Reaction analysis of initial oxidation of silicon by UV-light-excited ozone and the application to rapid and uniform SiO₂ film growth

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UV-light-excited O₃ prepared by irradiation of nearly 100% pure O₃ with a KrF excimer laser (λ = 248 nm, irradiated area = 30 × 10 mm²) was utilized for low-temperature Si oxidation. The initial oxidation rate was determined, and the activation energy was shown to be almost zero (0.049 eV). To clarify the optimum oxidation conditions, the dependence of the SiO₂ film growth rate on the total photon number and the photon density was investigated. The evolution of O₃ density after UV-light irradiation was experimentally measured, and the O(³P) density change is discussed. O(³P) density changes are successfully explained by using a second-order reaction model, indicating that a pulse supply of oxygen atoms is essential in the initial oxidation process. The uniform oxidation of 8 in. Si wafer has been carried out using a wafer-transfer type chamber by irradiating the wafer with KrF excimer laser light expanded linearly to the wafer width by a concave lens. © 2007 American Institute of Physics. [DOI: 10.1063/1.2433750]

I. INTRODUCTION

The low-temperature Si-oxidation method has been extensively studied for use in the fabrication of poly-Si thin-film transistors formed on glass or plastic substrates. The plasma enhanced chemical vapor deposition (PECVD) method is the most common way to stack oxide films; however, the quality factor of films prepared by this method is not as good as with the thermal oxide method. The use of high annealing temperatures to improve chemical vapor deposition (CVD) film and interface quality is limited by the deformation temperature of the substrates (e.g., T < 200 °C and <400 °C for plastic and glass substrates, respectively). As one of the solutions to utilize CVD film, it has been reported that high-quality SiO₂ thin-film fabrication before stacking the CVD film improves film quality. To fabricate a high-quality “interface film,” a several nanometer film to control the interface, it is necessary to develop a low-temperature Si-oxidation method.

In high-temperature (>800 °C) oxidation of Si in an O₂ atmosphere, molecular oxygen diffuses through the oxide film and reacts with silicon at the SiO₂/Si interface via dissociative adsorption to silicon at the interface. On the other hand, in low-temperature oxidation, some other method for the generation of atomic oxygen is necessary because O₂ does not dissociate.

UV radiation has been used to dissociate O₂ molecules at a lower temperature. The following are some of the dissociation processes:

O₂ + hν(λ = 172 nm) → O(³P) + O(³D),

O₂ + hν(λ = 126 nm) → O(³P) + O(¹S).

O(³P) and O(¹S) are excited states of atomic oxygen, which are expected to strongly oxidize silicon. In fact, Fang et al. showed that the growth rate of SiO₂ was very high (8 nm/min) in an O₂/Ar atmosphere irradiated with light (λ = 126 nm). However, quality factors of such films, such as limited leakage current density through the oxide film, are not as high as those of films prepared by the thermal oxide method. The dissociation of O₂ by 172 or 126 nm light is less effective because (1) the photodissociation rate is low, (2) light at these wavelengths cannot penetrate through air, and (3) irradiation at these wavelengths induces defects in SiO₂ film.

O₃ oxidation is also expected to be a potentially useful process for silicon oxidation at a low temperature because O₃ is easily decomposed into atomic oxygen at the silicon wafer at temperatures as low as 400 °C. Nishiguchi et al. reported that the SiO₂ films fabricated using nearly pure O₃. The electrical properties such as the interface trap density and the leakage current are 10⁻⁹ A/cm² at 5 MV/cm, respectively, which shows that O₃ oxidation method is acceptable for use in the most recent gate oxides. However, growing SiO₂ films thicker than 2 nm below 400 °C is difficult because of the low oxygen-atom density due to the low decomposition rate of O₃ on low-temperature SiO₂ surfaces.

The Si oxidation method using UV-light-excited O₃ that we previously proposed satisfies the need for both high growth rate and good film quality. The experimental results for 12 × 12 mm² silicon tips show that (1) the growth rate of...
SiO$_2$ film is 5.2 nm/10 min at 300 °C and 3.6 nm/10 min at 70 °C, and that (2) the film quality is as good as that of the thermal oxide using O$_2$. From an industrial standpoint, however, the method must be applicable for the oxidation of large wafers.

In this paper, we report the initial oxidation of Si using UV-light-excited O$_3$ and the application to larger Si wafer oxidation. First, we describe the method used to prepare nearly 100% O$_3$ and UV-light-excited O$_3$. Next, we refer the initial oxidation using UV-light-excited O$_3$. To analyze the time-resolved distribution of atomic oxygen, we made time-resolved O$_3$ density measurements, and the supplied O$_3$ density will be discussed. Finally, we describe a wafer-transfer-type oxidation chamber and report on the results obtained with the chamber.

II. PRODUCTION OF UV-LIGHT-EXCITED OZONE

UV-light-excited O$_3$ was prepared from almost 100% pure O$_3$ irradiated with light from a KrF excimer laser ($\lambda$ =248 nm). KrF excimer laser light was used because (1) irradiation by 248 nm light is expected to generate excited atomic oxygen, O$^1D$, which should be a powerful oxidizing agent; (2) a high density of O$^1D$ will be formed because of the high photon density of KrF excimer laser light (in our case, $\approx 10^{16}$ cm$^{-3}$); and (3) 248 nm light will not induce defects in SiO$_2$ film, because the absorption coefficient of ideal SiO$_2$ for 248 nm light is practically zero.

The nearly pure, highly concentrated (HC) O$_3$ was supplied from a pure-ozone generator (Meidensha Corp., MPOG-SM1C1). HC O$_3$ gas was produced by the following procedure: O$_3$ gas of 5%–7% purity prepared with a conventional ozonizer was introduced into an ozone vessel cooled to 90 K. Since O$_3$ exists as a liquid and O$_2$ as a gas at 90 K, pure liquid O$_3$ was obtained by pumping out the O$_2$ gas. Then, nearly pure O$_3$ gas was produced in the chamber by increasing the vessel temperature (typically to 110–125 K).

Silicon was oxidized by UV-light-excited O$_3$ in a mechanochemically aluminum chamber as shown schematically in Fig. 1. The base pressure of the chamber was $10^{-3}$ Pa or lower, and the O$_3$ pressure was kept between 200 and 800 Pa during the oxidation. The flow rate of the O$_3$ gas was maintained between 100 and 170 SCCM (SCCM denotes cubic centimeter per minute at STP). The KrF excimer laser (Lambda Physik, Compex 110, irradiation area 10 $\times$ 30 mm$^2$, 180–260 mJ/pulse, 1–100 Hz) was positioned to irradiate the Si wafer from above. The laser light was a pulse of approximately 10 ns duration. Note that the net irradiation time was not equal to the oxidation time. The irradiation area could be expanded by using a cylindrical concave lens ($f$ = 45.2 mm). The HF terminated silicon wafer was heated with a halogen lamp through an opaque glass substrate holder from the bottom side of the wafer and the typical temperatures are in the range of room temperature to 260 °C. The linear motion system used to transfer the Si wafer is described in Sec. VI.

The oxidation temperature was measured with a K-type thermocouple spot welded to the surface of the Si wafer. The irradiation by the KrF excimer laser heated the outermost surface of the Si wafer. On average, the temperature increase caused by the laser light irradiation, as measured by thermal tape attached to the wafer, was less than 50 °C. In this paper, therefore, the temperature rise of the Si surface due to laser irradiation is not fully taken into account.

III. INITIAL OXIDATION OF SILICON BY UV-LIGHT-EXCITED O$_3$

To determine whether the UV-light-excited O$_3$ process was effective enough for the formation of the “interface film” mentioned in the introduction on a large-size Si wafer, the initial growth rate of the process was investigated. The growth rate is shown in Fig. 2. The oxidation was carried out in a temperature range between room temperature and 300 °C.

The growth rate can be represented by a linear kinetics equation, $d = d_0 + At$, where $d$ is the SiO$_2$ thickness, A the linear rate constant, $t$ the oxidation time, and $d_0$ the thickness that has grown barrierlessly in the initial period of the UV-ozone oxidation. The calculated value of $d$ using $A$ =0.076 nm/min (at RT), 0.136 nm/min (at 200 °C), 0.159 nm/min (at 260 °C), and $d_0$=1.75 nm are shown also in Fig. 2 and fit the experimental results well. The value of $d_0$=1.75 nm is thicker than the nascent oxide film, which is typically 1 nm for O$_3$. The thick initial oxide film means that the oxidation occurs within an unusually short period of time. The experiment showed that a 1.7±0.1-nm-thick SiO$_2$ film grew in only 20 s. From these results, we estimate that a 1.7-nm-thick SiO$_2$ film can be fabricated within 6.7 min by oxidation of an 8 in. wafer using the oxidation system described in Sec. VI.
An activation energy ($E_a$) of 0.049 eV was obtained from the Arrhenius plot shown in Fig. 3. Though only a few reports on initial oxidation of Si are available, this $E_a$ is much lower than that determined for other methods, such as the Kr and O$_2$ mixture plasma process (0.14 eV) or the HC O$_3$ process (0.32 eV). The low $E_a$ indicates that UV-light-excited O$_3$ is applicable to low-temperature oxidation.

IV. DEPENDENCE OF SiO$_2$ FILM GROWTH ON PHOTON DENSITY AND TOTAL PHOTON NUMBER

The area irradiated by the KrF excimer laser light (10 $\times$ 30 mm$^2$) must be expanded with a lens to oxidize a large Si wafer. Therefore, clarifying the dependence of growth thickness of SiO$_2$ film on the number of irradiated photons or the photon density is important. When the photon density is constant the film thickness apparently depends on the total photon number of irradiated photon, but as O$_3$ is excited impulsively by the laser light, a nonlinear effect might occur when the photon density is changed. The relation between SiO$_2$ film thickness and the total photon number is shown in Fig. 4. The relation between the SiO$_2$ thickness and photon density was made in the case of Si oxidation using UV-light-excited O$_3$ and the transition time is 5 min. Therefore, the relation between the SiO$_2$ film thickness and photon density was made in the two oxidation modes (<5 min and >5 min). For oxidation times longer than 5 min [Fig. 5(b)], there seems to be a following relation between the SiO$_2$ thickness and photon density. When the constant total photon numbers are $1.3 \times 10^{21}$ and $8 \times 10^{20}$ cm$^{-2}$, the lower photon density results in thicker SiO$_2$ films. When the constant total photon number is $4.5 \times 10^{20}$ cm$^{-2}$, the SiO$_2$ film thickness seems to have a maximum value around photon density $= 5 \times 10^{15}$ cm$^{-2}$. On the other hand, for oxidation times shorter than 5 min [Fig. 5(a)], there is no relationship between SiO$_2$ film thickness and photon density.

The thickness of grown SiO$_2$ film is mainly determined by the supply and diffusion of atomic oxygen. For oxidation times above 15 min, SiO$_2$ film growth must be limited by oxygen diffusion. The rate constant of the reaction of O$(^1D)$ with O$_2$ is high (2.4 $\times$ 10$^{-10}$ cm$^3$), and the lifetime of O$(^1D)$ will be very short (e.g., the lifetime can be calculated to be 86 ns at 200 Pa by the reaction rate constant). Therefore, the short lifetime of O$(^1D)$ may cause a pulsed supply of O$(^1D)$ to the Si wafer. The fact that higher photon density (with low repetition rate) results in thinner SiO$_2$ films may indicate that there is an excess of oxygen atoms that cannot be used for oxidation within the lifetime of O$(^1D)$ because of a limitation of diffusion. To discuss the effect of the supply of O$(^1D)$ on SiO$_2$ film growth, understanding the behavior of O$(^1D)$ is necessary. In the next section, the time-resolved distribution of the O$(^1D)$ density will be discussed.

![Fig. 3. Arrhenius plots of linear rate constants A.](image)

![Fig. 4. The relation between SiO$_2$ film thickness and number of irradiated photons.](image)

![Fig. 5. The relation between SiO$_2$ film thickness and photon density. The total numbers of irradiated photon are (a) $4.8 \times 10^{20}$ cm$^{-2}$ (solid squares), $6.7 \times 10^{18}$ cm$^{-2}$ (open triangles), (b) $1.3 \times 10^{21}$ cm$^{-2}$ (open circles), $4.5 \times 10^{20}$ cm$^{-2}$ (solid triangles), and $8 \times 10^{20}$ cm$^{-2}$ (open squares). The oxidation times are (a) 5 min (solid squares), 3 min (open triangles), (b) 17.2 min (open circles), 15 min (solid triangles), and 15 min (open squares).](image)
V. ESTIMATION OF THE CHANGE OF O(1D) DENSITY BY EXPERIMENTAL MEASUREMENT OF THE TIME-RESOLVED DISTRIBUTION OF THE O3 DENSITY

For application to rapid and large-size wafer oxidation, determining the time-resolved and spatially resolved distribution of the O(1D) density is helpful. However, because the deexcitation occurs nonradiationally, the direct detection of O(1D) is not easy. Therefore, we instead measured the time-resolved distribution of the O3 density and estimated the time-resolved distribution of the O(1D) density.

A. Experimental setup

The time-resolved distribution of the O3 density was measured by using two KrF excimer lasers. One served as an “excitation light,” and the other as a “probe light.” The power densities of the KrF laser were 70 and 2 mJ/cm2, and the irradiation areas were 10×30 and 10×10 mm2, respectively. The pulse duration of both laser lights was about 10 ns.

The experimental setup is shown schematically in Fig. 6. The features of the chamber and the preparation method of UV-light-excited O3 are described in Sec. II. A synthetic quartz window that was made for the O3 density measurement was placed on the top of the chamber. Boxes made of synthetic quartz were welded to the window to enclose the process region. The dielectric multilayer mirrors that reflect the probe light were set so as to pass through the process region. The probe light passed through the O3 atmosphere for a length of 43 mm. Excitation light was irradiated into this region vertically from the top, as in the case of silicon oxidation.

The intensity of the probe light was measured using a photodiode (Hamamatsu Photonics S1226-18BU, rise time 0.15 µs). The intensity of the probe light through a vacuum is defined as $I_0$. The probe light intensity traveling through O3 atmosphere is weakened to $I_1$ because O3 molecules absorb light. After the excitation-light irradiation, the intensity of the probe light $I_2$ becomes greater than $I_1$ because the excitation light, whose photon density is much greater than that of the probe light, decomposes a large portion of the O3. A time-resolved measurement of O3 density after excitation-light irradiation was made by detecting the intensity of the probe light while varying the delay time of the probe light with respect to the excitation light.

The ratio of $I_2/I_0$ is converted to O3 density $N$ by

$$N = \frac{1}{\sigma_0} \ln \left( \frac{I_2}{I_0} \right),$$

where $\sigma_0$ is the absorption cross section ($1 \times 10^{-17} \text{cm}^2$ for $\lambda = 248 \text{ nm}$). In the case of laser light irradiation which has a high photon density, $\sigma_0$ must be corrected by taking into account the saturation absorption effect. The corrected $\sigma$ is expressed as

$$\sigma = \frac{\sigma_0}{1 + \frac{I}{I_{sat}}}$$

where $I_{sat}$ is the correction term given by

$$I_{sat} = h\nu Nl.$$  

The corrected $\sigma$ is 1%–4% smaller than $\sigma_0$ in a pressure range between 150 and 350 Pa. We confirmed that the calculated values of $I_1/I_0$ using the corrected $\sigma$ when the power density of the probe light was 2 mJ were in fair agreement with the experimentally measured $I_1/I_0$ (without the excitation light) at pressures lower than 330 Pa.

B. Decomposition of O3 molecules after UV-light irradiation

The experimental results of the time-resolved distribution measurements of O3 density are shown in Fig. 7. The O3 pressure before the irradiation of the excitation light was either 200 Pa (filled circles) or 300 Pa (filled triangles). The O3 density was calculated from Eqs. (1)–(3) with a path length of 43 mm. The results show that there were three time
regions of O₃ density change [Fig. 7(a)]; (A) The density started to decrease immediately after the excitation-light irradiation to about 10⁻⁵ s, (B) O₃ density greatly decreased between approximately 10⁻³ and 10⁻⁴ s, and (C) O₃ density started to increase after approximately 10⁻⁴ s. The third region (C) was the recovery process due to the supply of fresh O₃ gas into the process region.

C. Decomposition of O₃ molecules after UV-light irradiation

In this subsection, the decomposition of O₃ and the O₃ density calculation method are presented. The decomposition of O₃ by irradiation of the excitation light is expressed as follows:

\[ O₃ + h\nu(\lambda = 248 \text{ nm}) \rightarrow O^1(D) + O₂^1(S_g^+) \]  
(4)

The number of absorbed photon density can be calculated by using Eqs. (1)–(3) and the excitation KrF laser power (60 mJ/cm² at a single shot). The estimated value for the absorbed photon density was 1 × 10¹⁶ cm⁻³ at 200 Pa and 2 × 10¹⁶ cm⁻³ at 300 Pa.

\[ O^1(D) \text{ and } O₂^1(S_g^+) \] are further consumed by reacting with residual O₃ molecules as follows:

\[ O^1(D) + O₃ \rightarrow O₂ + 2O₂^2(P) \]  
(5)

\[ \rightarrow O^1(P) + 2O₃ \]  
(6)

\[ \rightarrow 2O₂^1(Δ_g) \]  
(7)

\[ \rightarrow O₂^1(S_g^+) + O₂^1(S_g^-) \]  
(8)

\[ \rightarrow 2O₂^1(S_g^+) \]  
(9)

\[ O₂^1(S_g^+) + O₃ \rightarrow O + 2O₂ \]  
(10)

\[ \rightarrow 2O₂^1(Δ_g) + O₃ \]  
(11)

\[ \rightarrow 2O₂^1(S_g^-) + O₃ \]  
(12)

The total rate constant of the reactions of \( O^1(D) \) with \( O₃ \) \((k_O)\) and the total rate constant of the reactions of \( O₂^1(S_g^+) \) with \( O₃ \) \((k_O)\) are 2.4 × 10⁻¹⁰ and 2.5 × 10⁻¹¹ cm³/molecule s, respectively.\(^{17,18}\) Because definite branching ratios of the reactions are not available, we calculated the O₃ density using the total rate constant.

D. Precise analysis of the O₃ density

The O₃ density shown in Sec. V B was obtained from the ratio of the probe light \((I_p/I_b)\), which was experimentally measured, and a calculation using Eqs. (1)–(3) with a path length of 43 mm. Although the actual path length of the probe light was 43 mm, the area of the excitation light was 30 mm, as shown schematically in Fig. 8. In this subsection, we introduce a correction to the O₃ density in order to analyze the reaction involving \( O^1(D) \) more accurately. The probe light passed through a “no excitation light area” before and after the “excitation light area.” The path lengths were

E. The O₃ density calculation

1. \( O^1(D) \) and \( O₂^1(S_g^+) \) reactions with \( O₃ \)

The time-resolved distributions of \( O^1(D) \) and \( O₂^1(S_g^+) \) densities can be calculated by means of the second-order reaction model using total rate constants, as described in Sec. V C. The reaction rate of \( O^1(D) \) with \( O₃ \) was much larger than that of \( O₂^1(S_g^+) \) with \( O₃ \). Therefore, for the first time region [as in Sec. V B (A)], we must calculate only the decrease in \( O₃ \) density due to reaction with \( O^1(D) \). The change of \( O^1(D) \) density \([O^1(D)]\) can be expressed as

\[ -\frac{d}{dt}[O^1(D)] = k_O[O^1(D)][O₃], \]  
(15)

\[ = k_O(m_O - x_O)(m_O - x_O), \]  
(16)

where \( m_O \) is the initial density \((t=0)\) of \( O^1(D) \), \( m_O \) is that of \( O₃ \), and \( x_O \) is the decrease of \( O^1(D) \). Since \( x_O=0 \) at \( t=0 \), \( k_O \) can be calculated by

FIG. 8. The schematic view of the probe light and the excitation light configuration.

6.5 mm for \( x_{ab} \), 30 mm for \( x_{bc} \), and 6.5 mm for \( x_{cd}(=x_{ab}) \). The intensity of the probe light at \( d(I_p) \) is expressed as follows:

\[ I_d = I_a \exp(-2N\sigma_b x_{ab}) \exp(-N'\sigma_{bc} x_{bc}). \]  
(13)

The \( O₃ \) density at excitation light area \((N')\) is given by

\[ N' = \frac{1}{\sigma_{bc} x_{bc}} \ln \left( \frac{I_d}{I_a \exp(-2N\sigma_b x_{ab})} \right). \]  
(14)

The results for \( O₃ \) density calculated using Eq. (14) are shown in Fig. 7 as open circles (200 Pa) and open triangles (300 Pa). Using this corrected density \((I_d)\) which satisfies the condition, \( I_d < I_a \exp(-2N\sigma_b x_{ab}) \) can be analyzed.
In this case, where \( x \) corrected experimental results well. The calculation of \( O_2 \) density should involve more-complex reactions. In this subsection, we take into account \( O_2 \) molecules generated by the reaction of \( O^1(D) \) with \( O_3 \). Since the rate constant of these generated \( O_2 \) molecules with \( O_3 \) is not available, we assumed that it was equal to \( k_{O_2} \). At time \( t \), the generated \( O_2 \) density [which is not primary generated \( O_2 \)] is \( 2x_0 \). Therefore the change of \( O_2 \) density is calculated by

\[
-\frac{d}{dt}[O_2] = k_{O_2} [O_2][O_3]
\]

The decrease of \( O_2 \) density is calculated by

\[
x_o = \left( \frac{m_{O_2}+2x_0)}{(m_{O_2}+2x_0)} \right) \left( 1 - \exp[-(m_{O_2}-m_{O_3}+3x_0)k_{O_2}t] \right)
\]

The results for \( O_3 \) density calculated by Eqs. (19) and (28) are shown in Fig. 7 as dotted curves. The results fit the corrected experimental results well (open symbols).

F. The time distribution of \( O^1(D) \) density

The agreement between the calculated values (dotted curves) and the experimental results (open symbols) shown in Fig. 7 indicates that our calculation, which involved the reactions of \( O^1(D) \), reflected well the actual \( O^1(D) \) density. The calculated \( O^1(D) \) density is shown in Fig. 9. The density of \( O^1(D) \) decreased to 1% of the initial value at \( t=5 \times 10^{-6} \) s, indicating that the supply of \( O^1(D) \) to the silicon wafer surface was intermittent with a short duration of approximately \( 10^{-6} \) s.

As shown in the previous section, \( SiO_2 \) thickness did not depend on the photon density at a constant total photon number in the initial oxidation region (<5 min), whereas the thickness did depend on the photon density after the initial oxidation region (>5 min). In the initial oxidation region (<5 min), the \( SiO_2 \) film thickness was small enough for the oxygen atoms to diffuse to the interface without a considerable barrier. Therefore, the \( SiO_2 \) thickness did not depend on the photon density at a constant photon number. On the other hand, after the initial oxidation region (>5 min), the oxidation rate was limited by the diffusion of atomic oxygen through the thicker \( SiO_2 \) film. Although a detailed discussion of oxygen diffusion is difficult, we can state that the mechanism of oxygen diffusion for the case of an oxidation method using a pulsed supply of atomic oxygen (\( O_2 \) and pulsed KrF excimer laser light) may be different from that using a continuous supply of atomic oxygen (e.g., \( O_2 \) and Ar lamp).

VI. OXIDATION OF AN 8 IN. WAFER

A wafer-transfer-type oxidation chamber (Fig. 1) was developed for large-wafer oxidation. Our chamber includes the following features: (1) the irradiation area of KrF laser light is expanded in one direction by a cylindrical concave lens.
(f = -45.2 mm), and (2) the silicon wafer is transferred in one direction. The transfer speed can be varied between 3 and 30 mm/min. Si wafers up to 8 in. can be oxidized in this chamber. The O₂ supply system and other features are described in Sec. II.

The SiO₂ thickness distribution on an 8 in. Si wafer using this system is shown in Fig. 10. The oxidation temperature was 200 °C, and the scan speed was 9.5 mm/min. The outline of an 8 in. wafer was also drawn.

The SiO₂ thickness profile. Oxidation temperature is 200 °C and the transfer speed is 9.5 mm/min. The outline of an 8 in. wafer was also drawn.

(FIG. 10)

The SiO₂ thickness distribution on an 8 in. Si wafer using this system is shown in Fig. 10. The oxidation temperature was 200 °C, and the scan speed was 9.5 mm/min. The average thickness of the SiO₂ film was 2.1 nm, and the deviation of the SiO₂ film thickness was 0.1 nm, which indicates that the fabrication of a uniform SiO₂ film is possible with this system.

The relation between the film thickness and the wafer transfer speed is shown in Fig. 11. Since the initial oxidation rate by the UV-light-excited O₃ was high, as mentioned in Sec. III, the thickness of SiO₂ films grown at a transfer speed of 12 mm/min was 1.75 nm. We have not yet measured the electrical characteristics for a whole wafer sample since our measurement system is only capable for small chip samples and the film thickness is anyhow too small for the measurement using the simple metal-insulator-semiconductor structure (MIS) structure. However, since the quality factors of the film fabricated by UV-excited O₃ were as good as those of a film fabricated by a thermal oxide process, the 1.7-nm-thick SiO₂ film is expected to be an “interface film” that improves the interface character between a CVD stacked film and poly-Si. The application to poly-Si oxidation by UV-light-excited O₃ is a future issue. In order to apply the method to processes in most advanced industries such as the gate oxide formation, further optimization of the process conditions such as the control of the laser beam profile and the ozone flow rate must be done.

VII. SUMMARY

A low-temperature oxidation method using UV-light-excited O₃ was developed. A 1.7-nm-thick SiO₂ film could be grown in only 20 s at room temperature. The activation energy of the oxidation using the method was almost zero (0.049 eV). The oxidation rate depended on the photon density when the oxidation time was longer than 5 min.

To estimate the evolution of O₁⁷(¹⁸)D density after an excitation laser pulse, the time-resolved distribution of O₃ density was experimentally observed. The O₃ density change was calculated using a second-order reaction model, and the calculated results reproduced the experimental results well. We concluded that O¹⁷(¹⁸)D was supplied to the Si wafer surface as a pulse. We developed a wafer-transfer-type oxidation chamber, and by using the chamber, we successfully grew SiO₂ films on 8 in. Si wafers by the UV-light-excited O₃ oxidation method.

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