Temporal Variations of Optical Emission Spectra in Microwave-Excited Plasma in Saturated Water Vapor under Reduced Pressure during Photoresist Removal

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Mechanisms of photoresist removal were investigated using microwave-excited plasma in saturated water vapor under a reduced pressure condition (approx. 6 kPa). A few seconds of white emission were observed at the beginning of photoresist removal. To ascertain the species of spectra, optical emission spectroscopy was used for photoresist removal from a Si wafer. Emission spectra of OH (A²Σ – X²Π), Hα (656 nm), and O (777 nm) derived from dissociation of water molecules were observed. Other emission spectra attributed to CO molecules were also detected and identified as the Ångström system (B¹Σ – A¹Π). This result indicates CO molecule generation during photoresist removal. The CO molecule emission intensity reached a maximum value at 1.1 s after plasma ignition, whereas those of OH, Hα, and O reached a minimum value at almost identical time. Furthermore, normalized emission spectra shape from CO molecules during photoresist removal were almost identical for Δν = +1, 0, -1, -2, -3, and -4. Rotational and vibrational temperatures of the CO molecules during photoresist removal were found to be almost constant and to be 1500 and 2500 K, respectively. These results suggest increased CO molecular density above the Si wafer at 1.1 s.

Keywords: Microwave, Optical emission spectroscopy, Photoresist removing, Water vapor plasma, CO molecular band spectra

1. Introduction

A photoresist is used for manufacturing semiconductor devices such as integrated circuits (IC) and large-scale integrated circuits (LSI). Photoresist patterns are made using three processes: spin coating, exposure, and development. Later, etching and ion implantation processes are conducted using the photoresist as a mask. For positive-tone photoresist films, an unexposed photoresist film keeps a patterned structure but an exposed photoresist is removed during development. Finally, the photoresist film mask is removed using a conventional photoresist removal technique. A mixture of sulfuric acid and hydrogen peroxide mixture (SPM) and/or O₂ plasma is used for photoresist removal [1–10]. When using the SPM, large amounts of environmentally unfriendly chemicals are used. Additionally, reuse of the chemicals is expensive. Furthermore, using SPM makes it difficult to remove hardened photoresists by ion implantation. Alternatively, if using O₂ plasma, photoresist removal rates are typically low; poor uniformity over large areas presents other difficulties. To increase photoresist removal rates, the Si wafer is usually heated to temperatures higher than 250 °C to enhance chemical reactivities on the photoresist film. This heating might degrade the efficiency of the semiconductor devices and increase defect rates. Reportedly, H₂O addition to the O₂ plasma was applied to photoresist removal. This addition might reduce the activation energy of the ashing reaction and raise photoresist removal rates in microwave-excited O₂ downstream plasma at a 2.45 GHz frequency and at 107 Pa [3]. Reportedly, photoresist
removal rates doubled to about 1 mm/min when the water vapor mixing ratio was increased from 0% to 10%. However, the operating temperature range was 140–200 °C. The photoresist removal rates showed strong dependence on the temperature. Moreover, particles were emitted during removal of the ion-implanted photoresist from the O₂ plasma.

Recently, photoresist removal using wet ozone instead of the conventional methods described above has been proposed. This low-temperature (approx. 100 °C) process is environmentally friendly. Wet ozone is produced by mixing ozone gas with a small amount of water vapor. However, using wet ozone entails some reported difficulties for removing ion-implanted photoresists [6–10]. Some other methods have been reported for photoresist removal, such as using CO₂ plasma [11]. The CO₂ plasma method has been evaluated for its economy and safety. Recent reports revealed its potential, compared to using O₂ plasma, for reducing low-k damage during photoresist removal. However, CO₂ ions can damage the Si wafer at chamber pressures as low as 6.7 Pa.

Using a slot antenna, we developed microwave-excited plasma produced in water bubbles under a reduced saturated vapor pressure condition [12–15] and applied it to photoresist removal [16]. Using this method, ultrapure water is used as a source gas for the microwave-excited plasma. A scroll pump was used to achieve saturated vapor pressure of approx. 6 kPa in the chamber. A Si wafer is cooled directly by water during photoresist removal. Results showed that an environmentally friendly and low-temperature photoresist removal was realized using this method. The 6 kPa operating pressure is about two orders higher than that using conventional O₂ plasma ashing. Furthermore, microwave plasma is generated in a narrow region of a few millimeters between the Si wafer and the slot antenna, which is expected to expose high radical flux density. To date, we have confirmed photoresist removal rates higher than 1 µm/min using this method, even for a positive-tone Novolak photoresist film stiffened by ion-implantation [16]. Application of this method using the slot-antenna-excited microwave plasma to a large-area process appears to be possible by customizing a suitable microwave frequency, a slot length, and slot patterns [17–22]. In such a case, clarification of photoresist removal using this method is important for application to practical industrial semiconductor manufacturing processes.

This study investigated temporal variations of optical emission images and spectra during photoresist removal using microwave-excited plasma with video camera observation and optical emission spectroscopy. The results were discussed to elucidate the mechanisms of photoresist removal using microwave-excited plasma.

2. Experiment setup to assess microwave-excited plasma for photoresist removal and to diagnose its spectral

Figure 1 portrays the setup of a microwave-excited plasma experiment to elucidate photoresist removal under conditions of saturated water vapor under the reduced pressure condition: (a) front view and (b) side view.
partially filled with 1 L of ultrapure water. The slot antenna was maintained under saturated water vapor during photoresist removal to avoid optical emission scattering because of bubbles. The chamber internal pressure reduced to approx. 6 kPa using a scroll pump.

A half-inch Si wafer (φ = 12.5 mm) for a Minimal Fab System [26, 27] was used for this study. Using a minimal coater (Litho Tech Japan Corp.), a positive-tone Novolak photoresist (OFPR-5000; Tokyo Oka Kogyo Co., Ltd.) for g/i line lithography was spin-coated onto the wafer at 800 rpm for 3 s and at 4000 rpm for 65 s. The photoresist film thickness was 1.0 µm. The wafer was baked at 90 °C for 60 s after spin-coating.

A magnetron-oscillation type microwave generator (MMG-213VPT; Micro Denshi Co., Ltd.) was used as a plasma source. A water-cooled dummy load was equipped between the microwave generator and the plasma to protect the magnetron from damage [25]. Non-modulated 2.45 GHz microwaves were injected into the water vapor through the slot antenna [12–15]. Forward and reflected microwave powers were measured using a mean-responding power detector that had been set for use in high-frequency receiver and transmitter signal chains up to 2.5 GHz (MMO-220HP; Ohta Electronics Co. Ltd.). We adjusted the impedance matching using an E-H tuner to reduce the reflected microwave power. For this experiment, the net microwave power was set at 200 W. Plasma was generated for 30 s after plasma ignition.

Video camera measurements and optical emission spectroscopy were conducted simultaneously during photoresist removal. Optical emission images were obtained from a viewing window equipped on the chamber. The video camera frame rate was set at 30 fps. Optical emission spectra were measured using a compact spectrometer (USB2000+ UV-VIS; Ocean Optics Inc.) with a grating of 600 lines/mm, slit width of 25 mm, and optical resolution of 1.5 nm for full width at half maximum. An optical fiber rod (φ = 6 mm, SOG-70S; Sumita Optical Glass Inc.) was connected in series to an optical fiber (φ = 50±5 µm, UV-VIS High OH content; Ocean Optics Inc.) and a spectrometer. The optical fiber rod was installed at a viewing port on the chamber side wall. The distance between the edge of the optical fiber rod and the center of the slot antenna was set at 17 mm. Optical emission spectra were recorded at every 100 ms with integration time of 10 ms.

3. Temporal variations of optical emission images and spectra during photoresist removal using microwave-excited plasma

White emission was observed at the moment of a microwave-excited plasma ignition (t = 0 s) when a Si wafer with photoresist was located below the slot antenna. Figure 2 presents temporal variations of optical emission images of the plasma during photoresist removal at t = 0, 1.0, and 5.0 s. From visual observation, we inferred that the white emission intensity reached its maximum at around t = 1 s. The white emission immediately turned to red-purple color in a few seconds, which was the same color as that observed in the case of a bare Si wafer. The red-purple emission derived from Hα (656 nm)
of the hydrogen atomic line spectrum. This drastic color change suggests that the compositions of radicals, chemical species, and their densities in the plasma changed considerably in a few seconds.

Figure 3 shows widely various spectra in 250–800 nm at $t = 0$, 1.0, and 5.0 s. The emission spectra of OH ($A^2S - X^2P, \Delta v = 0$), H$_a$, and O (777 nm) derived from dissociation of water molecules were observed clearly [12, 28–31]. The OH band spectrum of 309 nm was the strongest among the observed spectra. OH radicals are produced mainly by electron-impact dissociation of water molecules [28] as

$$e + H_2O \rightarrow H + OH + e \quad (1).$$

Therein, OH ($A^2 \Sigma - X^2 \Pi$) is a spontaneous emission observed when electrons in an excited state ($A^2 \Sigma$) return to the ground state ($X^2 \Pi$) [31]. Because OH radicals have high oxidation potential [30], OH radicals decompose the photoresist [16].

Emission spectra of CO (third positive system, $b^3 \Sigma - a^3 \Pi$) [1, 2, 32–35] and another CO (Ångström system, $B^1 \Sigma - A^1 \Pi$) [1, 2, 32–40] are presented respectively in Tables 1(a) and 1(b) [35]. These spectra are readily apparent. The same is also true for spectra of H$_\beta$ (486 nm) and H$_\gamma$ (434 nm) in the 250–650 nm range at around $t = 1.0$ s, as shown in Figs. 4(a) and 4(b).

Figure 5 shows temporal variations of emission intensity of OH ($A^2 \Sigma - X^2 \Pi, \Delta v = 0$), H$_a$, O, and CO ($B^1 \Sigma - A^1 \Pi, \Delta v = -1, 484$ nm). The CO emission intensity of $\Delta v = -1$ increased and reached a peak.

Table 1. List of the band-heads of (a) CO (third positive system, $b^3 \Sigma - a^3 \Pi$) and (b) CO (Ångström system, $B^1 \Sigma - A^1 \Pi$) [35]

| Wavelength (nm) | Sequence $\Delta v = (v' - v'')$ | Transition $(v', v'')$ |
|-----------------|-----------------------------------|----------------------|
| 297.74          | -1                                | (0,1)                |
| 313.44          | -2                                | (0,2)                |
| 330.57          | -3                                | (0,3)                |
| 349.33          | -4                                | (0,4)                |

| Wavelength (nm) | Sequence $\Delta v = (v' - v'')$ | Transition $(v', v'')$ |
|-----------------|-----------------------------------|----------------------|
| 412.36          | +1                                | (1,0)                |
| 451.09          | 0                                 | (0,0)                |
| 483.53          | -1                                | (0,1)                |
| 519.82          | -2                                | (0,2)                |
| 561.02          | -3                                | (0,3)                |
| 607.99          | -4                                | (0,4)                |
maximum value at $t = 1.1$ s. Subsequently, the CO emission intensity of $\Delta v = -1$ decreased monotonically for 10 s until it became undetectable. However, the emission intensities of OH, H$_a$, and O respectively reached minimum values at $t = 1.1$ s, in contrast to the results found for CO.

Figure 6 portrays the CO molecular band spectra obtained using the Ångström system ($B^1\Sigma - A^1\Pi$) for 470–570 nm, which will be used for deeper investigation of the temporal variation of the CO band spectra shape. The CO emission spectra at $t = 0$, 1.0, and 2.0 s are shown. The continuum compositions [41, 42] in these spectra were subtracted and normalized at 484 nm ($\Delta v = -1$). The CO molecular spectra shapes almost all mutually overlapped even though these CO molecular intensities varied greatly, as portrayed in Fig. 4(b).

4. Evaluating CO molecule rotational and vibrational temperatures

Rotational and vibrational temperatures of CO molecules were ascertained from calculations of optical emission spectra of $B^1\Sigma - A^1\Pi$ electronic transitions of the CO molecule. The electronic transitions take place from the rotational levels of the various levels of one electronic state to the rotational and vibrational levels of another electronic state. The energy of a molecule is calculated using the sum of electronic energy $T_e$, vibrational energy $G(v)$, and rotational energy $F_v(J)$, as shown below.

$$E = T_e + G(v) + F_v(J)$$

(2)

Therein, $v$ represents a vibrational state; $J$ denotes a rotational state. The energy difference $\Delta E$ from an upper state to a lower state is presented below.

$$\Delta E = \Delta T_e + \Delta G(v) + \Delta F_v(J)$$

$$= T_{e'} - T_{e''} + G(v') - G(v'') + F_{v'}(J') - F_{v''}(J'')$$

(3)

Therein, the upper state and the lower state are represented respectively by apostrophes and double quotation marks. Each molecular band emission spectrum depends on the rotational and vibrational states according to the rotational and vibrational temperatures. Assuming that the number density of excited molecules in the upper state follows a Boltzmann distribution, the spectrum is calculated using spectrum emission coefficients. The spectrum emission coefficients of diatomic molecules are calculated using the following equations [38, 43].

Figure 5 Temporal variations of emission intensities of (a) OH, (b) H$_a$, (c) O, and (d) CO ($B^1\Sigma - A^1\Pi$, $\Delta v = -1$, 484 nm) before and during photoresist removal.
Emission coefficient:

\[
\varepsilon_{n'n''v'v''J'J''} = \frac{1}{h \lambda} N_{n'n''v'v''J'J''} A_{n'n''v'v''J'J''} \cdot \exp\left(-\frac{\hbar c J' J''}{k T_{ex}}\right) \cdot \exp\left(-\frac{\hbar c G(v')}{k T_{rot}}\right)
\]

Therein, \(N_{n'n''v'v''J'J''}\) denotes the number density of molecules in an upper state, \(A_{n'n''v'v''J'J''}\) denotes a transition probability from an upper state to a lower state, \(n', n'', v', v'', J', J''\) respectively denote an electronic state, a vibrational quantum number, and rotational quantum numbers of upper and lower states.

Number density in the upper state:

\[
N_{n'n'v'J'} = \frac{N}{(T_{ex}, T_{vib}, T_{rot})} \cdot Z(T_{ex}, T_{vib}, T_{rot}) \cdot \left(\frac{J' + 1}{2J' + 1}\right) \cdot \exp\left(-\frac{\hbar c g(J')}{k T_{ex}}\right) \cdot \exp\left(-\frac{\hbar c G(v')}{k T_{rot}}\right)
\]

Transition probability:

\[
A_{n'n''v'v''J'J''} = A_{n'n''q'v''} S_{J'}
\]

\[
A_{n'n''} = \frac{64\pi^4 \alpha_e^2}{3\hbar^4 c^3 \lambda_n^3} |R_{e}^{n''}|^2
\]

Hönl–London Factors for \(P, Q,\) and \(R\) branches:

\[
S_{J'}^P = \frac{(J' + 1 + \Lambda')(J' + 1 - \Lambda')}{J' + 1}
\]

\[
S_{J'}^Q = \frac{(2J' + 1 + \Lambda^2)}{(J' + 1)^2}
\]

\[
S_{J'}^R = \frac{(J' + \Lambda')(J' - \Lambda')}{J'}
\]

Rotational energy:

\[
F_v(J) = B_v J(J + 1) - D_v J^2 (J + 1)^2
\]

Vibrational energy:

\[
G(v) = \omega_e \left(\frac{v + \frac{1}{2}}{2}\right) - \omega_e x_e \left(\frac{v + \frac{1}{2}}{2}\right)^2
\]

In those equations, \(N\) represents the total number density of molecules, \(Z\) stands for the internal state sum of molecules, \(q'v''\) are Franck–Condon factors, \(S_{J'}\) is the intensity factor, \(|R_{e}^{n''}|\) denotes the electronic transition moment deduced from the average radiative lifetimes of the \(B'\Sigma - A'\Pi\) states of CO [37], \(\hbar\) is Planck’s constant, \(k\) is Boltzmann’s constant, \(c\) represents the velocity of light, \(T_{ex}\) stands for the excitation temperature, \(T_{rot}\) denotes the vibrational temperature, \(T_{rot}\) expresses the rotational temperature, \(\alpha_e\) and \(\omega_e x_e\) are vibrational constants, \(L\) represents the total orbital angular momentum. Also,

\[
\Delta E = \frac{1}{\lambda_{n'n''v'v''J'J''}}
\]

where \(\lambda_{n'n''v'v''J'J''}\) (cm) represents the wavelength of
transition spectra from an upper to lower state. For this study, we measure the emission spectra of the CO molecule band (Ångström system, B'Σ - A'Π, which is presented in Table 1(b)). Figure 7 portrays calculated spectra with experimentally obtained spectra at t = 1.0 s during photoresist removal in the 400–650 nm range. A continuum light component [41, 42] in the experimental spectra was subtracted. Fitting the calculated theoretical spectra as functions of rotational and vibrational temperatures with experimentally obtained spectra, the respective rotational and vibrational temperatures were found to be 1500 and 2500 K.

5. Discussion

For this study, we performed a spectroscopic diagnosis during photoresist removal using microwave plasma in saturated water vapor. The characteristic band spectra were found. These band spectra appeared especially at the beginning of photoresist removal in the 250–650 nm range, although they were much weaker than the emission spectra of OH (A'Σ – X2Π), O, and H, as depicted in Fig. 3. By comparing the observed band spectra with reference spectra of CO (Ångström system, B'Σ – A'Π) [1, 2, 32–40], CO (Herzberg system, C'Σ – A'Π) [35], CO (Asundi bands, a13Σ – a3Π) [35, 40], CO (Triplet bands, d1Δ – a3Π) [35, 40], CO2 (carbon monoxide flame bands, 1B2 – X1Σ) [35], CO2+ (Fox, Duffendack, and Barker’s system, A2Π – X2Π) [11, 35, 40], C2 (Swan system, A3Π – X2Π) [35, 43], CH (4300 Å system, A2Δ – X2Π) [35], and CH (3900 Å system, B'Σ – X2Π) [35] including carbon component, we identified the measured spectra as CO molecule bands of the Ångström system (B'Σ – A'Π) and the third positive system (b3Σ – a3Π) [1, 2, 32–40], as shown in Figs. 4(a) and 4(b).

Results show that the Ångström system (B'Σ – A'Π) was spectrally isolated from the other systems, although the third positive system was partially overlapped with the OH (A2Σ – X2Π) band system. The electronic energy of the upper state of CO (B'Σ) and CO (b3Σ) is lower than that of Hα, Hβ, Hγ, and O [32, 33, 36, 45, 46], suggesting that there might be sufficient electrons with high energy to excite CO molecules to the states of (B'Σ, b3Σ) in microwave-excited plasma. Observation of the CO molecular band system indicates clearly that CO arises from plasma-induced oxidation of the polymeric photoresist material.

The CO band spectra were also observed in radiofrequency (rf) O2 plasma during photoresist removal [1, 2]. The plasma is produced using rf coils at rf frequency of 13.56 MHz, pressure of 27 Pa, power of 300 W, and an O2 flow rate of 55 sccm. The photoresist (SC-180; Fujifilm Hunt Chemicals USA Inc.) was coated onto a 2-inch Si wafer. The photoresist thickness was 3 mm. For O2 plasma ashing, excited oxygen atoms decompose the photoresist film and produce excited-state CO molecules as well as hydrogen atoms. The measured CO molecular band intensity was almost comparable with the OH band spectral intensity [1, 2]. However, from this study, we observed intense OH band spectra and H-and-O atomic lines, whereas the intensity of CO band spectra is much weaker than that of other spectra. This finding suggests that the reactive radical densities of, for example OH, H, and O supplied from water molecules, are much greater than the CO molecular density from the photoresist film compared with the O2 plasma ashing case.

Regarding the existence of CO2 ions, the emission spectra of CO2 ions (288 nm) were confirmed only in CO2 plasma under the condition of higher CO2 gas composition [11]. The CO2 plasma was produced at an rf frequency of 2.0 and 13.56 MHz, 6.7 Pa pressure, 300 W power, and a CO2 gas flow rates of 40 to 500 sccm. The energies for dissociation and ionization of CO2 molecules are presented below.

\[
\text{CO}_2 + e \rightarrow \text{CO} + \text{O}^+ + e \quad 5.4 \text{ eV} \quad \text{(dissociation)} \quad (16)
\]

\[
\text{CO}_2 + e \rightarrow \text{CO}_2^+ + 2e \quad 13.8 \text{ eV} \quad \text{(ionization)} \quad (17)
\]

When the plasma is generated using an rf

| Table 2. Molecular constants of electronic states for CO (Ångström system, B'Σ – A'Π) [34, 38, 39] |
| --- |
| State | \( T_e \) (cm\(^{-1}\)) | \( \alpha_c \) (cm\(^{-1}\)) | \( \alpha_c x_c \) (cm\(^{-1}\)) | \( B_c \) (cm\(^{-1}\)) | \( \alpha_c \) (cm\(^{-1}\)) | \( D_c \) (cm\(^{-1}\)) |
| B'Σ | 86948 | 2150.41 | 34.09 | 1.961 | 0.027 | 6.48 \times 10^{-6} |
| A'Π | 65075 | 1515.61 | 17.25 | 1.612 | 0.022 | 6.45 \times 10^{-6} |
generator with a lower frequency, the electron energy presumably increases because the electrons are likely to be accelerated by the electric field in such a low pressure condition of 6.7 Pa. The emission spectra of CO$_2$ ions are also observed at low pressure [35]. The emission intensity of CO$_2$ ions (288 nm) was higher than that of the oxygen line of 777 nm in CO$_2$ plasma ashing [11]. The CO$_2$ ion emission intensity was too low to be measured in this study, indicating that the CO$_2$ molecular density was sufficiently low during the ashing process.

In addition, a broad continuum emission was observed in the 250–650 nm range, especially at $t = 1.0$ s, as shown in Figs. 4(a) and 4(b). Because the operating pressure is as high as 6 kPa and because the microwave-excited plasma was produced in the narrow region, high-density plasma might be generated above the Si wafer including high-density neutral molecules. The broad continuum emission might be attributed to Bremsstrahlung [41, 42]. It is noteworthy that, $N_2$ second positive system ($C(\Pi \Delta - B(\Pi \Delta))$ [35] was not observed clearly in this study, but it was observed in the O$_2$ ashing plasma [1, 2] as shown in Figs. 4(a) and 4(b). This result suggests that the presence of negligibly small molecular nitrogen in the system accounts for the observable emission bands.

The emission intensity of CO ($B(\Sigma \Delta - A(1\Pi), \Delta \nu = -1, 484$ nm) reached a maximum value at 1.1 s after plasma ignition, whereas that of OH ($A(\Sigma \Delta - X(2\Pi), \Delta \nu = 0)$, H$_\alpha$, and O reached a minimum value simultaneously, as presented in Fig. 5. The temporal variations of other CO ($B(\Sigma \Delta - A(1\Pi), \Delta \nu = +1, 0, -2, -3, \text{and} -4)$ as well as CO ($b(3\Sigma - a(3\Pi), \Delta \nu = -1, 298$ nm) band spectra intensity followed an almost identical tendency as that of CO ($B(\Sigma \Delta - A(1\Pi), \Delta \nu = -1)$ (not shown here). These results indicate that the compositions of radicals and chemical species, and their densities in the plasma, were changed drastically during a few seconds after plasma ignition, which suggests that the photoresist on the half-inch Si wafer, where the optical rod was located, has been removed completely in a few seconds. Consequently, monitoring the emission intensity of CO molecules becomes a matter of endpoint detection. This endpoint detection technique will be useful to control damage to the Si wafer during manufacturing. Temporal variations of CO ($b(3\Sigma - a(3\Pi), 297.7$ nm), CO ($B(\Sigma \Delta - A(1\Pi), 519.8$ nm), H$_\alpha$, and O (615.6 nm) were reported when using O$_2$ plasma ashing [1, 2]. As one earlier study found [2], the emission intensity of CO ($B(\Sigma \Delta - A(1\Pi), 519.8$ nm) reached a maximum value at around 6.3 min after plasma ignition ($t = 0$ s). The H$_\alpha$ emission intensity also increased concomitantly with increasing treatment time [2]. By contrast, this study demonstrated that the H$_\alpha$ emission intensity decreased slightly and reached a minimum value, in contrast to results obtained for O$_2$ plasma ashing, when CO band spectra reached a maximum value during photoresist ashing. Furthermore, the H$_\alpha$ intensity increased and became saturated rapidly after the CO band spectra started to decrease, suggesting abstraction of H atom from the photoresist film [2]. The emission intensity of O decreased when CO overlapped with OH, and CO intensities (283.0, and 308.9 nm) increased in O$_2$ plasma ashing. However, OH and O intensities decreased and increased gradually when CO ($B(\Sigma \Delta - A(1\Pi), b(3\Sigma - a(3\Pi)$ band spectra increased in this study. Temporal variations of OH, O, and H show clearly that the origins of H atom differ greatly from that of OH and O species, supporting the hypothesis of the H abstraction reaction on the photoresist film surface. It is noteworthy that rapid variations of OH and O radicals show an excess amount of radical species derived from water vapor, resulting in enhancement of surface reaction on the photoresist film and a high-speed ashing process.

To investigate the temporal variation of the rotational and the vibrational temperatures of CO molecules, measured CO band spectra were compared at $t = 0, 1.0,$ and 2.0 s, as depicted in Fig. 6. These spectra are overlapped almost completely for 2 s after plasma ignition, indicating that the rotational and vibrational temperatures of the CO molecules were stable and almost constant during photoresist removal, even though the CO, O, and H$_\alpha$ intensities were altered dramatically. Therefore, the increase of emission intensity of CO molecules, as presented in Fig. 5(d), showed a rapid increase of CO molecule density above the Si wafer.

The following scenario is proposed for a photoresist removal mechanism in the case of using microwave-excited plasma in saturated water vapor under the reduced pressure condition. First, radicals such as OH, H, and O derived from water vapor are produced by microwave plasma. Then these reactive species react with the photoresist film and cause desorption of carbon-including molecules such as CO$_3$ and C$_2$H$_6$. Subsequently, the molecules which contain desorbed carbon increase in number. Electron impacts oxidize and excite them. They are de-excited above the Si wafer because of the increased CO emission intensity. Finally, the CO emission intensity decreases when the photoresist
film is removed by the plasma. For the 400–650 nm range, we conducted calculations of C₂ swan band spectra [44] to elucidate the possibility of appearance and overlap. In doing so, we found out that the C₂ swan spectra intensity would be negligibly small. Carbon-containing species would most likely be CO molecules, although we were unable to detect unexcited radical species. In this study, the calculated CO spectra show very good agreement with experimentally obtained spectra for obtained CO rotational and vibrational temperatures, respectively, of 1500 and 2500 K.

6. Conclusions
Optical emission images and optical emission spectra during photoresist removal were investigated using microwave-excited plasma. In this study, the microwave plasma was generated at a power of 200 W, and at a water vapor pressure of approx. 6 kPa. The distance between the bottom of the slot antenna and the wafer surface was fixed at 2 mm. A film thickness of positive-tone Novolak photoresist was 1.0 μm. White emission was observed at the moment of microwave-excited plasma ignition (t = 0 s). After a few seconds, the white emission turned to a red-purple color. The emission spectra of OH (A’Σ – X’Π, Δv = 0), H_a (656 nm), H_b (486 nm), H_f (434 nm), and O (777 nm) derived from dissociation of water molecules were observed clearly during photoresist removal. The emission spectra of CO (third positive system, b’Σ – a’Π) and CO (Ångström system, B’Σ – A’Π) were also observed at around t = 1.0 s. The emission intensity of CO (B’Σ – A’Π, Δv = -1, 484 nm) reached a maximum value at t = 1.1 s, whereas those of OH, H_a, and O reached their respective minimum values at t = 1.1 s. The CO molecular spectra shapes almost overlapped during photoresist removal. These results indicate the occurrence of a high-speed ashing process. Rotational and vibrational temperatures of the CO molecules during photoresist removal were found, respectively, to be 1500 and 2500 K.

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References
1. E. O. Degenkolb, C. J. Mogab, M. R. Goldrick, and J. E. Griffiths, Appl. Spectrosc., 30 (1976) 520.
2. J. E. Griffiths and E. O. Degenkolb, Appl. Spectrosc., 31 (1977) 134.
3. S. Fujimura, K. Shinagawa, M. T. Suzuki, and M. Nakamura, J. Vac. Sci. Technol., B 9 (1991) 357.
4. K. Taniguchi, K. Tanaka, T. Inomata, and M. Kogoma, J. Photopolym. Sci. Technol., 10 (1997) 113.
5. K. Tanaka, T. Inomata, and M. Kogoma, Plasmas Polym., 4 (1999) 269.
6. H. Horibe, M. Yamamoto, T. Ichikawa, T. Kamimura, and S. Tagawa, J. Photopolym. Sci. Technol., 20 (2007) 315.
7. H. Horibe, M. Yamamoto, Y. Goto, T. Miura, and S. Tagawa, Jpn. J. Appl. Phys., 48 (2009) 026505.
8. Y. Goto, Y. Angata, M. Igarashi, M. Yamamoto, T. Nobuta, T. Iida, A. Kono, and H. Horibe, Jpn. J. Appl. Phys., 51 (2014) 026504.
9. M. Takahashi, H. Ishikawa, T. Asano, and H. Horibe, J. Phys. Chem. C, 116 (2012) 12578.
10. Y. Goto, Y. Angata, E. Tsukazaki, S. Takahashi, K. Koike, T. Yamagishi, and H. Horibe, Jpn. J. Appl. Phys., 53 (2014) 02BB04.
11. Y. Susa, H. Ohtake, Z. Jianping, L. Chen, and T. Nozawa, J. Vac. Sci. Technol. A 33 (2015) 061307.
12. T. Ishijima, H. Hotta, and H. Sugai, Appl. Phys. Lett., 91 (2007) 121501.
13. T. Ishijima, H. Sugiiura, R. Saito, H. Toyoda, and H. Sugai, Plasma Sources Sci. Technol., 19 (2010) 015010.
14. R. Saito, H. Sugiiura, T. Ishijima, and H. Toyoda, Curr. Appl. Phys., 11 (2011) S195.
15. T. Takahashi, N. Takada, and H. Toyoda, Jpn. J. Appl. Phys., 53 (2014) 07KE01.
16. T. Ishijima, K. Nosaka, Y. Tanaka, Y. Uesugi, Y. Goto, and H. Horibe, Appl. Phys. Lett., 103 (2013) 142101.
17. N. Sato, S. Izuka, Y. Nakagawa, and T. Tsukada, Appl. Phys. Lett., 62 (1993) 1469.
18. T. Ikushima, Y. Okuno, and H. Fujita, Appl. Phys. Lett., 64 (1994) 25.
19. D. Korzec, F. Werner, R. Winter, and J.
Engemann, *Plasma Sources Sci. Technol.*, 5 (1996) 216.
20. R. Winter, D. Korzec, and J. Engemann, *Surf. Coat. Tech.*, 93 (1997) 134.
21. C. Tian, T. Nozawa, K. Ishibashi, H. Kameyama, and T. Morimoto, *J. Vac. Sci. Technol.*, A 24 (2006) 1421.
22. H. Suzuki, S. Nakano, H. Itoh, M. Sekine, N. Hori, and H. Toyoda, *Jpn. J. Appl. Phys.*, 55 (2016) 01AH09.
23. H. G. Booker, *J. IEE III A* 93 (1946) 620.
24. W. H. Watson, The physical principles of waveguide transmission and antenna systems, Oxford University Press, Clarendon, pp.137 (1947).
25. F. Werner, D. Korzec, and J. Engemann, *Plasma Sources Sci. Technol.*, 3 (1994) 473.
26. S. Khumpuang, H. Maekawa, and S. Hara, *IEEE Trans. Sensors Micromachines*, 133 (2013) 272.
27. S. Khumpuang and S. Hara, *IEEE. T. Semiconduct. M.*, 28 (2015) 393.
28. A. A. Joshi, B. R. Locke, P. Arce, and W. C. Finney, *J. Hazard. Mater.*, 41 (1995) 3.
29. J. S. Clements, M. Sato, and R. H. Davis, *IEEE Trans. Ind. Appl.*, 32 (1996) 106.
30. P. Sunka, V. Babicky, M. Clupek, P. Lukes, M. Simek, J. Schmidt, and M. Cernak, *Plasma Sources Sci. Technol.*, 8 (1999) 258.
31. P. Bruggeman, D. C. Schram, M. G. Kong, and C. Leys, *Plasma Process. Polym.*, 6 (2009) 751.
32. Raymond T. Birge, *Phys. Rev.*, 28 (1926) 1157.
33. O. S. Duffendack, and G. W. Fox, *Astrophys. J.*, 65 (1927) 214.
34. P. H. Krupenie, The Band Spectrum of Carbon Monoxide, Institute for Basic Standards National Bureau of Standards, Washington D.C. (1966).
35. G. Herzberg, The Identification of Molecular Spectra, Chapman and Hall, London (1976).
36. I. Tobias, R. J. Fallon, and J. T. Vanderslice, *J. Chem. Phys.*, 33 (1960) 1638.
37. J. Rogers, and R. Anderson, *J. Opt. Soc. Am.*, 60 (1970) 278.
38. G. Herzberg, Molecular Spectra & Molecular Structure Vol. 1, Chapman and Hall, London (1975).
39. R. Kepa and M. Rytel, J. Phys. B: *At. Mol. Opt. Phys.*, 26 (1993) 3355.
40. C. Rond, A. Bultel, P. Boubert, and B. G. Cheron, *Chem. Phys.*, 354 (2008) 16.
41. H. R. Griem, Principle of Plasma Spectroscopy, Cambridge University Press, Edinburgh (1997).
42. S. Park, W. Choe, H. Kim, and J. Y. Park, *Plasma Sources Sci. Technol.*, 24 (2015) 034003.
43. G. Herzberg, The spectra and structures of simple free radicals, Dover Publications, New York (1975).
44. Y. Haruta, K. Fujimoto, S. Horita, Y. Tanaka, Y. Uesugi, and T. Ishijima, *J. Phys. Conf. Ser.*, 441 (2013) 012017.
45. R. J. Fallon, I. Tobias, and J. T. Vanderslice, *J. Chem. Phys.*, 34 (1961) 167.
46. Atomic Spectra Database NIST, https://www.nist.gov/pml/atomic-spectra-database.