

Low-Temperature Nitridation of Fluorinated Oxide

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A new technique of growing nitrided oxide is proposed. As a first step a few-tens nanometer thick fluorinated oxide layers have been produced by fluorine-enhanced thermal oxidation of silicon in an O_2+NF_3 gas mixture at temperatures between 600 and 800 °C. Subsequent annealing of the oxide in a pure ammonia gas at the same temperature results in the formation of nitrided oxide as a consequence that fluorine atoms incorporated in as-grown oxide are substituted by nitrogen atoms during NH_3 annealing. The dielectric breakdown strength of the fluorinated oxide is improved by the nitridation. The nitrided oxide is found to behave as a protective layer against alkaline ion contamination.

1. Introduction

Low-temperature growth of high-quality gate insulator would be necessary for fabricating miniaturized VLSI devices. The nitridation techniques of thermally grown oxide have been extensively developed so far in order to obtain higher resistance against alkaline ion migration in the insulator, sufficient dielectric breakdown strength, and radiation hardness. However, the efficient nitridation rate has never been achieved at temperatures lower than 900 °C. Recently, the authors have found for the first time that a remarkable increase in the silicon oxidation rate can be obtained in the temperature range of 600 to 800 °C when an NF_3 gas is added to a dry oxygen atmosphere and that the fluorine atoms are incorporated in the resulting oxide films.^{4,5)} Fluorine atoms incorporated in the oxide are substituted by oxygen atoms during the post-annealing in dry oxygen at the same temperature as the oxidation.⁶⁾

In this paper, we describe a new technique to produce nitrided oxide (nitroxide) at temperatures below 800 °C. This technique consists of fluorine-enhanced thermal oxidation of Si in an O_2+NF_3 gas mixture⁴⁻⁶⁾ and subsequent nitridation of the fluorinated oxide ($SiO_{2-x}F_{2x}$) in an ammonia atmosphere.

2. Experimental

The fluorine-enhanced thermal oxidation

procedure has already been reported elsewhere.⁴⁻⁶⁾ Si wafers in a cold-wall type quartz tube reactor were placed on a silicon susceptor heated by irradiation with halogen lamps and oxidized first in O_2+NF_3 . Subsequent thermal nitridation was performed in the same reactor. Chemically cleaned p-type (2.5-3.5 Ω cm) and n-type (3.0-6.0 Ω cm) CZ Si(100) wafers were oxidized at a temperature between 600 and 800 °C for 30 min in a dry oxygen atmosphere containing 60 ppm NF_3 gas at 800 °C and 475 ppm at 600 °C, and the resulting oxide layer as thick as a few hundred Å was annealed at the same temperature for 5-300 min in a pure ammonia gas. The atomic compositions, their in-depth profiles, and chemical-bond configurations of the resulting films were determined by the quantitative analysis of x-ray photoelectron spectroscopy (XPS). The refractive index and thickness of the films were measured by ellipsometry.

3. Results and Discussion

3.1 Structural Characterization

The in-depth profiles of the atomic concentrations in the oxide produced by the fluorine-enhanced oxidation technique^{4,5)} are compared with those of the nitrided oxide in Fig. 1. As revealed by the XPS analysis, fluorine atoms in the oxide form chemical bonds only with silicon and there exists no F-O bond.^{4,5)} The fluorine content of the as-grown fluorinated oxide ($SiO_{2-x}F_{2x}$) (Fig. 1(a)) is significantly decreased

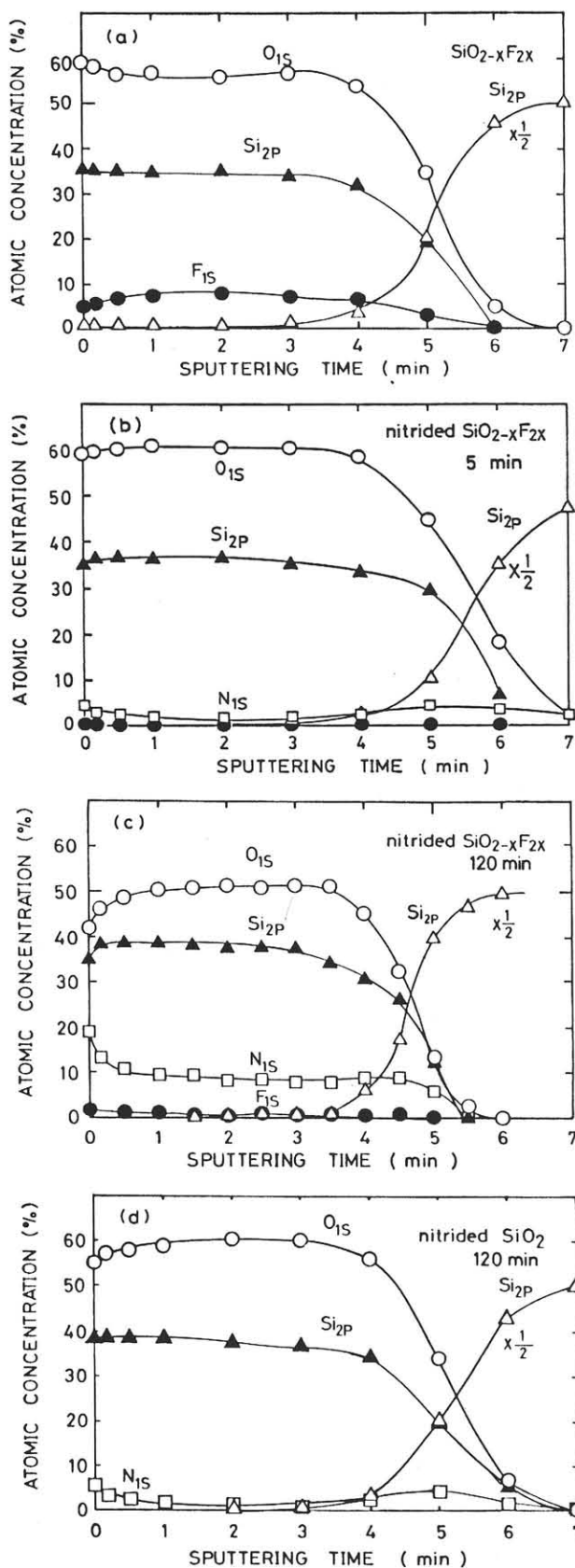


Fig. 1 In-depth profiles of atomic concentrations for the oxide obtained by fluorine-enhanced oxidation at 800 °C (a) for the oxide nitrided at 800 °C for 5 min (b), and 120 min (c). The profiles (d) refer to conventional SiO₂ annealed at 800 °C in NH₃.

with 5 min ammonia annealing (Fig. 1 (b)). Note that the nitrogen content in the nitrided SiO_{2-x}F_{2x} is already as large as that of pure SiO₂ annealed in NH₃ for 120 min (Fig. 1 (d)). The existence of Si-F bonds in the fluorinated oxide appears to enhance the diffusion of nitrogen radical because the oxide network is a little soft compared with pure SiO₂.⁵⁾ Consequently, incorporated Si-F bonds are substituted by Si-N bonds through a local nitridation reaction such as SiF + NH → SiN + HF. Considering the difference in the coordination numbers of N and F atoms, the oxide network must change its local chemical-bond configuration during nitridation. This implies that the oxide network under nitridation is softened, and hence further nitridation reaction and progressive reconstruction of the nitrided oxide take place during the course of annealing as shown in Fig. 1 (c). In this figure the reduction of the nitride thickness and a little surface pile-up of residual fluorine atoms are observed as a result of further nitridation. In addition to this, a decrease of the oxygen content throughout the bulk layer and in particular on the surface is observed, showing the existence of the substitution reaction between oxygen and nitrogen. It is important to note that the nitrogen content of the nitrided SiO_{2-x}F_{2x} (Fig. 1 (c)) is as high as that in pure SiO₂ nitrided at 1000 °C for 120 min.

For the purpose of investigating the chemical bonding features of nitrogen in the nitrides,

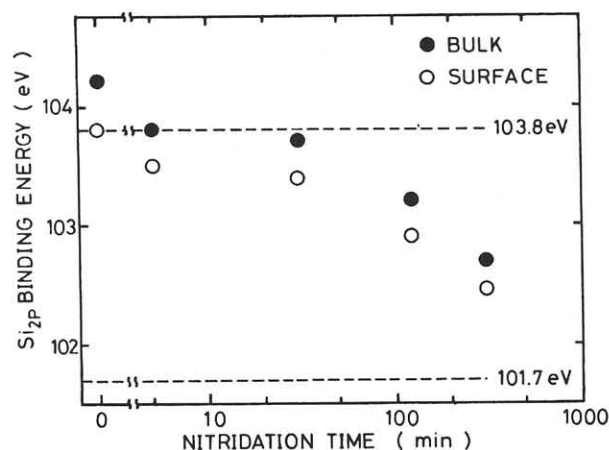


Fig. 2 Si_{2p} binding energies measured on the surface and in the bulk of nitrided oxides as a function of nitridation time at 800 °C.

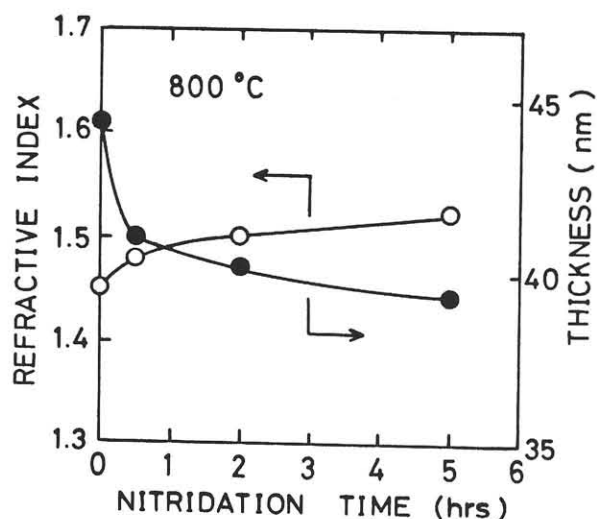


Fig. 3 Refractive index and thickness of nitrided oxides determined by ellipsometry as a function of nitridation time.

Table I Etching rate of fluorinated and nitrided oxides.

Oxidation gas	Oxidation Temperature [°C]	NH ₃ annealing time [hours]	Etching rate [Å/sec]
O ₂ /NF ₃	800	---	30.3
	800	2	5.6
	800	5	1.5
O ₂	1000	---	2.2

the binding energy of Si_{2p} XPS signal is measured as a function of nitridation time as shown in Fig. 2, where the binding energies of thermally grown SiO₂ (103.8 eV) and of stoichiometric Si₃N₄ (101.7 eV) are given as references. The shift of the Si_{2p} binding energy arises from the movement of partial electron cloud between silicon atom and the four nearest-neighbor atoms bonded with the silicon. The extent of the energy shift is proportional to the electronegativity sum of the four nearest-neighbor atoms. When some of Si-O bonds are substituted by Si-N bonds through nitridation, the Si_{2p} binding energy shifts toward a lower energy because the electronegativity of nitrogen is smaller than that of oxygen and the electron cloud partially comes back to silicon. Therefore, the result of Fig. 2 indicates the increase of Si-N bonds in the oxide as a

consequence of nitridation. The Si_{2p} binding energy from the bulk layer in the nitrided oxide is a little large compared with that from the surface. This is basically explained by the result of Fig. 1 (c), because in the nitrided oxide the surface concentration of oxygen is smaller than the bulk. The refractive index and the thickness of nitrided oxide layer measured as a function of nitridation time are shown in Fig. 3. The refractive index increases with nitridation time due to the substitution reaction between fluorine and nitrogen together with the fluorine-assisted substitution reaction of oxygen with nitrogen. This substitution reaction is accompanied with the volume reduction of the nitrided oxide, and a corresponding decrease of the film thickness takes place in consistence with the results of Fig. 1 (a) and (c).

The etching rates of as-grown and nitrided oxides measured by using the solution of 50 % HF:40 % NH₄F:H₂O= 1: 7: 80 are summarized in Table I, where the etching rate of thermally oxidized SiO₂ at 1000 °C is also given as a reference. The etching rate of the nitrided oxide becomes low with the increase of nitridation time, because the film is densified through nitridation accompanied with the removal of fluorine bonds in the nitrided oxide (see Fig. 1).

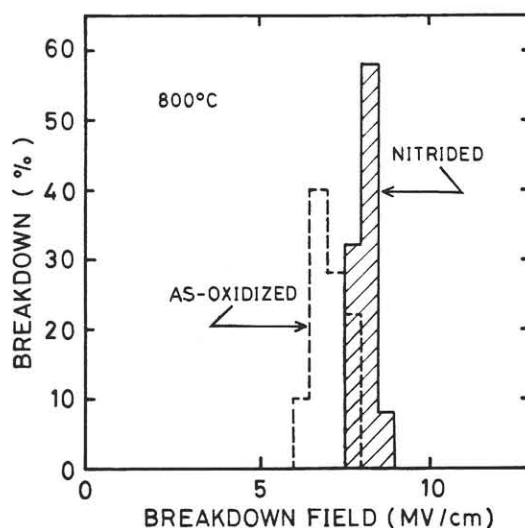


Fig. 4 Histograms of dielectric breakdown strength for 300 Å thick as-grown SiO_{2-x}F_{2x} and nitrided oxide. Area of gate electrode was 1 mm in diameter.

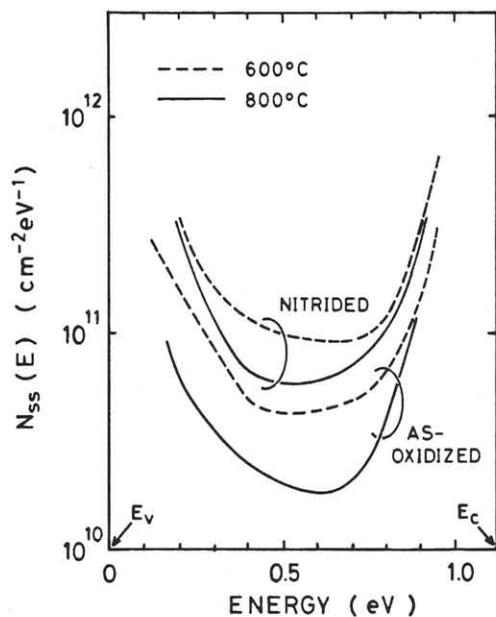


Fig. 5 Typical interface state density distributions of as-oxidized and nitrided specimens.

Table II The mobile Na ion densities [$\times 10^{11} \text{ cm}^{-2}$]

TVS Meas.Temp.	150 °C	200 °C	250 °C
Nitrided $\text{SiO}_{2-x}\text{F}_x$	1.0	4.0	7.3
$\text{SiO}_{2-x}\text{F}_{2x}$	4.1	7.0	8.0
SiO_2 (control)	7.5	9.7	11.0

3.2 Electrical Characterization

The histograms of the dielectric breakdown strength of as-grown oxide and nitroxide on n-type Si substrates are shown in Fig. 4, in which the breakdown strength was defined by an electric field strength at which the leakage current level exceeds $1 \mu\text{A}$ for a positive gate bias ramping rate of $1 \text{ MV cm}^{-1} \text{ sec}^{-1}$. The breakdown strength of the oxide is improved by the nitridation as shown in the figure, and even for 600 °C nitridation the breakdown strength of about 5.5 MV cm^{-1} is obtained.

Figure 5 represents the typical interface state density distributions of as-grown and nitrided

oxides on p-type Si substrates prepared at 600 and 800 °C. The state density near midgap is $6 \times 10^{10} \text{ cm}^{-2} \text{ eV}^{-1}$ for 800 °C nitridation and kept below $1 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$ even for 600 °C nitridation although the density tends to be increased with ammonia annealing as in the case of nitridation of pure SiO_2 . The increase in the state density could be related to the incomplete structural relaxation of the nitroxide near the interface.

The barrier effect of the nitrided oxides against mobile ions was estimated by the triangular voltage sweep (TVS) method.⁶⁾ The samples with an oxide thickness of about 27 nm were contaminated with boiling NaCl solution prior to Al electrode evaporation. The mobile Na ion densities in pure SiO_2 , fluorinated oxide $\text{SiO}_{2-x}\text{F}_{2x}$ and nitrided oxide are summarized in Table II. The result indicates that the nitrided $\text{SiO}_{2-x}\text{F}_{2x}$ can act as a protective layer against Na ion contamination. Even as-grown oxide is protective against Na ions due to the presence of fluorine atoms which trap Na ions.

4. Conclusions

It is demonstrated that newly developed oxide $\text{SiO}_{2-x}\text{F}_{2x}$ prepared by the fluorine-enhanced oxidation of Si can be efficiently nitrided at temperatures below 800 °C by substituting silicon-fluorine bonds with silicon-nitrogen in addition to substitution of silicon-oxygen bonds with silicon-nitrogen. Structural and electrical characterizations of the resulting nitrided oxide have revealed the future potential of this material as a new dielectric material which can be grown at low temperatures.

References

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