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Modification of Plasma-Polymerized Organosiloxane Films by Irradiation with He^+, Ne^+, Ar^+, and Kr^+ Ions

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The effects of ion irradiation on the composition, structure, compactness, and surface hardness of polyorganosiloxane films synthesized by plasma-enhanced chemical vapor deposition were investigated as a function of the ion mass and fluence. The films were obtained from a glow discharge plasma of a hexamethyldisiloxane (HMDSO)−O_2−Ar mixture, and the irradiations were carried out with 170 keV He^+, Ne^+, Ar^+, and Kr^+ ions at fluences between 1×10^{14} and 1×10^{16} cm^{-2}. To characterize the film elemental composition, two ion-beam analysis techniques were used: Rutherford backscattering spectroscopy (RBS) and forward recoil spectroscopy (FRS). The ion-beam-induced hydrogen loss from the films was significant. For the He^+-irradiated samples, a H loss of about 50% with respect to the pristine or unirradiated film was observed for the highest fluence. The surface hardness measurements, performed with a nanoindenter, in films irradiated at a fluence of 1×10^{16} cm^{-2} were 8.1, 6.0, 4.7, and 1.6 GPa for He^+, Ne^+, Ar^+, and Kr^+, respectively. To examine the ion-induced structural transformations in the films, infrared reflection−absorption spectroscopy (IRRAS) was employed. From analysis of the spectra of the irradiated samples several conclusions could be drawn. For example, as the ion fluence increased, (i) the densities of methyl- and Si−O-related groups changed, (ii) film disorder increased, and (iii) groups such as Si−CH_2−Si, and Si−OH, which were not present in the pristine film, were formed at lower fluences but disappeared when the latter attained their highest values. Furthermore, some of the absorption peaks that appeared at low fluences and increased with increasing fluence strongly indicate formation of carbon domains in the film. Finally, differences in the ion-induced modifications produced by the different ion species were analyzed in terms of the electronic and nuclear collisions of the ions traversing the film using the well-known SRIM simulation program.

1. Introduction

Energetic ions may cause significant modifications in the structure and composition of polymers, thus changing their chemical and physical properties. In both C-based[1−3] and Si-based[4−7] polymers the effects of ion irradiation have been intensively investigated for more than a decade. Motivations for these studies include understanding the polymer−energetic ion interaction process and use of ion irradiation to produce controllable changes in the polymer properties, rendering the material useful to various technical applications.[8−11]

In recent years much attention has been given to changes in the tribological properties of Si-based polymers induced by thermal treatment and ion irradiation. The latter has been used to produce ceramic materials from precursors such as polysiloxanes, polycarbosilanes, and polysilazanes.[5,12] Usually better improvement of compaction, hardness, and chemical stability can be achieved with ion irradiation in comparison to thermal treatment. While thermally treated precursors can be totally carbon-depleted, in the ion-treated ones the final carbon content is relatively high, forming highly cohesive structures such as oxycarbide (SiOC) or silicon carbonitride (SiCN). In fact, the hardness of some ion-treated Si-based polymers can be much higher than that of SiO_2.[12]

Thus far conventional polymers have been the target of most studies on ion-induced modifications of polymers.

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Modifications of plasma-deposited polymers, i.e., polymers produced by the plasma-enhanced chemical vapor deposition (PECVD) technique, have been investigated to a much lesser extent. Nevertheless, in these materials the ion-induced changes in hardness,[13] surface biocompatibility,[14] and electrical and optical properties[15] are usually as remarkable as those observed in their conventional counterparts. Typically, the thickness of plasma-deposited polymers ranges from tenths to about one micrometer. However, since the ion beams normally used in ion irradiation produce surface or near-surface modifications not too far beyond a micrometer, plasma-deposited polymers can compete with conventional polymers as precursor materials for ion irradiation.

In this work polysiloxane films synthesized by PECVD from a hexamethyldisiloxane (HMDSO)$-$O$_2$$-$Ar mixture were irradiated with 170 keV ions of widely different masses (He$^+$, Ne$^+$, Ar$^+$, and Kr$^+$) at ion fluences, Φ, in the range between 1×10^{14} and 1×10^{16} cm^{-2}. A detailed investigation of the changes in the film chemical structure was made by infrared spectroscopy as a function of ion mass and fluence. To obtain a more complete picture of the ion-induced transformations, the atomic composition was determined using ion-beam analyses. Surface hardness and film compactness measurements were also made and correlated with the ion-beam and infrared data.

In studies of ion-induced structural modifications in polymers, a fundamental parameter is the well-known linear energy transfer density (LET), defined as the energy lost per unit length by the ion as it traverses the polymer network. Several results reported in the literature are interpreted on the basis of the two components of the total LET, namely, the electronic LET, $(\mathrm{d}E/\mathrm{d}x)_e$, and the nuclear LET, $(\mathrm{d}E/\mathrm{d}x)_n$.[16] This procedure is used in this work. Both LETs are simulated using the SRIM computational program,[17] which is also used to evaluate the projected range of the ions in the films.

In the interpretation of the infrared spectra of thin films such as those in this work, a possible drawback is the low signal-to-noise ratio of the spectrometer, which may partially or totally preclude band identification. To avoid this problem, signal-enhancing experimental conditions comprising p-polarized light and an oblique incidence angle were used to obtain IR spectra with a high signal-to-noise ratio. Such conditions are well known and related to the metal surface selection rule.[18] Due to optical effects that are explained elsewhere,[19−21] signal intensification brought about by these conditions is related to detection of oscillators that vibrate perpendicular to the metal surface. Although the metal surface selection rule applies to both strong and weak oscillators on a metal surface, it has important implications for detection of the former, causing not only signal enhancements but also band shifts. At this point it is necessary to bring to our discussion the notion that for one single vibrational transition two different modes exist, according to their means of propagation throughout a solid: the transverse and longitudinal optical modes (TO and LO, respectively).[22,23] The splitting between their frequencies is termed LO$-$TO splitting ($\Delta_{\mathrm{LO-TO}} = \nu_{\mathrm{LO}} - \nu_{\mathrm{TO}}$, where ν_{LO} and ν_{TO} are the frequencies of the LO and TO modes, respectively) and is proportional to both the oscillator density and its strength.[24] It is known that for weak oscillators, such as a C$-$H stretching, the frequencies of the TO and LO modes are very close to each other and $\Delta_{\mathrm{LO-TO}}$ is not appreciable even for solids bearing a high density of C$-$H oscillators. On the other hand, the asymmetrical stretching mode of high-strength oscillators such as Si$-$O,[25−27] Ti$-$O,[28−31] and W$-$O[32] give rise to high LO$-$TO splittings. As previously outlined, use of p-polarized light and oblique incidence intensifies the signal related to vibrations preferentially oriented perpendicular to the metal surface, which means that an experiment carried out under these conditions is able to detect LO modes, which is not possible in normal or near-normal incident IR measurements. Such a phenomenon is known in the literature as the Berreman effect due to the pioneering work of D. W. Berreman.[33]

In previous work we investigated the LO$-$TO splitting of Si$-$O-group-related bands in plasma polymers.[26,27] These studies will be useful in the interpretation of several results of the present work. To our knowledge, this is the first time the LO$-$TO splitting is used to investigate ion-irradiated Si-based polymer films.

2. Experimental Section

Films were synthesized by the PECVD technique from a HMDSO$-$O$_2$$-$Ar mixture in a stainless steel vacuum chamber fitted with two circular electrodes capacitively connected to a 40 MHz power generator. The chamber was pumped by a 150 m^3/h Roots pump, and the pressure was measured by a capacitance manometer. High-purity (better than 99.99%) oxygen and argon were introduced into the chamber by means of precision mass flow meters. Since

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HMDSO is a liquid at room temperature and atmospheric pressure, a vaporization cell was used to introduce HMDSO vapor in the chamber. The cell consists of a borosilicate tube containing the liquid and is connected to the chamber through a precision gas-metering valve. To keep the liquid HMDSO at constant temperature during vaporization, the bulb was immersed in a room-temperature water bath. Since no mass flow meter was used with the cell, control of the HMDSO admittance to the chamber was made with the capacitance manometer. Using a mass flow rate−pressure calibration curve previously obtained for the chamber, the HMDSO pressure indicated by the manometer could be converted to mass flow rate. All films were synthesized in batch depositions with up to 12 substrates under the same conditions: HMDSO, O_2, and Ar flow rates of 4.0, 12.0, and 40.0 sccm, respectively, rf power of 35 W, and deposition time of 14 min. Because the deposition rate varies according to the substrate position onto the substrate holder, the film thicknesses varied between 280 and 310 nm.

Ion irradiations were carried out with 170 keV He^+, Ne^+, Ar^+, and Kr^+ ions at fluences ranging from 1×10^{14} to 1×10^{16} cm^{-2} using an ion implanter (Eaton GA-4R) of the Center of Semiconductor Components (CCS) of the State University of Campinas. The ion beam was set to sweep a 7.5×7.5 cm^2 area on the sample holder. Since the area of the substrates did not exceed 2×2 cm^2, the films were uniformly irradiated.

For film thickness measurements of the pristine samples a step was created by partial removal of the film from the substrate using a sharp needle. The height of the step, i.e., the film thickness, t, was then determined using a high-resolution profile meter. The step height was also measured after ion irradiation to determine film thickness change induced by the latter. Film thickness values were taken as the average of at least four measurements, performed in different regions of the step. Using this procedure the errors in t ranged between 0.5% and 5%.

Elemental analyses of the films were made using Rutherford backscattering spectroscopy (RBS) and forward recoil spectroscopy (FRS) at the Laboratory of Analysis of Materials by Ion Beams (LAMFI) of the Institute of Physics, University of São Paulo, Brazil. RBS was used to detect C, Si, and O using a beam of singly ionized 2.4 MeV helium atoms aligned normal to the film surface with detection at 10° off-normal. Hydrogen was detected by FRS. A 2.0 MeV He^+ ion beam at an incidence angle of 80° to the normal of the film surface was employed with detection of the recoiling H^+ ions at a forward angle of 70° to the normal. Before detection the H^+ ions passed through a 6 μm Al foil (stopper) and a collimating aperture. Single-crystal (100) Si wafers were used as substrates. From the RBS and FRS data the areal densities of C, Si, O, and H atoms of the film were obtained using the SIMNRA computational program.[34] With the use of this program simulations of RBS and FRS spectra were carried out using sets of tentative input values for the areal densities of the chemical elements in the film. The simulations were repeated with different sets of values until an optimum match of the simulated to the experimental spectra was found. An optimum set of values for the areal densities was thus obtained. Errors in these values were no higher than 2% for H and 10% for C, O, and Si.

To investigate the chemical bonds in the films, infrared reflection−absorption spectroscopy (IRRAS) was employed using a Bomen MB-101 FT-IR spectrometer. The spectra covered the 400−4000 cm^{-1} range at a resolution of 4 cm^{-1} and were taken from films deposited onto Al-coated glass substrates. Unpolarized and p-polarized IR beams were used. A variable-angle attachment was employed to obtain incidence angles of 10° and 70° for unpolarized and p-polarized radiation, respectively. All spectra were referenced to a bare Al-coated glass substrate.

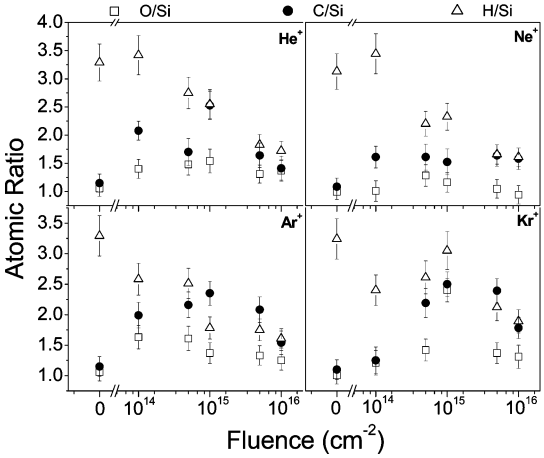

Figure 1. O/Si, C/Si, and H/Si atomic ratios as a function of ion fluence for He^+, Ne^+, Ar^+, and Kr^+ irradiations. The error bars were determined by propagation of the errors in the areal densities of H, C, O, and Si.

Hardness measurements were made using a Nanoindenter IIs (Nanoinstruments). The indentations were performed at peak indentation loads ranging from 0.05 to 16 mN.

3. Results

3.1. Elemental Composition and Film Compactness. The areal densities of C, O, Si, and H atoms were determined from RBS and FRS spectra of the pristine and each of the irradiated films. From these data the formula $SiOC_{1.1}H_{3.3}$ was determined for the pristine film, and the atomic ratios (H/Si, C/Si, and O/Si) were calculated. The dependence of the latter on the ion fluence is shown in Figure 1. The relatively large scattering of the data points is due to the low signal-to-noise ratio of the RBS data caused by the small film thickness and the relatively low scattering cross sections of C, O, and Si for He^+ ions.[35]

As can be seen in Figure 1, the film composition is significantly changed by ion irradiation. For all ion species used in the irradiations several common trends for the H/Si, C/Si, and O/Si atomic ratios can be observed as the fluence is increased: (i) the H/Si ratio decreases, (ii) the O/Si ratio increases to a maximum and then decreases, and (iii) there is an overall increase in the C/Si ratio, and its value at the highest fluence (1×10^{16} cm^{-2}) is higher than that of the pristine film. As discussed later, the increase in the O/Si ratio for intermediate fluences is, at least in part, due to oxygen uptake from ambient air after the irradiation process.

In the irradiation of a conventional silylene copolymer with high-energy ions[4] it is reported that the C/Si atomic ratio decreases with increasing ion fluence, while in our results an increase of the C/Si ratio is observed. Our data, however, unmistakably reveal that ion irradiation increases the C/Si ratio, since the measured C/Si values for the four ion species at all fluences are higher than that of the pristine film.

Ion-induced dehydrogenation of polymers is a significant and commonly reported effect.[4,36,37] The strong decrease of

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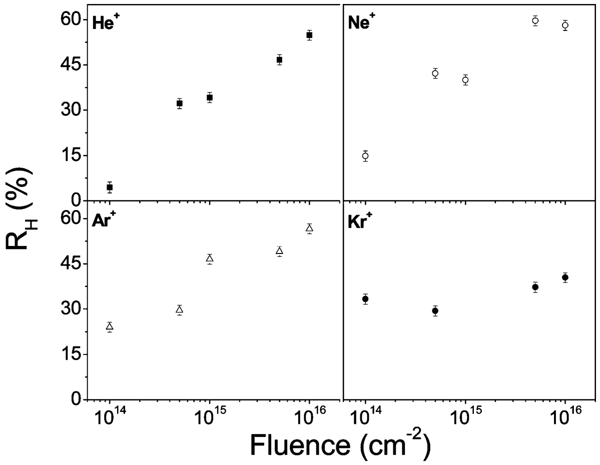

Figure 2. H loss as a function of ion fluence for He$^+$, Ne$^+$, Ar$^+$, and Kr$^+$ irradiations. The error bars were calculated by propagation of the errors in the areal densities of H.

the H/Si atomic ratio for increasing ion fluence, shown in the plots of Figure 1, are compatible with hydrogen loss. To better evaluate such an effect, only the H data obtained by FRS was considered, and the percent H loss of the films, R_H, was calculated by the equation $R_H = [(z_0 - z)/z_0] \times 100$, where z_0 and z are the areal densities of H in the pristine and the irradiated films, respectively. Plots of R_H as a function of the fluence are shown in Figure 2. The dehydrogenation of the samples is remarkable for all of the ions. For He$^+$, Ne$^+$, and Ar$^+$ irradiation at a fluence of 1×10^{16} cm^{-2}, R_H is around 55%.

In the ion irradiation of polymethylhydroxysiloxane and polyphenylmethylhydroxysiloxane (polymers known as SR350 and SR355, respectively) with 200 keV He$^+$ ions at $\Phi = 1 \times 10^{16}$ cm^{-2}, R_H values of 50% and 80% can be deduced from the experimental data for SR355 and SR350, respectively.[37] Considering the structural differences between our films and SR350 and SR355 and the fact that we used a lower energy (170 keV) it can be concluded that our results for He$^+$ irradiation are in good agreement with those of ref 37.

In the literature on ion irradiation of Si-based polymers hydrogen loss is frequently correlated to film compactness, K_t, expressed as the percent decrease in film thickness and defined as $K_t = [(t_0 - t)/t_0] \times 100$, where t_0 and t are the thicknesses of the pristine and irradiated films, respectively. Figure 3 shows the film compactness as a function of fluence and ion species. Within experimental errors, for a given fluence, compactness does not vary systematically with the ion mass. For each ion species, however, K_t strongly increases with fluence. At $\Phi = 1 \times 10^{16}$ cm^{-2}, the K_t values lie between 40% and 50% for all ion species. These values are comparable to earlier results,[37] from which percent thickness decreases of 20% and 40% are deduced for SR355 and SR350, respectively, irradiated with 200 keV He$^+$ ions at $\Phi = 1 \times 10^{16}$ cm^{-2}.

3.2. Pristine Film Baseline. As pointed out in the Experimental Section, infrared reflection−absorption spectra of both the pristine and the ion-irradiated samples were acquired at 10° and 70° incidence angles using nonpolarized and p-polarized light, respectively. Figure 4 shows both spectra for the pristine film, thus illustrating the differences between the two acquisition conditions. The intense signal enhancement generated by use of the more oblique incidence angle and p-polarized light can be clearly seen in the figure, especially in the low-frequency region (1500−400 cm^{-1}) of the spectra. Such an enhancement is expected according to the pioneering work of Greenler.[20] Also noteworthy are the blue shifts undergone by the most intense bands in the spectra. This is due to the fact that acquiring spectrum taken at 70° at oblique incidence angles gives rise to detection of the LO counterpart of the vibrational modes, which was first described by Berreman.[33] Profiting from this signal enhancement, our infrared analysis will be based on spectra taken at 70° with p-polarized light.

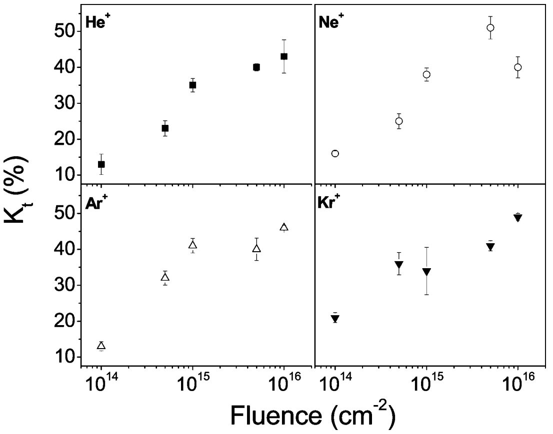

Figure 3. Film compactness as a function of ion fluence for He$^+$, Ne$^+$, Ar$^+$, and Kr$^+$ irradiations. The error bars were determined by propagation of the errors in the film thickness determinations.

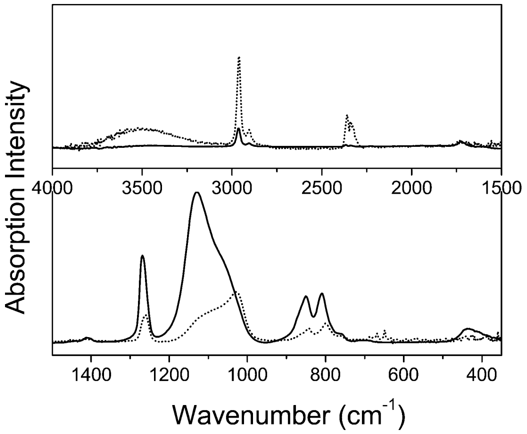

Figure 4. IRRAS spectra of the pristine film taken with an unpolarized infrared beam at a 10° incidence angle (dotted line) and with a p-polarized infrared beam at a 70° incidence angle (continuous line). The intensity of the spectra taken at 10° was multiplied by 10.

The spectra of Figure 4 are typical of a PECVD siloxane film produced from oxygen-diluted HMDSO plasmas, and band assignments are made from refs 26, 27, 38, and 39. The intense bands at 1027 ($\theta = 10°$) and 1129 cm^{-1} ($\theta = 70°$) are due to an antisymmetric stretching (AS) motion in

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which the O atom moves back and forth along a line parallel to the axis through the two Si atoms. The observed LO−TO splitting of 102 cm^{-1} is close to that observed in our previous papers for siloxane networks.[26,27] These bands will be termed AS1-TO and AS1-LO, respectively, in analogy to those observed for vitreous silica (v-SiO_2) for which they lie at 1072 and 1257 cm^{-1}, respectively.[25] In v-SiO_2 the AS1-TO band exhibits a high-frequency shoulder at ca. 1200 cm^{-1}, which, as suggested by Kirk,[40] is due to a motion (termed AS2 mode) in which adjacent O atoms execute the AS motion 180° out of phase with each other. Again, in analogy with v-SiO_2, the shoulder at ca. 1100 cm^{-1} in the spectrum of the pristine film at 10° is assigned to the AS2 motion. As for the low-frequency shoulder observed in the spectrum taken at 70°, it can be due to the AS1-TO mode but also be assigned to the AS2 mode since in v-SiO_2 the LO−TO splitting is negative, i.e., opposite to that of the AS1 mode.[40]

The spectra taken at 70° show a band at 430 cm^{-1} which is due to Si−O bond rocking in Si−O−Si groups. In thermal SiO_2 the TO mode for these groups appears at ca. 450 cm^{-1},[40] but lower values have been observed for SiO_x-like materials. The reasons why this mode cannot be observed in the spectrum taken at 10° are either because of the extremely low signal-to-noise ratio in the region or because it lies outside the detection range of the spectrometer (4000−400 cm^{-1}). Also noteworthy is a band that appears at nearly 1723 cm^{-1}, which is due to C═O groups.[41]

Other absorptions clearly seen in the spectra taken at 70° are related to vibrations in methyl groups: asymmetric and symmetric C−H stretching at 2961 and 2903 cm^{-1}, respectively; asymmetric and symmetric methyl deformations in Si−Me_x at 1408 and 1269 cm^{-1}, respectively; the group of bands between 900 and 600 cm^{-1} involving coupling of the rocking of the methyl groups and stretching of Si−C bonds.[42]

3.3. Structural Transformations Brought About by Ion Irradiation. Spectra of the He^+-irradiated films at five different fluences are given in Figure 5. For the sake of brevity, in Figure 6 only the spectra of films irradiated with the other ion species for the lowest and the highest fluences are shown. From inspection of the spectra of either Figure 5 or Figure 6 it can be readily concluded that ion irradiation produces significant changes in the film structure, manifested by strong modifications in the absorption band intensities and line shapes and formation of new bands. A discussion regarding such modifications follows.

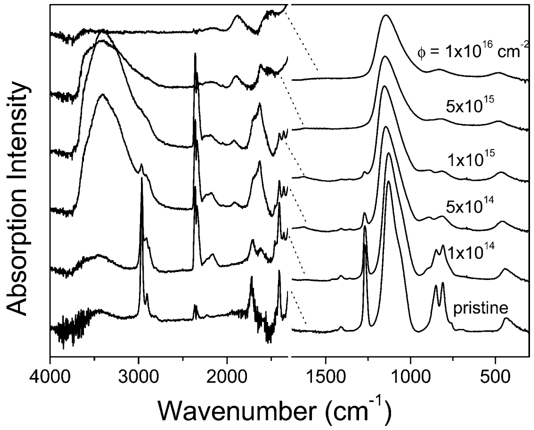

Figure 5. IRRAS spectra of the pristine and He^+-irradiated films taken with a p-polarized infrared beam at a 70° incidence angle. The intensity scale for the spectra in the region from 4000 to 1400 cm^{-1} is 5 times higher than that in the 1700−400 cm^{-1} interval. The dotted line joining each pair of spectra indicates that both correspond to the same sample.

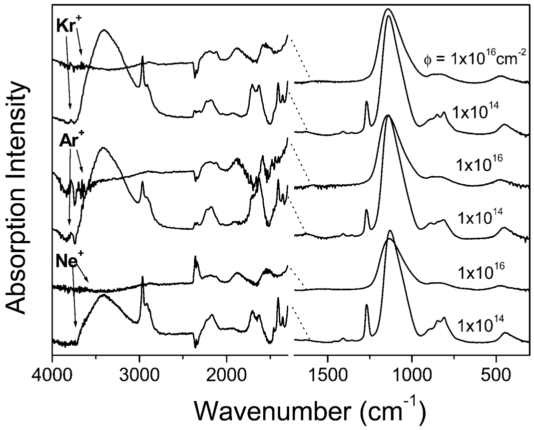

Figure 6. IRRAS spectra of the Ne^+-, Ar^+-, and Kr^+-irradiated films taken with a p-polarized infrared beam at a 70° incidence angle. The intensity scale for the spectra in the region from 4000 to 1400 cm^{-1} is 5 times higher than that in the 1700−400 cm^{-1} interval. The dotted line joining each pair of spectra indicates that both correspond to the same sample.

Methyl-Related Groups. Methyl-related groups are strongly depleted by ion irradiation as demonstrated by the strong intensity decrease of their corresponding bands as the fluence is increased. This observation is compatible with the H-loss measurements made by FRS since a possible mechanism for depletion of a methyl-related group involves scission of C−H bonds. Actually, most methyl-related groups seem to disappear in films irradiated at higher fluences, regardless of the ion species used in the irradiation, as shown by the bands assigned to methyl deformations in Si−Me_x groups at 1408 and 1269 cm^{-1}. Evolution of the asymmetric methyl deformation band with ion fluence for He^+-irradiated films is shown in Figure 7. The intensity dependence of this band with the ion fluence for the other ion species is very similar to that shown in Figure 7. The absorption at 2961 cm^{-1}, which in the pristine film is due to C−H asymmetric stretching in Si−Me_x groups, disappears in the He^+-irradiated film at the highest fluence. Absorptions in the region around 2960 cm^{-1}, however, are present in films irradiated with Ne^+, Ar^+, and Kr^+ ions at the highest fluence.

As shown in Figures 5 and 6 the line shape of the C−H stretching bands changes with ion irradiation, indicating an increasing variety of chemical environments surrounding the C−H bonds as the fluence increases. The well-defined, narrow bands at 2961 and 2903 cm^{-1} in the spectrum of the pristine film increase their line widths, and a broad and featureless C−H stretching band appears in spectra of films irradiated at higher fluences. It is thus possible that, in these films, the C−H groups may exist independently of the methyl groups, as discussed later.

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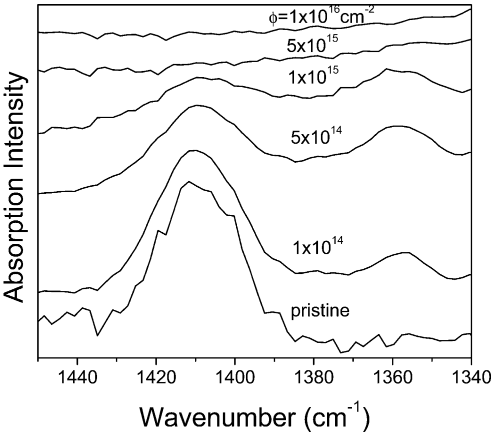

Figure 7. IRRAS spectra of the He$^+$-irradiated films in the 1450−1340 cm^{-1} interval. The spectrum of the pristine film is also shown.

The decrease of the methyl groups with ion irradiation is also shown by the decrease in the intensity and line shape changes of the bands in the 900−700 cm^{-1} interval, assigned to coupling of rocking of methyl units and stretching of Si−C bonds associated to Si−Me$_x$ groups with $x = 1$, 2, and 3,[42] which will be also discussed later.

O−H and C═O Bond-Related Groups. For intermediate fluences an intense hydroxyl absorption due to O−H stretching and peaking at ca. 3450 cm^{-1} can be observed in Figure 5. The shoulder at the high-energy side of the O−H band indicates that part of the O−H groups are bonded to Si atoms, forming silanol groups. The intensity and line shape of the hydroxyl band exhibits a peculiar behavior: as the He$^+$ fluence is increased, the O−H band intensity increases, goes through a maximum, and then decreases, becoming negligible for the highest fluence. An identical behavior is noted in the spectra of the samples irradiated with the other three ion species. The appearance of the O−H groups is linked to the formation of free radicals from ion-induced bond scissions in the film network. Similarly to what happens in plasma-deposited polymer films, the O−H bonds appear from reactions between the free radicals and water vapor or oxygen from the atmosphere.[43] Incorporation of oxygen from the atmosphere due to reactions with free radicals produced by ion irradiation of conventional polymers has been observed by various investigators.[37,44]

Oxygen or water vapor uptake is related to their diffusivity in the film, which depends on network compactness, decreasing as the latter is increased. According to the results reported in the previous section, compaction is strongly increased by ion irradiation. This explains the low or even negligible O−H bond content observed in the samples irradiated at higher fluences.

For films irradiated with the four ion species (Figures 5 and 6) the decrease of the C═O groups with ion irradiation is clearly demonstrated by the decrease of the intensity of the C═O stretching band at about 1723 cm^{-1} as the ion fluence is increased. Depletion of the C═O groups may be due to various reasons, such as their dissociation (e.g., by nuclear collisions with the energetic ions) and transformation into C−O−Si, C−OH, and other groups. The C−OH groups, in particular, may be formed from rearrangements of C═O bonds with groups originating from water vapor uptake from the atmosphere, thus contributing to the intensity of the O−H absorption band seen in the spectra of most irradiated films (Figures 5 and 6). It should be mentioned, on the other hand, that C═O groups are probably generated in the postirradiated films. Carbon dangling bonds formed by ion irradiation may lead, from reaction with incorporated oxygen, to C═O groups, according to a reaction scheme previously proposed by Yasuda et al.[45] However, as in He$^+$-irradiated films, in those irradiated with the other ion species the intensity of the C═O stretching band monotonically decreases with increasing ion fluence, thus indicating that depletion of C═O groups is more significant than their formation.

Si−O Bond-Related Groups. The AS1-LO band observed in the spectra of Figure 5 blue shifted from 1129 to 1150 cm^{-1} with increasing ion fluence, which is consistent with a mineralization of the material. However, it did not blue shift enough for the material to have been converted into vitreous silica, for which the AS1-LO lies at 1257 cm^{-1}.

A similar behavior is observed for Si−O−Si rocking bands observed at 430 cm^{-1} in the pristine film, which shift to 480 cm^{-1} for He$^+$ and 475 cm^{-1} for Kr$^+$ at the highest fluence. However, these shifts are not as high as those for v-SiO$_2$, for which the TO band can be observed at 450 cm^{-1} and the LO at 505 cm^{-1}.[25]

Formation of New Groups and Structures. The breaking of bonds, induced by the ion beam, and their subsequent recombination may lead to formation of other important groups, such as Si−O−C. However, since the Si−O−C asymmetrical stretching mode in organosilicones occurs around 1100 cm^{-1},[42,46] a conclusion on the formation of these groups in the irradiated films is hampered by the possibility of overlapping of the Si−O−C AS and Si−O−Si AS bands.

Other ion-generated functional groups are related to the bands peaking at nearly 2200 and 1357 cm^{-1} and in the 1000−700 cm^{-1} interval (Figures 5 and 6). The former is associated with the Si−H stretching vibrations in Si−H groups.[47] The band at 1357 cm^{-1} is assigned to scissoring deformation of methylene in Si−CH$_2$−Si groups,[38,48,49] and for the He$^+$-irradiated films it is represented in Figure 7. From this figure it is shown that Si−CH$_2$−Si groups are not present in the pristine film and are generated in the films irradiated at lower fluences. For films irradiated at higher fluences, Si−CH$_2$−Si groups are no longer observed. The trend followed by the Si−CH$_2$−Si deformation band in Figure 7 is also observed in spectra of the Ne$^+$-, Ar$^+$-, and Kr$^+$-irradiated films.

For the methylene wagging mode in Si−CH$_2$−Si a strong absorption is assigned in the 1080−1040 cm^{-1} region.[49] The

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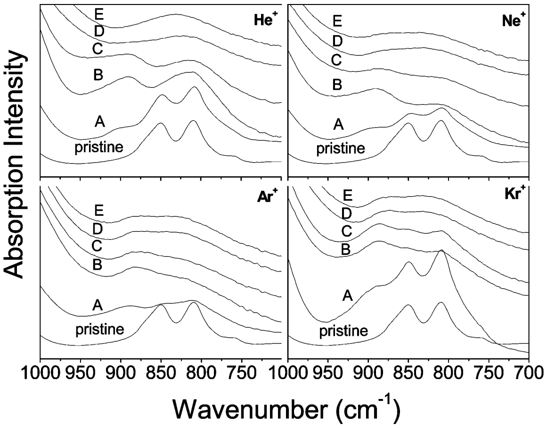

Figure 8. IRRAS spectra in the 1000−700 cm^{-1} interval for films irradiated with He$^+$, Ne$^+$, Ar$^+$, and Kr$^+$ ions at fluences of 1 × 10^{14} (A), 5 × 10^{14} (B), 1 × 10^{15} (C), 5 × 10^{15} (D), and 1 × 10^{16} cm^{-2} (E). The spectrum of the pristine film is also shown.

latter is, however, masked by the strong AS1 band. Because the absorption due to methylene wagging is much stronger than that of the methylene scissoring mode, the Si−CH$_2$−Si groups are important constituents of the films irradiated at low to intermediate fluences. A possible mechanism of formation of the Si−CH$_2$−Si groups involves generation of C dangling bonds by H detachment from the abundant Si−CH$_3$ groups existing in the film. The resulting Si−CH$_2$ units may further react with Si atoms, thus forming Si−CH$_2$−Si. Since Si−CH$_3$ and Si atoms are in the polymer chains, Si−CH$_2$−Si will be part of the cross-linked network. Actually, this mechanism would be also responsible for cross-linking, since, before reacting, Si−CH$_2$ and Si must be in close proximity in neighbor chains.

Figure 8 shows spectra of films irradiated with the four ion species in the 1000−700 cm^{-1} region. Regardless of the ion species, at low to intermediate fluences, a well-defined band appears at about 890 cm^{-1} as a shoulder on the high-energy side of the broad band already assigned to coupling between the CH$_3$ rocking and the Si−C stretching modes. Two absorptions may contribute to this band: Si−O stretching vibrations in silanol groups[50] and Si−H deformation.[51] For the He$^+$-irradiated films at a fluence of 1 × 10^{16} cm^{-2} the band at 890 cm^{-1} disappears and only one band, at 830 cm^{-1}, is observed. The latter is attributed to the Si−C stretching mode[52] since in the spectrum of the He$^+$-irradiated films for 1 × 10^{16} cm^{-2} (Figure 5) CH$_3$- or OH-related bands are no longer observed. Absorptions due to the Si−C stretching mode are also present in the spectra of Ne$^+$-, Ar$^+$-, and Kr$^+$-irradiated films. In these, in contrast to the He$^+$-irradiated samples, the absorption at about 890 cm^{-1} is present even for irradiation at the highest ion fluence. As pointed out before, a relatively large hydrogen concentration is present even in films irradiated with the highest fluence, as demonstrated from the FRS data. Thus, existence of the band at about 890 cm^{-1} for samples irradiated at 1 × 10^{16} cm^{-2} strongly indicates that SiH groups remain in the film.

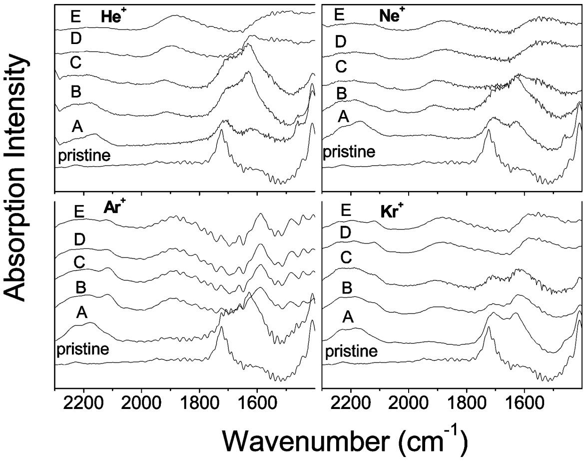

Figure 9. IRRAS spectra in the 2300−1400 cm^{-1} interval for films irradiated with He$^+$, Ne$^+$, Ar$^+$, and Kr$^+$ ions at fluences of 1 × 10^{14} (A), 5 × 10^{14} (B), 1 × 10^{15} (C), 5 × 10^{15} (D), and 1 × 10^{16} cm^{-2} (E). The spectrum of the pristine film is also shown.

In the spectra of the films irradiated with each of the ion species, exhibited in Figure 9, a clearly defined absorption band appears at about 1890 cm^{-1} whose intensity and line width monotonically increase with increasing ion fluence. Differences in the evolution of these bands reflect different structural modifications produced by the different ion species. For Kr$^+$ irradiation the absorption at 1890 cm^{-1} can be clearly noted in the spectrum of the sample irradiated at the lowest fluence. In the spectra of the He$^+$-irradiated samples this absorption is only noted for fluences of 5 × 10^{14} cm^{-2} and higher. Furthermore, the position of the band for any given fluence varies according to the ion species.

To our knowledge, this is the first time the bands around 1890 cm^{-1} are observed in ion-irradiated Si-based polymer films. Their origin is not yet clearly defined. From a literature search, C$_n$-type chains (n = integer), mainly with $n > 10$, exhibit bands in this region.[53] Concomitant with the appearance of these bands, another band, at about 1620 cm^{-1}, appears and is assigned to stretching vibrations of C═C bonds. The shoulder at the high-energy side of the latter is assigned to C═O bonds, whose intensity decreases with increasing ion fluence. The bands at 1620 cm^{-1} disappear at higher fluences, while the appearance of broad bands at about 1550 cm^{-1} can be clearly noted, suggesting a graphene-structured carbonaceous compound[54] or a disordered graphitic structure.[55,56]

From these results it seems possible that a carbonaceous material consisting of domains of graphitic structures interconnected by C$_n$-type chains exists in the films irradiated at the highest fluences. These structures may evolve from domains of amorphous hydrogenated carbon (a-C:H) formed at lower fluences, as indicated by the C═C and diffuse C−H stretching bands. Conversion of the a-C:H structures seems to be complete only for the film irradiated with He$^+$ at the highest fluence, as no trace of C−H bonds is observed in

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the spectrum. For the films irradiated with the other ion species at their highest fluences, the weak and diffuse C−H stretching band remaining in the spectra may indicate that C−H bonds still exist in the carbonaceous domains. It should be noted that the bands at about 1890 and 1550 cm^{-1} could not be observed in the IRRAS spectra obtained in the unpolarized mode at near-normal incidence.

Comparison with Infrared Spectra of other Ion-Irradiated Films. There are few reports on the investigation of ion-irradiated effects in conventional Si-based polymers by infrared spectroscopy. However, since our films are polysiloxanes, there is a close similarity between the spectrum of our pristine sample and that of a pristine polysiloxane such as SR350, exhibited in ref 37. The evolution of the spectra of our films as the ion fluence is increased is very similar to those of SR350 irradiated with 500 keV C^+ ions as the fluence increases from 5×10^{13} to 5×10^{16} cm^{-2}, i.e., several common trends can be seen, such as the strong decrease in the methyl- and Si−O-related band intensities and the increase and subsequent decrease of the O−H-related bands.

3.4. Hardness. Surface hardness measurements were carried out on the pristine film and films irradiated with the highest fluence (1×10^{16} cm^{-2}). While the surface hardness of the pristine film was 1.3 GPa, values of 8.1, 6.0, 4.7, and 1.6 GPa were measured for the He^+-, Ne^+-, Ar^+-, and Kr^+-irradiated samples, respectively. Thus, the surface hardness monotonically increases with decreasing ion mass. In both C-[13,57,58] and Si-based[12,59] polymers surface hardness usually increases with increasing ion fluence. Thus, these hardness values were expected to be highest for films irradiated with each ion species.

At least in part the hardness increase can be associated with a process whose initial step is formation of free radicals by ion-induced scission of hydrogen bonds in close proximity in neighboring chains. Owing to the thermal mobility of the network chains, the free radicals recombine, forming a highly cross-linked compact three-dimensional network. As expected, material compactness accompanies the hardness increase due to the decrease in the average bond length. Other mechanisms may also contribute to hardness increase, such as bond rearrangements different than those arising from H-bond breakage and diffusion of carbon atoms, forming diamond-like domains.[5,12,59]

For conventional polysiloxane and polycarbosilane films irradiated with 200 keV He^+ ions at $\Phi = 1 \times 10^{16}$ cm^{-2}, hardness values in the range between 10.9 and 17.0 GPa can be deduced from ref 12. Since we have measured a surface hardness of 8.1 GPa for the 170 keV He^+-irradiated sample at $\Phi = 1 \times 10^{16}$ cm^{-2}, our pristine films are competitive with the above-mentioned Si-based polymer films for producing hard-surfaced ceramic materials.

3.5. Role of Electronic and Nuclear LET on Film Modification. Using the SRIM code we determined the average electronic and nuclear LET and the ion-projected ranges for the pristine and irradiated films at the highest (1×10^{16} cm^{-2}) fluence. The thickness and atomic areal densities of Si, C, O, and H, determined by ion-beam analysis, were used as input data. The results are displayed in Table 1 and define the minimum and maximum LET and projected range values for any of the ions.

Table 1. Average Electronic and Nuclear LET (eV/ion/nm) and Projected Range for the Pristine Film and Films Irradiated at $\Phi = 1 \times 10^{16}$ cm^{-2}

	pristine film			films irradiated at $\Phi = 1 \times 10^{16}$ cm^{-2}		
ion	$(dE/dx)_e$	$(dE/dx)_n$	projected range (nm)	$(dE/dx)_{e.}$	$(dE/dx)_n$	projected range (nm)
He^+	122	0.6	1590	241	1.2	970
Ne^+	182	39.8	600	359	80	360
Ar^+	312	176	500	548	291	270
Kr^+	271	284	370	502	465	172

The first conclusion to be drawn from the table arises from the extremely low nuclear LET values for He^+ as compared to the electronic LET for the same ion. Because the hydrogen loss of our films is significant for He^+ irradiation, electronic collisions are, most likely, the dominant mechanism for C−H and Si−H bond scission. Consequently, in He^+-irradiated films electronic collisions are responsible for film hardening and for the appearance of O−H and Si−OH groups, since they are formed from reactions between the free radicals resulting from C−H and Si−H bond scission and oxygen and water vapor from the atmosphere.

The He^+-irradiated films are those in which the methyl-related groups are most drastically reduced. As can be seen in Figure 5, there is no trace of C−H stretching bonds in the films irradiated at a fluence of 1×10^{16} cm^{-2}. For this fluence, however, C−H stretching bonds are present in films irradiated with the other ions, as can be noted in Figure 6. A more intense reduction of C−H-related groups would be expected for ions of heavier masses since their electronic LET values are higher. A possible explanation for this apparent contradiction is due to the fact that the projected ranges for Ne^+, Ar^+, and Kr^+ at a fluence of 1×10^{16} cm^{-2} are comparable to, or even smaller than, the film thickness and much smaller than the He^+-projected ranges at the same fluence. Consequently, the Ne^+, Ar^+, and Kr^+ ions do not traverse the entire film or if they do their energy before completing the film traversal becomes too low to produce significant structural changes. In both cases an undamaged, or weakly damaged, layer remains in the films, which may be responsible for the C−H stretching absorption band seen in the spectra of Figure 6 for the films irradiated at the highest fluence.

As previously outlined, for all ion species the bandwidths of the C−H stretching modes increase with increasing fluence, indicating an increment in film structural disorder. At any given fluence the increases in the bandwidth for the He^+-, Ne^+-, Ar^+-, and Kr^+-irradiated films are comparable. Thus, electronic collisions play an important role in the increasing structural disorder.

However, nuclear collisions are expected to contribute to disorder as they produce atomic displacements and breaking of the polymer chains. As shown in Table 1, the average nuclear LET is significant for Ar^+ and Kr^+ and higher increases in the bandwidths would be expected for these ions.

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The probable reason such an expectation is not confirmed is, again, due to the fact that the penetration depth in the film is smaller for the heavier ions and thus the structural modifications do not extend to the entire film volume.

To explain the observation that the hardness of the He^+-irradiated film was the highest it should be remembered that the hardening of polymer films depends on the balance between electronic and nuclear LET. While the former is responsible for the increase in cross-linking and thus for improvement in network cohesion, the latter produces atomic displacements from nuclear collisions, which are detrimental to hardness improvement. Thus, the He^+ ions do not produce significant chain degradation since their LET is almost exclusively electronic. For Ne^+, Ar^+, and Kr^+ ions, whose nuclear LET are higher than that of He^+, the beneficial effects of the electronic LET for hardness are overriden by the nuclear LET, responsible for chain degradation.

4. Conclusions

Ion-beam effects on film structure were investigated in detail using IRRAS spectra obtained with an unpolarized infrared beam at near normal incidence (unpolarized mode) and with a p-polarized beam at a 70° incidence angle (polarized mode). The polarized-mode spectra proved to be extremely useful in this work since they exhibited several clearly defined bands not seen in the spectra taken in the unpolarized mode due to the low signal-to-noise ratio.

Significant conclusions drawn from the infrared analysis can be summarized as follows. (1) Several new groups, such as $Si-CH_2-Si$, $Si-OH$, and $C=C$, were formed at low and intermediate ion fluences, the latter being compatible with formation of amorphous carbon domains. The origin of the well-defined absorption band at 1890 cm^{-1} is not yet established, and we proposed that it could be assigned to carbon clusters of the C_n-type, mainly with $n > 10$. (2) $Si-CH_2-Si$, $Si-OH$, and $O-H$ groups, among others, disappeared at higher fluences. Because these groups, upon dehydrogenation, may recombine forming strongly bonded units such as $Si-C-Si$, $Si-O-Si$, and $Si-O-C$, they may play an important role on the formation of a compact and high-strength network.

Film stoichiometry was strongly affected by irradiation. Hydrogen loss was a pronounced effect, but an overall increase in the C/Si atomic ratio was observed with increasing ion fluence. For the highest He^+ fluence, H loss was nearly 50% and the C/Si atomic ratio increased by about 20%.

Film compactness and hardness were found to be in a direct correlation with the H loss, and this can be understood as recombination of the free radicals formed by the ion-induced scission of the $C-H$ bonds, giving rise to a tighter, strongly bonded structure. Such a structure is at least in part responsible for the high surface hardness of the irradiated films. It is possible that diamond-like carbon domains also contribute to hardness.

Several results of this work were interpreted in terms of the electronic and nuclear LET of the ions traversing the film network. Both the electronic and the nuclear LET increase with increasing ion mass. Because the nuclear LET is not significant as compared to electronic LET in the He^+-irradiated films, electronic collisions are responsible for increases in compactness and surface hardness of the latter. Despite the fact that the electronic LET increases from He^+ to Kr^+, the lower surface hardness of the Ne^+-, Ar^+-, and Kr^+-irradiated films, as compared to the He^+-irradiated ones, was attributed to the higher density of nuclear collisions that are detrimental to hardness improvement. On the other hand, the fact that the film disorder was not increased at the same pace as the ion mass was interpreted as due to the decreasing ion penetration depth in the film network as the ion mass was increased.

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