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Oxidation of Silicon Substrates in the Flowing Afterglow by Using O_2, N_2O, and H_2O

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Silicon was directly oxidized by using O atoms and OH radicals produced from the Ar afterglow reactions of O_2, N_2O, and H_2O at substrate temperatures below 350 °C. Uniform thin SiO_2 films were grown in all cases. The maximum film thickness was limited to about 20 Å by diffusion of oxidation species across the grown film.

The thermal oxidation of silicon is an important process in the fabrication of silicon MOS devices. The SiO_2 film is usually produced in dry O_2 ambient at relatively high temperatures (>900 °C). In recent years, formation of high quality SiO_2 film at low substrate temperatures below 500 °C is required for the development of smaller and faster silicon devices. One promising technique for silicon oxidation at low temperatures is a flowing-afterglow (FA) method.1-3) In the previous FA experiments,1-3) oxygen atoms generated by a microwave discharge of either pure O_2 or a mixture of Ar/O_2 were used for the direct oxidation of silicon substrates. A thin SiO_2 film of a uniform thickness below 300 Å was grown during 0.5-12 h. In the present new type of FA experiment, silicon substrates are oxidized by using O atoms and OH radicals produced from energy transfer reactions of the metastable $Ar(^3P_{2,0})$ atoms with O_2, N_2O, and H_2O at low substrate temperatures below 350 °C.

The schematic illustration of the experimental arrangement is shown in Fig. 1. The metastable $Ar(^3P_{2,0})$ atoms were generated by a microwave discharge (2.45 GHz, 200 W) of the pure Ar gas in a quartz flow tube. They

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flowed downstream past an oxidant inlet placed about 20 cm downstream from the center of the discharge. The Ar gas pressure was 1-1.5 Torr and the oxidant pressure was 0.05-0.1 Torr (1 Torr=133.3 Pa). Radical species resulting from the reactions of Ar($^3P_{2,0}$) with O_2, N_2O, and H_2O arrived at a silicon wafer placed about 3-5 cm downstream from the oxidant inlet. The silicon wafer was a 2 inch p-type (100)-oriented, Cz single crystal. The temperature of the silicon substrate was varied from 30 to 350 °C. The oxide thicknesses were measured by ellipsometry using a single wavelength Shimadzu AET-100 at a fixed oxide refractive index of 1.462. On the basis of ellipsometric measurements, a uniform stable native oxide with a thickness of 20±2 Å was present on the silicon prior to oxidation.

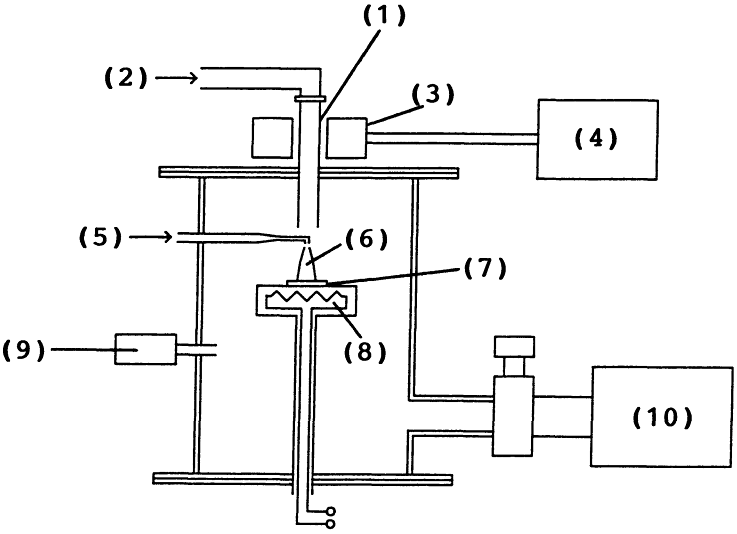

Fig. 1. The schematic diagram of the flowing-afterglow CVD apparatus: (1) Quartz flow tube, (2) Ar gas inlet, (3) Microwave cavity, (4) Microwave generator, (5) Oxidant inlet, (6) Flame, (7) Si wafer, (8) Heater, (9) Vacuum gauge, (10) Rotary pump

When O_2, N_2O, and H_2O were used as oxygen donors, hard colorless thin films were grown at substrate temperatures between 30 and 350 °C. A typical IR spectrum of this film is shown in Fig. 2 together with that of thermally grown oxide obtained at 1000 °C by Richter et al.[4] The following vibrational bands are identified: Si-O stretching (1060 cm^{-1}), O-Si-O bending (850 cm^{-1}), and Si-O-Si rocking (450 cm^{-1}). It is therefore concluded that the grown thin film is SiO_2. It has been shown that Si-O stretching frequency in SiO_x is linearly related to the oxygen concentration, x, whereas the bandwidth is mainly determined by the O-Si-O bond angle variation.[5] Since the peak position of the Si-O band (1060 cm^{-1}) is the same as that in the thermally grown oxide, the bulk of the SiO_2 is stoichiometric and shows no oxygen deficiency. The bandwidth of Si-O stretching (FWHM = about 200 Å) is wider than that of SiO_2 film prepared by thermal oxidation (FHHM = about 100 Å), indicating that the SiO_2 film obtained in the present study has higher structural disorder like large variations in the O-Si-O bond angle.

The thickness of grown film, 20±5 Å, was independent of the oxidant (O_2, N_2O, and H_2O), its pressure (0.05-0.1 Torr), Ar buffer gas pressure (1.0-1.5 Torr), oxidation time (1-3 h), and substrate temperature (30-350 °C). The degree of thermal oxidation was verified under the same experimental conditions but with the microwave discharge tuned off. It was found that the SiO_2 layer could hardly be distinguished from the native oxide present. This indicates that thermal oxidation was negligible under the operating conditions.

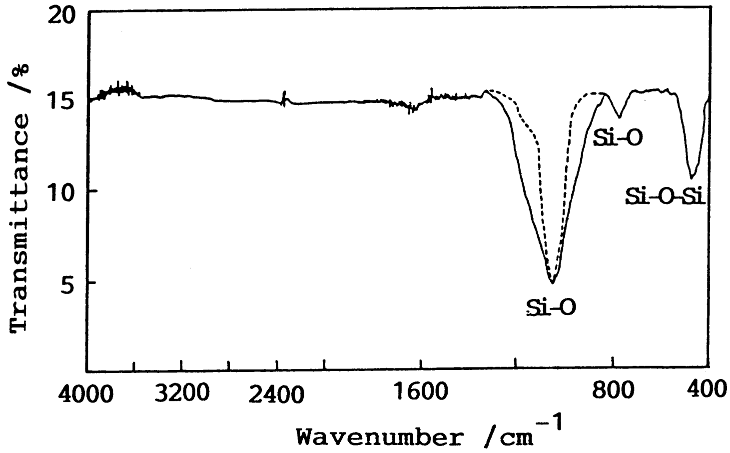

Fig. 2. IR spectra of SiO_2 film grown by using flowing-afterglow CVD apparatus (solid line) and by thermal oxidation[4] (broken line).
Oxidant: H_2O,
Ar pressure: 1 Torr,
H_2O pressure: 0.05 Torr,
Oxidation time: 3 h.

The metastable argon atoms with electronic energies of 11.55 eV ($^3P_2$) and 11.72 eV ($^3P_0$) are suitable to dissociate oxidants. According to the FA studies by Balamuta and Golde,[6], Velazco et al.,[7] and Gundel et al.,[8] exit product channels of the reactions of $Ar(^3P_{2,0})$ with O_2, N_2O, and H_2O leading to precursor species of oxidation are as follows:

$$Ar(^3P_{2,0}) + O_2 \longrightarrow 2O + Ar, \qquad (1)$$

$$k_1 = 2.1 \times 10^{-10}\ cm^3s^{-1} \text{ for } ^3P_2 \text{ and } 2.4 \times 10^{-10}\ cm^3s^{-1} \text{ for } ^3P_0,$$

$$Ar(^3P_{2,0}) + N_2O \longrightarrow O + N_2(B) + Ar, \qquad (2)$$

$$k_2 = 5.0 \times 10^{-10}\ cm^3s^{-1} \text{ for } ^3P_{2,0},$$

$$Ar(^3P_{2,0}) + H_2O \longrightarrow O + 2H + Ar, \qquad (3a)$$

$$\longrightarrow OH + H + Ar, \qquad (3b)$$

$$k_{3a} = 2.2 \times 10^{-10}\ cm^3s^{-1} \text{ and } k_{3b} = 2.6 \times 10^{-10}\ cm^3s^{-1} \text{ for } ^3P_2.$$

On the basis of these kinetic data, precursor species of oxidation are O atoms for O_2 and N_2O, while O atoms and OH radicals for H_2O. For the film growth, these radicals must arrive at the interface between Si and SiO_2 layers. When emission spectra resulting from reactions (1)-(3) were measured in the 200-700 nm region by using a Jarrell Ash 50 cm monochromator, no emission was found for O_2, whereas strong N_2(B-A) and OH(A-X) emission systems were observed for N_2O and H_2O, respectively. These spectral observations are consistent with the previous FA optical spectroscopic data.$^{6,8-10)}$ The observation of the above emissions just above the silicon wafer indicated that O atoms and OH radicals arrived at the wafer without significant quenching by collisions with buffer Ar gas and source gases. The radial intensity distribution of the emission intensity on the wafer showed that the number densities of excited species decreased with increasing the radial distance from the center of wafer. Although similar radial distributions of the precursor O atoms and OH radicals were expected, ellipsometric measurements of the SiO_2 layer thickness over the entire wafer surface showed that a uniform layer of 20±5 Å was grown. This can be explained by the fast saturation of film thickness under the operating conditions. Namely, the maximum film thickness was limited to about 40 Å including the native SiO_2 film due to limited diffusion of O atoms and OH radicals across the grown film.

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