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Fluorine-enhanced thermal oxidation of silicon in the presence of NF_3

M. Morita, T. Kubo, T. Ishihara, and M. Hirose
Department of Electrical Engineering, Hiroshima University, Higashihiroshima 724, Japan

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The oxidation rate of silicon has been dramatically increased at temperatures between 600 and 800 °C by adding NF_3 gas to a dry oxygen atmosphere. The chemical analysis of the resulting oxide has revealed that fluorine atoms in SiO_2 are incorporated as Si–F bonds. The existence of such bonded-fluorine atoms enhances the diffusion of oxidant through the oxide layer. The oxidation reaction rate in the SiO_2-Si interface is also remarkably increased because fluorine atoms in the interface create silicon dangling bonds and weakly positively charged silicon atoms as well. The kinetics of the fluorine-enhanced oxidation has primarily been interpreted in terms of the Deal–Grove model.

Efficient thermal oxidation of silicon at low temperatures is one of the important subjects in fabrication of large scale integrated circuits. One possible approach for this purpose is to utilize chemical reactions enhanced with a catalytic gas such as chlorine or fluorine. In fact, a little increase in the silicon thermal oxidation rate has been observed in a dry O_2/HC1 system,[1,2] while the plasma oxidation rate in Si has been significantly increased by adding CF_4 to an oxygen plasma.[3] In the case of thermal oxidation in silicon, NF_3 gas added to dry oxygen is expected to enhance the oxidation reaction, because NF_3 can be thermally decomposed even at temperatures below 600 °C. NF_3 gas is noncorrosive at temperatures below 70 °C, is a minor toxic substance compared with F_2 gas,[4] and is widely used as an etching gas in semiconductor industries. In this letter, it is demonstrated for the first time that at least one order of magnitude increase in the silicon oxidation rate is achieved in the temperature range of 600–800 °C by mixing NF_3 gas with dry oxygen. The oxidation mechanism is discussed based on the chemical analysis of the resulting oxide films and on the growth kinetics.

High purity oxygen gas and NF_3 diluted with oxygen were admitted into a cold-wall type quartz tube reactor, in which Si(100) wafers (2.5–3.5 Ω cm) were placed on a silicon susceptor heated by irradiation with halogen lamps so as to maintain the wall temperature as low as possible in order to minimize the fluorine-quartz tube interaction. It was thoroughly checked that the gas system is leak tight and the NF_3 gas concentration in the gas system is kept at less than 1%. Chemically cleaned wafers were oxidized at a temperature of 600, 700, or 800 °C in an oxygen atmosphere containing NF_3 up to 800 ppm. The compositions and chemical bonding features of the oxides obtained were determined by Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS) using Shimadzu ESCA 750.

A very large increase in the silicon oxidation rate by admixed NF_3 gas in dry oxygen is verified by the plots of oxide thickness versus NF_3 concentration as shown in Fig. 1 for *p*-Si(100) substrates. The oxide thickness sharply increases with an increase of NF_3 concentration until it reaches 70 ppm at 800 °C, 165 ppm at 700 °C, and 475 ppm at 600 °C, above which the thickness starts to decrease. This is because etching reactions on the oxide surface by flourine radicals become competitive with the oxidation process. The NF_3 concentration providing maximum oxide thickness shifts toward the higher value as the substrate temperature decreases, since the lower decomposition rate of NF_3 at a lower temperature needs higher NF_3 concentration to obtain a similar amount of reactive fluorine on the oxide surface. In the etching region the higher the substrate temperature is, the thinner the final oxide thickness becomes, and the oxide thickness as a function of oxidation time remains constant as a result of balance between oxidation and etching. This implies that the etching reaction is more temperature dependent than the oxidation reaction. Almost the same result as shown in Fig. 1 is obtained for *n*-Si(100) substrates, indicating that the type of free carriers of the position of the Fermi level in silicon has no influence on the fluorine-enhanced oxidation process. The deposition of SiO_2, which comes from the quartz tube wall to the silicon surface, is quite unlikely because the sapphire substrate surface exposed to $O_2 + NF_3$ gas at 600, 700, or 800 °C for 30 min showed no Si_{2p} XPS signal.[5]

The compositions obtained from AES measurements for an as-grown oxide are uniform in the direction of thickness, and a significant amount of fluorine atoms is incorporated throughout the oxide. There was no fluorine pile-up in the SiO_2-Si interface, suggesting that the fluorine atoms directly enhance the oxidation reaction rate in the interface. Typical compositional ratios of Si, O, and F in the oxide, determined by the quantitative analysis of XPS spectra,[6,7] are summarized in Table I for specimens oxidized at 600 and 800 °C. The result shows that the total number of silicon bonds N[Si] is approximately equal to the sum of the total oxygen bonds N[O] and total fluorine bonds N[F]. There-

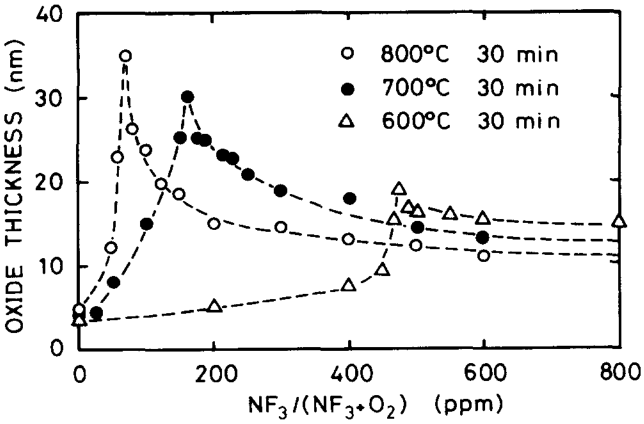

FIG. 1. Oxide thickness vs NF_3 concentration for the oxidation of *p*-Si(100).

TABLE I. Typical atomic concentrations of fluorinated oxides grown at 600 and 800 °C.

Oxidation temperature (°C)	Element X	Coordination number $n[X]$	Atomic concentration (%):$C_A[X]$	$n[X]\,C_A[X] = N[X]$
600	Si	4	32.8	131.2
	O	2	64.1	128.2
	F	1	3.1	3.1
800	Si	4	32.0	128.0
	O	2	60.4	120.8
	F	1	7.6	7.6

fore, it is evident that fluorine atoms in the oxide form only Si–F bonds and no O–F bond. The termination of Si bonds with fluorine atoms reconstructs the oxide network and hence the local structure of such a fluorinated oxide would be a little different from that of pure SiO_2.

Figure 2 represents the oxide thickness plotted against oxidation time for a typical NF_3 concentration in the enhanced oxidation region, where the oxide thickness increases with NF_3 concentration (see Fig. 1). The oxidation curve at 600 °C is approximately fitted to the parabolic growth law over a wide range. For oxidation at 700 °C, the growth rate obeys a linear law in the initial oxidation, and a parabolic law in the longer time region. Even for 800 °C oxidation, a similar feature is observed although there is little deviation from the parabolic law, possibly because some unknown mechanisms are involved. From the result of Fig. 2, it is likely that the kinetics of fluorine-enhanced oxidation is basically explained by the Deal–Grove model,[8] where the parabolic rate constant B and the linear rate constant B/A determined from the plot of Fig. 2(b) are $4.9\times10^{-4}\,\mu\text{m}^2/\text{h}$ and $2.6\times10^{-2}\,\mu\text{m/h}$, respectively. Both values are larger than those for the conventional dry oxidation at 700 °C ($B = 3.6\times10^{-4}\,\mu\text{m}^2/\text{h}$, $B/A = 2.6\times10^{-4}\,\mu\text{m/h}$). In particular, the linear rate constant B/A for the fluorine-enhanced oxidation is two orders of magnitude larger than that for dry oxidation. This indicates that fluorine radicals in the oxygen atmosphere primarily enhance the oxidation reaction rate in the interface. The increase in the diffusion coefficient could be explained by the fact that the oxide layer contains a significant number of Si–F bonds, because fluorine bonds slightly modify the microstructure of the oxide and enhances the oxygen diffusion slightly.

A possible model of the fluorine-enhanced oxidation mechanism derived from the growth kinetics and the XPS analysis is inferred as follows: NF_3 molecules are thermally dissociated on the surface of silicon and produce fluorine radicals such as NF, NF_2, F and F_2. The fluorine species reach the oxide-silicon interface by diffusion through the oxide. The cleavage of the Si–Si bond in the interface by one fluorine atom results in the formation of one Si dangling bond together with one Si–F bond because the electronegativity of a fluorine atom is significantly larger than for Si and the Si–F binding energy (129.3 kcal/mol) is considerably larger than that for the Si–Si bond (42.2 kcal/mol).[9] Furthermore, the silicon atom bonded with the fluorine atom is slightly positively charged because of the large electronegativity difference between fluorine and silicon. Therefore, both types of silicon atoms created in the interface might be highly reactive with oxygen. Also, the diffusion of oxidant may be enhanced a little because the packing density of Si and O in the fluorinated oxide might be slightly less than for pure dry oxide.

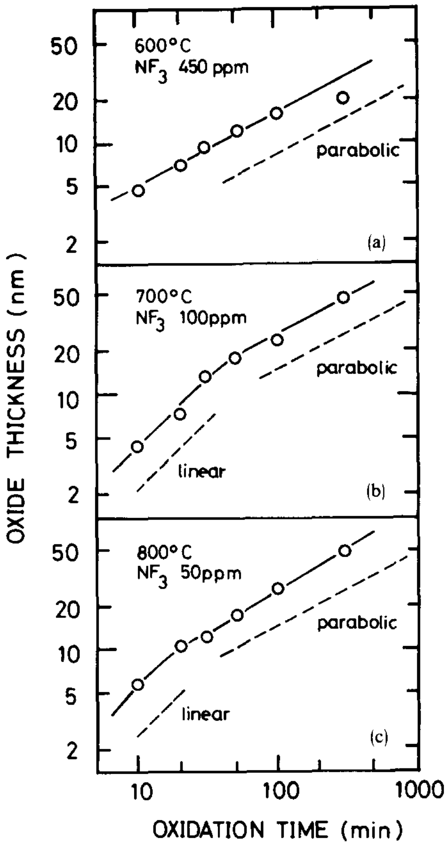

FIG. 2. Oxide thickness vs oxidation time for p-Si(100).

The etching mechanism of the oxide by NF_3 could be explained as follows: Since the binding energy of a Si–F bond is larger than that of Si–O (88.2 kcal/mol), some of the fluorine atoms produced by the thermal dissociation of NF_3 on the SiO_2 surface cleave the surface Si–O bonds to form Si–F bonds, a part of which becomes volatile molecules such as SiF_4. Formation of volatile N_2O or NO_2 molecules on the surface would also be possible through reactions between NF_3 and SiO_2.[10] This model implies that the necessary number of fluorine atoms to etch out one surface Si–O–Si bond is larger than that for producing one Si–O–Si bond in the interface. This is consistent with the result of Fig. 1 because an increase in the fluorine atoms first enhances the oxidation rate and then etching of SiO_2 becomes competitive with oxidation at higher NF_3 concentrations.

The electrical properties of the oxide-silicon interface were studied by employing aluminum-oxide-silicon structures. The fixed interface charge density is less than 1×10^{11} cm^{-2}. The typical interface state density is as low as 2×10^{10} $\text{cm}^{-2}\,\text{eV}^{-1}$ near midgap for the 800 °C sample, and is $6\times10^{10}\,\text{cm}^{-2}\,\text{eV}^{-1}$ at 600 °C, despite the presence of Si–F bonds in the oxide. The electronic states induced by Si–F bonds in the oxide might presumably be located far away from the silicon band edges.

In conclusion, we have demonstrated that fluorine radicals produced by thermal dissociation of NF_3 dramatically enhance the thermal oxidation rate of silicon. The rate is nearly one order of magnitude larger than that of conventional dry oxidation. The fluorine atoms in the oxide are incorporated as Si–F bonds and there are no detectable O–F bonds. The kinetics of the fluorine-enhanced oxidation can primarily be understood on the basis of the Deal–Grove model. The increase in the oxidation rate might originate in the remarkable enhancement of the oxidation reactions in the interface and in the enhanced oxygen diffusion through the oxide as well. The fluorine-enhanced thermal oxidation can yield a high quality oxide-silicon interface at temperatures below 800 °C.

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High-speed modulation and switching with gain in a GaAlAs traveling-wave optical amplifier

J. Hegarty and K. A. Jackson
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

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We demonstrate optical amplification of 10-ps-long pulses in a traveling-wave type GaAs double heterostructure laser diode. A continuous train of mode-locked pulses from a dye laser focused end on into the GaAs active region is amplified by a factor of 10 under injection by a synchronous train of current pulses and attenuated by a factor of 10 in the absence of current injection. This gives a switch/modulator with modulation depths of 100, overall gain, and measured switching speed of many GHz. A cw beam can be modulated at similar gains and speeds and since the device is capable of integration the performance of many optical functions without loss is possible.

Single mode fibers transmitting optical pulses in the 1.3–1.5-μm range have bandwidth products greater than 100 GHz km at the present time. To take full advantage of the large bandwidth requires new and novel modulation techniques for generating and switching optical pulses at high speeds. The modulation techniques being used to date include direct current modulation of semiconductor laser diodes and electro-optic switching in nonlinear media such as $LiNbO_3$. Direct modulation of a laser diode can give up to about 4 Gbit/s data rates.[1] Higher bit rates can be achieved by time division multiplexing many of these lasers but the maximum number that can be multiplexed is limited by the pulse length. At present the shortest pulse is in the region of 50–100 ps.[1] Shorter pulses are obtainable by microwave current injection[2] or by mode locking a laser but this requires subsequent switching of the continuous optical pulse train. Such switching can be accomplished with electro-optic devices[3] but at the expense of some loss. In the present paper we demonstrate a novel but simple switch that has built-in gain, that is capable of speeds greater than 1 GHz, and that is capable of integration. This switch can be used to modulate a cw beam with gain at similar speeds to give subnanosecond pulses. The gain aspect of the device in addition to giving rise to simple amplification also opens the possibility in integrated optics of performing a variety of functions with no net loss.

The basis of the switching device is a GaAlAs laser-type diode; this device, when biased by an electronic pulse, can amplify an external optical pulse which is focused into the active area and which is coincident in time with the current pulse. Optical amplification has hitherto been observed in GaAs structures under dc current injection[4,5] and has been proposed as a necessary ingredient in coherent communications systems.[6] The characteristics of a Fabry–Perot type laser amplifier have already been examined in detail.[7] In the present work we show for the first time amplification of optical pulses, only a few picoseconds long, in a traveling-wave type amplifier configuration. The GaAlAs diode, under a dc bias, can amplify a 1-GHz pulse train without significant pulse-to-pulse interference. When the diode is injected with short current pulses synchronous with the optical pulses amplification by a factor of 10 is observed as compared to an attenuation by a factor of 10 in the absence of injection. This gives a modulation depth of 100. Modulation rates greater