Study of the changes in the infrared transmission of SiO$_2$ spin-on-glass due to ion implantation

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The ion implantation of phosphorus into spin-on-glass (SOG) SiO$_2$ thin-film films modified the infrared transmission spectrum of the films. Two SOG types, polysiloxane and silicate, were ion implanted with doses in the 1×10^{14}–1×10^{15} cm^{-2} range and an energy of 40 keV. The Fourier-transform infrared spectrum of such films on silicon substrates was measured and the results are presented as a function of the implanted dose. The effect of the ion implantation on the silicate SOG was minute while significant changes were observed in the polysiloxane SOG. The major absorption peaks in the transmission spectrum were numerically analyzed and fitted to a set of Lorentzian functions. The peak heights, width, and area were measured. The ion implantation reduces the number of CH$_3$ groups while the location of the Si-O absorption peak is shifted towards a shorter wavelength, i.e., a denser material. A physical interpretation of the absorption peak dependence on the ion-implanted dose is presented.

Spin-on-glasses (SOG) are sol-gel materials, i.e., are initially liquid and can be solidified by a chemical process, typically at elevated temperatures. The properties of annealed SOG are comparable to those of chemically vapor-deposited (CVD) SiO$_2$, which is widely used in very-large-scale-integration (VLSI) technology.[1] SOG is used as part of the interlevel dielectric where its role is to smooth the upper topography and hence improve the upper metal level step coverage. SOG materials for VLSI are processed at temperatures below 450 °C, to be compatible with aluminum technology. Higher-temperature annealing may improve the material properties but cannot be incorporated after the first aluminum level. Ion implantation of SOG has been proposed[2] as a technique to improve the low-temperature annealed SOG properties and still be compatible with aluminum technology.

The transmission infrared spectrum of polysiloxane and silicate SOG materials is discussed here. Both materials have silicon and oxygen in their polymer backbone, but they differ in their carbon content when annealed at low temperatures. After a high-temperature anneal, typically above 850–900 °C, both materials are fully converted to silicon dioxide.[1] The silicate SOG contains only a small amount of carbon after a 260 °C anneal. It is typically used for thin-film coating, less than 100 nm thick, since it tends to crack for thicker layers. Adding phosphorus, 2%–4% in weight, improves its resistance to cracking. Polysiloxane SOG contains carbon when annealed at temperatures as high as 600–700 °C. It is less vulnerable to cracking and its typical maximum use thickness is about 400–500 nm.

SOG processing involves spin casting and an annealing step. The final material properties depend on the temperature cycle, ambient gas properties (i.e., composition, partial pressure, and humidity), and substrate. SOG film formation includes polymerization, solvent evaporation, and by-product out-diffusion. The chemical and structural characteristics of the material depend on each one of these mechanisms. The annealing process has a detrimental effect on the material reliability, i.e., defect density, cracks, structural instabilities that effect overlaying layers,[3] and residual polymerization during plasma etching.[4]

Ion implantation can be also used for SOG annealing.[2] The implanted ions transfer their energy to the material atoms through a series of collisions. The result is a compositional and structural change which is apparently similar to those that appear after thermal annealing: i.e., volume shrinkage and lower etch rate. To understand some of the effects of ion implantation on the molecular structure of the SOG, an infrared spectroscopy study was conducted. The infrared transmission spectrum of SOG is characterized by the absorption of the following bonds: Si—O, CH$_3$, water, and Si—H.[5,6] Each peak was identified and numerically analyzed by a nonlinear fitting program to a Lorentzian function. The relative concentration of the infrared absorbing species was calculated as a function of the implanted dose.

The spin-on-glass materials under study were (1) Allied Signal 110 & 111 polysiloxane-type materials, and (2) Tokyo Ohka OCD-2P and Allied Signal 112P silicate-type SOG. The SOG was dispensed on the polished side of 100-oriented, n-type, 5–10 Ω cm, Czochralski-grown single-crystal silicon wafers with low oxygen content (less than 30 ppm). The coated wafers were baked on a hot plate at 80, 180, and 260 °C sequentially. This was followed by a 30-min furnace anneal at 450 °C in a nitrogen ambient. The annealed wafers were implanted with phosphorus and sil-
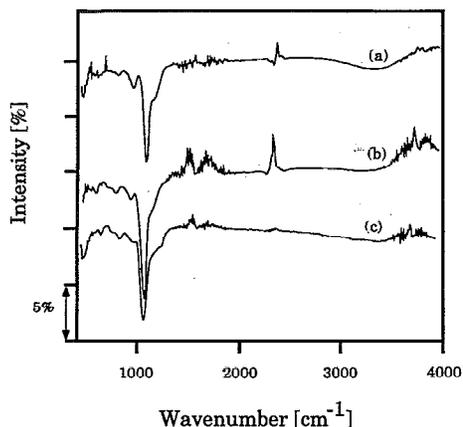
FIG. 1. Transmission FTIR spectra of silicate SOG samples. (a) After 120 °C hot-plate anneal for 90 s in air, (b) after 120, 180, 260 °C hot-plate anneal for 90 s at each temperature followed by 420 °C furnace anneal in nitrogen ambient for 30 min, and (c) like (b) followed by a phosphorus implant. The curves are aligned such as the flat region is approximately at 100% transmission.

FIG. 2. Transmission FTIR of four polysiloxane SOG samples before (a) after (b, c, and d) a 40-keV phosphorus ion implant.

icon with an energy of 40 keV and a dose of 1×10^{14}–1×10^{15} cm^{-2}. The ion-implanted SOG layer thicknesses were measured by ellipsometry.

The Fourier-transform infrared (FTIR) spectrum of the coated wafers was measured with the Cygnus 25 system made by Mattson Instruments Inc. The samples were tilted about 20° off the beam path to eliminate the interference effect due to the internal multiple reflection inside the wafer. The data was transferred to an HP9845B workstation and was fitted to a set of Lorentzian curves, each given by

$$f(x) = A/[(X - X_0)^2 + \delta^2], \qquad (1)$$

where X_0 is the local peak wave number and δ is its width. The procedure included a nonlinear regression analyses using a least-square-root minimization algorithm.

Typical infrared transmission spectra of silicate SOG annealed to 120 °C, 420 °C, and by ion implantation are shown in Fig. 1. The lines are plotted such that the flat region is about 100% and the y-axis marks are 5% separated. The significant absorption peaks, as shown in Fig. 1, are as follows:

(a) Near 1050 cm^{-1}: Due to the Si—O stretching vibration mode. This peak is composed of a major peak plus a smaller absorption mode at about 1200 cm^{-1}. After the ion implantation the shape and the location of the two peaks remain almost the same.

(b) At 940 cm^{-1}: This peak almost disappears after the ion implantation.

(c) At 800 cm^{-1}: This peak remains unchanged after the implant.

Typical infrared transmission spectra of polysiloxane SOG before and after the ion implantation are shown in Fig. 2. The data covered the range between 400 and 1600 cm^{-1} where five major absorption peaks could be observed:
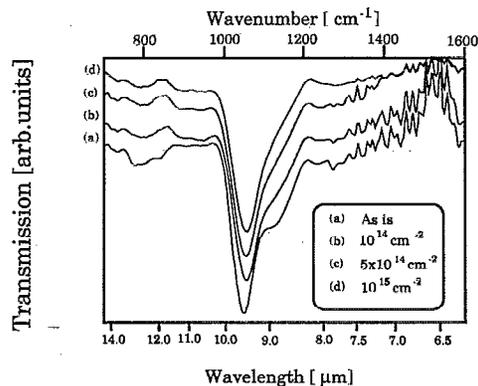
(a) At 1050 cm^{-1}: This peak is due to absorption of the stretching vibration of the Si—O group.

(b) Near 1120 cm^{-1}: This peak is most probably due to the stretching vibration mode absorption of Si—O—R groups where R is assumed to be CH$_3$.[2]

(c) Near 1250 cm^{-1}: This absorption peak is identified as due to the stretching vibrations of the (Si)—CH$_3$ group.

(d) Near 800 cm^{-1}: This peak can be related to the weaker absorption of the Si—CH$_3$ or Si—H groups.

(e) Near 920 cm^{-1}: This peak is due to Si—OH bonds.

The two first peaks in Fig. 2 are close enough so they were analyzed together as a superposition of two Lorentzian curves (see Fig. 3). The rest of the peaks were analyzed separately. The results for the first three peaks are summarized in Table I. In this table, we also present the peak normalized magnitude, A/δ, that is proportional to the area under the absorption curve. Each magnitude was normalized so the maximum magnitude for every peak is 1. The magnitude of the fourth peak, near 920 cm^{-1}, is very small for the unimplanted SOG and increases after the ion implantation. The increase has only a slight dependence on the implant dose. The magnitude of the fifth peak, near 800 cm^{-1}, decreases after the ion implantation, independently of the implant dose.

The first peak (a) wave number increases with dose as does its width, while its magnitude remains constant. This may be explained by the increase of the SOG density of the implanted SOG[1] compared to the nonimplanted one. The change is probably due to the average bond energy increase as the material density increases. This leads to a stronger coupling between the molecules and higher vibration frequency. The number of absorbing centers remains constant, as found from the relative magnitude. This means that the effect of the ion implantation is to rearrange the Si—O—Si groups in a denser form. The ion implantation breaks many of the Si—O bonds and may also knock atoms from their sites. However, most of the atoms, silicon or oxygen, bond again shortly after being dislodged.

The second peak (b) is shifted toward lower energies, its magnitude decreases and its width increases with in-
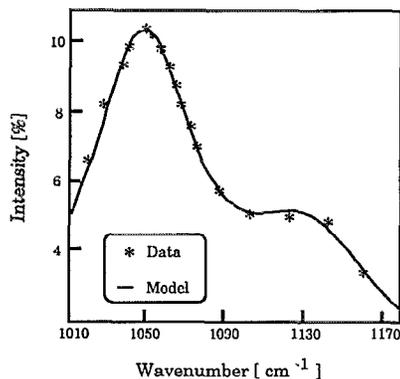
FIG. 3. Detailed plot of the major absorption peak of polysiloxane SOG near 1050 cm^{-1}. The data is marked by stars and the continuous curve is the sum of two Lorentzian functions fitted to the data with a total of six unknown parameters that were found by the nonlinear minimum square-root method.

creasing dose. A similar effect has been reported for furnace-annealed SOG, as reported in Ref. 5. The decrease in the relative magnitude can be related to a loss of the methyl groups, and the shift may be due to loss of water or OH bonds which may be attached to the methyl group.

The third peak (c) was shifted to higher energies as the doses increase while the peak width remains unchanged. This peak is also related to the Si—CH$_3$ bond and also related to the change in the material density. The peak relative magnitude was reduced by half after the ion implantation. The total number of hydrogen in the SOG, as measured by using a foreword recoil elastic scattering (FRES) probe with He ions, decreased in a similar ratio. Therefore, it is assumed that the hydrogen atoms actually leaves the glass.

The fourth peak is assumed to be due to Si—CH$_3$ bond absorption. The maximum absorption was shifted to higher energies as the doses increase while the peak width remains unchanged. The absorption magnitude decreases with increasing doses and it may indicate that the ion implantation breaks the silicon-carbon bonds. The carbonyl ion may recombine with hydrogen and disappear or become attached to a free oxygen bond.

The last peak is assumed to be due to a Si—OH bond. The magnitude of that peak increases with increasing dose. However, this increase in hydrogen content is less than the decrease in Si—O—R groups. The increase in the OH-related absorption can be due to water adsorption from the atmosphere by dangling silicon bonds after the process. This increase may affect the SOG reliability since water is not a stable component in the solid matrix.

The infrared study of the polysiloxane SOG indicates the following effects of the ion implantation.

(1) A decrease of the amount of carbon and hydrogen bonded to silicon.

(2) An increase of the number of the Si—OH bonds.

(3) A change in the oxide structure as shown in the major Si—O bond absorption peaks.

The measured increase of the Si—OH bonds after the implant is similar to the increase after furnace anneal in oxygen ambient. The ion implantation breaks enough oxygen bonds that become available to bond hydrogen molecules from the ambient. This result is important since it indicates a higher sensitivity of the implanted SOG properties to the ambient humidity. Capacitance measurements show that the material dielectric constant decreases after the ion implantation. On the other hand, the presence of more OH bonds would be expected to result in an increase in the dielectric constant. Therefore, we may assume that the increase in the material density may negate the expected polarization of the excess hydrogen in the implanted samples.

It is shown that detailed FTIR analysis can be used for the investigation of the chemical and physical changes in SOG due to the ion implantation. The relative magnitude of the absorption peaks describes the total number of absorbing centers in the material. Although the SOG is very thin, the signal was found to be sufficient for a useful analysis. 100-nm thin SOG absorbs about 20% of the radiation near the Si—O major peak at 1050 cm^{-1}. Therefore, the peak absorption coefficient is about 2.2×10^4 cm^{-1}.

TABLE I. The parameters of the Lorentzian functions fitted to the three major absorption peaks of polysiloxane SOG (see Figs. 2 and 3).

Peak	Dose (cm^{-2})	X_0 (cm^{-1})	δ (cm^{-1})	Relative mag.
(a)	0	1048	32.7	0.92
(a)	10^{14}	1053	33.5	0.82
(a)	5×10^{14}	1053	38.7	1.00
(a)	10^{15}	1053	38.9	0.97
(b)	0	1133	44.6	0.5
(b)	10^{14}	1122	58.7	0.53
(b)	5×10^{14}	1120	59.4	0.44
(b)	10^{15}	1112	61.9	0.43
(c)	0	1232	76.7	1.00
(c)	10^{14}	1235	86.1	0.81
(c)	5×10^{14}	1246	79.7	0.68
(c)	10^{15}	1266	74.2	0.53

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