were made under by constant field stress of $10\sim 12MV/cm$. This electric field was calculated using the effective thickness.

Ⅲ. Results and Discussion

The thickness of silicon oxide grown on a silicon substrate and on a silicon nitride as a function of wet oxidation time was shown in Fig. 1. It can be seen that the oxidation rate of the silicon is much larger than that of the silicon nitride and that both curves are nearly straight lines. By curve-fitting the thickness (T) versus oxidation time(t) in the form of T $= At^n$, where A is a constant, the values of n were determined to be 0.85 and 0.5 for oxidation of the silicon and the silicon nitride, respectively. These facts imply that, when wet oxidation is carried out at $900°C$, the oxidation rate of the silicon is dominated by a surface-reaction-controlled mechanism(n=1.0) and that of the silicon nitride by a diffusion-controlled mechanism(n=0.5). The conversion ratio of the oxide thickness grown on the nitride to the thickness of consumed silicon ni-
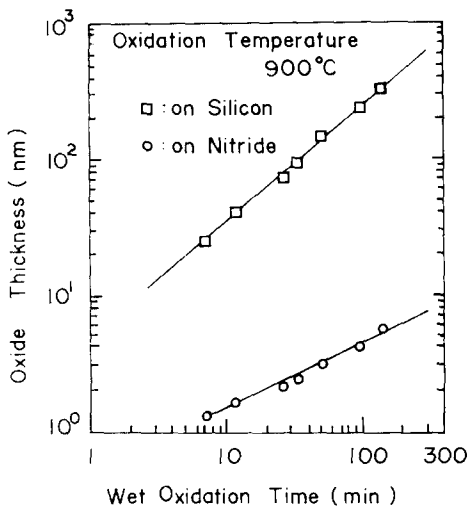
Fig. 1. Silicon oxide thickness on silicon and silicon nitride as a function of wet oxidation time.

tride was determined to be 1.72, which is close to the theoretical value of 1.75[10].

The capacitance of oxidized silicon nitride with and without the top oxide as a function of oxidation time are shown in Fig. 2. The capacitance of the oxide/nitride composite films decreases with oxidation time. Since the value of capacitance is proportional to the dielectric constant of a material, and inversely proportional to the thickness of the material, the thicknesses of the dielectric materials were measured and are shown in Fig. 3 as a function of oxidation time. Comparing Figs. 2 and 3, we see that the decrease in capacitance is much greater than the increase in thickness for the capacitors with oxide/nitride composite because of the changes in the effective dielectric constant of the composite.

The dielectric constant determined from the measured values of capacitance and total thickness is in general defined as the effective dielectric constant of composite dielectric material. The effective dielectric constants of the capacitors of Fig. 2 are shown in Fig. 4. It is interesting to note that the effective dielectric constant of the nitride film before oxidation($t = 0$) is only 5.4 and is much less than the well
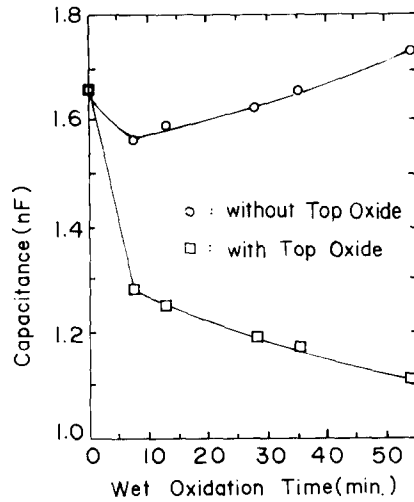

Fig. 2. Capacitances of capacitors with dielectric layers consisting of oxidized silicon nitride with and without top oxide as a function of wet oxidation time.
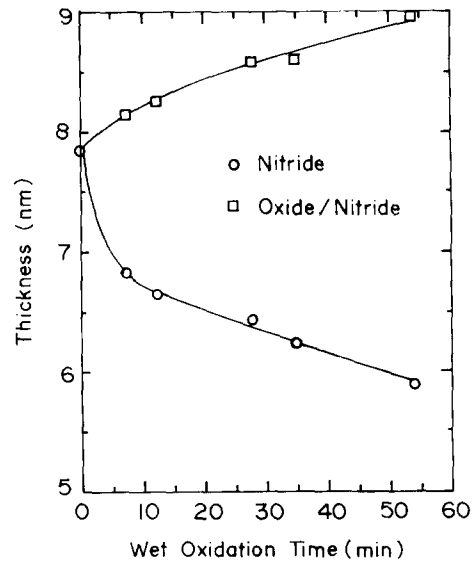

Fig. 3. Variation of thickness of wet oxidized silicon nitride with and without top oxide as a function of wet oxidation time.

known value of 7.5 for amorphous silicon nitride. This phenomenon, often observed for capacitors with ultrathin nitride layer, is usually explained in terms of the composite nature of the silicon nitride and the native oxide which supposedly foremd before the formation of the

nitride[11]. The presence of a thin native oxide on silicon after the exposure to ambient is well-known. Thus, the measured value of 5.4 can be explained if we assume the presence of the native oxide with thickness of 1.6nm in our samples.

Figure 4 also shows that the effective dielectric constant of the film decreases during the wet oxidation period. E. G. Lee et al [12] observed using Auger electron microscope that the large change in composition of silicon nitride occurs with the wet oxidation period up to 7.5min and then the compositional change takes place with a much slower rate. Figure 5 shows X-TEM of the inter-polysilicon dielectric film oxidized at 900℃ for 35min. It can be seen that total~10nm thick film consists of three layers; top oxide grown on nitride, nitride, and native oxide.

Figure 6 shows the breakdown field of the oxide/nitride film and the oxynitride film as a function of wet oxidation time. The breakdown field of the capacitors with oxide/nitride composite increases sharply with the increase in the wet oxidation time up to 7.5min and than increases slowly with further increase in the
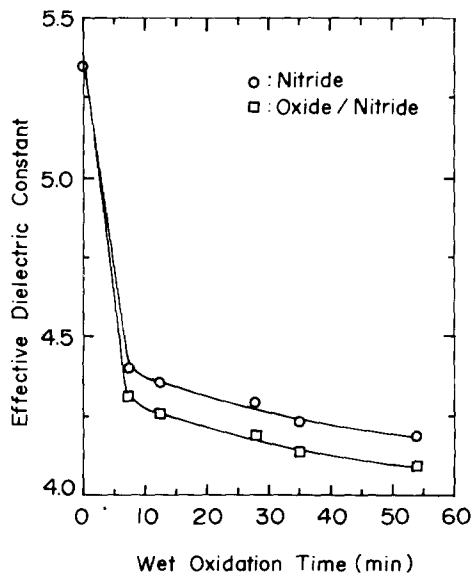

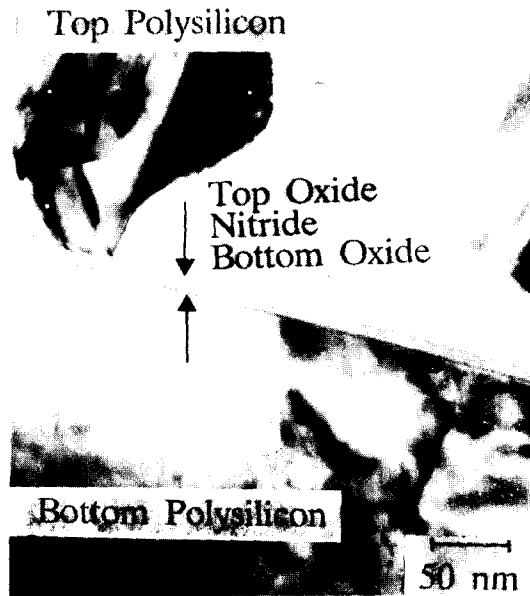Fig. 5. X-TEM micrograph of inter-polysilicon dielectric film with top oxide/nitride/native oxide film wet oxidized at 900℃ for 35min.

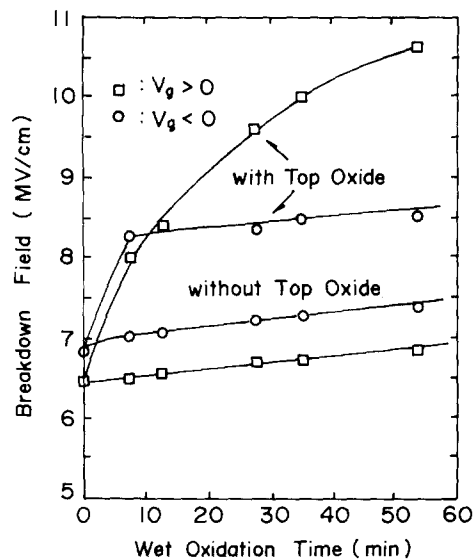Fig. 6. Breakdown field of the capacitors of Fig. 2.

Fig. 4. Effective dielectric constant of capacitors of Fig. 2.

oxidation time. We note that polarity dependence of the breakdown field is larger the thicker the top oxide layer. K. Kobayashi et al. [13] explained this phenomenon in terms of blocking of hole current by the top oxide. The breakdown field of oxynitride film increases

slightly with increasing oxidation time, and the breakdown field for negative gate voltage(Vg) is larger than that for positive Vg, contrary to the case of oxide/nitride composite film. This may have been caused by the presence of a thin bottom native oxide layer. It is worth while to note that the capacitor with oxynitride film oxidized for longer than 35min at 900 ℃ has higher values of capacitance and break-down field than those of the capacitor with sili-con nitride(t=0).

It was reported that the electrical conduc-tions of both silicon nitride and oxynitride film are limited by the hole current [14, 15]. In order to investigate the change of leakage cur-rent during charge injection, the electrical field dependence of the I-V characteristic was measured by the constant bias stress method. Figures 7 and 8 show the stress time depen-dence of the leakage current shift dielectric films under positive(Vg>0) and negative(Vg<0) bias, respectively. In contrast to the oxide layer, it is found that the leakage current of the oxide/nitride composite film(1.3/8) in-creases with increasing stress time especially
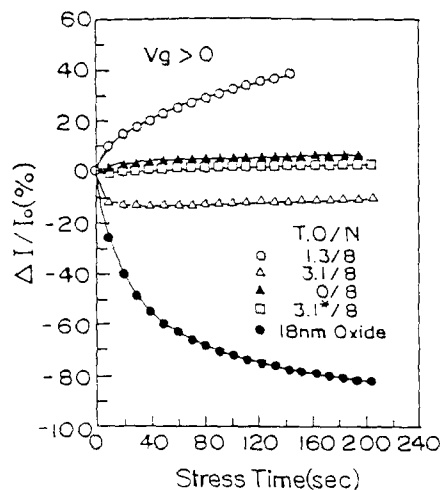
under negative bias polarity. In case of thick top oxide/nitride composite film(3.1/8), the leakage current decreases with stress time under the positive bias polarity however, in-creases with stress time under the negative bias polarity. It is probably due to the fact that the stress causes charges to tunnel the top oxide and accumulate at the oxide/nitride in-terface and increase the total leakage current of oxide/nitride composite film. However, the leakage currents of the oxynitride film and the as-deposited nitride film are almost constant with stress time. This result suggests that the oxynitride film has a strong resistance to trap charge under electrial stress.
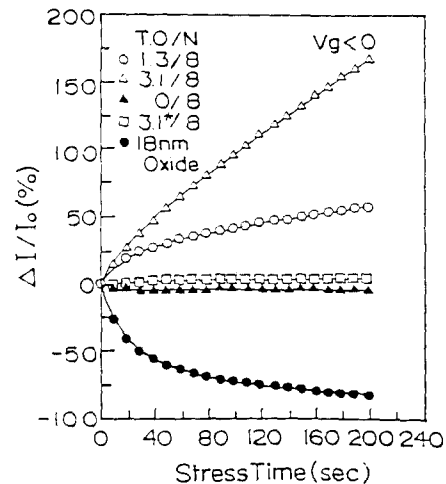

Fig. 8. The stress time dependence of leakage cur-rent shifts for several kinds of dielectric films under negative constant voltage stress of 9MV/ cm. The asterisk(*) denotes oxynitride film formed by removing the top oxide.

Figure 9 show that the TDDB stress time de-pendence of cumulative failure of the ON com-posite film has a lower early failure rate and better TDDB characteristics than the as-de-posited nitride film. This seems to be the fact that oxidation of the nitride removes the de-fects inherent in the deposited nitride film or misaligns the thin film defects. the TDDB life time under positive bias is longer than that
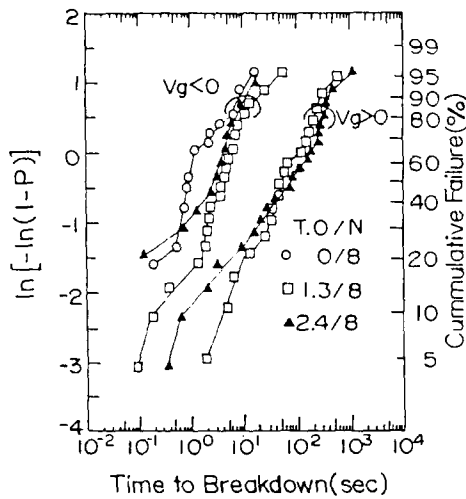

Fig. 7. The stress time dependence of leakage cur-rent shifts for several kinds of dielectric films under positive constant voltage stress of 9MV/cm. The asterisk(*) denotes oxynitride film formed by removing the top oxide.

Fig. 9. TDDB plot for oxide/nitride composite film with different oxide thickness as a function of gate bias polarity undr constnat field of 11MV/cm.

under negative bias due to the presence of the top oxide, which prevents hole injection from the electrode. In order to verify the effect of wet oxidation on the TDDB chacteristics of oxynitride film, the stress time dependence of cumulative failure of oxynitride film was measured with different oxidation time.

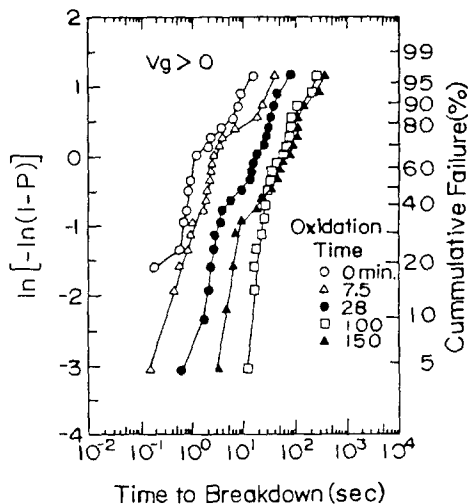Figure 10 shows that the TDDB chacterization is improved with oxidation time. As com-

Fig. 10. TDDB plot for oxynitride film as a function of wet oxidation time under constant field of 11MV/cm.

pared with Fig. 9, the improvement in TDDB characteristics of oxynitride film is much stronger than that of the ON composite film. It is found that oxidation of the nitride film markedly improves the intrinsic TDDB characteristics and the dielectric integrity of the nitride film itself by removing the latent defects in the deposited nitride film. However, the TDDB characteristics of nitride film is nearly constant for more than 100min oxidation. From the consideration of the capacitance, breakdown strength and TDDB life time, it is evident that the nitride film prepared by removing the top oxide is suited for further scaled DRAM devices.

IV. Conclusions

Based on analysis of physical and electrical properties of ultrathin(sub-10nm) oxide/nitride composite and oxynitride films, the following conclusions are drawn :

The wet oxidation growth rate of silicon oxide on silicon nitride at 900℃ from 7.5 to 150 min is dominated by a diffusion-controlled mechanism. The effective dielectric constant of an oxide/nitride composite layer decreases sharply, but the breakdown field increases, with the increase in wet oxidation period, because of the increase in thickness of the oxide layer.

The capacitance of silicon oxynitride layers, created by removing top oxide of the oxidized silicon nitride films, increases with the increase in oxidation time, because of the reduction in the film thickness. The breakdown field also increases slightly, probably because of the removal of latent defects such as pinholes and microcracks. Oxynitride films have strong resistance to trap charge under electrical stress. and can be used in devices with further decreased dimensions.

Acknowledgments

preparation and TEM works.

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