Study of Electrical Characteristics on Thermally Nitrided SiO_2 (Nitroxide) Films

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ABSTRACT

A significant influence of thermal nitridation on the electrical characteristics of nitroxide films was found in this study. Nitridation at temperatures lower than 1000°C results in a great negative shift of flatband voltage V_{FB}. However, the value of V_{FB} continuously decreases with the increasing of nitridation time at nitridation above 1000°C. After annealing of nitroxide films in N_2 gas at 1000°C for 30 min, a decrease of V_{FB}, compared with the same nitridation conditions, was observed. From quasi-static C-V measurements, it shows that not only interface fixed charge Q_{SS} but also surface-state density N_{SS} are reduced in the decreasing of V_{FB} after annealing the films in N_2 gas. This effect is more prominent for nitridation at lower temperatures; however, there still exists some degree of reduction in V_{FB} for nitridation at higher temperature and longer time. The negative bias-temperature instability, sometimes called "slow trapping," is revealed by accelerated aging with negative gate bias at elevated temperatures. It is found that the instability problem is more severe for samples which are nitrided at lower temperatures but N_2 annealing can reduce the negative bias-temperature instability. After N_2 annealing, nitroxide films prepared with nitridation above 1150°C provide good properties for MOS devices.

Currently, thermally grown SiO_2 film is used as a gate insulator in MOSLSI's. According to the scaling method (1), a reliable thin insulator is required for VLSI applications. However, due to several serious problems of thin SiO_2 films, including low resistivity to the diffusion of impurities (2, 3), high field instabilities (4-7), and hot electron effects (8-9), we can expect that the quality of SiO_2 films becomes inadequate for VLSI devices when the thickness of the gate oxide is getting thinner.

Thermal nitridation of SiO_2 is considered to be the best candidate to replace SiO_2 as the gate insulator in films less than 300Å thick since this material has demonstrated excellent masking characteristics against diffusion of impurities, remarkable improvement in dielectric breakdown voltages, larger dielectric constant, and good stability of MOS structure (10-12).

In this study, relatively thick nitroxide films (around 650Å), instead of thinner nitroxide films, were chosen because we could eliminate the poor quality factor caused from unreliable thin oxide films. This paper shows that the interfacial characteristics of MOS structure can be improved by applying N_2 annealing on nitrided oxide films.

Experimental

Electrical measurements were made on MOS structures. In this experiment, n-type, (100) oriented silicon wafers, with resistivities ranging from 4 to 7 Ω-cm, were used. These wafers were cleaned in a hot solution of $H_2SO_4 + H_2O_2$ and rinsed in deionized water. Oxide films with thicknesses of around 650Å were thermally grown on the wafers in the ambient of wet oxygen gas. The oxidized wafers were proceeded to thermal nitridation in ultrapure ammonia gas. The nitridation temperature and time were varied from 900° to 1200°C and from 30 min to 3h, respectively. After this process, the wafers were divided into two groups. There was a group with no additional processing, the others were annealed in nitrogen gas at 1000°C for 30 min. 1 μm in thickness of aluminum was deposited on the wafers, and a metal pad of 100 mil^2 was then patterned using the conventional lithography and etching techniques. After metallization, the wafers were sintered at 450°C in forming gas for 30 min.

The value of flatband voltage V_{FB} was calculated on C-V curves. Bias-stress tests using an applied voltage of −20V were made on MOS capacitors at 300°C for 3 min to reveal the negative bias-temperature instability. A quasi-static C-V technique was used to determine the interface fixed charge Q_{ss} and surface-state density N_{ss}.

Results

For samples without N_2 annealing, the changes of flatband voltages V_{FB} with respect to nitridation temperature and time are shown in Fig. 1. Nitridation at temperatures lower than 1000°C results in a great

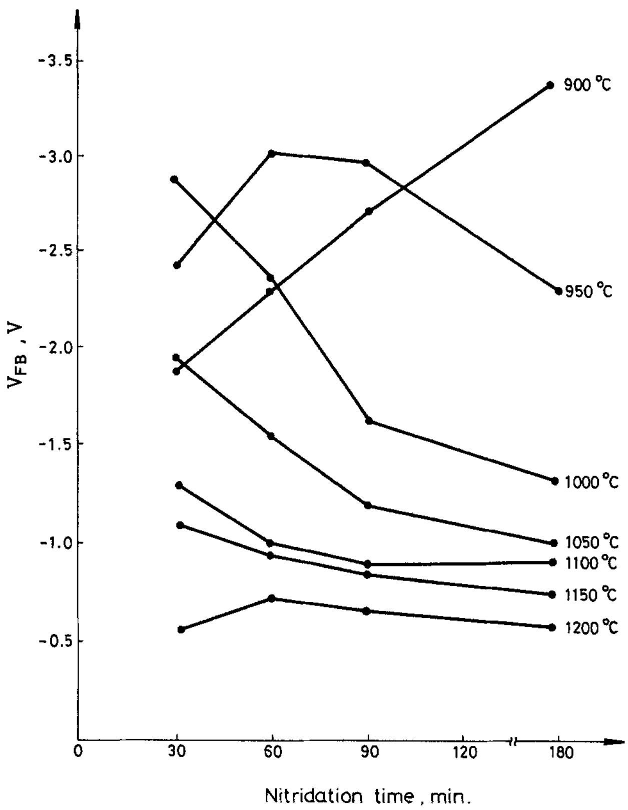

Fig. 1. The changes of flatband voltages V_{FB} with respect to different nitridation temperature and time for samples without N_2 annealing.

Table I. Q_{SS} and midgap N_{SS} vs. nitridation time for samples that were nitrided at 950°C and received N_2 or no N_2 annealing

	NO N_2 annealing				N_2 annealing			
	30 min	60 min	90 min	180 min	30 min	60 min	90 min	180 min
Qss (cm^{-2})	6.6×10^{11}	5.07×10^{11}	4.92×10^{11}	2.2×10^{11}	5×10^{11}	3.18×10^{11}	2.14×10^{11}	1.04×10^{11}
Nss ($cm^{-2}ev^{-1}$)	7.82×10^{10}	4.68×10^{11}	5.08×10^{11}	5.55×10^{11}	5.78×10^{10}	4.4×10^{11}	4.55×10^{11}	4.96×10^{11}

negative shift of V_{FB}. However, as temperature increases above 1000°C and nitridation time exceeds 90 min, the V_{FB} value rapidly decreases. Figure 2 shows the changes of V_{FB} for samples that were N_2 annealed, the curves have similar tendency of variation to Fig. 1, but V_{FB} is smaller compared with the same nitridation conditions. As temperature increases above 1100°C and reaction for 180 min, the samples have nearly the same value of V_{FB}.

For samples that were N_2 annealed, the decrease of V_{FB} corresponds to the reduction of N_{SS} and Q_{SS}. This can be clearly seen in the representative data shown in Table I. These data are obtained from samples which were nitrided at 950°C by using quasi-static C-V technique.

Table II shows data of midgap N_{ss} and Q_{ss} for samples which were nitrided at 1150°C and had been annealed in N_2 gas. Both Q_{ss} and midgap N_{ss} can be reduced to the order of 10^{10} for a nitridation time longer than 90 min.

Upon negative bias-temperature aging, the slow trapping is revealed in the shift of the high frequency C-V curve to a more negative direction. The magnitude of flatband voltage difference ΔV_{FB} reflects the degree of instability. The dependence of ΔV_{FB} on nitridation temperatures with reaction time varied from 30 to 180 min and is shown in Fig. 3. ΔV_{FB} increases with the increasing of nitridation time for temperatures lower than 1150°C and nearly saturates at higher temperatures of 1150° and 1200°C. However, samples that were N_2 annealed consistently achieve lower ΔV_{FB} values.

Table II. Data of Q_{SS} and midgap N_{SS} for samples that were nitrided at 1150°C and had been annealed in N_2 gas

	30 min	60 min	90 min	180 min
Qss (cm^{-2})	1.3×10^{11}	1.1×10^{11}	4.1×10^{10}	3.6×10^{10}
Nss ($cm^{-2}ev^{-1}$)	5.0×10^{10}	4.7×10^{10}	3.5×10^{10}	1.0×10^{10}

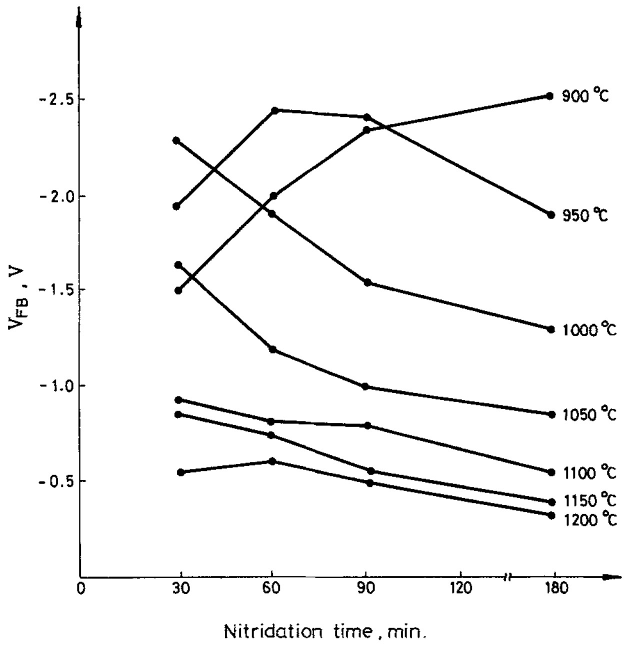

Fig. 2. The changes of flatband voltages V_{FB} vs. various nitridation temperatures and times for samples that were N_2 annealed.

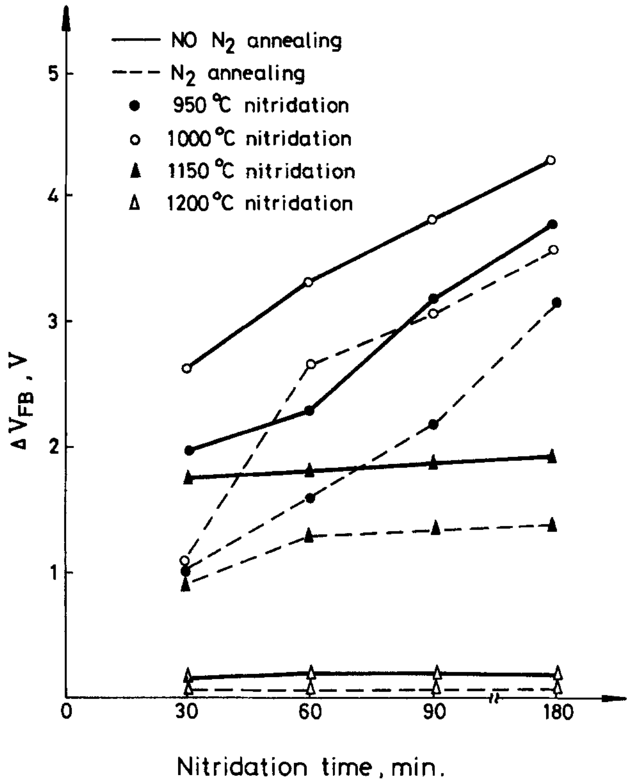

Fig. 3. The dependence of flatband voltage of different ΔV_{FB} on various nitridation temperatures and time for samples with and without N_2 annealing.

Discussion

As seen in Fig. 1, with the increase of nitridation time the negative shift of V_{FB} increases significantly at 900°C and decreases explicitly at elevated temperatures above 1000°C. This phenomenon might be interpreted as the following mechanism. At first, the hydrogen gas produced during ammonia nitridation processing dissolves into the SiO_2 skeleton. Then, the dissolved hydrogen molecules react with the surrounding Si-O bondings, forming the dangling bonds. Both N_{ss} and Q_{ss}, therefore, increase significantly and cause the V_{FB} shift phenomenon (2). The V_{FB} shift consequently is strongly related to the solubility of hydrogen gas in a SiO_2 layer. Since the hydrogen molecule is very small in molecular diameter and has nonpolar characteristics, the solubility of hydrogen in SiO_2 may be assumed to be similar to its solubility in aqueous solution (13). That is, the hydrogen solubility in a SiO_2 layer may decrease with the increase of temperature and be negligibly small at elevated temperatures above 1000°C compared with that at 900°C. Consequently, the dangling bond formation at temperatures above 1000°C is not explicitly seen.

The slow trapping instability can be a major threat to reliability of p-channel MOSFET. The mechanism of slow trapping has not been established. However, the effect is greater when initial Q_{ss} or N_{ss} is large (14, 15). In the case of Table I, N_{ss} exhibits the reverse. Comparing Fig. 3 with Table I, we can conclude that the increase of ΔV_{FB} is due to the increase of N_{ss}.

After N_2 annealing, the atomic bonds at the interface of silicon and nitroxide can be rearranged (16). Both N_{ss} and Q_{ss} are reduced to a certain amount, therefore, V_{FB} and ΔV_{FB} also decrease. This effect is clearly shown in Fig. 2 and Fig. 3.

Conclusion

The electrical characteristics of the nitroxide films were studied. The negative direction shift of V_{FB} due to the deterioration of hydrogen gas can be alleviated by N_2 annealing. Such an anneal also reduces the negative bias-temperature instability. N_2 anneal is recommended for nitroxide films which are prepared with nitridation above 1150°C to achieve stable device operational characteristics.

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Submicron Epitaxial Films

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ABSTRACT

This work focuses on the quality of epitaxial silicon deposited when the total thickness grown is in the range of 0.5-0.9 μm from the initial physical interface. Shallow junctions were fabricated to evaluate device potential of the thin films. Defect levels were evaluated. The ability to reproduce doping profiles was also evaluated. The studies have shown that the epitaxial silicon deposited to 0.5 μm thickness is suitable for device fabrication.

This study has focused on evaluation of the quality of the epitaxial silicon deposited to thicknesses in the 0.5 μm range. The concerns with regard to the silicon quality this close to a physical interface included: (*i*) whether doping profiles could be reproduced and thicknesses controlled, (*ii*) whether defect levels arising from the interface would have an effect on devices, and (*iii*) whether the silicon obtained would be suitable for device fabrication.

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Experimental

The concentration profiles in this study were obtained by spreading resistance measurement technique. Figures containing spreading resistance data show either the raw data of spreading resistance in ohms *vs.* depth in microns, or data converted to log of the dopant concentration *vs.* depth from the surface. The spreading resistance data was obtained on samples beveled to angles of 20 min. An Automatic Spreading Resistance Probe (Solid State Measurements, Incorpo-