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Low temperature photo-oxidation of silicon using a xenon excimer lamp

Jun-Ying Zhang^{a)} and Ian W. Boyd

Electronic and Electrical Engineering, University College London, Torrington Place, London WC1E 7JE, United Kingdom

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Low temperature (250 °C) photo-oxidation of silicon initiated by a Xe_2^* excimer lamp operating at a wavelength of 172 nm has been investigated. The induced reaction rate of 0.1 nm/min is 90 times greater than thermal oxidation at 612 °C and more than three times greater than that previously obtained at 350 °C using a low pressure mercury lamp. It was found to be strongly dependent upon oxygen pressure with the highest rates being achievable below 10 mbar. Ellipsometry, Fourier transform infrared spectroscopy, capacitance–voltage, and current–voltage measurements have been employed to characterize the oxide films and designate them as high quality. © *1997 American Institute of Physics*. [S0003-6951(97)01346-6]

The oxidation of silicon is one of the most important steps in the fabrication of Si based integrated circuits and has traditionally required high temperatures, typically about 1000 °C. Low-temperature oxidation of Si would be highly desirable for reduced thermal budget processing in device fabrication, but unfortunately purely thermally driven reactions are much too slow to be of use. In recent years, various methods to enhance low temperature growth of thin high quality silicon dioxide (SiO₂) films have been investigated using different approaches, involving plasmas,¹ ion beams,² and visible,³ and ultraviolet $(UV)^4$ radiation. UV and vacuum UV (VUV) radiation, has been shown to increase the oxidation rates, in some cases by more than an order of magnitude over the thermal rate, by photoexciting the silicon and/or directly dissociating the O_2 bond (5.1 eV) and liberating atomic species.^{5,6} These can either react directly with the silicon or, through collisional processes, form O₃, which is also much more reactive than its allotropic cousin.

Recently, a new generation of excimer UV lamps capable of producing high power radiation over large areas and extended availability of wavelengths from the near UV (354 nm) to the deep UV (126 nm) has been developed.^{7,8} The principle underlying the operation of these lamps relies on the radiative decomposition of excimer states created by a dielectric barrier discharge (*silent* discharge). The excimer molecules, once formed, rapidly decompose within a few nanoseconds giving up their excitation energy in the form of a VUV or UV photon. For example, in the case of the rare gas, Xe

$$Xe_2^* \rightarrow 2Xe + hv(\lambda = 172 \text{ nm}).$$

Since the excimer molecules readily dissociate there is no self-absorption of the emitted radiation. Thus, the sources can emit high UV intensities very efficiently (efficiencies between 7%-15% are readily achievable⁹). The development of these novel lamps offers enormous potential for materials processing. Several possibilities of applications of the UV sources have already been shown and include material deposition, polymer etching, and surface modification.¹⁰⁻¹² These have been also used to photodeposit good quality silicon

dioxide and silicon nitride films at low temperature by irradiating silane, nitrous oxide, and ammonia mixtures.^{10,13} In this letter, we report the direct photo-oxidation of silicon at 250 °C using 172 nm radiation from a Xe excimer lamp. The films grown were characterized using ellipsometry, Fourier transform infrared spectroscopy (FTIR), and capacitance– voltage (C-V) techniques.

The (100) orientation silicon wafers used were p-type with a resistivity of $2-10 \Omega$ cm and *n*-type with a resistivity of 2–4 Ω cm. The photon source was an excimer lamp filled with Xe and provided intense narrow-band radiation at λ = 172 nm from a dielectric barrier discharge. The distance between the silicon and the lamp was 1 cm with the power density incident on the sample being about 100 mW/cm². More details about this particular excimer deep UV source and the emission spectrum of Xe_2^* can be found elsewhere.^{7,8} The mica heater used provided uniform background heating over the entire surface of the sample, and the temperature, measured with a thermocouple, was fixed at 250 °C. Prior to UV irradiation at different exposure times the chamber was evacuated and filled to the required pressure (between 1 and 1000 mbar) with electronic grade oxygen (99.999%). The thickness of the films grown was determined using a Rudolph AutoELII ellipsometer at a fixed refractive index (n =1.462). The error of measurements for the thickness is about ± 4 Å.

Figure 1 shows the oxide thickness of the films grown at 5 mbar as a function of exposure time compared with previously published data for layers grown using a low pressure mercury lamp. As can be seen, the excimer lamp induced oxidation rate at 250 °C is more than three times greater than that obtained previously using a low pressure mercury lamp at 350 °C. It is also 90 times greater than thermal oxidation at 612 °C.⁶

The bond energy of O_2 is known to be close to 5.1 eV. Therefore, with 172 nm radiation (photon energy 7.2 eV), O_2 can be readily dissociated

$$O_2 + h v (\lambda = 172 \text{ nm}) \rightarrow O(^3p) + O(^1D).$$

The oxygen atoms released can subsequently form ozone by the following reaction:

$$O_2 + O(^3p) + M \rightarrow O_3 + M$$
 (M is a third body).

^{a)}Electronic mail: j.zhang@eleceng.ucl.ac.uk

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FIG. 1. Oxide thickness grown as a function of exposure time of the Si to 172 nm radiation from a Xe excimer lamp and a low pressure mercury lamp.

The ozone can then be decomposed by further absorption of the VUV light, producing excited state ${}^{1}D$ oxygen atoms.

 $O_3 + h \nu (\lambda = 172 \text{ nm}) \rightarrow O_2 + O(^1D).$

The active oxygen species thus formed subsequently react with the silicon leading to the formation of SiO₂. It is reasonable to assume that the oxidation process involves: (1) transport of the oxygen species to the oxide surface, (2) diffusion through the oxide, and (3) reaction with Si at the Si–SiO₂ interface, and that the overall reaction rate will be governed by the slowest process. During the initial stages of oxidation, the reaction at the silicon–oxide interface will most likely be the controlling factor, whereas in the later stages, once a significant film thickness has formed, the diffusion of reactant through the oxide layer may become important, as is the case for conventional silicon oxidation.

The oxidation rate was found to be strongly dependent upon oxygen pressure. Figure 2 shows the thickness of oxide grown as a function of oxygen pressure. At higher pressures the oxidation rate is much lower than that obtained at lower pressures. Several effects could cause this, but here we con-



FIG. 2. Oxide thickness grown as a function of pressure during a fixed irradiation time of 50 min using a 172 nm Xe excimer lamp.

TABLE I. Comparison of electrical properties and position of the Si–O–Si stretching absorption band maximum of UV grown oxides after different annealing times (172 nm lamp, 1000 mbar O_2 , 400 °C).

Annealing time (h)	Fixed oxide charge density (cm ⁻²)	Leakage current density at 1.0 V (A/cm ²)	Si–O–Si stretching absorption band maximum (cm ⁻¹)
0	2.4×10^{11}	1.2×10^{-6}	1069
1	7.5×10^{10}	7.0×10^{-7}	1073
2	4.5×10^{10}	9.0×10^{-8}	1075

sider two of the most likely contributors. First, at higher pressures the short wavelength radiation produced by the lamps (172 nm) will be more strongly attenuated in the gas phase by the absorbing oxygen. This would result in the photogenerated species being formed further away from the sample as well as less radiation reaching the silicon itself both of which could conceivably lead to reduced oxidation activity. Second, it is well known that as a consequence of the high voltage and signal frequency applied and the resulting distribution of charge on the dielectric tubes, plasma formation can occur around the exterior of the lamp at reduced pressures. The presence of this plasma can also possibly enhance the photo-oxidation rate of silicon in this pressure regime. Further work is clearly required to elucidate these points, and will be reported at a later date.

The FTIR spectra obtained for the annealed films were very similar to those recorded for thermally grown oxides,¹⁴ with peaks at 1075 cm⁻¹ (asymmetric stretching vibration), 800 cm⁻¹ (bending vibration), and 450 cm⁻¹ (rocking mode). The full width at half-maximum of the stretching peak at 1075 cm⁻¹ was 75 cm⁻¹, much smaller than that reported for excimer laser grown oxides (133 cm⁻¹).¹⁵ Besides the above mentioned SiO₂ bands, no other absorption bands (e.g., hydroxyl groups, etc.) were detected in the 4000–400 cm⁻¹ range.

Simple metal-oxide-semiconductor (MOS) capacitors have been fabricated using 11-nm-thick layers with an evaporated Al top contact of area 3.2×10^{-3} cm². Table I shows the fixed oxide charge density and the leakage current density of as-grown films to be 2.4×10^{11} cm⁻² and 1.2 $\times 10^{-6}$ A/cm² at 1.0 V, respectively. The electrical properties of these films are clearly not comparable with the best high temperature thermal oxide films grown under strict clean room conditions. However, even the rapid thermal oxides grown at 950 °C contain fixed oxide charge density in the high 10¹¹ cm⁻² range.¹⁶ It has been recently found that UV-O₃ annealing of Ta₂O₅ films improves their electrical properties significantly.¹⁷ This technique has been applied to our films, which were subsequently annealed in 1 atm of O_2 radiated by a 172 nm excimer lamp at 400 °C. A comparison of the electrical properties of our films after different annealing times is shown in Table I. After 2 h/ UV annealing, the fixed oxide charge density (Q_f/q) decreased from 2.4 $\times 10^{11}$ cm⁻² for the as-grown material, to 4.5×10^{10} cm⁻² while the interface trap density (D_{it}) was found to be 4 $\times 10^{10} \text{ eV}^{-1} \text{ cm}^{-2}$. These are comparable to that for thermally grown oxide on Si at 1030 °C.¹⁶ It was also found that the Si-O-Si stretching peak shifted to higher wave numbers



FIG. 3. Leakage current density vs applied electric field characteristics for a MOS capacitor fabricated using as-grown films and annealed films.

after this annealing step (Table I), indicating a possible increase in film density.^{18,19}

The I-V characteristics of the MOS capacitors also showed that after UV annealing, the leakage current density reduced dramatically as summarised in Table I. Figure 3 shows the leakage current density versus electric field characteristics for the MOS capacitor fabricated using as-grown films and annealed films. It can be seen that the as-grown films exhibited high leakage current densities (about $1 \,\mu$ A/cm²), in comparison to those that were annealed oxides, which showed a decrease of over an order of magnitude. One possible mechanism explaining the UV annealing effect involves the active O species formed by 172 nm light irradiation reducing the density of donor levels in SiO_x film, such as oxygen vacancies which lead to an increased leakage current. Further studies in the UV annealing effect are clearly necessary to more fully elucidate this point. Breakdown fields of 7-10 MV/cm were readily achievable in the annealed samples, almost as high as for thermally grown oxides.¹⁶ Figure 4 shows the C-V characteristics of the MOS capacitors at a frequency of 1 MHz after annealing for 1 and 2 h. Without annealing the flatband voltage $V_{\rm fb}$ was slightly positive, indicating the expected presence of negative fixed charges near the SiO₂/Si interface. After annealing the C-V curve shifted towards the negative voltage axis and the flatband voltage $V_{\rm fb}$ decreased, indicating a reduction in negative surface charge. This is most likely due to unreacted oxygen ions combining with Si and/or Si suboxides to create SiO₂. Clearly, very good electrical properties can be obtained for the SiO₂ layers by this UV-induced low temperature oxidation and annealing technique. It is important to note at this stage that the optimum growth and annealing steps may not yet have been achieved. This is the subject of a more extensive study now underway.



FIG. 4. 1 MHz C-V characteristics of the MOS capacitors for different UV annealing times at 400 °C (1000 mbar O₂).

Significant photo-oxidation of silicon at low temperature (250 °C) by using 172 nm radiation from a xenon excimer lamp has been demonstrated for the first time. Excellent electrical properties of the films grown, e.g., low fixed oxide charge densities $(4.5 \times 10^{10} \text{ cm}^{-2})$, low leakage current density $(9 \times 10^{-8} \text{ A/cm}^2 \text{ at } 1.0 \text{ V})$ and high breakdown fields in the range of 7–10 MV/cm, are achieved, properties comparable to those reported for thermally grown oxide on Si. This UV-induced low temperature oxidation process would appear to be very attractive for future ultralarge scale integration technology, especially when followed by a UV/O₃ annealing step, since the lamp technology used can, in principle, be readily extended to large areas wafers.

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