JOURNAL OF MATERIALS SCIENCE LETTERS **19**, 2000, 1883 – 1885

# Chemical structure modification of silicone surfaces by plasma immersion ion implantation

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Polymer materials with surface chemical structures that exhibit properties different than the bulk properties are of great interest in many applications such as adhesion, friction, and biocompatible materials [1, 2]. In this paper, we report on the modification of the chemical structure of silicone surfaces by Ar plasma immersion ion implantation (PIII). Surface modification of silicon based polymers has been investigated using ion beams [3, 4] and plasma treatment [5–7]. Suzuki *et al.* reported on the effects of ions beam implantation on the wettability of silicone rubber [3, 4]. Morra *et al.* investigated the hydrophobic recovery of oxygen plasma treated polydimethylsiloxane (PDMS) surfaces [5]. The mechanisms of hydrophobic recovery of plasma treated PDMS were addressed by Owen and Smith [6]. Everaert *et al.* showed that the aging of plasma treated silicone rubber can be slowed down by repeating the plasma treatment [7].

Plasma immersion ion implantation (PIII) is a relatively new technique for the surface modification of materials. In recent years, the PIII technique has been used in semiconductor processing applications with promising results in shallow junction formation, polycrystalline silicon thin film transistor hydrogenation, and the formation of silicon on insulator materials [8]. Recently, we showed that PIII treatment of silicone and EPDM at high doses reduced the surface coefficient of friction considerably [9]. In the PIII treatment, the sample to be treated is immersed in a plasma that is usually maintained at low pressure (between 0.03–1 Pa) and plasma densities between $10^8$–$10^{11}$ ions $cm^{-3}$. Then a series of negative high voltage pulses (typically few volts to 300 kV) are applied to the sample. The plasma ions are accelerated across the surrounding sheath and are implanted into the sample surface. This implantation technique offers many attractive features over the conventional ion beam implantation method [8]. Large areas and three-dimensional objects can be processed by PIII at a rate orders of magnitude faster than by the conventional implantation and without the need for sample manipulation. And in applications requiring low energy implantation (less than 10 keV) and high doses, the conventional ion beam technique is limited by the focusing optics [8]. The PIII treatment, discussed here, differs from the previously reported plasma treatment methods in [5–7]. In those studies, the plasma treatment was conducted at high pressure (usually 40–500 Pa) and no high voltage pulses are applied to the sample during the treatment process.

The silicone rubber samples, provided by Acushnet Rubber Company, Inc. (New Bedford, MA), were cut into $5 \times 6.4 \times 0.16$ $cm^3$ pieces and cleaned by isopropyl alcohol and then washed by distilled water prior to the PIII treatment. The samples were treated in an inductively-coupled plasma system where the plasma is generated by a planar antenna coil placed on top of a fused quartz window outside the vacuum chamber. The coil is connected in series with a capacitive matching network to the RF input. A detailed description and illustration of this system can be found in [8]. The samples were processed under the following conditions: base pressure $= 6 \times 10^{-6}$ Torr ($8 \times 10^{-4}$ Pa), processing pressure $= 0.2$ mTorr ($\sim$0.03 Pa), RF power = 430 W, and plasma density of $\sim 6 \times 10^{10}$ $cm^{-3}$. The plasma ions were accelerated by applying negative voltage pulses of $-8$ kV with pulse widths of 8 $\mu$s and repetition frequencies of 2 kHz to the sample holder. The samples were treated for 30 min to achieve an approximate dose of $8 \times 10^{17}$ $cm^{-2}$ [8]. The sample holder temperature was maintained around 30 °C by cooling it during the treatment.

The chemical composition and the nature of the chemical bonds were determined by the attenuated total reflectance Fourier transform infrared spectroscopy (FTIR-ATR) and by X-ray photoelectron spectroscopy (XPS) analysis of the survey and high resolution spectra of the Si 2p, O 1s, and N 1s lines. The FTIR-ATR spectra of a silicone surface before and after PIII treatment are shown in Fig. 1. The spectrum shows the range between 600–1800 $cm^{-1}$. Only two weak bands of interest associated with the $CH_3$ asymmetric stretch at 2960 $cm^{-1}$ and the $CH_3$ symmetric stretch at 2880 $cm^{-1}$ occur outside this range. The intense absorption bands around 1020 $cm^{-1}$ and 1080 $cm^{-1}$ (numbered 1 and 2 respectively) in Fig. 1a are characteristic of the Si-O-Si chain asymmetric stretch in siloxanes

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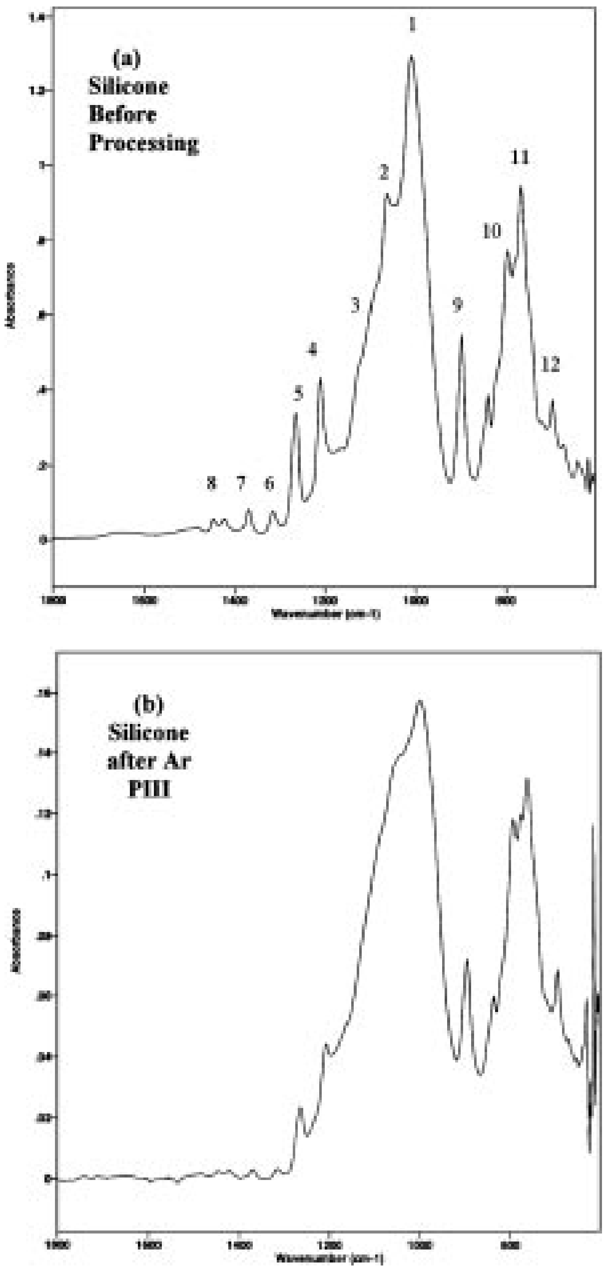

*Figure 1* FTIR-ATR absorbance spectra of a silicone surface. (a) Before processing; (b) after Ar PIII treatment.

[10–12]. The PIII modified surface in Fig. 1b shows a wide band with an asymmetric shape between 1000 and 1200 $cm^{-1}$, which is a characteristic of the asymmetric stretch of the Si-O-Si chain in silica [10, 11]. The C-F symmetric stretch band occurs around 1150 $cm^{-1}$ (band 3) overlapping with the Si-O-Si asymmetric stretch bands and appearing like a shoulder in Fig. 1a. The intensity of the absorption band at 1210 $cm^{-1}$ (band 4) which is associated with the C-F asymmetric stretch [12] decreased significantly after PIII treatment.

The bands in the FTIR spectrum of the PIII modified surface that are associated with the methyl ($CH_3$) group and methyl groups attached to silicon atom also showed a decrease in their intensity. The Si-$CH_3$ symmetric bend (umbrella mode) around 1265 $cm^{-1}$ (band 5), the $CH_3$ symmetric bend at 1370 $cm^{-1}$ (band 7), and the $CH_3$ asymmetric bend around 1460 $cm^{-1}$ (band 8) all decreased in intensity after Ar PIII [10–12]. The two weak bands assigned to the $CH_3$ asymmetric stretch and the $CH_3$ symmetric stretch at 2960 and 2880 $cm^{-1}$ respectively (not shown in Fig. 1) were difficult to observe in the PIII modified sample. The remaining bands in Fig. 1 at the wave numbers 910, 845, 800, and 765 $cm^{-1}$ are assigned to the Si-O stretch in silanol (Si-OH), the Si$(CH_3)_2$ rocking mode, the Si-O-Si symmetric stretch, and the Si$(CH_3)_2$ rocking mode respectively [10, 11].

The XPS survey analysis results of an untreated silicone surface and an Ar PIII treated silicone surface are summarized in Table I. The atomic composition of the PIII modified silicone surfaces show a significant increase in oxygen and silicon by comparison with the untreated surface. This change is accompanied by a decrease in the amount of carbon and fluorine in the implanted sample. This is in agreement with the decrease in the intensity of the FTIR-ATR bands that are

TABLE I XPS survey analysis of a silicone surface before and after Ar PIII modification

| | Surface composition (at%) | | | | | |
|---|---|---|---|---|---|---|
| | C | O | Si | N | F | Cl |
| Silicone | 47.8 | 20.0 | 16.8 | 0.4 | 14.5 | 0.2 |
| PIII modified | 10.7 | 51.7 | 29.6 | 1.5 | 6.6 | — |

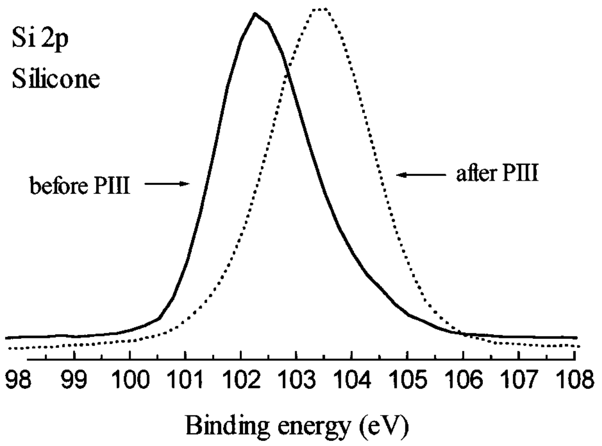

*Figure 2* Comparison of the XPS Si 2p spectrum of a silicone surface and an Ar PIII modified surface.

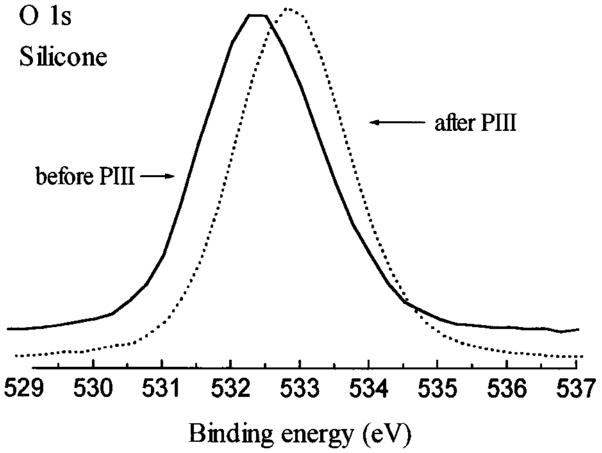

*Figure 3* Comparison of the XPS O 1s spectrum of a silicone surface and an Ar PIII modified surface.

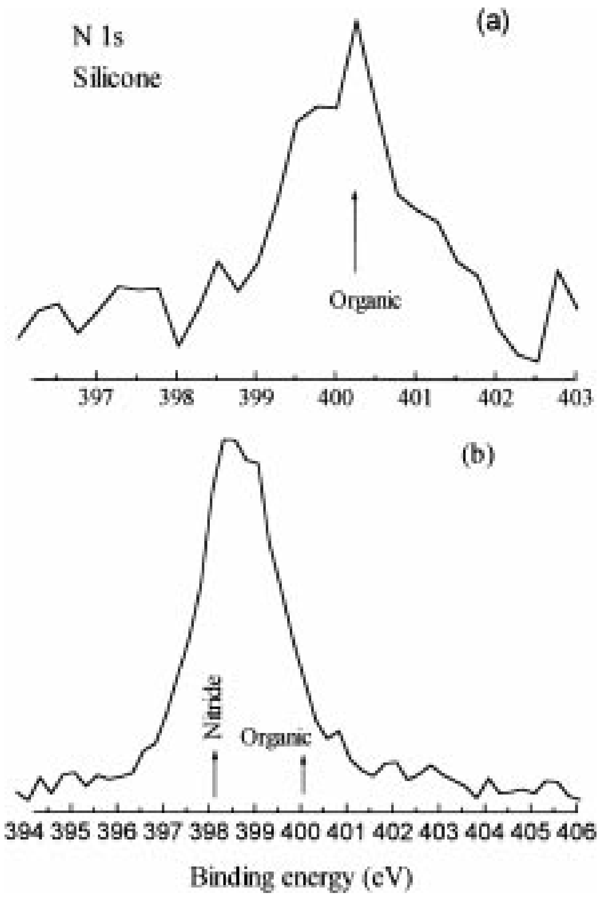

*Figure 4* XPS N 1s spectra of a silicone surface. (a) Before treatment; (b) after Ar PIII treatment.

associated with methyl, methyl groups attached to silicon, and carbon-fluorine stretching vibrations.

The XPS high-resolution spectra of the Si 2p, O 1s, and N 1s lines for a silicone surface and an Ar PIII modified surface are shown in Figs 2–4 respectively. The binding energy of the Si 2p peak of the untreated sample in Fig. 2 is around 102 eV which is consistent with the reported values for silicone [5, 6, 13, 14]. After PIII treatment, the Si 2p binding energy is shifted by about 1.5 eV higher (at a B.E. = 103.5 eV). This energy shift is too high to be assigned for organic silicone species and is more consistent with binding energies assigned to silica type surfaces. Also, the peak of the O 1s spectrum of the PIII modified surface occurs at a higher binding energy than that of the untreated silicone surface by about 0.5 eV as shown in Fig. 3.

Fig. 4a shows the XPS high resolution spectrum of a silicone surface for the N 1s region. The peak occurs around a binding energy of 400 eV which is consistent with the existence of nitrogen in an organic form [14]. The N 1s peak of the PIII modified surface (Fig. 4b) is shifted toward lower binding energies (around 398.5 eV) which indicates the formation of nitrides after implantation. In conclusion, the XPS and the FTIR-ATR measurements suggest the formation of a ceramic-like layer on the Ar PIII treated silicone surface.

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*Received 19 April*
*and accepted 15 May 2000*