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ArF Excimer Laser-Enhanced Oxidation of Silicon in O_2/NF_3 Gas Mixture

Mizuho Morita, Seiichi Aritome and Masataka Hirose

Department of Electrical Engineering, Hiroshima University

Higashihiroshima 724, Japan

Low-temperature oxidation of silicon by using ArF excimer laser irradiation in an O_2/NF_3 gas mixture is studied. More than 60 A thick oxide can be grown even at 400°C for 20 min in the NF_3 gas concentration range less than 0.5 % . The considerable enhancement of the oxidation rate by 193 nm laser irradiation is caused by fluorine radicals created by the photo-dissociation of NF_3 molecules in the gas phase and of adsorbed NF_3 on the oxide surface. The XPS analysis of the resulting oxide has revealed that the oxide film produced under laser irradiation contains Si-F bonds as in the case of thermally grown fluorinated oxide at higher temperatures without laser irradiation.

1. Introduction

Photo-enhanced oxidation of silicon has been attemped for aiming at the low-temperature growth of gate insulator, although photo-irradiation still has very little influence on lowering the oxidation temperature. The silicon oxidation has been carried out in dry or wet oxygen under ultraviolet or visible light irradiation from various light sources such as high-pressure mercury arc and iodine-vapor lamp,[1] argon-ion laser,[2-5] krypton-ion laser[3] and XeCl excimer laser.[6] The increase of the oxidation rate in these studies is not significant except for the case that employs heating of silicon substrate to near or above its melting point by a laser irradiation with high energy densities.

Recently, the authors have developed fluorine-enhanced thermal oxidation of silicon in the presence of an NF_3 gas with dry oxygen, and found that fluorine radicals produced by the thermal dissociation of NF_3 dramatically enhance the linear rate constant of silicon oxidation defined by the Deal-Grove model.[7,8] It is also found that the NF_3 gas concentration necessary for the relevant enhancement of oxidation rate considerably increases as the substrate temperature decreases because the thermal decomposition rate of NF_3 for producing fluorine radicals becomes extremely low at low temperatures.[7,8] The plasma excitation can be utilized for supplying significant amount of fluorine radicals even at low temperatures.[9] However, the use of plasma always encounters the problem of ion bombardment damage.

In this paper, we describe the effect of ArF excimer laser irradiation on the oxidation rate of silicon in O_2/NF_3 gas system and demonstrate a significant increase in the oxidation rate by laser-irradiation even at 400 °C.

2. Experimental

A schematic diagram of ArF excimer laser-induced oxidation system is shown in Fig. 1. A high purity NF_3+O_2 gas mixture was introduced into a cold-wall type quartz tube reactor. An ArF excimer laser beam (193nm, 20 $mJcm^{-2}$/shot) at a

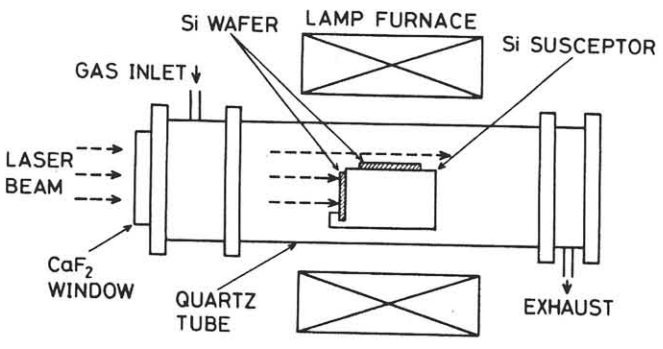

Fig. 1 Schematic diagram of ArF excimer laser-induced oxidation system.

repetition rate of 1-50 Hz was irradiated in the direction normal or parallel to Si substrates. In the parallel irradiation the distance between the laser beam and substrate surface was kept nearly zero. P-type (2.5-3.5 Ωcm) CZ Si(100) wafers placed on silicon susceptor were heated with halogen lamp irradiation in O_2+NF_3 at atmospheric pressure. Both NF_3 and O_2 gases are photochemically decomposed by 193 nm irradiation. The oxide thickness was measured by ellipsometry. The atomic compositions and their in-depth profiles of the oxide film were determined by the quantitative analysis of x-ray photoelectron spectroscopy (XPS).

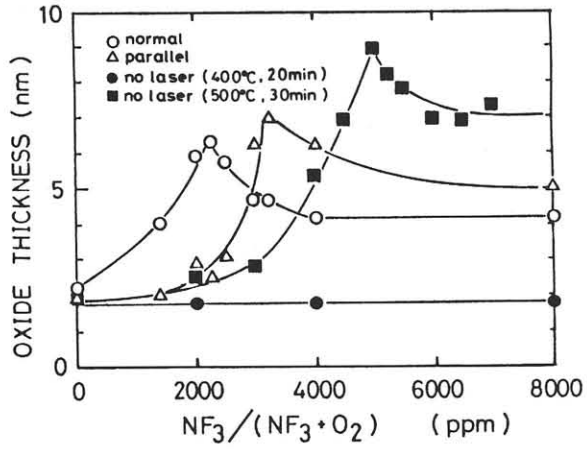

Fig. 2 Oxide thickness versus NF_3 gas concentration for two different conditions of 193 nm pulsed laser irradiation for 20 min at 20 mJ cm^{-2}/shot. The laser-pulse repetition rate was 50 Hz and the substrate temperature was 400 °C.

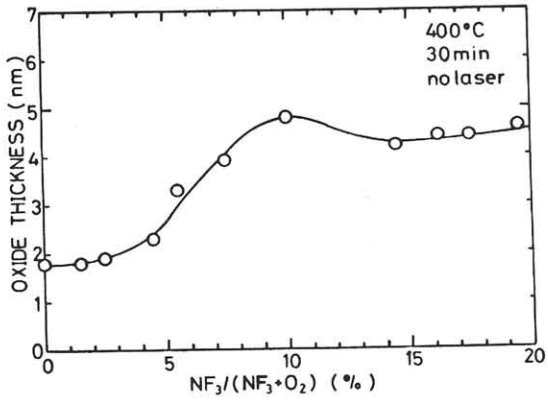

Fig. 3 Oxide thickness versus NF_3 gas concentration without laser irradiation. Note the difference of the horizontal scale with respect to that in Fig. 1.

3. Results and Discussion

Remarkable increase in the Si oxidation rate at 400 °C by ArF excimer laser irradiation is shown in Fig. 2. The curves comprize the enhanced oxidation region at the left side of the peak and the etching region at the right side as in the case of the thermal oxidation in O_2+NF_3 at temperatures above 600°C.[7,8] For the parallel irradiation to Si surface, the enhanced oxidation can be explained by the presence of fluorine radicals which are created by the photo-dissociation of NF_3 gas and break Si-Si bonds in the SiO_2/Si interface to promote the oxidation reaction.[8] In fact Si oxidation hardly proceeds in the O_2+NF_3 system at 400°C without laser irradiation when NF_3 concentration is less than 2 % as indicated in Figs. 2 and 3. The gradual increase in the oxidation rate at NF_3 concentrations above 2 % in Fig. 3 is due to the generation of fluorine radicals produced by the thermal decomposition of NF_3. Therefore, the primary role of the laser irradiation is to promote the gas phase dissociation of NF_3 molecules even at low temperatures. There exists the other important effect of the photo-irradiation as already shown in the case of normal incidence of the laser beam (see Fig. 2). For the normal irradiation more significant enhancement of the oxidation rate is observed at low NF_3 concentrations and the NF_3 concentration which yields the maximum oxide thickness is lower than that for the parallel irradiation. This implies that the normal irradiation causes the direct photo-dissociation of NF_3 molecules adsorbed on the oxide surface in addition to the gas phase dissociation and hence the etching reaction on SiO_2 begins to occur at a lower NF_3 concentration. This idea is consistent with the fact that the final oxide thickness in the etching region becomes thinner for the normal irradiation because of the presence of more reactive fluorine which attacks the SiO_2 surface. The temperature rise in the normal irradiation case is hardly responsible for the enhancement of the oxidation rate at NF_3 concentrations below 3000 ppm, because the maximum temperature rise due to the laser pulse energy is estimated to be at most 110°C[10] and the oxide

thickness obtained by the thermal reaction at 500 °C is appreciably low in the enhanced oxidation region as clearly shown in Fig. 2. From the above discussion, it is likely that the enhancement of the oxidation rate by the laser irradiation originates in fluorine radicals photochemically produced in the gas phase for the parallel irradiation case, while in the normal irradiation, radicals created by photo-dissociation of adsorbed NF_3 on the SiO_2 surface are more important for the enhancement. This interpretation is also supported by the result of Fig. 4, where the oxide thickness is plotted as a function of the accumulated number of laser pulses. The oxide thickness for the normal irradiation rapidly increases with the increasing number of laser pulses and then saturates over 1.5×10^4 shots, while in the parallel irradiation the thickness slowly increases. This indicates that, since the major source of fluorine radicals for the parallel irradiation is the photochemical dissociation of NF_3 in the gas phase, the number density of the radical impinging onto the SiO_2 surface is significantly low compared with the case of direct excitation of NF_3 adsorbed on the surface. The rapid saturation of oxide thickness for the normal irraidation is due to the balance of oxidation reaction with etching reaction induced by a plenty of fluorine. The in-depth profiles of Si, O, and F atomic concentrations in the oxide grown with and without laser irradiation are compared with Fig. 5. The fluorine content in the oxide produced under laser irradiation is rather uniform in the direction of thickness and is about 3 at. %, which is not very much different from the fluorinated oxide thermally grown at 600 °C without laser irradiation. The reason why the depth profile does not clearly exhibit the flat concentration region is that the oxide thickness (~ 50 A) is not thick enough with respect to the escape depths of Si_{2p} and O_{1s} photoelectrons.

A possible model of the fluorine-enhanced photo-oxidation mechanism based on the above results as well as on the model of the fluorine-enhanced thermal oxidation[7,8] is inferred as

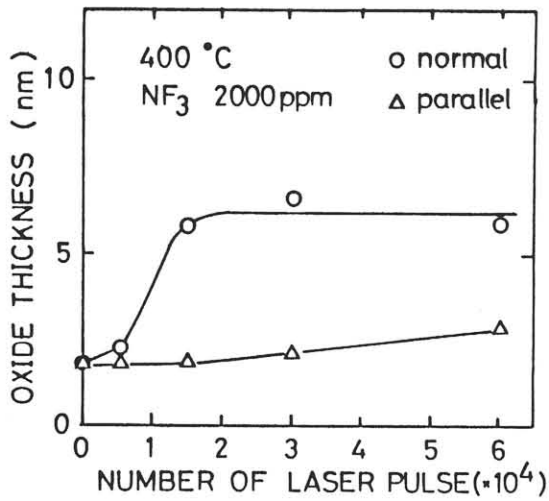

Fig. 4 Oxide thickness versus accumulated number of laser pulses for normal and parallel irradiation to Si surface. The repetition rate is 50 Hz and 6×10^4 pulses corresponds to 20 min.

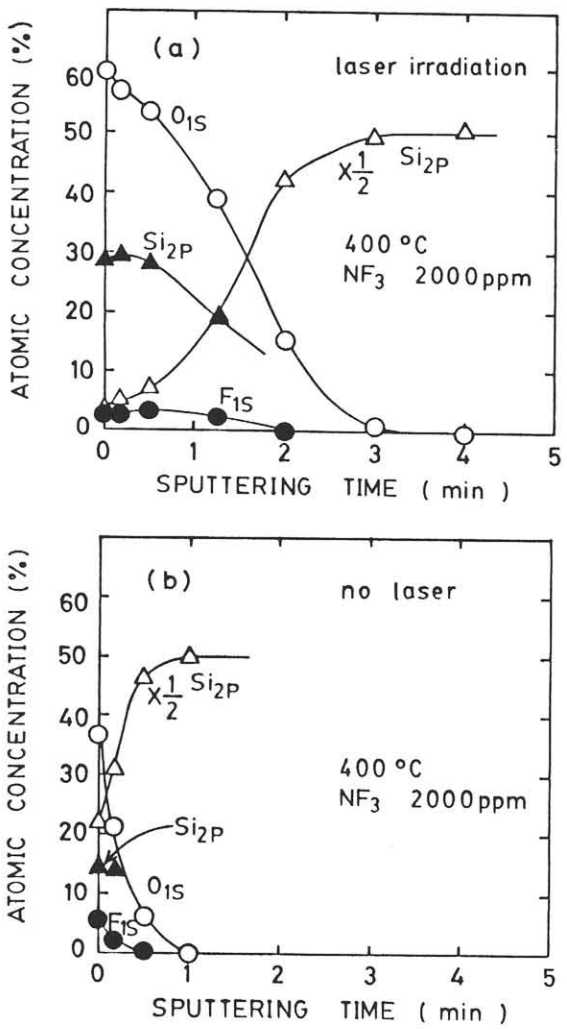

Fig. 5 In-depth profiles of atomic concentrations measured by XPS for the oxide grown under normal laser irradiation (a) and without irradiation (b) for 20 min.

follows: NF_3 molecules are dissociated in the gas phase by ArF excimer laser excitation and the fluorine radicals such as NF, NF_2, F, and F_2 impinge onto the oxide surface. The NF_3 molecules adsorbed on the oxide surface are also efficiently photo-dissociated when the laser beam is incident in the direction normal to the surface. Such fluorine species diffuse into the SiO_2/Si interface and the fluorine atoms in the interface cleave the Si-Si bond, resulting in the formation of one Si dangling bond together with one Si-F bond. Since the electronegativity of fluorine atom is extremely large compared to that of silicon, the silicon atom at the site of Si-F bond is positively charged and becomes highly reactive with diffused oxygen. The difference of oxidation rate for the normal and parallel incidences of the laser beam is explained by the different number densities of fluorine radicals existing on the SiO_2 surface for the both cases. Laser excitation of SiO_2 matrix is unlikely because the energy gap of SiO_2 is much larger than 193 nm photon energy. The silicon band gap photo-excitation in the SiO_2/Si interface may give rise to the enhancement of oxidation reaction rate because of the presence of highly reactive Si-F bonds in the interface, but the result of Fig. 3 indicates the primary importance of fluorine radicals for enhanced oxidation.

4. Conclusions

The fluorinated silicon dioxide has been grown at a temperature of 400 °C for 20 min by using ArF excimer laser irradiation in O_2+NF_3 at atmospheric pressure. Fluorine radicals created by photo-dissociation in the gas phase and on the oxide surface enhance the oxidation rate and more than 60 A thick oxide can be grown even at 400 °C. Further lowering of the oxidation temperature down to 300 °C would be possible in the higher NF_3 concentration range.

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References

1) R. Oren and S. K. Ghandhi, J. Appl. Phys. 42 (1971) 752.
2) S. A. Schafer and S. A. Lyon, J. Vac. Technol. 19 (1981) 494.
3) S. A. Schafer and S. A. Lyon, J. Vac. Technol. 21 (1982) 422.
4) E. M. Young and W. A. Tiller, Appl. Phys. Lett. 42 (1983) 63.
5) I. W. Boyd, Appl. Phys. Lett. 42 (1983) 728.
6) T. E. Orloeski and H. Rrichter, Appl. Phys. Lett. 45 (1984) 241.
7) M. Morita, T. Kubo, T. Ishihara and M. Hirose, Extended Abstracts of the International Conference on Solid State Devices and Materials, Kobe 1984, p. 451.
8) M. Morita, T. Kubo, T. Ishihara and M. Hirose, Appl. Phys. Lett. 45 (1984) 1312.
9) R. P. H. Chang, C. C. Chang and S. Darac, Appl. Phys. Lett. 36 (1980) 999.
10) C. P. Christensen and K. M. Lakin, Appl. Phys. Lett. 32 (1978) 254.