AIP Applied Physics Letters

Photooxidation of silicon monoxide to silicon dioxide with pulsed farultraviolet (193 nm) laser radiation

S. E. Blum, K. H. Brown, and R. Srinivasan

Citation: Applied Physics Letters **43**, 1026 (1983); doi: 10.1063/1.94216
View online: http://dx.doi.org/10.1063/1.94216
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/43/11?ver=pdfcov
Published by the AIP Publishing

Photo-oxidation of silicon monoxide to silicon dioxide with pulsed far-ultraviolet (193 nm) laser radiation

S. E. Blum, K. H. Brown, and R. Srinivasan
IBM Thomas J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598

(Received 14 June 1983; accepted for publication 12 September 1983)

Silicon monoxide films (1000–5000 Å thick) are converted to silicon dioxide when irradiated in air with pulses (~ 15 n half-width) of 193-nm radiation (40–110 mJ/cm^2) from an excimer laser. The quantum efficiency of the process has a minimum value of 0.014.

PACS numbers: 77.55. + f, 61.80. − x, 81.20.Pe, 81.60. − j

Silicon monoxide and silicon dioxide are insulating films that are commonly used in microelectronic devices. In silicon device technology the insulating silicon dioxide films are formed on the silicon wafers by direct oxidation at elevated (~ 1000 °C) temperatures. It would be desirable to form these films at lower temperatures[1] since the high temperature is known to result in surface depletion of impurities[2] and generation of stacking faults.[3,4] Deposition of silicon monoxide at room temperature followed by a low-temperature conversion to the dioxide is a possible way to obtain silicon dioxide films at low temperature. The monoxide, deposited at or near room temperature, is used in Josephson device technology because the high temperature required for silicon dioxide deposition irreversibly damages the metal in these devices and precludes its use. Unfortunately the monoxide does not lend itself to etching and patterning. It would therefore be beneficial for personalization and packaging purposes if the monoxide could be converted to the dioxide at room temperature. In this letter we describe work on such a conversion using far-ultraviolet (UV) (193 nm) irradiation in air.

The silicon monoxide films used were prepared by the evaporation of the monoxide onto polished ⟨100⟩ silicon wafers at a pressure of 10^{-8} Torr. The substrates were at room temperature and the source silicon monoxide (Cerac, 4–9's superoptical grade) was heated to 1300 °C in an rf heated hearth. The substrates were cleaned *in situ* before the deposition using an argon plasma. The thickness of the deposit was monitored with an Inficon XMS-3 Al_2O_3-Au crystal monitor. The uniformity of the films across the wafers was better than 5%. The film thickness was also checked with a Sloan Dektak and the agreement between the two methods was good ($\sim 5\%$). Silicon monoxide films of thicknesses between 500–5000 Å were used but it was generally more convenient to monitor the $SiO \rightarrow SiO_2$ conversion with films 4000–5000 Å thick.

A Lambda-Physik EMG-500 excimer laser with argon-fluorine gas was used as the source of 193-nm laser radiation. The laser beam impinged on the sample through a rectangular mask (0.8×1.5 cm) and with a fresh gas charge provided a fluence of approximately 110 mJ/cm^2 per pulse (15 ns) at half-width) over the area irradiated. A GenTec joulemeter was used to measure the laser output. The laser was used at repetition rates of 1–5 Hz with most of the experiments being done at 1 Hz. The output was measured both before and after an experiment to obtain an average.

The procedure followed in these experiments was to allow the unfocused beam from the laser to impinge directly onto the SiO film surface in an air atmosphere. Alteration of the beam flux was done with Spectrosil^{TM} (high purity synthetic vitreous silica) lenses and plates.

The course of the oxidation of the SiO films was analyzed by infrared spectrometry and by helium backscattering. A Perkin–Elmer 180 IR spectrophotometer was used in the mid-infrared region, 4000–500 cm^{-1}. The SiO/Si films (hereafter this designation for film and substrate is used) exhibit an absorption peak at 980 cm^{-1} while thermally grown SiO_2 films have an absorption peak at 1060 cm^{-1}.

Although there is interest for device purposes in producing SiO_2 films of $\leqslant 1000$ Å, it was best for this study to use films of 4000–5000 Å in order to obtain sufficient absorption intensities at the peaks.

Several oxide films, both before and after irradiation, were analyzed by helium backscattering to confirm that the IR transmission peak shift represented the oxidation of the monoxide to the dioxide. A High Vacuum Technology accelerator was the source of the 2.3 MeV helium ions used in these analyses. In one case a direct comparison of backscattering analysis and IR spectrum was made using a 5000-Å SiO/Si sample. In several samples 1000 Å of SiO was deposited on carbon and helium backscattering analyses were done both prior to and after irradiation. The films on carbon were used because the carbon substrate backscattered helium less than silicon and therefore the sensitivity and precision of the analyses were enhanced.

Ellipsometry is a much favored analysis for thermally produced silicon dioxide films. An attempt was made to confirm the $SiO \rightarrow SiO_2$ reaction by this technique. The ellipsometry studies proved difficult. However, the results were not in disagreement with the IR and backscattering results. Ellipsometry of unirradiated SiO/Si gave thicknesses and re-

TABLE I. Helium backscattering analyses of SiO films irradiated with 193-nm pulsed laser.

No.	Film	# Pulses at 110 mJ/cm^2	Atom % O	Atom % Si	O/Si	IR peak (cm^{-1})
1	5000 Å SiO/Si	none	50.5	49.5	1.02	980
2	5000 Å SiO/Si	1200	68	32	2.13	1080
3	1000 Å SiO/C	none	47.6	52.4	0.91	···
4	1000 Å SiO/C	100	60.5	39.5	1.53	···
5	1000 Å SiO/C	1000	67.2	32.8	2.05	···

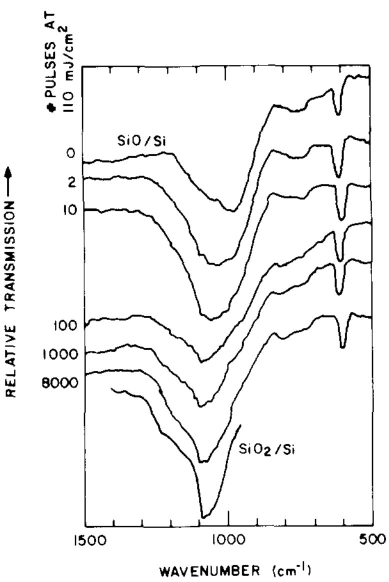

FIG. 1. IR spectra of 4000 Å SiO/Si films irradiated at 110 mJ/cm^2/pulse for various number of 193-nm pulses. Unirradiated SiO film is shown at top and thermally formed SiO_2 at bottom. Curves are vertically displaced for clarity.

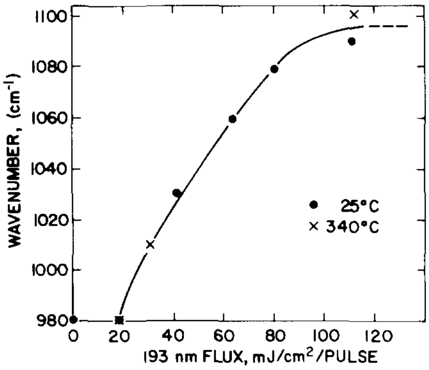

FIG. 2. IR transmission peak position as a function of fluence. Each sample exposed for a total of 110 J/cm^2. 4000 Å SiO/Si.

fractive index values in good agreement with thickness monitors and established refractive index values of 1.9–2.0.[5] After irradiation the refractive index decreased to 1.3–1.8 indicating conversion towards SiO_2, with some samples having a refractive index equal or close to that of SiO_2 (1.46).

The results are summarized in Table I and Figs. 1 and 2. Helium backscattering data in Table I show that with progressive irradiation with 193-nm pulses, the atomic composition ratio of O to Si changes from 1 to 2. At the same time the infrared peak position shifts from 980 to 1080 cm^{-1}. Infrared spectra which are presented in Fig. 1 further demonstrate that the gradual shift in the peak position can be used to obtain a qualitative idea of the change from an initial composition of SiO to SiO_2.

The backscattering data allow the determination of a quantum yield for the formation of SiO_2. On the basis that 100 pulses of 110 mJ of energy were required to convert partially 1000 Å of SiO in the irradiated area to a composition of $O/Si = 1.53$, a quantum yield of 0.014 is obtained. This must be viewed as a minimum value since the assumption is made here that every incident photon is absorbed by the reactant(s). This is hardly likely to be the case. The apparent quantum yield for the 5000 Å film was even smaller than the value given above.

The influence of fluence at room temperature and at 340 °C is given in Fig. 2. Since all samples were irradiated to the same total energy, the results suggest an increase in the formation of SiO_2 with increasing fluence but no detectable influence of temperature up to 340 °C.

Three mechanisms can be considered for the oxidation of SiO to SiO_2b by 193-nm pulses. The first would be a disproportionation (reaction 1) between excited SiO and an unexcited molecule.

$$SiO^* + SiO \rightarrow Si + SiO_2. \tag{1}$$

The free-silicon atom can subsequently undergo oxidation by the oxygen in air so that the ratio of silicon to oxygen can change with conversion. It is not essential that one molecule of the SiO in reaction (1) be in an excited state because intense local heating by the laser can also lead to a disproportionation. It is known[6] that such a reaction can occur at as low a temperature as 1200 °C.

Two other mechanisms in which oxygen in air provides the oxygen atom for the oxidation process can also be proposed. In Eq. (2), photoexcited

$$\begin{aligned} &SiO^* + O_2 \rightarrow SiO_2 + O, \\ &O + SiO \rightarrow SiO_2. \end{aligned} \tag{2}$$

SiO abstracts an oxygen atom from O_2 while in Eq. (3) the oxygen is provided by the photolysis of O_2

$$\begin{aligned} &O_2 + h\nu \rightarrow 2O^\bullet, \\ &O^\bullet + SiO \rightarrow SiO. \end{aligned} \tag{3}$$

Obviously, O can react with O_2 to give O_3, a process that is readily observed at this wavelength. Both of these mechanisms would be consistent with the observed difficulty in photo-oxidizing thick as opposed to thin SiO films. Attempts to test these mechanisms by carrying out the laser irradiation in a controlled atmosphere have not yet produced definitive results because the laser pulses caused considerable outgassing of material from the window and walls of the cell in which the SiO film was enclosed.

We are especially indebted to R. J. von Gutfeld for his many helpful discussions and D. R. Vigliotti for his generous technical help. We also wish to thank S. Renick for preparation of the SiO films, R. Serino for aid in the IR analyses, M. Levanoni and H. Kaiser for the ellipsometry analyses, and P. Saunders for the backscattering analyses. R. S. wishes to thank J. Siejka and C. Cohen of the Solid State Physics Group at E.N.S., University of Paris for an enlightening discussion concerning the mechanism.

[1] A. K. Ray and A. Reisman, J. Electrochem. Soc. **128**, 2424 (1981).
[2] B. E. Deal, A. S. Grove, E. H. Snow, and C. T. Sah, J. Electrochem. Soc. **112**, 308 (1965).
[3] S. M. Hu, J. Appl. Phys. **48**, 1567 (1974).
[4] S. P. Murarka, J. Appl. Phys. **48**, 5020 (1977).
[5] E. Ritter, Opt. Acta. **9**, 197 (1962).
[6] J. Simpson, *Inorganic Chemistry*, edited by M. F. Lappert (Butterworths, England, 1972), p. 241.