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TOPICAL REVIEW

Silicon oxidation by ozone

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Abstract

Understanding the oxidation of silicon has been an ongoing challenge for many decades. Ozone has recently received considerable attention as an alternative oxidant in the low temperature, damage-free oxidation of silicon. The ozone-grown oxide was also found to exhibit improved interface and electrical characteristics over a conventionally dioxygen-grown oxide. In this review article, we summarize the key findings about this alternative oxidation process. We discuss the different methods of O₃ generation, and the advantages of the ozone-grown Si/SiO₂ interface. An understanding of the growth characteristics is of utmost importance for obtaining control over this alternative oxidation process.

(Some figures in this article are in colour only in the electronic version)

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1. Introduction

1 The continued dominance of silicon as the semiconducting
2 material of first choice within the microelectronics industry
3 is, arguably, due primarily to the ease with which insulating
4 silica may be grown upon it. Aside from any desirable
4 intrinsic electronic properties of silicon, the ability to fabricate
4 devices on wafers at the nanoscale depends upon this
4 essential interfacial property. The continuing drive towards
7 miniaturization, however, places ever greater demands upon
8 the resulting oxide, particularly in the sub-4 nm thickness
8 regime, where it exhibits a compositional and structural
12 transition region extending up to a nanometre in depth [1]. The
12 insulating properties of SiO₂ can therefore be compromised,
leading to device failure.

15 Conventional oxide growth involves exposure of silicon
16 to molecular dioxygen at high temperatures (usually greater
16 than 800 °C [2, 3]) in order to achieve a fast oxide growth
16 rate and ensure the high quality Si/SiO₂ interface needed for
16 device applications. As an alternative strategy, low temperature
17 oxidation would not only reduce the risk of inducing dopant
17 migration, but also enable the processing of temperature-
17 sensitive materials. Among various approaches, advanced
low temperature oxidation methods include microwave plasma

oxidation, photo-oxidation in O_2 , and different techniques using ozone (O_3) as oxidant. It is this latter approach that forms the basis of this review.

Ozone is more environmentally friendly than other oxidizing species such as N_2O and NO_2 , since simply by heating it decomposes into molecular oxygen [4]. Compared to other radical oxygen species, O_3 can be generated in high concentrations, while the molecules exhibit only low kinetic energies according to the thermal velocity distribution. This is a clear advantage over plasma oxidation techniques, which often cause sample damage due to highly energetic particle bombardment. Similarly, photo-oxidation in O_2 requires irradiation by high energy photons (>7.2 eV), which increases the risk of defect formation at the interface [5].

While ozone is well known for its beneficial role in the upper atmosphere (due to its photochemistry ozone acts as a shield for harmful ultraviolet light), it is usually less well known that it is used in large volumes in large-scale industries such as water purification and paper and pulp processing [6]. In the semiconductor industry, the chemical reactivity of ozone has already found applications in the cleaning of wafers.

In 1989, the first to study ozone for silicon oxidation was Chao *et al* [7]. The authors observed an increase in the oxidation rate when O_3 was present at low concentration in O_2 gas. The potential of ozone for low temperature oxidation was soon recognized by Kazor *et al* [8, 9], and with the development of high-purity ozone generators [10, 11, 4] silicon oxidation by ozone has turned into a vibrant research field. In particular, a series of experiments has revealed that the Si/SiO₂ interface formed by the more reactive O_3 is of higher quality than the interface formed by regular O_2 . Amongst these advantages, the ozone-grown interface exhibits less strain [12] and the notorious transition layer is reduced [13–15]. Ozone's oxide has also been tested for MOS-FET operations, where improved reliability characteristics were observed due to the improved interface properties [16].

Most recently, it was shown that the oxidation rate of UV-light excited ozone did not depend on the orientation of the Si crystal surface, which enabled the growth of a high quality oxide film at room temperature even on polycrystalline silicon [17].

Because of these advantages in the oxidation of silicon, ozone has also been tested in the oxidation of other materials, most prominently metal oxides. These materials exhibit a high dielectric constant (κ) and are therefore heavily investigated to replace the silicon oxide, which exhibits only a low dielectric constant, to allow further miniaturization of semiconductor devices.

This topical review will summarize and connect the available literature in the field of silicon oxidation by ozone. First, the different types of ozone generators will be introduced and discussed. Then, the advantages of ozone as oxidant will be presented in more detail. This is followed by an investigation of the growth characteristics. Here, we will find that the growth process is influenced by many parameters, which make a direct comparison between the growth studies difficult. Therefore, due to missing pieces in the puzzle, we will provide a qualitative picture of the oxidation by ozone.

Finally, a brief overview of other oxide materials will be given, where ozone has been successfully applied as an oxidant.

2. Ozone generators

Here, we present a brief overview of the type of ozone generators employed in the study of silicon oxidation by ozone. Chao *et al* [7], who originally studied the potential of ozone as a more reactive oxidant in the oxidation of silicon, employed a commercially available ozone generator, which uses a low pressure mercury UV-light source 'UV/O₂' (two main wavelengths at 185 and 254 nm, at a ratio $\approx 1:10$). This setup, however, only generated an O_3 concentration of 2.25 ppm in the O_2 stream. In order to avoid any UV exposure of the silicon sample, since high energy photons might lead to defect formation at the interface, the UV-ozone generator is kept outside the oxidizing furnace. The same type of ozone generator was also employed by Cui and co-workers [18], who achieved a concentration of 950 ppm of O_3 in the O_2 gas.

Kazor and Boyd [8, 9] used a barrier discharge ozonizer (BDO), sometimes also called silent discharge ozonizer [19], reaching higher O_3 concentrations between 3 and 4% in the O_2 gas. In this approach an AC voltage of several kV is applied across two dielectric coated electrodes, between which O_2 gas is pumped. The electric field produces an avalanche of electrons that directly dissociate the O_2 molecules into O atoms, which subsequently form O_3 molecules. Thus the oxidizing gas pumped into the oxidizing chamber is a mixture of O_2 , O_3 , and O (stated with decreasing concentration).

To move beyond the low-concentration limit, Ichimura and co-workers developed several types of high-concentration ($>70\%$) O_3 generators [10, 20, 11, 21, 4] and tested their applicability in the oxidation of silicon. A key issue for these generator types is the safe handling of the highly-concentrated ozone gas, since at these high ozone concentrations the potential danger of an explosive conversion of O_3 into O_2 has to be considered.

Therefore, any factor, which would favour such an explosive conversion (e.g. catalytic exposure, sudden temperature changes, or mechanical vibrations) has to be eliminated in the generator design (figure 1).

It has also been confirmed that O_3 , despite its high concentration, exhibits a long enough lifetime in the gas phase to react with the silicon sample, as long as the temperature ($<100^\circ\text{C}$) and the pressure ($<4 \times 10^4$ Pa) are controlled [21]. Thus, to avoid decomposition of gas-phase ozone, the heating should be limited to the surface only.

The first type of high-concentration O_3 generator ('Ozone Jet Generator I') [10, 20] utilizes the difference in equilibrium vapour pressure between the liquid phases of O_3 and O_2 . These vapour pressures differ by three-to-four orders of magnitude at 90 K, which are the typical temperature conditions during the ozone 'collecting' cycle.

This allows to selectively liquefy ozone from the incoming O_3/O_2 mixture gas, which is generated from a commercial ozonizer with an ozone concentration of $\approx 5\%$. In this way, liquefied ozone is progressively stored in an ozone vessel with a volume of <0.5 cm³ (in the most recent design, this volume

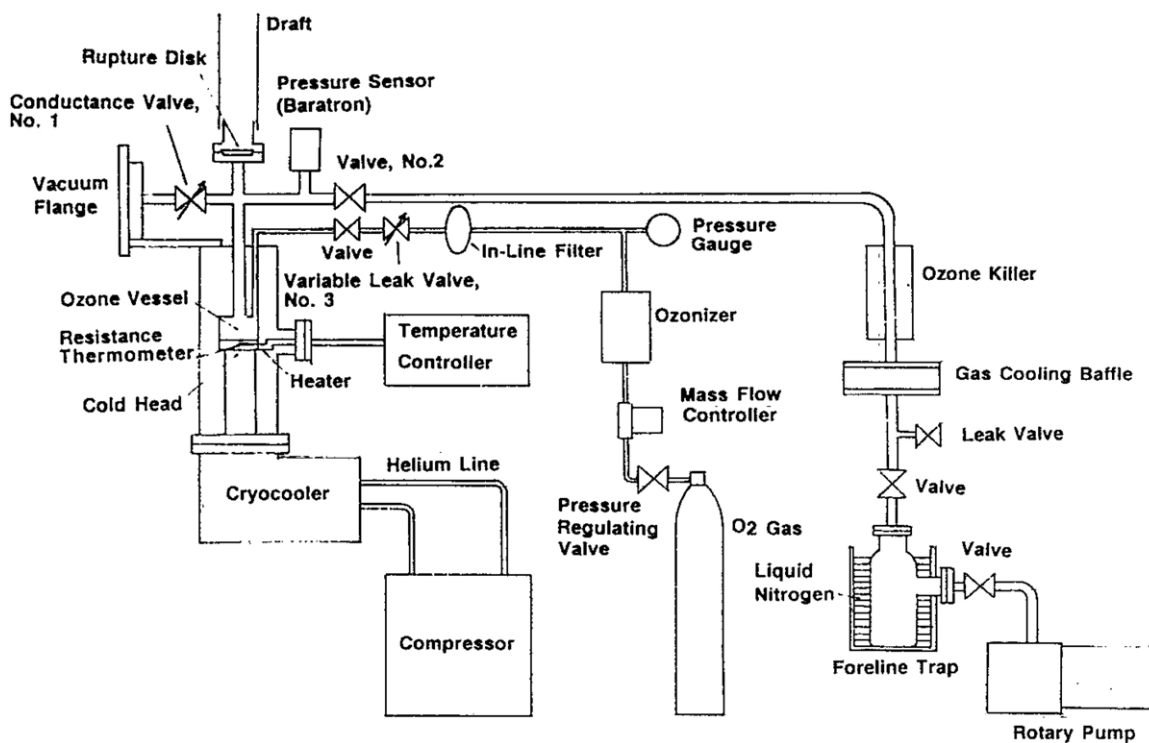


Figure 1. Ozone Jet Generator I: the first type of high-concentration ozone generator as used for low temperature oxidation of silicon. Reprinted with permission from [10]. ©1991, American Institute of Physics.

was further increased to store over 5 cm^3 of liquid ozone). Then, upon slowly heating this ozone vessel, the liquid ozone vaporizes and high-purity ozone gas passes through a nozzle into the oxidation chamber. Due to an undesired trapping of impurity gases, however, the ozone vessel has to be evacuated after only a few collection cycles.

To ensure *continuous* high-concentration O_3 supply, this generator type has been further developed to comprise four ozone vessels ('Ozone Jet Generator II') [4], which independently address the four modes of operation (i.e. accumulation/storage; vaporization/supply; evacuation; and cooling). Still, one major limitation is that this generator type (due to safe-handling considerations) can only supply high-concentration O_3 at low pressure conditions ($< 2 \times 10^3 \text{ Pa}$). This type was therefore mainly used to study how ozone adsorbs on the silicon surface and its initial oxidation stage.

In order to supply high-concentration ozone at high pressure conditions (between 10^3 and 10^5 Pa), and thus study the formation of thin oxide films, an entirely different generator was developed, which employs an adsorption-desorption technique via a silica gel ('ozone silica gel') [11]. Here, instead of liquefying the ozone, the O_3/O_2 gas from the commercial ozonizer passes through a column of silica gel, which is kept at $\approx 213 \text{ K}$. In this gel, the O_3 molecules selectively adsorb. In contrast to the liquid storage, O_3 is stabilized in this adsorption state, which prevents a spontaneous decomposition.

Subsequently, to supply the O_3 into the oxidation chamber, the silica gel is heated to room temperature and the adsorbed ozone gas desorbs. Even though this generator allows in principle a maximum ozone concentration of $\approx 70\%$, even

at high pressure conditions (10^5 Pa), to strictly avoid any explosive decomposition the ozone concentration is usually kept below 30%. To continuously supply high-concentration ozone gas, this generator consists of three such ozone columns containing silica gel, which sequentially cycle through the three modes of operation (i.e. cooling; adsorption/storage; desorption/supply).

To achieve a controllable supply of ozone molecules, a collimated hyperthermal O_3 beam was generated by a technique based on pulsed laser deposition (PLD) [21]. In this design, high-purity O_3 gas, supplied from the previously-described ozone jet generator, passed over a sapphire plate, which was cooled to 30 K , and formed a $100 \mu\text{m}$ thick solid ozone film. A pulsed KrF excimer laser ($\lambda = 254 \text{ nm}$) is aimed at this film and ablates for each laser shot a constant flux of O , O_2 and O_3 molecules (a total of $\approx 10^{17}$ molecules $\text{cm}^{-2}/\text{shot}$) with a small angular spread (6°). The O_3 concentration in the beam was estimated to be $\approx 80\%$, which decreased to $< 10\%$ at higher laser fluences. Nevertheless, since the species received higher translational energy, and in addition the O atom concentration increased, higher laser fluences also resulted in a faster oxidation rate. In general, since the oxygen species in the beam have a much higher kinetic energy than thermal O_3 , the oxidation rate by PLD was faster than by any other generator type. The kinetic energy (KE) distribution was found to be very similar for all three oxygen species, and revealed a mean KE of 0.4 eV and a maximum KE of 2 eV per molecule or atom.

Finally, a high-concentration ozone generator was used in combination with a laser source, which directly illuminated the O_3 gas in the oxidation chamber (UV/O_3) [22]. Different

Table 1. O₃ generators used in the oxidation of silicon by ozone.

Type	Abbrev.	O ₃ conc (%)	References	Remarks
UV-based generator (Hg lamp)	UV/O ₂	<0.1	[7, 18]	
Barrier discharge ozonizer	BDO	3–4	[19]	
Ozone jet generator	OJG	99	[10, 20, 4]	Low pressure (<2 × 10 ³ Pa)
Ozone silica gel	OSG	30–70	[11]	High pressure (<10 ⁵ Pa)
Pulsed laser deposition	PLD		[21]	Hyperthermal beam
UV-assisted (KrF lamp)	UV/O ₃		[22]	Additional UV source

irradiation conditions were tested, including UV-light in a perpendicular and horizontal direction with respect to the silicon sample. The direct UV irradiation of the sample was found not to be mandatory for the increased oxidation rate. Instead, the UV induces the dissociation of O₃, leading to a direct supply of atomic oxygens for the oxidation, which allows a fast oxidation rate even at room temperature. Since O₃ has a high adsorption coefficient in the UV range between 220 and 310 nm, a KrF excimer laser source ($\lambda = 248$ nm) has been used, which provides the necessary high photon density. In comparison, the photo-oxidation of O₂ [23, 24] is less effective, since O₂'s photodissociation rate is only low and necessitates shorter laser wavelengths (usually 172 or 126 nm), which have a short penetration depth in air and are prone to induce defects at the Si/SiO₂ interface [25]. In contrast, the UV-light to dissociate O₃ does not cause any damage to the silicon sample.

A summary of the generator types is given in table 1 while further details on the oxidation kinetics and oxidation rates of each generator type will be discussed in a later section.

3. Advantages of oxidation by ozone

This section summarizes the experiments which have revealed three advantages of using ozone as oxidant. First, the more reactive O₃ gives a faster oxidation rate, which allows the silicon oxidation to proceed at much lower temperatures. Second, the oxidation rate in O₃ was found to be independent of silicon's crystallographic orientation. Finally, the ozone-grown oxide film yields a Si/SiO₂ interface of higher quality than a conventionally grown oxide film (800–900 °C). In this discussion we will include the processing conditions (temperature and ozone concentration), since they were found to influence the growth rate and film characteristics to a certain extent.

3.1. Fast oxidation at low temperatures

Originally, O₃ has been used as a more reactive oxidant to increase the oxidation rate and thus lower the oxidation temperature [7, 26]. By adding photogenerated O₃ (UV/O₂ with 2.25 ppm O₃) to the O₂ gas at oxidation temperatures of 700–800 °C the oxide film was for the same oxidation time 50–100% thicker than in pure O₂ [7]. At higher ozone concentrations (BDO, 3–4 O₃) and lower temperatures (400–800 °C) this growth enhancement was even more pronounced [9, 26] and was found to increase with lower oxidation temperatures (e.g. at 400 °C the O₃/O₂ gas formed an oxide film which was 400% thicker than in pure O₂ [9]). Thus,

at a temperature of 550 °C oxidation in O₃ gave a comparable growth rate to oxidation in pure O₂ at 850 °C [9].

As an alternative, low temperature oxidation reduces the risk of inducing dopant migration and in addition enables processing of temperature-sensitive materials (e.g. plastic and glass substrates). Most recently, this growth rate enhancement was even further boosted, allowing oxidation at room temperature. By exposing high-concentration O₃ gas directly to UV-light (UV/O₃), high quality oxide films were even grown at room temperature [25, 17]. More details about the growth characteristic in an O₃-containing oxidant gas will be discussed in the specified section below.

3.2. Growth rate independent of surface orientation

Conventional oxidation by molecular oxygen shows a strong dependence on the surface orientation, leading to significantly faster growth rates on Si surfaces with {111} orientation than {001}. Therefore, on poly-silicon, which exhibits various crystallographic orientations separated by grain boundaries, oxidation in O₂ leads to the formation of non-uniform films. In contrast, oxygen atoms oxidize silicon at a rate independent of its orientation [1].

To confirm the same behaviour for the oxidant ozone, Kameda *et al* [17] studied the oxidation of various silicon orientations by UV-excited ozone at temperatures of 20 and 400 °C. The authors found that the oxide film formed on Si{111} and Si{001} after UV–ozone exposure had the same thickness independent of the surface orientation. Similarly, the oxidation of poly-silicon by UV–ozone resulted in a homogeneous oxide film (figure 2), which even at room temperature resulted in the formation of a high quality Si/SiO₂ interface with a low leakage current and a high breakdown voltage.

3.3. Improved interface characteristics

Two kinds of transition layers have been identified at the Si/SiO₂ interface, namely the compositional and the structural transition layers [1]. The compositional transition layer corresponds to the formation of a substoichiometric oxide, SiO_x, where the Si atoms are not fully oxidized (thus species of Si¹⁺, Si²⁺ and Si³⁺ are present). This suboxide lowers the insulating qualities and the lifetime of the oxide and is usually limited to one-to-two atomic layers within the oxide.

The structural transition layer, in contrast, is due to the volumetric expansion of the SiO₂ film relative to the silicon lattice, which implies a strained region, usually found on both sides of the interface (Si and SiO₂). On the Si side of the

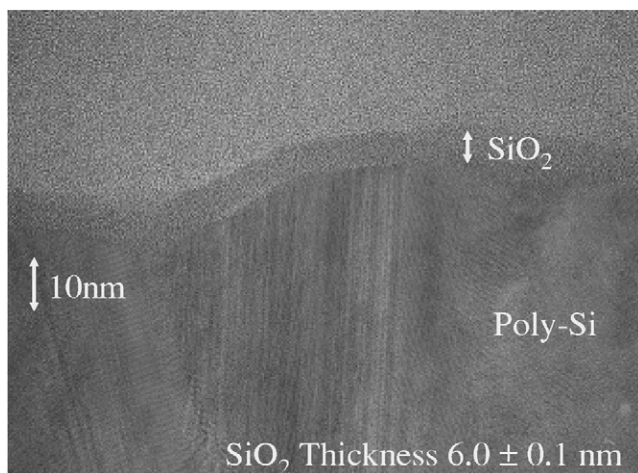


Figure 2. Transmission electron microscopy image of cross section of poly-Si with SiO₂ film. A homogeneous 6.0 nm thick SiO₂ film formed after UV–ozone exposure for 30 min at 20 °C (thickness of SiO₂ film and 10 nm reference labelled). Reprinted with permission from [17]. ©2007, The Electrochemical Society.

interface, this distortion is limited to only one or two layers, while on the oxide side this region has been found for thermally grown oxide to extend up to 1 nm thickness. The structure of this transition region exhibits a distortion of the Si–O bond lengths and bond angles with respect to bulk SiO₂.

Experimentally, the existence of a transition layer is inferred from changes in the XPS spectrum, HF etching rate, MEIS, and FTIR vibrational analysis. These techniques have been applied to elucidate the interface properties of the ozone-grown oxide.

3.3.1. Diminished interfacial transition layer. The first indication that ozone gives improved interface characteristics over a conventionally grown oxide, was found by Awaji *et al* [13]. The authors applied difference x-ray reflectivity to study the silicon oxide growth in O₂ and O₃ (5%)/O₂ (generated by a discharge ozonizer, BDO-type) at temperatures between 800 and 1000 °C. They found an interfacial layer of ≈1 nm thickness which exhibited a higher density than bulk SiO₂. The thickness of this interfacial layer, however, decreased with higher oxidation temperatures and also in the presence of the more reactive ozone oxidant. Subsequently, the ozone-grown oxide and its interface properties were studied in greater detail.

3.3.2. Constant HF etching rate. The etching rate of silicon oxide in hydrofluoric acid (HF) is sensitive to the density, porosity, and composition of the oxide film and thus allows to probe the quality of the oxide. The HF etching rate of ozone-grown oxide has been studied and compared to thermally grown and native oxide³ [14, 27, 28].

Whereas the thermally grown oxide showed two etching rates, depending on the film depth, the etching rate of the ozone-grown oxide was found to be independent of the film depth (see figure 3). For the O₂-grown film, the etching rate

³ A native oxide refers to the oxide film that forms naturally on the silicon sample when exposed to air.

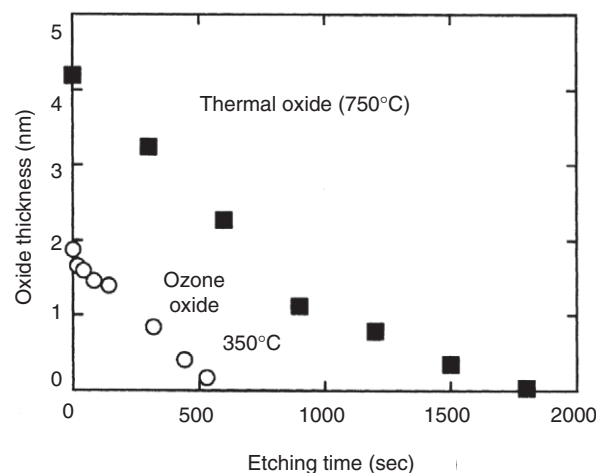


Figure 3. Oxide thickness on Si{001} during etching process (0.1 wt% HF solution at 25 °C) for thermally grown oxide (■, wet oxidation at 750 °C) and ozone-grown oxide (○, $p = 10^5$, $T = 350$ °C, $c > 30\%$). Reprinted with permission from [29]. ©2000, Elsevier.

decreased at a thickness of around 1.2 nm, which indicates a transition region of higher density near the Si/SiO₂ interface. In contrast, high-concentration O₃ exposure at low pressure ($p = 10^{-4}$ Pa) [14] and high pressure ($p = 10^5$ Pa) [27] conditions confirmed that the etching rate of the ozone-grown oxide is constant even close to the interface.

The conditions of how the oxidant O₃ is supplied, however, were found to be critical for the quality of the ozone oxide. Since very long exposure times are necessary to form the oxide film at room temperature, the lifetime of the reactive O₃ starts to play a significant role. By filling the processing chamber with high-concentration O₃ gas and storing, instead of replacing, the gas during the oxidation process, O₃ decomposes into the less reactive O₂. It was found that in these processing conditions the HF etching rates of the films were as high as those of a native oxide [27]. In contrast, by constantly supplying the O₃ gas [28], a film of comparable quality to the best thermally grown oxide was formed even at room temperature.

Interestingly, it was also observed that it is possible to upgrade the poor film quality of a native oxide by exposure to ozone at appropriate temperature conditions [28]. The native oxide exhibits a high HF etching rate, which is nevertheless constant throughout the film. After ozone exposure above 350 °C, the etching rate of the oxide decreased, which relates to an increase in film density, and stayed independent of the film depth. In contrast, an already present structural transition layer of a thermally grown oxide was not affected by O₃ oxidation [28].

3.3.3. Less Si displaced at interface. To explain the observations of the different HF etching rates, the structural properties of the SiO₂ film near the Si/SiO₂ interface were studied by medium energy ion spectroscopy (MEIS) [15, 16]. The displacement profile of Si atoms near the interface confirmed that, while thermally grown oxide

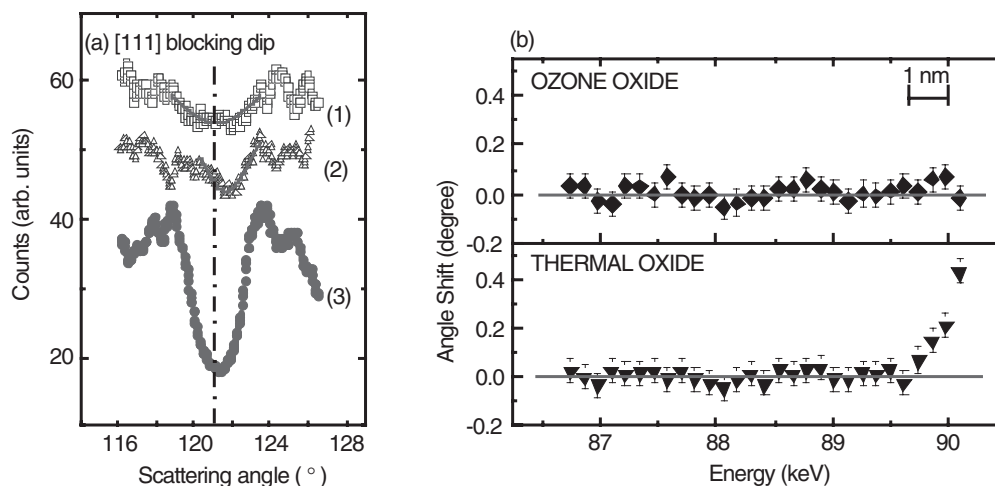


Figure 4. (a) Angular spectra around the Si blocking dips of (1) the ozone oxide and (2) the thermal oxide, and (3) the crystalline Si substrate in the [111] direction for a 4 nm oxide (parabolic fittings used to determine the dip positions). (b) Shift in blocking dip positions of the Si peak as a function of depth for the ozone oxide and thermal oxide in the [111] direction. Reprinted with permission from [16]. ©2002, Japan Society of Applied Physics.

exhibits a structural transition layer, the ozone-grown film is homogeneous even at the interface, supporting the observation of the constant HF etching rate.

In their experiments, Kurokawa *et al* [15] prepared a 3.3 nm thick oxide film by exposing Si{001} to atmospheric-pressure ozone at a substrate temperature of 375 °C, and compared it to a film of the same thickness prepared by wet oxidation at 700 °C.

Even though the XPS Si 2p spectra showed that the stoichiometry of the ozone-grown oxide is the same as that of the thermally grown oxide, the MEIS revealed differences in the displacement profile. At high incident energies, which corresponds to a penetration depth near the interface, the blocking dips of the thermal oxide shifted to a higher angle with respect to the blocking dip of bulk Si. This shift indicates the presence of a compressively strained SiO₂ layer near the interface.

In contrast, the ozone-grown oxide does not exhibit this shift, but the blocking dips near the interface keep the same angle. Thus, the oxide grown by ozone oxidation shows a negligible strain and a thinner interfacial transition layer than the thermal oxide.

The same MEIS characteristics of ozone-grown oxide were found by Chang *et al* [16] as shown in figure 4, who used slightly different processing conditions. The authors compared an ozone-grown oxide formed at 600 °C in a concentration of 3% ozone to an oxide film formed by dry oxidation (O₂) at 800 °C. Only the O₂-grown oxide formed a ≈1 nm thick structural transition layer, while the ozone-grown oxide is homogeneous even close to the interface.

Similar interface improvements were also observed by photo-oxidation methods at low temperatures. Thus, there might be two reasons for this improvement. First, the lower processing temperature might suppress diffusion effects that lead to a disruption of the oxide network (e.g. Si outwards diffusion). Second, the more reactive diffusive species of atomic oxygen might be more successful in saturating interface

defects (e.g. Si dangling bonds) and so lead to a more defect-free SiO₂ network formation in the interface region. Interestingly, it was found that on a 4° tilted wafer even thermal oxidation by O₂ showed these improved interface characteristics [30]. There, it was argued that since O₂ dissociates more easily into atomic oxygens at the reactive step edges than on the planar surface, the vertical strain on the Si{001} substrate is reduced. This observation supports the second argument that the more reactive diffusion species is mainly responsible for the improved interface characteristics.

3.3.4. Si–O–Si vibrations. Since the Si–O–Si asymmetric stretching frequency is sensitive to the Si–O bond angle and bond length, it shifts towards lower wavenumbers near the interface, when strain and substoichiometric oxide are present [31, 32].

The structure of the ozone-grown oxide film near the Si/SiO₂ interface has been analysed by Fourier transform infrared spectroscopy (FTIR) [18, 12]. Even though both groups used different processing conditions and techniques to measure the thickness dependence, both found that the ozone-grown oxide exhibited different FTIR characteristics than the thermally grown oxide, suggesting improved interface characteristics.

Cui *et al* [18] oxidized a Si{001} sample in low-concentration O₃ (950 ppm in O₂ gas) at temperatures between 200 and 500 °C. They measured the longitudinal optical (LO) mode of the Si–O–Si asymmetric stretching frequency *in situ* as a function of oxidation time (increasing thickness). For short exposure times (equivalent to very thin oxide films) the LO mode was lower than the SiO₂ bulk value of 1050 cm⁻¹. As the film grew in thickness this peak shifted upwards and converged towards a frequency typical for the oxidation temperature. Higher oxidation temperatures led to an increase in the vibrational frequency, thus bringing it closer to the SiO₂ bulk value. In addition, the authors also found that ozone had a favourable effect, so that the Si–O vibrations were close

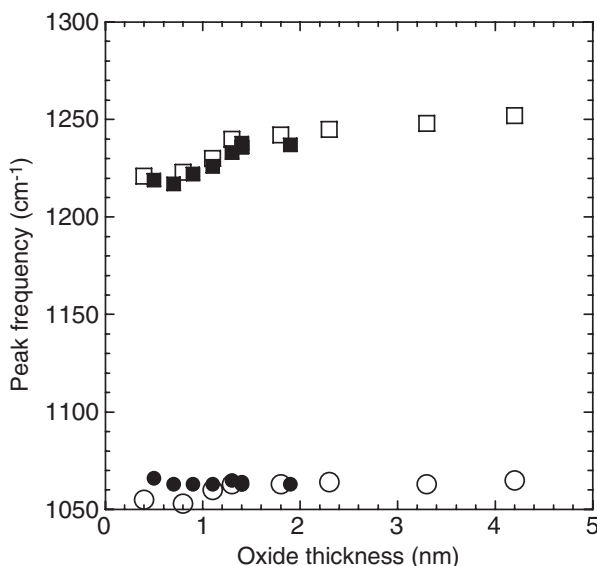


Figure 5. TO and LO mode of the Si–O–Si asymmetric stretching vibration of oxide films formed on Si{001} as a function of oxide thickness: (■) LO frequency and (●) TO frequency of ozone oxide, and (□) LO frequency and (○) TO frequency of thermal oxide. Reprinted with permission from [12]. ©2005, Japan Society of Applied Physics.

to the bulk value even after short exposure times. Cui *et al* also performed XPS measurements to quantify the amount of suboxide, which confirmed that both higher temperature conditions and the more reactive oxidant (ozone) reduced the amount of suboxide and thus improved the interface quality.

Nakamura *et al* [12] exposed a Si{001} surface with an already present native oxide film to high-concentration O₃ (>30%) at 350 °C. In addition to the LO mode of the Si–O–Si stretching vibrations, they also measured the transverse optical (TO) mode. In order to evaluate the thickness dependence, they first grew an oxide film of 1.9 nm thickness and then etched the oxide by HF back to the desired thickness (decreasing thickness). We note, that in this method the HF etching could have an additional influence on the FTIR spectra.

While the TO phonon peak of the thermally grown oxide exhibited a red-shift by 10 cm⁻¹ at a distance of 1.3 nm from the interface, the ozone oxide remained constant at 1065 cm⁻¹ down to 0.4 nm thickness (figure 5). Yet, the LO phonon peak yielded for both oxides a red-shift of ≈30 cm⁻¹ from its bulk value of 1250 cm⁻¹, as soon as the thickness reached values lower than 1.3 nm. While this shift of the LO mode alone is not fully understood⁴, the authors have argued that the TO mode in the thermal oxide decreases, because the Si–O–Si bond angle near the interface is more distorted (≈3°) [12]. The TO stretching frequency was also calculated to exhibit a strong dependence on the Si–O bond length, as a bond length increase of just 0.01 Å lead to a red-shift of 43 cm⁻¹ [32].

3.3.5. Improved reliability. The quality of the ozone-grown SiO₂ film and its Si/SiO₂ interface has also been tested for

⁴ The oxide composition and/or oxide density might be responsible for this shift.

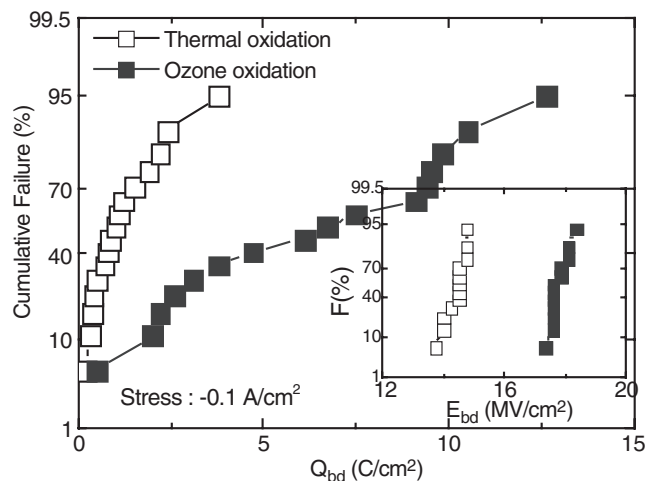


Figure 6. Charge-to-breakdown characteristics Q_{bd} under a constant current density of -0.1 A cm^{-2} of a 4 nm thermally grown (800 °C) and ozone oxide (600 °C). Inset highlights higher breakdown field strength of ozone oxide. Reprinted with permission from [16]. ©2002, Japan Society of Applied Physics.

device performance [16, 33]. The lifetime of the ozone-grown oxide has been measured under electrical stress [16] and the charge-to-breakdown characteristics were found to be significantly improved (figure 6). It has been suggested that the observed strain relaxation might be responsible for the improved reliability. Alternatively, the more reactive diffusive species of oxygen radicals might be more successful in saturating any Si dangling bonds, and thus lead to a lower defect density than in the O₂-grown oxide. The ozone-grown oxide was also found to exhibit less charge trapping [16].

4. Growth properties

In order to achieve a high degree of control in the silicon oxide formation by ozone, it is necessary to understand its growth characteristics.

In 1965, Deal and Grove [34] devised the now famous Deal–Grove model to describe the oxide growth in O₂ and H₂O at high temperatures. In this model, the oxidizing species is considered to undergo three stages: (I) diffusion from the bulk of the gas to the surface, (II) diffusion through the bulk oxide to the oxide–substrate interface, and (III) reaction at the interface. However, despite describing the formation of thick oxide films very accurately, this model fails to account for the formation of thin-film oxides (<20 nm) [35] and new models (considering diffusion of charged O₂, Si outwards diffusion, a reactive layer, etc) have been proposed to understand the ultrathin oxide growth by O₂ (see [36] and references therein). Interestingly, however, due to its general nature the Deal–Grove model has found validity in the case of silicon oxidation by ozone.

In most experimental studies that have investigated the relation between film thickness and oxidation time in ozone, the silicon oxide grew initially at a linear growth rate followed by a parabolic growth rate. While a linear growth rate usually indicates a surface or interface reaction-limited growth

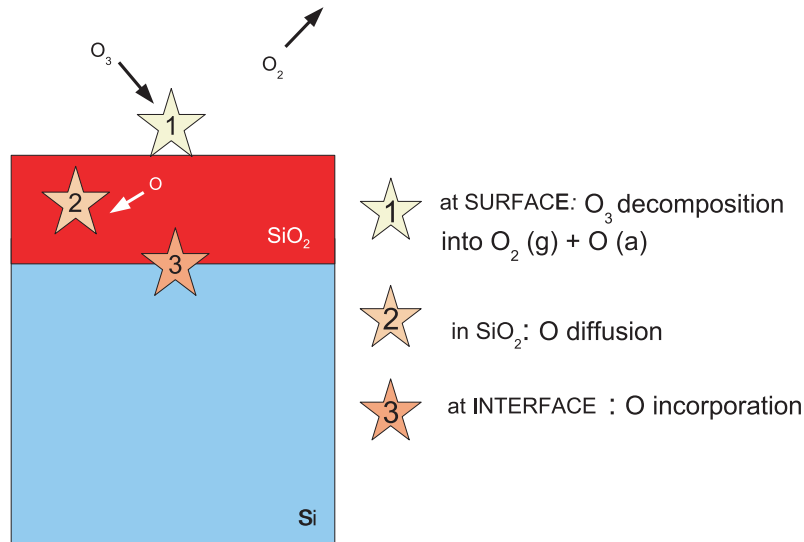


Figure 7. Schematic representation of how silicon oxide grows by oxidation in O₃.

(phenomenon III of Deal–Grove model), a parabolic growth rate suggests that the oxidation is governed by diffusion (phenomenon II). Each phenomenon can be expressed either by a linear or parabolic law with

$$x = At \quad (1)$$

$$x^2 = x_0^2 + Bt. \quad (2)$$

Here, x refers to the oxide film thickness (nm), t to the oxidation time (min), while A and B account for the linear and parabolic rate constant (nm min⁻¹ and nm² min⁻¹), respectively. Assuming that both growth constants follow an Arrhenius behaviour, they can be expressed as $A = A_0 \exp(-E_a^A/kT)$ and $B = B_0 \exp(-E_a^B/kT)$ to describe the temperature dependence of the growth rate.

In (2) x_0 is an empirical parameter, which refers to the oxide thickness until which linear growth is observed. Thus, x_0 marks the transition from the linear to the parabolic regime and has been estimated to be ≈ 0.6 nm [37]. Figure 7 gives a schematic representation of the oxide growth in ozone.

4.1. Initial oxidation: adsorption

The initial oxidation stage is governed by the interaction between ozone and the silicon surface and has been studied by numerous experimental techniques, which were complemented by first-principles molecular dynamics simulations. Since it was found that the surface termination has a strong influence on the adsorption process, we will discuss the adsorption of ozone on the two most important surface terminations, the clean and hydrogen-terminated surfaces, separately.

4.1.1. Clean Si{001}. Two scanning tunnelling microscopy (STM) studies [38, 39] were performed to elucidate the initial oxidation of clean⁵ Si{001} by ozone. It was observed that O₃

⁵ Due to its importance in the semiconducting industry, most studies have focused on the {001} surface.

exposure led to the emergence of bright and dark features on the surface. However, since STM is unable to unambiguously image oxygen atoms on the silicon surface ([40] and references therein), the interpretation of these observed features differs between the two studies. While Itoh *et al* [38] related the bright features to single oxygen adsorption sites, Narushima *et al* [39] suggested these to be ejected Si adatoms. Since we are unable to solve this ambiguity, we report both interpretations, independently.

Itoh *et al* [38] identified three types of bright features, which varied in brightness and in their location relative to the dimer rows. The two most common bright features were assigned to O adatoms in the dimer and back bond sites, while the third, less frequently observed bright feature was suggested to be an O adatom in the trough region, between the dimer rows. This assignment also coincides with the adsorption sites observed by first-principles MD simulations [41] (see below).

In contrast, Narushima *et al* [39] describes the bright features as ‘bumps’ and ‘elongated islands’, and relates their origin to ejected silicon surface atoms.

Yet, both studies agree in assigning the dark features, which emerge after O₃ exposure, to an increase in surface defects (‘etching’). Narushima *et al* [39] also argues that in surface areas, which have been etched to a high degree, the exposed sublayers reconstruct into new dimer rows.

To reveal the underlying ‘microscopic’ reaction mechanism, Fink and Jenkins [41] simulated the interaction between an impinging O₃ molecule and the clean p(2 × 2) dimer-reconstructed surface by first-principles molecular dynamics (FPMD). They found that ozone exhibited a very high reaction probability, corresponding to an initial sticking probability close to unity. Two dominant reaction pathways were observed, where O₃ dissociatively adsorbed either into a single O adatom and gas-phase O₂ (partial dissociation) or into three O adatoms (complete dissociation). The dissociation of ozone was highly exothermic and found to proceed without any activation barrier.

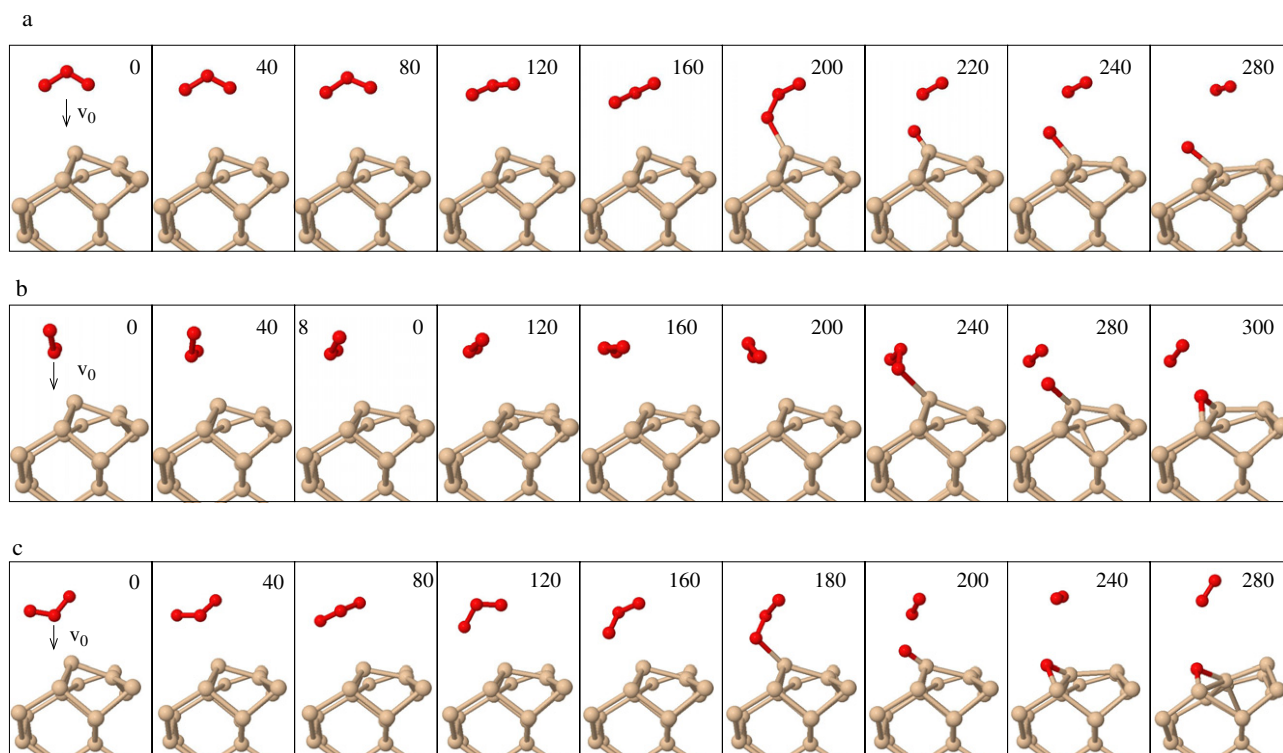


Figure 8. Molecular dynamics trajectories for O_3 approaching the Si-up dimer atom (Si^u) on the clean Si{001}. O_3 has been given a velocity of 5 \AA ps^{-1} towards the surface, while all surface atoms are initially at rest. The Si^u steers the O_3 into a favourable orientation, until the molecule is eventually stripped of one of its terminal O atoms and the remaining O_2 fragment desorbs from the surface. The O adatom either stays in its initial Si^u adsorption site (a) or it relaxes into the more stable lower back bond adsorption site (b), (c). Time evolution given in fs. Reprinted with permission from [41]. ©2008, American Physical Society.

On the surface two reaction centres were identified, where ozone reacted with either the up (Si^u) or the down (Si^d) dimer atom of the buckled Si dimer of the reconstructed surface.

The electron-rich up dimer atom, Si^u , was found to be more reactive and displayed a pronounced steering effect onto the incoming molecule. As the trajectories depicted in figure 8 reveal, O_3 is steered by the Si^u atom into a favourable position in order that one of ozone's terminal O atoms is able to react with the surface dangling bond. After adsorbing to the Si^u atom, this O atom relaxed (in most trajectories) into the more stable dimer bond or lower back bond site.

A study of the underlying electronic structure revealed several reaction stages during the dissociation process. In particular, responsible for the surface-induced steering was the maximization of overlap between the Si^u dangling bond and the O_3 LUMO.

In contrast, the less reactive down dimer atom, Si^d , did not exhibit this steering effect on to the incoming molecule, but was able to react (depending on the incoming orientation of O_3) with either a terminal or the central O atom. By reacting with the central O atom, the molecule was even able to dissociate completely, leaving three O adatoms on the surface. Since this complete dissociation is sterically more challenging, it has been suggested to be a rare event and that the partial dissociation is the preferred reaction pathway. As mentioned earlier, the products of partial dissociation coincide with the assignment of the STM data of Itoh *et al* [38], that single O atoms occupy the back bond and the dimer bond.

In comparison to O_3 , regular O_2 exhibits a much lower sticking probability, since the adsorption of O_2 on Si{001} proceeds only via a narrow dissociation pathway [42]. Therefore, the initial oxidation by O_3 proceeds much faster and at much lower temperatures than by O_2 .

The reason why O_3 exposure leads to the creation of surface defects even at low temperatures was also investigated [41]. Previously, the activation barrier for SiO ejection was found to have a strong dependency on the oxidation state of the Si atom [43], so that the barrier for ejection of a singly oxidized Si atom, Si^{1+} , is much lower (at around 2 eV) than for higher oxidized Si atoms (Si^{2+} , Si^{3+} , and Si^{4+}).

Putting this observation in the context of the oxidation by ozone, the hot O adatom from the partial dissociation of ozone has a large enough kinetic energy to enable a SiO ejection of the singly oxidized Si atom [41]. This SiO ejection mechanism is able to explain the microscopic origin for the experimentally observed increase in defects during ozone exposure [38, 39]. In contrast, the dissociation of O_2 leads to the formation of a doubly oxidized Si^{2+} species; due to its additional Si–O bond, this species is much stronger bound to the surface and therefore exhibits a much higher activation barrier of around 4 eV for SiO ejection [43].

Thus, while oxidation in O_2 results in etching only at the specific thermodynamic conditions of high temperature and low pressure, also referred to as the 'active oxidation' regime,

the dissociation of O_3 increases the likelihood for an early etching event even at low temperatures.

4.1.2. Hydrogen-passivated Si{111} and Si{100}. The hydrogen-terminated silicon surfaces, which are rather inert with respect to O_2 , were found to be readily oxidized by ozone even at low temperatures [44, 45]. This fact is significant, since it is common practice in industry to protect clean silicon surfaces with a passivating coverage of hydrogen prior to controlled oxidation.

Even though the sticking probabilities of both ozone and molecular O_2 were reduced with increasing hydrogen coverage, at a full hydrogen coverage only O_3 was still able to oxidize Si{111} at the processing temperature of 70°C [44], as shown in figure 9.

Nevertheless, compared to adsorption on clean Si{111}, O_3 exhibits a considerably lower sticking probability on the hydrogen-terminated surface. Here, the initial rate of oxide formation has been estimated to be reduced to one tenth at low temperature conditions (50°C) [45].

A similar behaviour was observed in the oxidation of hydrogen-terminated Si{001}. By measuring the stress evolution during oxidation by ozone, it was revealed that the hydrogen-terminated surface exhibited a rate of initial stress increase that was lower than for the clean surface [46]. This was linked to the effect that surface hydrogen would lower ozone's initial sticking probability. Nevertheless, after long enough exposure, the stress of both clean and H-terminated surface saturated at almost the same value and became by $\approx 0.3\text{ N m}^{-1}$ more compressive with respect to the sample prior to oxidation. This suggests that the later oxidation stage is independent of the surface termination.

First-principles molecular dynamics simulations have provided new insights into the microscopic surface reaction [47, 48]. The simulations confirmed that independent of the crystallographic orientation of the surface ({001} or {111}) a termination by hydrogen exhibits a repulsive interaction with ozone, and thus lowers ozone's sticking probability.

Nevertheless, the FPMD simulations revealed several low-barrier oxidation channels [48], where ozone succeeded in the direct oxidation of a Si-Si bond. Through a partial dissociation mechanism, where the O_2 fragment desorbed, one of O_3 's terminal O atoms was inserted into the dimer bond, back bond, or subsurface bond, which released a heat of adsorption of 5.57, 4.97, or 4.81 eV, respectively.

In addition, in the interaction between ozone and surface hydrogen an intriguing radical-mediated adsorption mechanism was observed [47], which allowed ozone to oxidize the Si-H bond itself (figure 10). Here, ozone was able to abstract a surface hydrogen atom and form a short-lived HO_3^\bullet radical. Due to the close proximity of an unpaired silicon surface dangling bond, which was created through the H-abstraction, the HO_3^\bullet species exhibited only a very short lifetime of $\approx 0.2\text{ ps}$. As summarized in figure 11, a variety of dissociation channels was observed, which independently led to the same reaction product of gas-phase O_2 and a surface hydroxyl -OH.

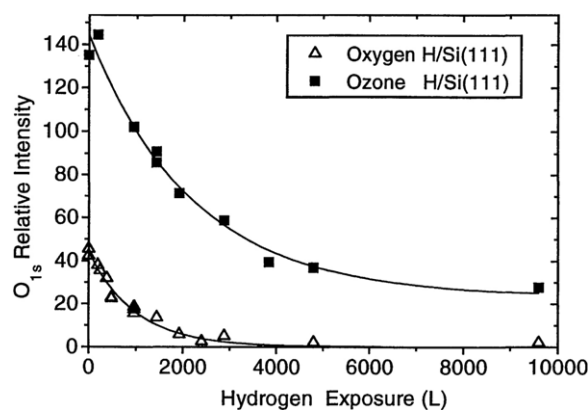


Figure 9. XPS signal of O 1s intensity on Si{111} with various hydrogen coverages after 4 L of ozone or molecular oxygen exposure (concentration of $O_3 > 80\%$, temperature at 70°C). Reprinted with permission from [44]. ©1995, Japan Society of Applied Physics.

Even though this abstraction mechanism was found to be sterically challenging, it exhibited only a low activation barrier of 0.04 eV [48] and was found to proceed in an 'autocatalytic' way [47]. Since the surface hydroxyl is able to form an H bond to one of O_3 's terminal O atoms [47, 49], the sticking probability of ozone is increased, which facilitated not only the Si-H oxidation (as depicted in figure 10(d)) but also the Si-Si oxidation.

Assuming that both Si-Si and Si-H oxidation take place, it is of interest to investigate how the oxidation proceeds after the initial stage. Interestingly, first-principles calculations [48] show that an increasing O coverage lowers the probability for the oxidation of the Si-H bond, since with increasing oxidation state of the Si atom, its Si-H bond increases in strength, too. Thus, only when abstracting an H atom from a Si atom with zero (Si^0) or one oxygen bonding partner (Si^{1+}) is the formation of the HO_3^\bullet reaction intermediate exothermic. In contrast, for the higher oxidized Si^{2+} and Si^{3+} , it is energetically more favourable for the H atom to stay bound to the oxidized Si atom than to bind to the O_3 . Thus, if the oxidation of the Si-H bond indeed takes place via the suggested mechanism, the transformation of Si-H into Si-OH would saturate soon after the initial oxidation stage.

Next, we relate this theoretical model that ozone not only oxidizes the Si-Si, but also the Si-H bond to available experimental data. We note that a direct oxidation of the Si-H bond has been already experimentally confirmed for another highly reactive oxidation gas, namely atomic O. Ikeda *et al* [50] exposed the H-terminated Si{001} to oxygen plasma and observed a sharp increase in the Si-OH stretching vibrations. The O atoms were simultaneously inserted into the Si-H and Si-Si bond, of which the latter proceeded faster. Nevertheless, we find that the Si-H oxidation by ozone has not been fully investigated by experiments yet.

Cui and Takoudis [51] have studied the initial oxidation of H-terminated Si{001} by O_3 (950 ppm)/ O_2 gas at temperatures between 50 and 300°C . The activation barrier for the initial oxidation regime was very low and estimated to be less than 0.05 eV.

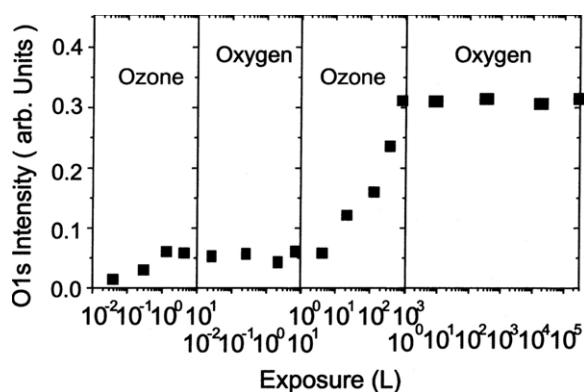


Figure 12. Change of O 1s intensity with exposure of H-terminated Si{111} sample to ozone and molecular oxygen gas. The gas exposure was performed in order of O₃, O₂, O₃, O₂ exposure. Reprinted with permission from [29]. ©2000, Elsevier.

higher vibrational modes, and so induces H₂ desorption) or by transformation of Si–H by oxidation into Si–OH. Since neither the signal of H₂O nor of any other OH-related desorption species were investigated by TPD, the latter cannot be ruled out.

Thus, we find that in order to clarify how ozone exposure affects the hydrogen termination (e.g. does ozone create surface hydroxyls as suggested by the simulations?), additional experiments are necessary. For example, IR measurements during the initial oxidation stage could probe the frequency range where hydroxyl vibrations occur (typically at $\approx 3750\text{ cm}^{-1}$).

Nevertheless, the later oxidation stage appears to be governed by diffusion, where silicon's surface termination appears to play a minor role.

4.2. Transition: O₃ reacts with partially oxidized Si{001}

Already in their early studies, Kazor and co-workers [26] concluded that the inward diffusion of atomic oxygen through the SiO₂ film would be the rate-determining process in the later oxidation stage. In order to understand the transition from the initial adsorption to the later growth mode, FPMD simulations have investigated the interaction between O₃ and an increasingly oxidized Si{001} [48].

The simulations revealed that with increasing O coverage ozone's sticking probability was reduced. Whereas on the clean surface each incoming molecule reacts with the surface, the preadsorbed O atoms exhibit a repulsive potential on the ozone. Therefore, in the vicinity of the O adatoms, ozone was repelled and either desorbed back into the gas phase or managed to get into the vicinity of an unoxidized Si–Si bond, where ozone would react. Here, the partial dissociation of ozone dominated, so that the Si adsorption sites were gradually filled by single oxygen atoms, while the O₂ fragments desorbed.

O₃ preferentially reacted with surface Si atoms which had a lower oxidation state [48]. This led to a uniform oxidation, which has been experimentally observed by atomic force microscopy (AFM) [53]. The experiments confirmed that

room temperature oxidation of Si{001} by ozone proceeded in a homogeneous layer-by-layer mode, where the step-terrace morphology of the clean surface was preserved both on the oxide surface and also at the SiO₂/Si interface.

Nevertheless, the simulations observe a clear transition in the oxidation rate. After more and more Si adsorption sites are filled, the rapid dissociative adsorption mechanism eventually gets blocked and only resumes when O atoms diffuse from the surface into the subsurface [48]. Such a diffusion mechanism, which leads to the oxidation of a Si–Si subsurface bond and the formation of a fully oxidized Si⁴⁺, is depicted in figure 13.

In brief, upon dissociative adsorption of a single O onto Si³⁺, a Si subsurface dangling bond is created. To saturate this defect, an O atom hops from a neighbouring surface site and occupies this subsurface site. This hopping itself creates a surface dangling bond, which is filled by subsequent diffusion of an O atom. All three events (creation of dangling bond, O hopping, O hopping) happen within a very short time period (<500 fs). Analogue diffusion reactions are expected to play an important role in the transition from the initial adsorption to the later oxidation stage.

Having obtained insight into how ozone reacts with a lightly oxidized silicon surface, we now turn to the full oxide growth.

4.3. Later oxidation: diffusion

In table 2 we provide a comparison⁶ of the oxide growth characteristics by ozone as experimentally observed.

It becomes clear that the oxidation kinetics depend on many parameters, as for example the reported values for the diffusion barrier show a large variation with values between $0.14\text{ eV} < E_a < 0.80\text{ eV}$. Interestingly, a similar variation in the activation energy has been observed for the plasma oxidation of silicon, where the space charge, which was different in each experimental setup, was found responsible for this variation [55].

In the oxidation by ozone, effects of charge transfer are expected to play an equivalent role in influencing the diffusion rate. This is because the diffusion barrier of the O atom, which diffuses through the oxide, exhibits a strong dependence on its charge. By looking at the results of first-principles calculations [56, 57] the diffusion barrier for neutral O⁰ and negatively charged O⁻ are revealed. The neutral species exhibits a much higher barrier of 1.3 eV [56], while charge transfer lowers the barrier of O⁻ to 0.27 eV [57]. The latter value is in much better agreement with the activation energies for the diffusive species related to ozone oxidation.

Of the experimental setup, the generator type, the O₃ concentration, and the total pressure in the chamber⁷, exhibit a strong influence of the growth characteristics, as table 2 highlights. These experimental conditions determine the supply of ozone to the surface.

⁶ Such a comparison has already been conducted by Narushima *et al* [54], which we have expanded here to include studies published after 2001.

⁷ Since the heating system (gas-phase heating or sample-only heating) is also expected to affect ozone's lifetime, gas-phase heating is explicitly labelled in the table.

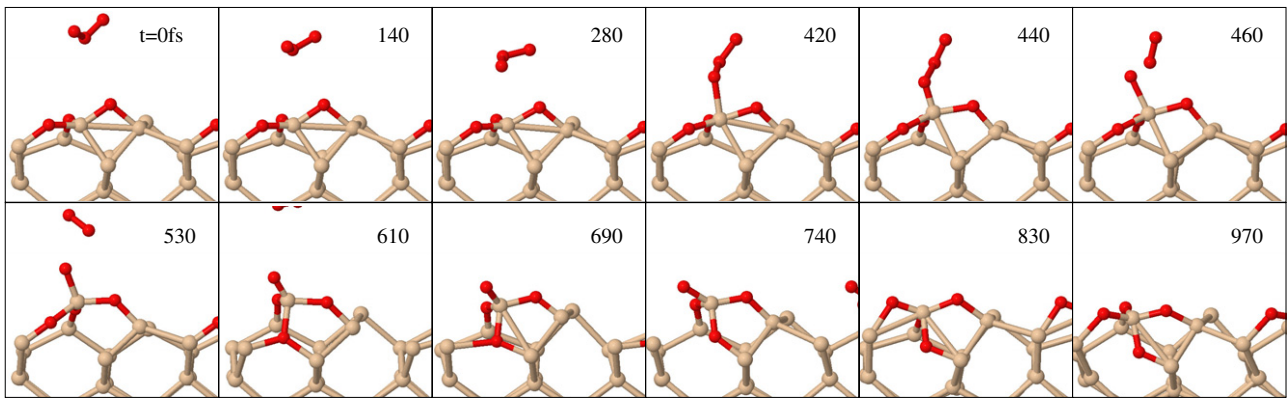


Figure 13. Molecular dynamics trajectory of O₃ impinging on a partially oxidized Si{001} (0.75 ML O coverage). O₃ has been given a velocity of 5 Å ps⁻¹ towards the surface, while all surface atoms are initially at rest. The O₃ is able to bring one of its terminal O atoms into the vicinity of the Si³⁺ site, which initiates the adsorption of a single O adatom and the subsequent migration of an O atom from the back bond into the subsurface site. Time evolution given in fs. Reprinted with permission from [48].

Table 2. Growth characteristics of silicon oxidation by ozone. Abbreviations of generator types are presented in table 1. *A* and *B* are linear and parabolic rate constant.

Year	Authors	Sample	Generator	O ₃ conc.	<i>T</i> (°C)	Mechanism	Rate constant, growth rate	<i>E_a</i> (eV)
1989	Chao <i>et al</i> [7]	Si{001}, clean	UV/O ₂	2.25 ppm	700–950		6.2 nm after 140 min at 700 °C	
2000	Cui <i>et al</i> [18]	Si{001}, H-pass.	UV/O ₂	950 ppm	125–530 ^a	2 linear regimes (fast < 5 min < slow)	2.2 nm after 20 min at 500 °C 2.6 nm after 75 min at 500 °C	0.13 (fast) 0.19 (slow)
1993	Kazor and Boyd [9]	Si{001}, H-pass.	BDO	3–4%	400–550	parabolic (up to 4 h)	<i>B</i> = 2.7 nm ² min ⁻¹ at 500 °C	0.80
1994	Kazor <i>et al</i> [26]		BDO	3–4%	600–1200	parabolic	<i>B</i> = 6.6 nm ² min ⁻¹ at 800 °C	0.22
2002	Narushima <i>et al</i> [54]	Si{001}, H-pass.	BDO	7%	700	parabolic	<i>B</i> = 40.2 nm ² min ⁻¹ at 700 °C	
2000	Nakamura <i>et al</i> [58]	Si{001}, clean	OJG	80% <i>p</i> < 10 ⁻³ Pa	RT–700	Linear (0.4–1.2 nm)	1.0 nm after 90 min at 600 °C	
2001	Maeda <i>et al</i> [53]	Si{001}, clean	OSG	30% <i>p</i> = 10 ⁵ Pa	RT	layer-by-layer growth	1.0 nm after 270 min at RT	
2002	Nishiguchi <i>et al</i> [33]	Si{001}, H-pass.	OJG	93% <i>p</i> = 900 Pa	260–830 ^a	Parabolic (3–11 nm)	6.0 nm after 3 min at 600 °C	0.32 (above 400 °C)
2005	Koike <i>et al</i> [59]	Si{001}, H-pass.	OSG	25% <i>p</i> = 1100 Pa	340–625	Parabolic (1–5 nm)	3.5 nm after 3 min at 625 °C	0.52
2001 (2002)	Nishiguchi <i>et al</i> [37] [60]	Si{001}, H-pass.	PLD	80%	RT–550	linear (<0.6 nm) parabolic (>0.6 nm)	1 nm synthesized by 1000 laser shots at 350 °C	0.0 ^b 0.14 (0.17)
2005	Tosaka <i>et al</i> [22]	Si{001}, H-pass.	UV/O ₃	93% <i>p</i> = 200–800 Pa	70–300	linear (<5 min) Parabolic (>5 min)	<i>A</i> = 0.5 nm min ⁻¹ at 70 °C <i>B</i> = 0.1 nm ² min ⁻¹ at 70 °C 3.6 nm after 10 min at 70 °C	0.025 0.14

^a Gas-phase heating.

^b Kinetic energy of O₃ ≈ 0.4 eV.

An additional impact on the growth rate, which we only mention briefly here, might come from the sample’s type of doping (n-or p-type) and dopant concentration, which is expected to facilitate the charge transfer into the diffusion

species. Yet, since the majority of samples presented in table 2 were of p-type, with a resistivity in the order of 5 Ω cm, it is difficult to quantify this impact. In any case, compared to the other factors this influence is expected to be negligible.

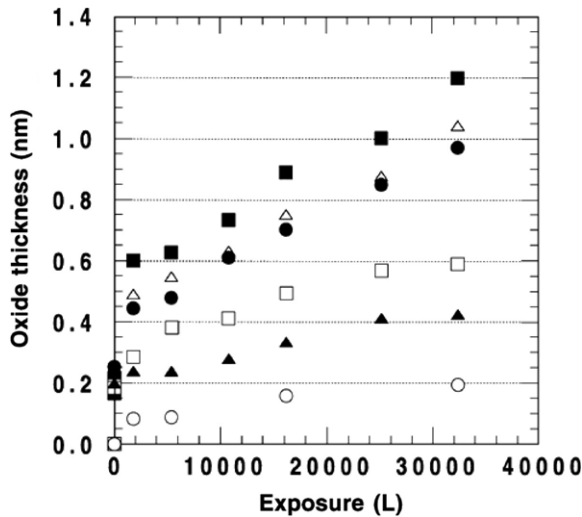


Figure 14. Growth kinetics during initial oxidation of Si{001} by ozone at low pressure conditions: the fast initial adsorption process is followed by ultrathin film growth. Yet, at substrate temperatures below 550 °C, the film saturates in thickness. Gas-phase pressure of ozone at 8×10^{-4} Pa with substrate temperatures at (○) RT, (▲) 300, (□) 500, (●) 550, (△) 600 and (■) 700 °C. Reprinted with permission from [58]. ©2000, Japan Society of Applied Physics.

In their pioneering work, Chao *et al* [7] found that, despite its low concentration, the presence of O₃ enhanced the oxide growth rate significantly. In the temperature range between 700 and 950 °C the oxidation in the UV-generated O₃ (2.25 ppm)/O₂ mix gas was up to 96% faster than in pure O₂. However, for thicker films and higher temperatures, where O₂ alone exhibits fast oxidation rates, this relative growth enhancement in the O₃/O₂ mix gas decreased.

Cui *et al* [18] also used a UV-based O₃ generator (UV/O₂) producing an ozone concentration of 950 ppm in the O₂ gas. By measuring the *in situ* IR intensity during the exposure of mixed O₃/O₂ and pure O₂ gas two linear oxidation regimes were identified for the growth of ultrathin oxide films (<3 nm). For O₃/O₂ the fast initial oxidation regime exhibited an activation barrier of 0.13 eV and changed after approximately 5 min exposure into a slower oxidation (up to ≈30 min exposure) with an estimated barrier of 0.19 eV. In comparison, oxidation in pure O₂ yielded higher barriers of 0.20 and 0.36 eV for the two oxidation regimes respectively.

In contrast to cold-wall processing in this setup a heating lamp was used, which thermally excites the gas-phase ozone and thus affects its lifetime. Therefore, it was found that at temperatures above 500 °C the ratio between the oxidation rates of O₃/O₂ and pure O₂ actually decreased. *In situ* FTIR measurements confirmed that at 530 °C a large proportion (≈75%) of the inlet ozone decomposed at steady state, while at 125 °C only a few ozone molecules (≈9.5%) decomposed. Since atomic O would have a much shorter lifetime, the decomposition of O₃ forms O₂, which is less reactive in the oxidation process. Based on a first-order reaction, the activation energy for ozone dissociation was estimated to be ≈0.17 eV. Since this activation barrier was very close to the barrier of the slower oxidation regime, the dissociation of ozone was suggested to be the rate-limiting step in

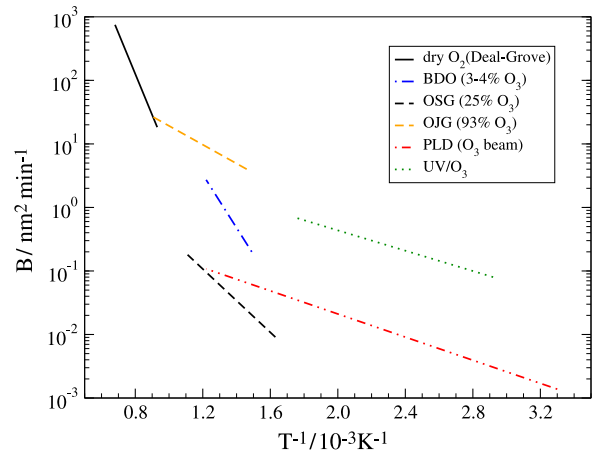


Figure 15. Comparison of parabolic rate constant *B*. Oxidation in ozone for different ozone supply: BDO barrier discharge ozonizer with 3–4% concentration of ozone (pressure in chamber, $p = 10^5$ Pa) [9], OJG ozone jet generator with 93% ($p = 900$ Pa) [33] and OSG ozone silica generator with 25% ($p = 1100$ Pa) [59], PLD pulsed laser deposition (one laser shot per second) [60]. As reference Deal–Grove model, parabolic rate constant of oxidation in dry O₂ [34] (valid for oxide thickness >20 nm).

this oxidation process [18]. This would also explain the observation of a linear, instead of a parabolic (diffusion-limited) growth.

Despite these low ozone concentrations in the O₂ gas (<4%), the oxidation is clearly governed by the presence of ozone, which supplies the more reactive oxygen atoms to the surface. Therefore, the value of the parabolic rate constant *B* was found to increase linearly with the ozone gas partial pressure (2–7%) [54].

At high ozone concentrations but at low pressure conditions ($p < 10^{-3}$ Pa), even though the O₃ concentration is close to 100%, the partial pressure of ozone and thus the oxidation rate is nevertheless low. This became particularly apparent in a study of the oxidation of clean Si{001} by a highly-concentrated ozone gas at very low pressure conditions (< 10^{-3} Pa, O₃ generator: OJG) [58]. Initially, the oxidation proceeded in accordance with Langmuir kinetics, which is typical for adsorption. Nevertheless, in the later oxidation stage, the oxide growth either saturated or followed linear kinetics, depending on the oxidation temperature (figure 14).

If the substrate was heated to temperatures ≤500 °C, the oxide thickness saturated after an exposure of 90 min at a thickness of 0.2, 0.4, or 0.6 nm for temperatures of 30, 300 or 500 °C, respectively.

On the other hand if the oxidation temperature was ≥550 °C, the film did not saturate, but the growth mode changed into linear kinetics as soon as the oxide reached a thickness of 0.6 nm. Thus, after 90 min exposure a 1.0 nm or 1.2 nm thick film was formed for a temperature of 550 °C or 700 °C, respectively. This transition at 0.6 nm describes the change of growth mode from adsorption to thin-film growth [58]. Yet, in this sub-2 nm regime, the growth follows a linear behaviour, which suggests that the oxidation is reaction-limited, rather than diffusion-limited (which should lead to

parabolic growth). We think that due to the low pressure of O_3 , there is a shortage of ozone molecules at the gas/oxide interface, which limits the growth.

To account for the growth saturation at temperatures below 500°C , the decomposition rate of ozone might be too low.

Similarly, in pure O_3 gas, but under slightly higher pressure conditions ($p > 250$ Pa, OSG), it was found that the oxidation rate decreased significantly at temperatures below 400°C [33]. This was linked to the low decomposition rate of O_3 , so that less O atoms could react with the surface. In order to supply reactive O atoms and guarantee a fast oxidation rate even at temperatures below 400°C , alternative methods are necessary, including the pulsed laser deposition (PLD) and UV-excited ozone (UV/ O_3) method.

Nishiguchi *et al* [37, 60] found that the oxidation rate by a hyperthermal ozone beam (PLD) was independent of the substrate temperature up to a thickness of ≈ 0.6 nm. Since the ozone molecules had a very high translational kinetic energy (between 0 and 2 eV) they could easily overcome any activation barrier related to the initial oxidation. Yet, at a thickness larger than 0.6 nm the growth mode changed from being linear into the parabolic regime, indicating that the oxidation kinetics became diffusion-limited. Thus, instead of being a surface reaction, which is influenced by the kinetic energy of the incoming ozone, the diffusion of the oxygen species through the growing oxide film was influenced by the substrate temperature. The activation barrier for this parabolic growth regime was estimated to lie between 0.14 [37] and 0.17 eV [60].

In addition to the higher reactivity, in this method the supply of ozone molecules is highly controllable. Tuning the repetition rate of the laser pulse gives precise control over the oxidation rate: e.g. 1000 laser shots formed a 1 nm thick oxide film at 350°C , which depending on a repetition rate of 1 or 10 Hz either takes 1000 or 100 s.

Alternatively, UV-excited O_3 also allowed oxidation at room temperature. Ozone has a strong absorption band between 220 and 310 nm, also referred to as the Hartley band. In this band the photodissociation of ozone results in a quantum yield of unity in the reaction products of O_2 ($^3\Sigma$) and $O(^1D)$. Thus, while thermal decomposition of ozone results in oxygen atoms in the ground state $O(^3P)$, the decomposition of ozone by UV-light leads to oxygen atoms in the more reactive $O(^1D)$ state. It has been suggested that the oxygen atoms in this excited $O(^1D)$ state [61, 25] are responsible for the increased reactivity of UV-light excited O_3 .

Tosaka *et al* [25] analysed the O_3 density after UV-light irradiation and discussed the change in the $O(^1D)$ density. They concluded that, even though the $O(^1D)$ atoms have only a very short lifetime ($\approx 1 \mu\text{s}$ at $p = 200$ Pa) due to their high density this excited O species was indeed supplied to the surface in a pulse like fashion with each laser shot [25].

Yet, the UV irradiation also affects the silicon sample. Upon direct UV illumination, even though no defects are created, the surface temperature increases by up to 50°C [17, 25]. In addition, the electron population in the UV-illuminated oxide is expected to be higher than the thermal equilibrium concentration, which promotes electron transfer into the diffusion species and affects the diffusion rate.

It was found that the growth rate during UV/ O_3 oxidation did not follow the parabolic law, but became slower as the oxide thickness increased [5]. To account for this behaviour it was argued that the quenching of $O(^1D)$ to $O(^3P)$ during the diffusion in the oxide would be responsible for these slower oxidation kinetics [61]. However, while the spin assignment of $O(^3P)$ as ground state for atomic oxygen in the gas phase is correct, in the oxide the oxygen atom interacts with the lattice and binds temporarily to neighbouring Si atoms. Through this interaction, the spin state of the atomic oxygen relaxes almost immediately into its ground state. In addition, charge transfer into the diffusing oxygen atom has to be considered, which alters its electronic configuration from O^0 to O^- . Instead of a spin quenching, we suggest to consider a reduction in charge transfer for this decrease in oxidation kinetics: with increasing oxide thickness, the probability decreases for electrons to tunnel from the Si valence band into the SiO_2 conduction band.

Finally, to visualize the influences on the growth characteristics, plots of the parabolic rate constant of representative studies are shown in figure 15. At temperatures between 350 and 800°C common O_3 generator types (including BDO, OJG, and OSG) offer a fast oxidation of silicon, whereas at temperatures below 300°C alternative methods are necessary. Here, because of the low thermal budget only the PLD or UV/ O_3 methods provide a fast oxidation, which is facilitated by either the high kinetic energy of the O_3 beam or by the UV-excitations.

Figure 15 highlights again the strong influence of the generator type on the oxidation rate. At temperatures between 350 and 800°C the growth rates between the three generator types (BDO, OJG, OSG) differ by several orders of magnitude. In this comparison, the ozone jet generator (OJG) [33] offered the fastest growth rate. With the highest ozone concentration of over 93% and a total pressure of 900 Pa, it supplied ozone at a partial pressure of 830 Pa. In contrast, the barrier discharge ozonizer (BDO) [9], even though it supplied ozone at a higher partial pressure (4000 Pa, 4% at 10^5 Pa), resulted in a slower oxide growth. As a possible explanation one could consider the influence of O_2 , which, at a concentration of 96%, constitutes to the majority gas and might block the fast oxidation channels of O_3 . In this temperature range the slowest growth rate was given by the ozone silica generator (OSG) [59]. Although the concentration of ozone was fairly high at 25%, the total gas pressure was low at 1100 Pa, which resulted in the lowest partial pressure of all three studies ($p_{O_3} = 270$ Pa).

We conclude that the O_3 concentration and the total pressure conditions, both of which are directly linked to each generator type, influence the growth rate of the oxide significantly.

4.4. Growth and improved interface

In an effort to understand how the growth in ozone leads to improved interface characteristics, the stress evolution during the oxidation of clean $\text{Si}\{001\}$ by O_2 and O_3 has been studied by the optical cantilever bending method [39]. During exposure to O_3 a monotonic increase towards the compressive stress side is observed, which saturates at a value of 0.33 N m^{-1} while the film thickness saturates at 0.6 nm.

In contrast, during exposure to O_2 at the same temperature and pressure conditions (room temperature, 0.2 Torr) the stress only increased marginally to 0.002 N m^{-1} . However, the SiO_2 film thickness after this O_2 exposure is not reported and it seems highly likely that at these low temperature and low pressure conditions, O_2 shows little to no reaction with the silicon surface. Therefore, the reported differences in the stress evolution during O_2 and O_3 exposure are not necessarily linked to the oxidation mechanism but might only reflect the higher reactivity of O_3 .

More interesting is the comparison with the stress evolution during plasma oxidation, which gives a very different profile [39]. In contrast to ozone's monotonic increase in compressive stress, plasma oxidation displays three stress stages, namely tensile-compressive-tensile. This complicated profile was linked to the $Si\{001\}$ surface structure, since it disappeared after the surface structure was destroyed by Ar bombardment [62].

From STM experiments ozone exposure was found to etch the surface and thus to affect the surface structure. This roughening of the surface was argued to be responsible for the release in tensile stress, which would allow a stress-free growth [39].

Despite this ozone-induced etching, which leads to a roughening of the surface, AFM experiments confirmed that the surface terraces of the ozone oxide film were nevertheless smooth [53]. While for a thickness of 1.0 nm the native oxide exhibited a root-mean-square value of the measured height $>0.20 \text{ nm}$, the ozone oxide's RMS value was much smaller. The RMS of the ozone oxide was 0.10 nm, which was comparable to thermally grown oxide ($O_2/900^\circ\text{C}$). Interestingly, further oxidation led to a flattening of the surface, since 1.0 nm thick ozone oxide had a slightly lower RMS (0.05 nm) than a 1 ML ozone oxide (0.07 nm). This could indicate that etching is induced only during the initial oxidation stage (also refer to our discussion how the oxidation state of Si affects its etching barrier, see 4.1.1).

In addition, the initial oxidation of clean $Si\{111\}7 \times 7$ by O_3 and O_2 was studied via second harmonic generation (SHG) [63]. Since this technique is particularly sensitive to resonances of dangling bond surface states and strain, it is interesting to note that oxidation in O_2 and O_3 resulted in different SHG signals.

Initially, the SH intensity exhibited a fast decay for both oxidants, which was related to the saturation of dangling bonds by the adsorption of oxygen. However, while O_2 exposure (at RT and 400°C) after reaching a minimum resulted in a slow gradual rise of the SHG signal, the signal during O_3 exposure (at RT), not only dropped to a lower minimum, but did not gradually rise. Instead, the SHG intensity of oxidation in O_3 exhibits a significant temporary increase between 5 and 10 Langmuir exposure, before it gradually decreases again. Ozone's SHG signal might reflect the temporary increase in etching-induced surface defects or indicate a favourable strain release, which takes place already in the early oxidation stage of ozone.

Nevertheless, the role of this ozone-induced etching in the formation of a less-strained interface, is not clear. We

think that the most likely origin for the improved interface characteristics, is related to ozone's diffusion species. In the oxidation by ozone the diffusion of the more reactive O atom, in contrast to a diffusion of O_2 , allows a structural relaxation of the SiO_2 network near the interface. Further studies are necessary, however, to shed light on the interface formation.

5. Outlook: oxidation in ozone beyond silicon

Having extensively discussed the oxidation of silicon by ozone, we now give a brief overview of how ozone has been used in the fabrication of other oxide materials, most notably in the growth of metal oxides.

5.1. Semiconductor materials

Crystalline SiGe was successfully oxidized in O_3 at low temperatures [64]. Similar to the oxidation in silicon, the growth followed a parabolic behaviour with an activation barrier of $\approx 0.12 \text{ eV}$, which is slightly lower than in pure Si. With increasing temperature ($125\text{--}530^\circ\text{C}$) the Ge content in the oxide decreased and also the suboxide (Si^{1+} , Si^{2+} , Si^{3+}) decreased in thickness.

With respect to pure germanium, a good quality and perfectly stoichiometric GeO_2 was fabricated via atomic layer deposition (ALD) based on a divalent Ge precursor combined with O_3 [65]. Here, the O_3 was crucial to transform the chemisorbed divalent Ge precursor into tetravalent Ge on the growing surface. Ozone has also been successfully used to passivate germanium in order to engineer a Ge/insulator interface [66].

In the low temperature oxidation of silicon carbide, O_3 exhibited a much higher oxidation rate than O_2 . In addition, the oxidation in ozone reduced the carbon content in the SiO_2 film, which is favourable for device operations [54].

Ozone's oxidizing abilities have also been studied with respect to different structures of carbon, most notably graphene [67], carbon nanotubes [68, 69], and, due to the effect of surface transfer doping, increasingly important diamond surfaces [70–74].

5.2. High- κ materials

Metal oxides are heavily investigated as replacements for SiO_2 in complementary metal-oxide-semiconductor (CMOS) devices, since these oxides (high- κ materials) have a higher dielectric constant. In general, using O_3 in the oxidation or ALD of three of the most promising metal oxides (Zr, Hf, Al) exhibited improved electrical characteristics over chemical methods or oxidation in O_2 .

Ozone has been studied with respect to formation of zirconium oxide (ZrO_2) [75–78], where the ozone-grown oxide resulted in improved electrical characteristics over oxidation in O_2 [76] and a chemical oxide [77]. Similarly, a study of the physical and electrical properties of $HfSiON$ confirmed that UV/O_3 forms a high quality oxide even at room temperature [79].

High quality hafnium oxide (HfO_2) has been grown on top of silicon using ozone [80–84]. HfO_2 films grown by ALD

with O₃ as oxidant yielded superior electrical characteristics, including a lower fixed charge density, a lower interface trap density, and lower leakage current density, compared to H₂O as oxidant [80]. Even though, it was found that during the oxidation process ozone formed an undesired interfacial silicate between HfO₂ and the silicon substrate [80, 81, 83], ozone allowed a better control of this interfacial layer than regular O₂ [81]. XPS data indicated that the introduction of O₃ significantly improved the bonding characteristics between hafnium and oxygen even at low temperature [84].

In the case of alumina [85, 86], the ozone-grown aluminium oxide layer was more dense and superior in its corrosion properties compared to the natural oxide [85]. The electrical characteristics of a HfAlON dielectric with a UV/O₃ interfacial oxide were superior over an interfacial chemical oxide [87].

Room temperature oxidation in UV/O₃ exhibited enhanced oxidation rates for growth of zirconia, hafnia, and alumina with oxidation rates as follows: Zr > Hf > Al [88]. To explain the enhancement by UV-light radiation during the oxidation of metals such as Zr a theoretical model has been devised which gives trends consistent with experiments [89]. Here, the tunnel electron current due to UV-light excitation plays a key role to enhance the oxidation process.

6. Summary

In this topical review we have summarized key issues relating to the oxidation of silicon by ozone, including the various types of ozone generator developed over the last twenty years, the unique (and advantageous) characteristics of ozone-grown silicon oxide, and known details of the growth process itself. Notably, SiO₂ grown by exposure to ozone has been shown to possess a diminished suboxide transition layer, reduced strain, and greater reliability. Furthermore, the oxide growth rate under ozone is independent of the crystal facet exposed, and oxidation can even occur readily on hydrogen-passivated surfaces. As an alternative oxidant to regular dioxygen, ozone presents a variety of benefits, going beyond the immediate case of silicon oxidation, and clearly warrants further study.

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