Analysis by Surface-sensitive Second Harmonic Generation of Si(111)7 × 7 Exposed to High-purity Ozone Jet for Oxide Film Formation†

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We observed an *in situ* process of ozone adsorption on Si(111)7 × 7 at different temperatures by second harmonic generation (SHG). On ozone exposure, the second harmonics (SH) intensity descreased close to a detectable limit on the surface at room temperature (RT). However, we observed the appearance of another SH intensity during ozone exposure at elevated substrate temperatures between 260 °C and 400 °C, after it decreased in the same way as that at RT. On these surfaces, the profile of SH intensity recovery by desorption of adsorbed species indicated that different adsorbed species were formed during surface exposure to ozone at different substrate temperatures: those at RT are weakly adsorbed species for termination of dangling bonds and insertion into backbonds, and those at higher temperatures have an Si–O–Si network which is more stable and desorbs at higher temperatures than 700 °C. We conclude that the SH intensity that appeared on the surfaces at elevated temperatures is due to more stable SiO_2-like Si–O–Si bonding as an initial step of oxide formation. © 1997 by John Wiley & Sons, Ltd.

INTRODUCTION

The microfabrication of electronic devices requires more and more controlled materials processing in a well-defined environment.[1] The formaton of silicon dioxide (SiO_2) thin film[2] is one such critical process because, with larger integration, a thinner oxide closer to that of native oxide is indispensable. In this range of thickness, oxidation at a lower substrate temperature is necessary to avoid thermal damage in the device structure. For such a purpose, more active oxidants such as ozone[3] must be used.

A conventional ozonizer can only supply <10% ozone in the mixture of ozone and oxygen. A high-purity ozone beam of constant flux can be obtained by an ozone jet generator system,[4] which proved to be effective for the formation of a thin film of CuO.[5] Recently, this high-purity ozone beam was exposed to room temperature (RT) Si(111)7 × 7.[6] With this ozone beam, the Si(111) surface at RT was oxidized and was observed by a shift in the Si 2p peak on x-ray photoelectron spectroscopy (XPS). A lower density of suboxide was formed by ozone on the surface at RT than by molecular oxygen at 400 °C. These are promising results for the effective use of ozone for oxide film formation at a lower substrate temperature, and they are due to the difference in oxidation mechanism between ozone and oxygen.

To synthesize an oxide film of good quality, the kinetics and mechanism of oxidation must be analysed and controlled under the appropriate conditions. Such good conditions for surface reaction can be obtained by *in situ* process analysis. Optical measurement with photon incidence/photon detection does not require a vacuum so it is applicable to *in situ* characterization of material processing. Surface second harmonic generation (SHG)[7,8] is one such characterization technique. It is a non-linear optical effect converting the wavelength of the incident laser beam into half its initial value. This phenomenon is allowed in those media without inversion symmetry. Hence, in the case of a single-crystal silicon surface, second harmonics (SH) are generated only at surfaces, so the signal gives information exclusively on surface phenomena.

We applied this method to the characterization of initial oxidation of a silicon surface using a high-purity ozone beam. In this paper, we investigated ozone adsorption on Si(111)7 × 7 at different temperatures and the subsequent initial step of oxide formation *in situ* by SHG. On surfaces at elevated temperatures between 260 °C and 400 °C we found that after the SH intensity had decreased, a small SH intensity appeared in the same exposure as it approached the detectable limit on an RT surface. On these surfaces, recovery of SH intensity by desorption of adsorbed species indicated the existence of different adsorbed species formed from ozone molecules at different substrate temperatures. Therefore, we conclude that this appearance of SH intensity on the surfaces at elevated temperatures during their exposure to ozone is due to the SiO_2-like Si–O–Si network formation. This was supported by the

measurement of O 1s peak intensity and Si 2p chemical shift by XPS.

EXPERIMENTAL

We used an ultrahigh vacuum chamber with a base pressure of $\sim 3 \times 10^{-8}$ Pa. As shown in Fig. 1, it is equipped with a high-purity ozone beam generator system for oxidation processing, and, for surface characterization, a low-energy electron diffraction (LEED) apparatus, an x-ray source with a double-pass cylindrical mirror analyser (CMA) for XPS and an optical set-up for surface SHG measurement.

After chemical cleaning to remove organic contaminants and placing in an ultrahigh vacuum chamber, Si(111) was first heated to 1200 °C with direct current to remove the native oxide thin film, and then cooled down to RT. The formation of a clean and reconstructed surface of Si(111)7 × 7 was confirmed by XPS and LEED.

The ozone jet generator system[4] has two main parts: a conventional ozonizer and an ozone vessel. The ozonizer generates an ozone–oxygen mixture gas with an ozone concentration of $\sim 5\%$ by electric discharge of pure oxygen. The mixture gas was introduced into a stainless-steel vessel. The temperature of this vessel was cooled down below 100 K and controlled to within an accuracy of 0.1 K by the cryocooler and heater. Ozone was liquefied and accumulated in the vessel separately only after the evacuation of oxygen gas by using the large difference in saturation vapour pressure of ozone and oxygen in the low-temperature region. Liquefied

ozone is estimated to have a purity of >98 mol.%.[5] After accumulation of liquid ozone, the vessel was isolated from the evacuation system. The flux of ozone beam coming into the chamber was controlled by the vessel temperature (i.e. saturated vapour pressure) and the conductance of the aperture between the ozone vessel and the chamber. The concentration of ozone at the sample position in the chamber was confirmed to be >80 at.% by mass spectrometry.[5]

For SH measurement, an Nd:YAG laser was used as the light source with a series of optical devices for rotation of the plane of polarization of incident light. The laser wavelength was 1.064 μm, with a pulse repetition rate of 10 Hz and a pulse width of 10 ns. The light was incident onto the surface through a viewing port and was focused in the spot of 2.5 mm diameter on the sample surface. The intensity of the incident beam was 70 mJ per pulse at the sample, i.e. 1.4×10^8 W cm^{-2}, which is under the threshold for optical breakdown.[9] Second harmonic light of 532 nm was detected in the direction of the reflectance angle by a photomultiplier after separating only SH light by a grating-type monochromator. In each measurement, the SH intensity averaged by boxcar for 100 laser shots was recorded.

X-ray photoelectron spectroscopy was applied for the measurement of O 1s and Si 2p peaks on clean Si(111)7 × 7 at RT and on the surfaces after they were exposed to 20L ozone at RT, 260 °C and 380 °C. Spectra were obtained by using a double-pass cylindrical mirror electron analyser (PHI15-255) with Mg Kα x-rays. The analyser was operated at a pass energy of 50 eV for each scan.

RESULTS

Adsorption of a high-purity ozone beam on Si(111)7 × 7 at different substrate temperatures was observed *in situ* by SHG as indicated in Fig. 2. In the initial exposure of <5L, because of the reaction of active and vacant dangling bonds with incident particles in the submonolayer regime, the SH intensity decreased
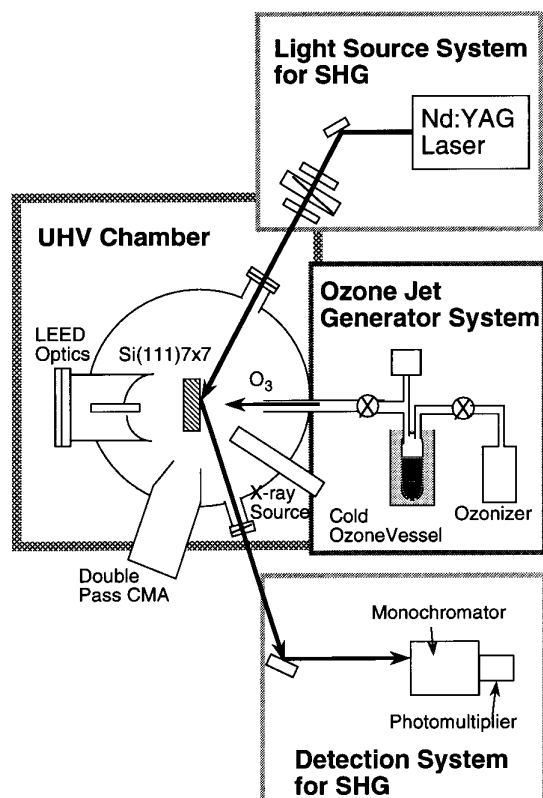

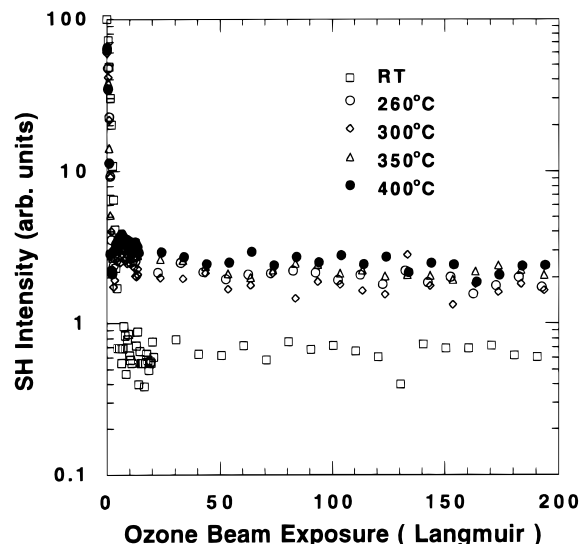**Figure 1.** Schematic diagram of the experimental system.

Figure 2. Second harmonic intensity decay during exposure of ozone with substrate temperature: RT (□); 260 °C (○); 300 °C (◇); 350 °C (△); 400 °C (●).

drastically. With exposures of > 5L, the SH intensity at RT for Si(111)7 × 7 reached close to the detectable limit. However, in the case of exposure of the surface to ozone at elevated temperatures such as 260 °C, 300 °C, 350 °C and 400 °C, the SH intensity was still observed but of low magnitude. It was almost constant for further increase of substrate temperatures and for increase of exposure doses. As already clarified in detail by Höfer *et al.*,[10] the SH intensity on a clean Si(111)7 × 7 surface is dependent on the substrate temperature: increasing substrate temperature decreases SH intensity. In our measurement, each SH intensity is plotted without any normalization of intensity for different temperatures, which is why each initial SH intensity with no exposure is not equivalent to each other, as shown in Fig. 2. The dependence of SH intensity that appeared at this elevated temperature on the intensity of the incident pump laser beam showed second-order non-linearity.

During the cooling procedure of this surface after its exposure to ozone at 380 °C, the temperature dependence of SH intensity was investigated and shown in Fig. 3. As the temperature decreased down from 380 °C to RT, the SH intensity was amost constant or slightly decreasing with decreasing substrate temperature, and it recovered to the same SH intensity after increasing the temperature again to 380 °C. This was a completely different temperature dependence from that on the clean surface.[10] We also checked the temperature dependence of clean Si(111)7 × 7 as shown in Fig. 4 in the temperature range between RT and 450 °C, and the dependence was found to be identical to that reported previously.[10]

The temperature effect on the SH intensity was observed in a wider temperature range for the same sample: the sample was exposed to ozone at 380 °C, cooled down to RT and then increased again to higher than 850 °C. The results are indicated by closed circles in Fig. 5. The almost constant or gradual increase of SH intensity continued until the temperature reached 700 °C, but between 700 °C and 800 °C we observed a rapid, sharp increase of SH intensity to reach an intensity more than five times as large as that at 380 °C. After
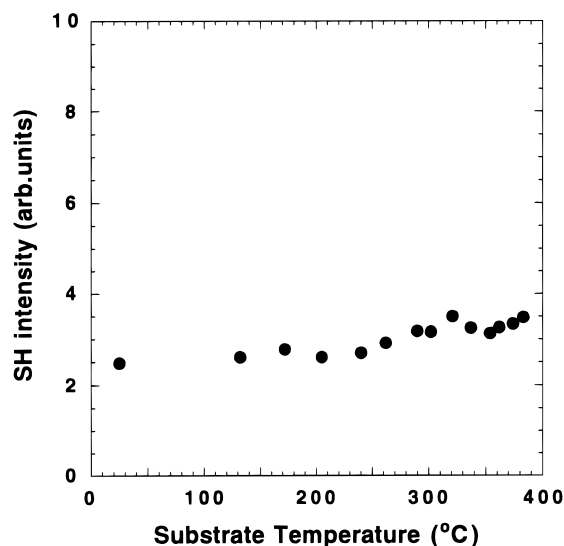

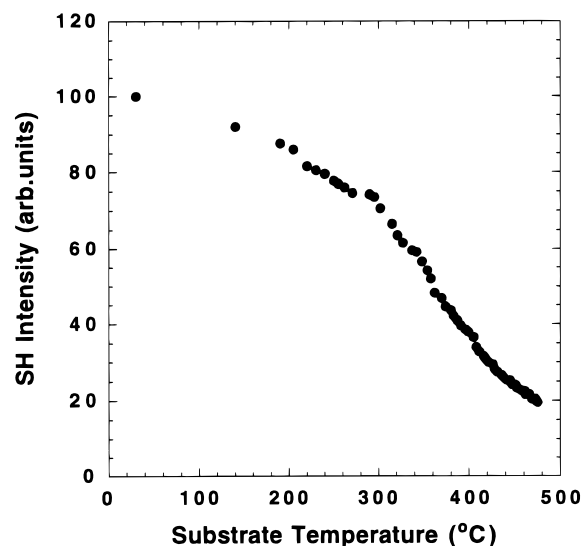**Figure 4.** Temperature dependence of SH intensity on clean Si(111)7 × 7.

this rapid increase, it reached a constant level that was almost equivalent to that of the clean Si(111)7 × 7 surface at the same substrate temperature.

We also observed the temperature effect on surface SH intensity after ozone exposure at other different temperatures. The open circles in Fig. 5 indicate the surface temperature effect of SH intensity after the sample was exposed to 20L ozone at 260 °C. In the lower temperature region (< 600 °C) the SH intensity started to recover with a faster increasing rate than that for ozone exposure at 380 °C. The increase in the temperature region between 700 and 800 °C was not as sharp as observed for ozone exposure at 380 °C (●) in Fig. 5. The open squares in Fig. 5 indicate the SH intensity increase after the sample at RT was exposed to a 20L ozone beam. The recovery of SH intensity started just after we started increasing the substrate temperature. No sharp increase in the limited temperature range between 700 and 800 °C was then observed.

As is explained above, the behaviour of the SH intensity change is completely different during increasing

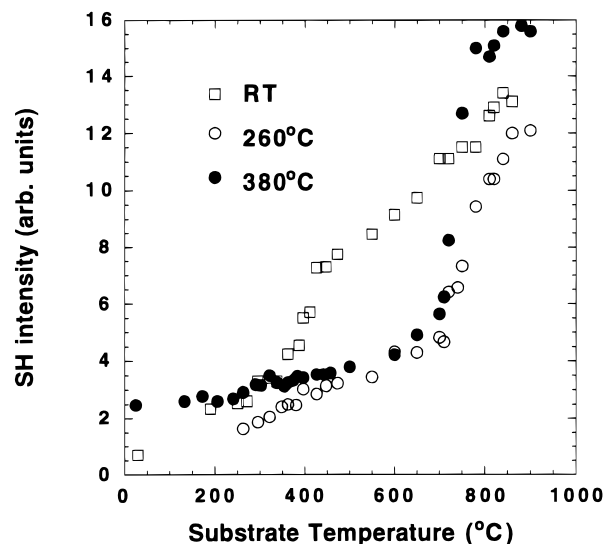**Figure 3.** Temperature dependence of SH intensity on the surface after exposure of Si(111)7 × 7 at 380 °C to an ozone beam.

Figure 5. Temperature dependence of SH intensity after exposure of Si(111)7 × 7 to an ozone beam at: RT (□); 260 °C (○); 380 °C (●).
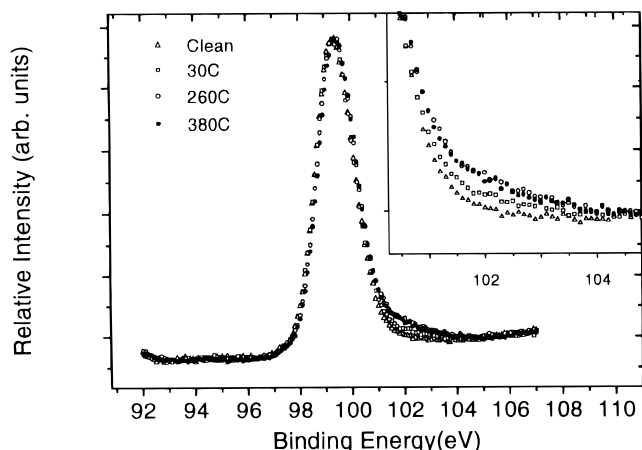
Figure 6. The XPS Si 2p chemical shift on a clean Si(111)7 × 7 surface at RT (△) and on the surfaces after exposure to an ozone beam at RT (□); 260 °C (○) and 380 °C (●).

temperatures of the samples after they were exposed to an ozone beam at different temperatures. However, the SH intensities recovered close to almost the same level. This level was recovered to the level of initial intensity of clean Si(111)7 × 7 surface when it was cooled down again to RT. Also, the recovered SH intensity showed the same temperature dependence as shown in Fig. 4.

The surfaces after their exposure to the 20L ozone at the three temperatures above were also observed by XPS after cooling down to RT. A chemical shift appeared in the shoulder of the Si 2p peak after the sample exposure to ozone at RT, although it is a small amount and inseparable. A further increase of shifted intensity in the case of exposure at 260 °C and 380 °C compared to that of RT was also detected as shown in Fig. 6. We also observed the appearance of an O 1s peak even on the surface exposed at RT, and it increased on surfaces at 260 °C and 380 °C as indicated in Fig. 7.

DISCUSSION

The SH intensity was reduced to close to zero during exposure of Si(111)7 × 7 at RT to ozone, as is shown in Fig. 2. However, with the same exposure at elevated temperatures, we observed second harmonics. The con-
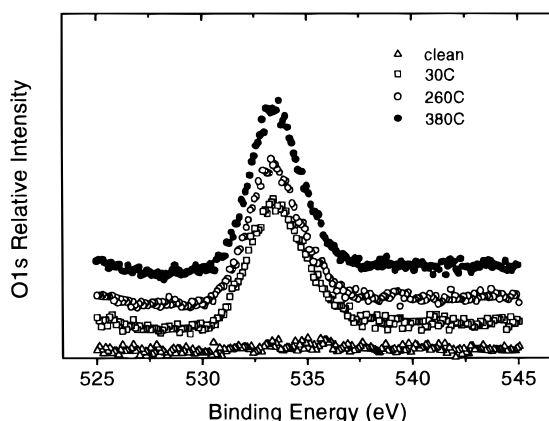

Figure 7. The XPS O 1s intensity on a clean Si(111)7 × 7 at RT (△) and on the surfaces after exposure to an ozone beam at RT (□); 260 °C (○) and 380 °C (●).

dition of SHG as a second-order non-linear optical effect is always the lack of inversion symmetry in the medium, which is satisfied always at surfaces and interfaces. One of the possibilities for the origin of SH light is that there is some clean surface with vacant dangling bonds still remaining. In fact it is reported, in such cases as molecular oxygen adsorption, that a higher temperature reduces the sticking probability on Si(111)7 × 7 because of unstable precursors[11] and it affects the SH intensity behaviour.[12] Another possibility is that a new SH source was formed during ozone exposure at elevated substrate temperatures, which satisfies the condition of SHG. From the comparison of the temperature effect of both ozone-exposed and clean Si(111) surfaces shown in Fig. 3 and Fig. 4, it is clear that the non-linear optical properties of Si(111) are largely modified by its exposure to ozone. This suggests that the formation of a new SH source is more probable.

As a new SH source, the formation of an SiO_2-like Si–O–Si network accelerated by elevated temperature is expected by the fact that the SH intensity showed a rapid increase between 700 and 800 °C during increasing the substrate temperature after exposure to ozone at 380 °C in Fig. 5 (●). Because of its recovery after this increase to the initial intensity equivalent to that of a clean surface, this increase is regarded to be due to a desorption process. The temperature range of rapid increase is coincident with the decomposition temperature of an ultrathin oxide film. Ishizaka and Shiraki[13] observed the removal of a chemically prepared thin oxide film on Si(111) and Si(100) around 800 °C. Decomposition was considered to occur with a reaction of Si and SiO_2 to produce vapourized SiO.[14] Thermal desorption spectroscopy (TDS)[15] also showed its desorption peak around 800 °C, although the position of the peak is dependent on the method of oxide formation and its pretreatment. On the contrary, for exposure of the surface at RT to ozone, which led not to the appearance of further SH intensity but to its disappearance, desorption started at a lower temperature [Fig. 5(□)]. We think that this disappearance of SH intensity in the initial ozone exposure was due to adsorption on the dangling bond and, probably, insertion into the backbonds of oxygen species by the ozone beam, because disappearance of SH intensity was also observed on RT Si(111)7 × 7 during molecular oxygen adsorption on the dangling bond and also insertion into Si–Si backbonds,[16] decreasing a small portion of SH intensity further.[17] Our data show that these adsorbed species by ozone beam at RT surface are much less stable than that formed on the surface treated at 380 °C and that they do not form any new SH source like that on the surface at 380 °C.

Therefore, appearance of further SH intensity at higher exposure suggests that existence of a new medium with SHG condition: the formation of an Si–O–Si network and/or Si/SiO_2 interfaces with most of the dangling bonds terminated. Interfaces of Si/SiO_2 satisfies the condition required for a source of second harmonics. In fact, with the use of transparent light for SiO_2, some researchers have reported SHG from the interfaces of Si/SiO_2. The origin of SHG at the interface is attributed to such reasons as strain,[18,19] interface charge and electric field,[20] preparation and roughness[21-23] and dangling bond creation.[24] The

effect of oxide thickness was also observed for SH intensity and considered to be due to multiple reflection of linear optics in the film.[25,26]

The temperature dependence of SH intensity on Si/SiO$_2$ interfaces prepared in conventional thermal oxidization was also observed and discussed in Refs 19, 24 and 27. Govorkov et al.[19] measured the temperature dependence of the SH intensity generated at the surface of Si/SiO$_2$ between 25 °C and 520 °C, and related the observed hysteresis to mechanical stress relaxation at the interface. Hirayama and Watanabe[24] also observed a linear increase of SH intensity generating from the interface while increasing its temperature to 500 °C. They considered this increase to be due to dangling bond creation at the interfaces. Tom et al.[27] observed a recovery in SH intensity on desorption of a thermally grown oxide layer from a surface kept at 900 °C. Although such behaviour is largely dependent on sample preparation treatment, the observed temperature dependence of SH intensity is completely different and the reverse of that for clean Si(111)7 × 7.[10] In our case with a small amount of ozone exposure, adsorbed species on the surface showed a temperature dependence of SH intensity similar to some of the reported results. This supports the idea that a stable Si–O–Si network similar to that of an interface of Si/SiO$_2$ is formed on the surfaces by ozone at elevated temperatures.

It is reported in Refs 25 and 26 that, in a much thicker oxide film, the effect of thickness on SH intensity is observed because of its multiple reflection effect in the film. However, it is different from our case, since our XPS data indicate that the oxide thickness formed at elevated temperatures is less than a few monolayers. Elevated substrate temperatures increased the O 1s intensity or the amount of oxygen after 20L ozone exposure in Fig. 7, but it was not a large increase proportional to an increase in the SH intensity. This SH intensity already appeared after a 5L ozone exposure to the surface at elevated temperatures, where it is not expected to obtain thick SiO$_2$ film, and kept its constant intensity during further exposure (see Fig. 2). Therefore, SH intensity cannot be related to the amount of oxygen species or to the thickness of the oxide film.

In the case of the Si 2p peak in Fig. 6, a chemical shift to higher oxidation number appeared on the surfaces exposed to ozone at RT, and this increased at 260 °C and 380 °C. On the surfaces at elevated temperatures where the appearance of another SH intensity was observed, the formation of a different chemical bond in the stage of initial oxidation was assured to proceed. On an RT surface, a smaller chemical shift of Si 2p compared to that at 260 °C and 380 °C surfaces was

observed, while the amount of oxygen estimated by the O 1s intensity increased from that of a clean surface. We think that ozone at an RT surface decreased the SH intensity by termination of dangling bonds and insertion into backbonds, thus shifting the Si 2p peak. It is expected that only a negligible amount of Si–O–Si network is formed on RT Si(111)7 × 7 and that such unstable intermediates as those on dangling bonds can easily desorb at the lower temperature to recover SH intensity.

Therefore, we can conclude that, under our experimental condition, the appearance of another SH intensity is not related to the thickness of bulk oxide film or to the amount of oxygen on the surface, but is due to more stable chemical bonding on the surface or interface, such as the Si–O–Si bond formed on Si(111) at elevated temperatures. In order to confirm our conclusion, it is necessary to use a characterization method such as thermal desorption spectroscopy (TDS) to detect directly stable Si–O–Si species. Further study is also required for investigations on kinetics and mechanism of adsorption of ozone on Si(111)7 × 7 at RT and elevated temperatures, on the decomposition mechanism of ozone to release atomic oxygen[28] on the surface, on an equivalent or alternative role of ozone for diffusion in oxide film in comparison with that of molecular oxygen[29] and on the growth mechanism of a thin oxide film.[30] We think that the monitoring of these processes is also possible by *in situ* SHG analysis.

CONCLUSION

We observed the appearance of another SH intensity during Si(111)7 × 7 exposure at elevated temperatures between 260 °C and 400 °C to a high-purity ozone beam, after it had decreased due to dangling bond adsorption of oxygen species from ozone. It was clearly indicated from the SH intensity change during desorption of adsorbed species that the characteristics of oxygen species formed by ozone on the surface at different temperatures are different from each other: those species at RT are weakly adsorbed for termination of dangling bonds and insertion into backbonds, while those at higher temperatures have an Si–O–Si network that is more stable and desorbs at higher temperatures than 700 °C. The formation of an Si–O–Si network was also shown from XPS results: an Si 2p peak chemical shift was observed at higher temperatures, although a weaker chemical shift was found with oxygen species on an RT surface.

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