

Large increase of refractive index and compactness in siloxane-type spin-on-glass induced by ion implantation

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Drastic changes in index of refraction and volume shrinkage of spin-on-glass films induced by P^+ implantation are reported. An increase in refraction index (n) as large as 20% (from 1.38 to 1.79) has been measured following $1.6 \times 10^{16} \text{ cm}^{-2}$ implantations. The changes in n are accompanied by a volume shrinkage of similar magnitude. However, at doses exceeding $\approx 10^{15} \text{ cm}^{-2}$ the shrinkage saturates while the index of refraction continues to increase indicating that material changes other than simple densification must be responsible for the observed rise in refractive index.

In recent years spin-on-glass (SOG) has found its application in the microelectronics industry mainly as a planarization material or as an insulating film between two metallic layers.¹⁻⁴ A difficulty encountered in the use of SOG for such applications is the requirement for high-temperature ($> 800^\circ\text{C}$) curing of the material; a process which is often noncompatible with device manufacture requirements. In the field of integrated optics efforts are directed into the search for high quality dielectric films needed for optical communication in which waveguides can be realized. To achieve this, one needs an optically transparent material the refractive index of which can be locally changed on a micron scale by a low-temperature process compatible with microelectronic technology. Little work has been published on this topic to date, and only most recently, Rochford and co-workers⁵ reported on the possibility of inducing changes (of up to 8%) in the index of refraction of a particular polymer (poly-4BCMU) by photoinduced bleaching. They demonstrate waveguiding in channels produced in this way.

In the present work we show that both optical and physical properties of SOG films can be drastically changed by ion implantation. Optically, increases in the index of refraction as high as 20% have been measured by us in SOG layers which were subjected to P or Si implantations. Physically, we show that ion implantation into SOG causes substantial increases in material density leading to films with physical properties comparable to those of high-temperature-treated SOG or native oxide layers, thus offering a simple low-temperature process which results in good quality dielectric layers.

The spin-on material used in the present investigation was a commercial siloxane-type SOG (Allied Ltd.), based

on silicon-organic compounds (5–15%), dissolved in an alcoholic solution. The films were produced by dispensing about 1 c.c. of the solution on a $\langle 100 \rangle$ 2 in. silicon wafer, followed by a spin at 7000 revolutions per minute for 20 s. The coated wafers were baked at 120 and 180 $^\circ\text{C}$ on an open hot plate for 5 min. Following this, the samples were inserted into a furnace (in air), in which the temperature was raised from 260 to 420 $^\circ\text{C}$ at a rate of 6.5 $^\circ\text{C}/\text{min}$ and kept there for an additional 30 min. This procedure has led to films with a uniform thickness of $\approx 1200 \text{ \AA}$.

Identical implantations of different elements (^{28}Si , sometimes ^{29}Si and ^{31}P) were performed at 40 and 70 keV to a dose of 10^{15} or 10^{16} cm^{-2} keeping the beam current density below $4 \mu\text{A}/\text{cm}^2$ to eliminate beam-induced heating effects. Since both Si and P implantations are expected to cause similar damage due to the proximity in ion mass, any difference in film properties which may be observed following the implantation must be attributed to chemical effects. No such difference in any one of the measured quantities (index of refraction and thickness changes—see below) could be detected. We therefore conclude that the major effect of the implantation is due to radiation damage—hence all following implantations were of P ions only. Different implantations with doses ranging from 10^{14} to $1.65 \times 10^{16} \text{ P}^+/\text{cm}^2$ were employed at 60 and 40 keV.

An estimate for the thickness of the layer affected by the implantation was obtained from TRIM computer simulations.⁶ These, however, face some difficulties when applied to the present case since the material density and composition, which are input parameters to the program, are not exactly known and both seem to gradually change during implantation. We have thus performed the TRIM calculation using a reasonable range of values for the material density (1.5–2.0 g/cm^3) and composition $\text{Si}_x\text{O}_y\text{C}_z$ ($x = 0.2\text{--}0.4$, $y = 0.3\text{--}0.6$, and $z = 0\text{--}0.4$) yielding for 60 keV phosphorus implants a range R_p of 900–1000 \AA with a

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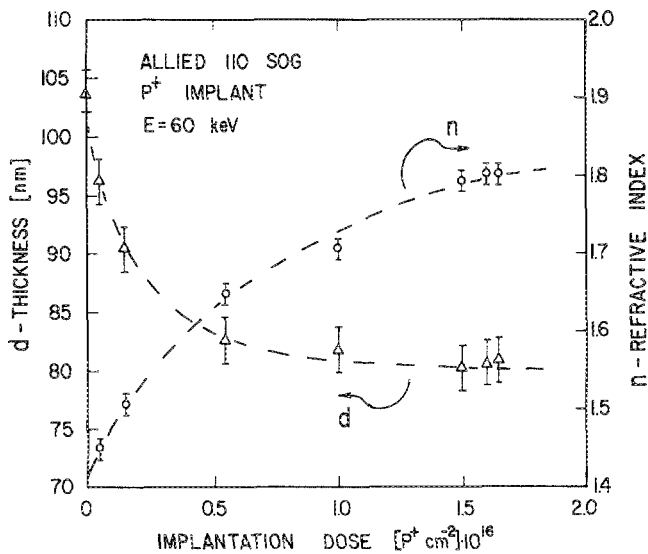


FIG. 1. Thickness and refractive index of P-implanted SOG as function of implantation dose in Allied 110.

straggling ΔR_p of 300–400 Å. Similar calculations for 40 keV P^+ yielded $\Delta R_p \approx 750$ –850 Å with $R_p \approx 250$ –350 Å. If we assume that the damage profile roughly overlaps that of the implant, we see that the better part of the SOG film has been affected by implantation. The similarity of the results obtained for 70, 60, and 40 keV implantations, regarding both optical and physical changes, verifies this assumption and shows that even if the tail of the implantation profile has somewhat penetrated into the substrate, this had no remarked effect on the results.

The coated wafers were analyzed, before and after implantation, by performing ellipsometry (at 633 nm) and profilometry measurements. The δ and ϕ values obtained from the ellipsometer were used to calculate the thickness and refractive index of the SOG film assuming it to be of uniform composition on a Si substrate of infinite thickness with $n = 3.85 - 0.018j$. To verify the thicknesses deduced from the ellipsometry, step height measurements were also performed on the same samples using two different instruments (TENCOR Alpha-step and Nanospec AFT-200). As all measurements yielded results which were in agreement to within 5%, we quote here the results of the ellipsometry measurements only and assign them an uncertainty of 5%.

Very significant changes in refractive index and in film thickness were observed following ion implantation. These changes are presented in Fig. 1 from which it can be seen that with progressive implantation the film thickness shrinks and its index of refraction increases. Both effects seem to go hand in hand for doses below $\approx 5 \times 10^{15} \text{ cm}^{-2}$. For higher implantation doses the material density saturates, while the index of refraction keeps increasing with dose.

In order to check whether the observed changes in index of refraction are just due to the increased compactness of the material, we have analyzed our data using the

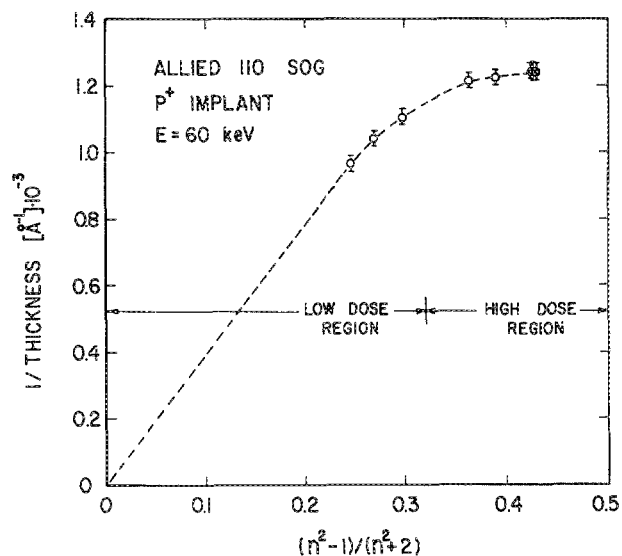


FIG. 2. Lorenz-Lorentz relation plot of $1/\text{thickness}$ vs $(n^2 - 1)/(n^2 + 2)$.

Lorenz-Lorentz relation.⁷ According to this relation the density of a dielectric material is proportional to $(n^2 - 1)/(n^2 + 2)$. Therefore, assuming no material loss during implantation, a plot of $1/\text{thickness}$ of the SOG film versus $(n^2 - 1)/(n^2 + 2)$ should give a straight line. Such correlation is indeed observed at low doses, up to $5 \times 10^{15} \text{ cm}^{-2}$, as shown in Fig. 2. At higher doses the film thickness reaches saturation and the changes in the refractive index must be due to other effects.

It is interesting to note that while the final compactness of the implanted spin-on-glass very much resembles that of high-temperature-baked SOG,⁸ their optical properties differ remarkably. In high-temperature-treated SOG (above 850 °C) the optical properties are similar to those of thermal oxide ($n \approx 1.4$), whereas those of the implanted layers reach an index of refraction as high as ≈ 1.8 .

The similarity in densification between high-temperature-treated and ion-implanted SOG can be related to possible molecular rearrangement in the material and to loss of remaining organic residues, both being the result of energy deposited to the material by either heat or by the implantation process. During implantation the ions lose energy by a series of collisions with electrons and atoms in the stopping medium. This may break existing bonds and knock atoms from their original location thus aiding rearrangement of the material. Such rearrangements may also be thermally induced, hence the similarity in the final results. Since the spin-casting deposition process, in contrast to the chemical vapor deposition technique, is a rapid process that takes place at low temperatures much below the material glass point, molecules which are probably trapped in a loosely packed mesh with some solvent may effuse or change position leading to a different, more dense, structure.

The observed large differences in index of refraction between high-dose-implanted layers and high-temperature-

treated SOG, despite both having rather similar final densities, is still unclear. One possibility to be considered to account for this difference is that a phosphorus doping effect, due to the high-dose implantation, is responsible for the further increase in index of refraction beyond the compactness saturation. This possibility can, however, be ruled out in light of the fact that similar, high-dose (10^{16} cm^{-2}) Si implantations (Si not being a dopant in SiO_2) has resulted in an increase in n identical to that caused by the P implantations. Nevertheless, those differences are being further investigated, and detailed infrared and dielectric measurements on implanted and thermally treated SOG are currently underway.

Both optical and physical effects that ion implantation has on SOG films, reported in the present work, may have important technological implications. The possibility to drastically alter the refractive index of the SOG layer by ion implantation, a technique which is well suited for sub-micron technology, may find uses in integrated optics applications. The compactness of SOG layers induced by ion implantation can offer a low-temperature process for the production of high quality dielectric films and may replace

the undesirable high-temperature curing stage currently employed in the very large scale integrated circuits technology.

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- ¹P. E. Riley and A. Shelley, *J. Electrochem. Soc.* **135**, 1207 (1988).
- ²P. Elkins, K. Reinhardt, and R. Tang, *VLSI Multilevel Interconnect Conference Proceedings* (VMIC, Santa Clara, CA, 1986), p. 102; G. E. Whitewell, *ibid.*, p. 292; J. K. Chu, J. Multani, S. Mittal, J. Orton, and R. Jecmen, *ibid.*, p. 474; S. K. Gupta and S. W. Kirtley, *ibid.*, p. 506.
- ³F. Dupuis, Y. Shacham-Diamand, and W. G. Oldham, *Proceedings of the VLSI Technical Conference* (VMIC, Kobe, Japan, 1985), p. 52.
- ⁴N. Moriya, R. Kalish, R. Brenner, and V. Richter, *Mater. Res. Soc. Symp. Proc.* **105**, 97 (1988).
- ⁵K. B. Rochford, R. Zanoni, Q. Gong, and G. I. Stegeman, *Appl. Phys. Lett.* **55**, 1161 (1989).
- ⁶J. P. Biersack and L. G. Haggmark, *Nucl. Instrum. Methods* **174**, 257 (1980).
- ⁷N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Saunders College, Philadelphia, 1976), p. 542.
- ⁸Pei-Lin Pai, A. Chetty, R. Roat, N. Cox, and C. Ting, *J. Electrochem. Soc.* **134**, 2829 (1987); Pei-Lin Pai, W. G. Oldham, and C. Ting, *Proceedings of the VLSI Multilevel Interconnect Conference* (VMIC, Santa Clara, CA, 1987), p. 111, and references therein.