

# The Effect of Plasma-Deposited Siloxane Coatings on the Barrier Properties of HDPE

M. MORRA, E. OCCHIELLO, and F. GARBASSI\*

Istituto G. Donegani S.p.A., V. Fauser 4, 28100 Novara, Italy

## SYNOPSIS

Thin polymeric films were deposited from siloxane plasma on the surface of polyethylene. The surface composition of the films was measured by X-ray photoelectron spectroscopy (XPS) and the permeability to O<sub>2</sub> by an analytic gas permeability fractometer. No significant improvement of barrier to O<sub>2</sub> was observed with 200 nm-thick coatings. When the siloxane layer was subjected to a further O<sub>2</sub> plasma treatment, a threefold decrease of permeability to oxygen was recorded. Results are discussed on the light of the effect of the O<sub>2</sub> plasma on the siloxane backbone. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Thin polymeric films deposited from plasma have been for the last several years the subject of much research, due to their interesting and often unique properties.<sup>1</sup> Possible applications of this class of materials ranges from friction and wear<sup>2</sup> to biocompatibility<sup>3-8</sup> and protective coating.<sup>9</sup>

Many studies also have been devoted to the permeability of plasma polymers, mostly with the aim of increasing permselectivity<sup>10-13</sup> (see also references in Ref. 1). As to barrier properties, it is generally agreed that the overall barrier effect to small permeants (such as O<sub>2</sub>) is very limited.<sup>1</sup> In fact, due to the absence of large-scale segmental mobility and the presence of a high degree of cross-linking, the permeation of small molecules does not strictly follow the "solution-diffusion" mechanism typical of common polymers, whereas a molecular-level sieve effect occurs. The dimensions of the sieve holes make the plasma-deposited thin film an excellent barrier against large permeants, whereas barrier properties to small permeants are practically nil.

A particular class of plasma-deposited polymers, namely, siloxanes, is, however, worthy of further in-

vestigation as to its barrier properties to O<sub>2</sub>. The reason is that polymers based on siloxane backbones have unique properties with respect to oxygen permeability. Although poly(dimethylsiloxane) (PDMS) is the one of the most permeable synthetic polymers,<sup>14</sup> inorganic silicates, such as glass, have been exploited for centuries as a barrier to oxygen (for instance, in food and beverage packaging). The interesting point is that the nature of plasma-deposited siloxanes can be shifted from organic to inorganic by controlling the plasma parameters<sup>15</sup> (in general, the higher the input energy per single molecule,<sup>1</sup> the more inorganic the nature of the film<sup>15</sup>). Another intriguing feature is that the effect of an O<sub>2</sub> plasma on organic siloxanes is to remove the organic pendant groups and to create an inorganic-like phase, greatly increasing the average number of O to Si bonds.<sup>16-20</sup> This postdeposition treatment seems more suitable for barrier applications, since the high power-to-flow rate ratio required to produce inorganic Si/O polymers directly from siloxanes plasma usually leads to defective or highly stressed films.<sup>1</sup> The production of inorganiclike Si/O films from organic precursor by O<sub>2</sub> plasma treatment is exploited, for instance, in microelectronics, where silicon-containing polymers are used as plasma-etching resistant resists.<sup>21</sup> On the other hand, this behavior is a recognized drawback of O<sub>2</sub> plasma treatment of siloxane contact lenses, whose goal is

\* To whom correspondence should be addressed.

to increase lens wettability but whose side effect is to decrease oxygen permeability.<sup>22</sup>

In this paper, we will discuss the effect of the deposition of thin polymeric films from siloxane plasmas on the barrier properties to O<sub>2</sub> of high-density polyethylene (HDPE), both in the as-deposited state and as a function of several postdeposition O<sub>2</sub> plasma treatments. The surface composition of the films and the effects of plasma treatments are measured by X-ray photoelectron spectroscopy (both core level and valence band), whereas the permeability is measured by an analytic gas permeability fractometer.

## EXPERIMENTAL

### Materials

HDPE plates (10 × 10 × 1 mm) (Heraclene, Eni-chem Polimeri) were used as substrate. Hexamethyldisiloxane (HMDSO), 99% pure, and tetramethyldisiloxane (TMDSO), > 98% pure, were purchased from Fluka and used without further purification. Oxygen from lecture bottles (Carlo Erba) was used both for plasma treatments and as a permeant.

### Plasma Deposition and Plasma Treatment

Plasma deposition and plasma treatment were performed using a parallel plate, aluminum reactor, coupled with a 13.56 MHz RF generator. The sample was located on the water-cooled grounded electrode. Oxygen was introduced by an MKS mass flow controller, at a flow rate of 16 cc(STP)/min. The pressure was maintained at 2 Pa (with the plasma off). The power was 100 W for O<sub>2</sub> plasma treatment and ranged from 40 to 100 W, as discussed in the following, for plasma deposition.

HMDSO and TMDSO were introduced into a glass vessel, connected to the reactor with a glass valve and a glass-metal joint. The temperature of the monomer in the vessel was maintained at 30°C throughout the cycle by a water bath. The flow rate, calculated by the initial increase in the system pressure with time after cutting off the vacuum pump, was about 100 cc(STP)/min.

The deposition rate was monitored by a quartz crystal microbalance (Intellemetrics) assuming a density of 1 g/cm<sup>3</sup>. A 200 nm-thick film of siloxane was deposited on each side of the HDPE samples intended for permeability measurements.

### X-ray Photoelectron Spectroscopy (XPS)

XPS analysis was performed with a Perkin-Elmer PHI 5500 ESCA system. The instrument is equipped with a monochromated X-ray source (Al anode), operated at 14 kV, 200 W. The diameter of the analyzed spot was 400 μm. The electron takeoff angle was varied between 25° and 75°, as discussed in the following. The base pressure was 10<sup>-10</sup> Torr. Peak deconvolution and quantitation of the elements was accomplished using the software and the sensitivity factors supplied by the manufacturer.

### Permeability Measurements

Permeability to O<sub>2</sub> was measured by a Lissy GPM-200 analytic gas permeability fractometer. This instrument measures isostatic permeability, that is, without substantial pressure differences between the two sides of the sample. The latter is fitted into a two-sector measuring unit, the upper one containing the probe gas (O<sub>2</sub> in this case), and the lower one, a circulating carrier gas (He). The unit was maintained at 27°C. The two sectors are separated by the sample, and O<sub>2</sub> can reach the lower part only by permeating through it. At fixed, preselected interval times (1 h in this case), a portion of the gas of the lower sector is carried by the flowing He to a gas-chromatograph (GC320, Gasukuro Kogio), equipped with a molecular sieve column and a thermal conductivity detector for determination of the volume of each gas. The peak area is calculated by a Carlo Erba DP 700 integrator. The permeability is calculated by the increase of the O<sub>2</sub> peak area (normalized to the peak area of a known amount of O<sub>2</sub>) as a function of time. Each measurement was repeated three times.

## RESULTS

### Deposition Rate

The deposition rate was deeply affected by the nature on the monomer, as shown in Table I. In general, the deposition rate of HMDSO was lower than that of TMDSO. The former could not be deposited with power lower than 60 W, whereas the latter, at 100 W, produced only white flakes of several millimeters diameter.

These data suggest that the reactive hydrogen atom linked to Si plays a fundamental role in the mechanism of polymerization or, in other words, that the molecular fragmentation induced by the

**Table I** Effect of Power on the Rate of Deposition of Polymeric Films from HMDSO and TMDSO Plasma

Monomer	Power (W)	Deposition Rate (nm/min)
HMDSO	40	<sup>a</sup>
HMDSO	60	<sup>a</sup>
HMDSO	80	3.1
HMDSO	100	5.2
TMDSO	40	5.71
TMDSO	60	8.57
TMDSO	80	16.67
TMDSO	100	<sup>b</sup>

<sup>a</sup> No deposition.<sup>b</sup> White flakes observed.

discharge is not so extensive, at least in these experimental conditions, to bridge the gap of reactivity between a fully methylated and a hydrogen-containing siloxane. This suggestion is supported also by the XPS results discussed in the following, and we will come back on this point in the discussion.

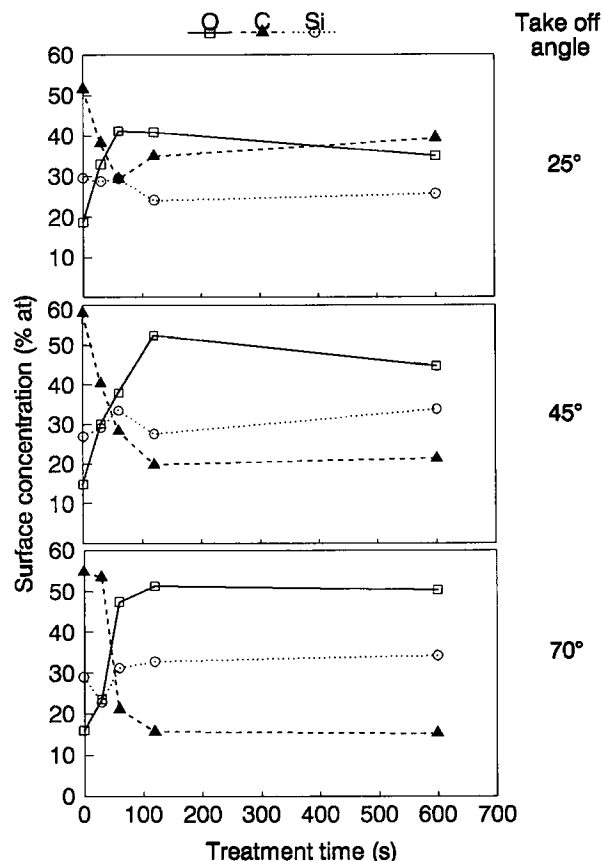
The results obtained with TMDSO at 100 W indicates that the rate of polymerization is too high and that macroscopic polymeric particles nucleate from plasma. Because of its very low deposition rate (at least in the present experimental conditions), HMDSO was discarded and experiments were further carried out only with TMDSO.

### XPS Analysis of Siloxane Films

The surface composition of polymeric films deposited from TMDSO plasma is shown in Table II. The takeoff angle was maintained, in this case, at 45°. At 40 W discharge power, the composition of the

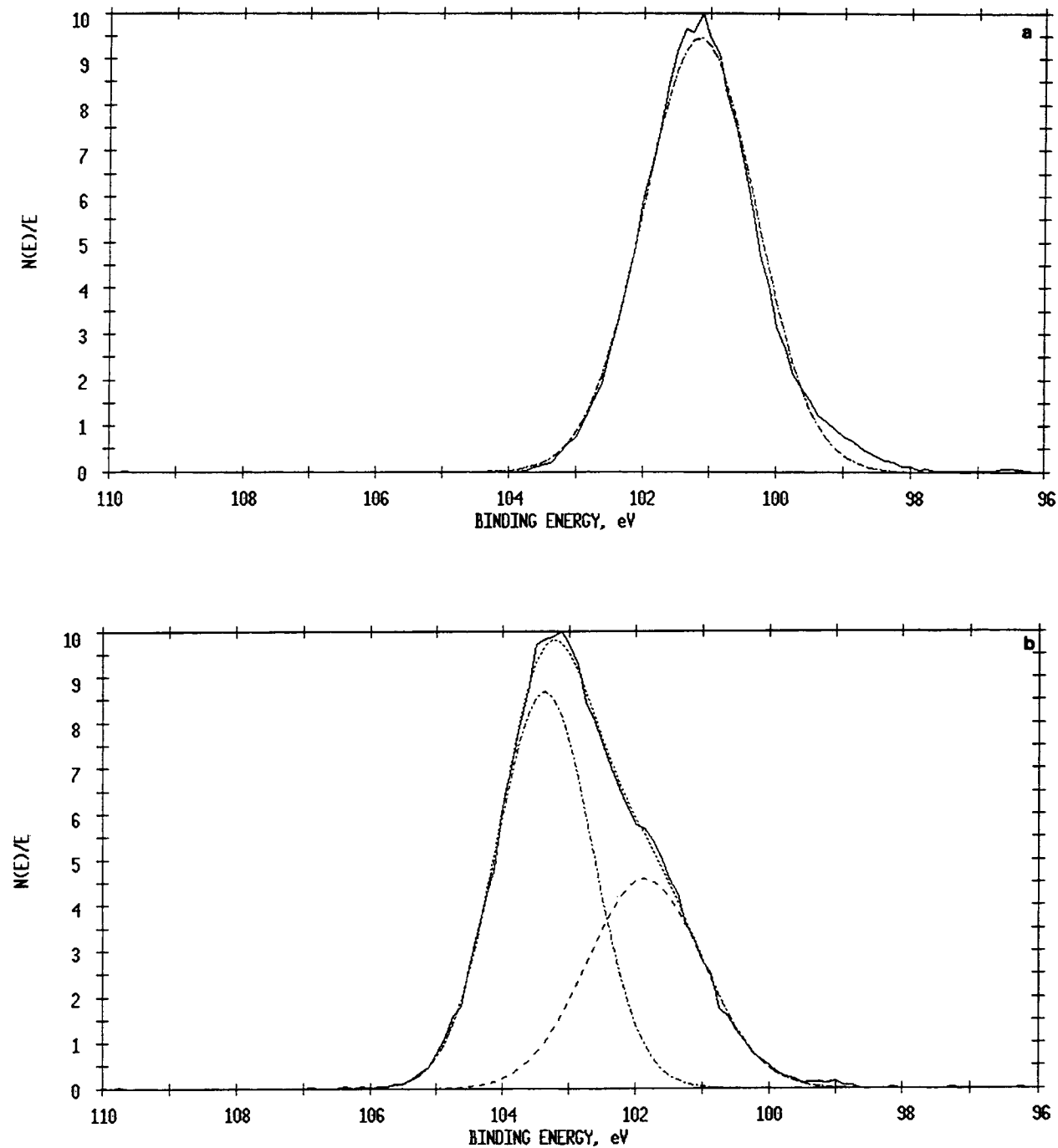
**Table II** Effect of the Power on the Surface Composition of Plasma-Deposited TMDSO Films

Power (W)	Surface Composition (% at)		
	O	C	Si
40	14.84	58.12	27.04
60	22.35	50.31	27.34
80	13.21	66.35	20.44
TMDSO (theoretical)	14.29	57.14	28.57

**Figure 1** Effect of O<sub>2</sub> plasma treatment on the surface composition of TMDSO deposited at 40 W at several takeoff angles.

film is very close to the theoretical composition of TMDSO. This finding confirms that, in the adopted experimental conditions, the fragmentation of the TMDSO molecule is not very marked, as suggested also by the previously discussed deposition rate. At 60 W power, a slight increase of the O-to-Si and a decrease of the C-to-Si ratio can be noticed, in agreement with the expected effect of increasing the power to the flow rate ratio.<sup>15</sup> On the other hand, at 80 W, the opposite is observed, and the atomic concentration of C reaches a very high and unexpected value. A likely explanation of this result is that, due to the very high deposition rate, a nonhomogeneous film is deposited and the substrate is exposed through cracks in the coating. This suggestion is strongly supported by the behavior observed at 100 W (flakes formation) and by permeability measurements, discussed in the following.

XPS analysis was performed also to evaluate the surface composition of samples subjected to adhe-



**Figure 2** Effect of  $O_2$  plasma treatment time on the  $Si_{2p}$  peak (takeoff angle  $45^\circ$ ): (a) TMDMSO deposited at 40 W; (b) TMDMSO after 30 s  $O_2$  plasma treatment; (c) TMDMSO after 60 s plasma treatment.

sion tests. Shortly, the surface composition of several samples, both as deposited and  $O_2$ -plasma-treated after deposition, was measured before and after the Scotch tape test.<sup>23</sup> No indications of adhesive fracture at the substrate-coating interface were ob-

served. These results are in agreement with current theories on plasma polymerization,<sup>1</sup> which suggest that a true covalent bonding is formed between a polymeric substrate and a plasma-deposited coating by the coupling of radicals created on the substrate

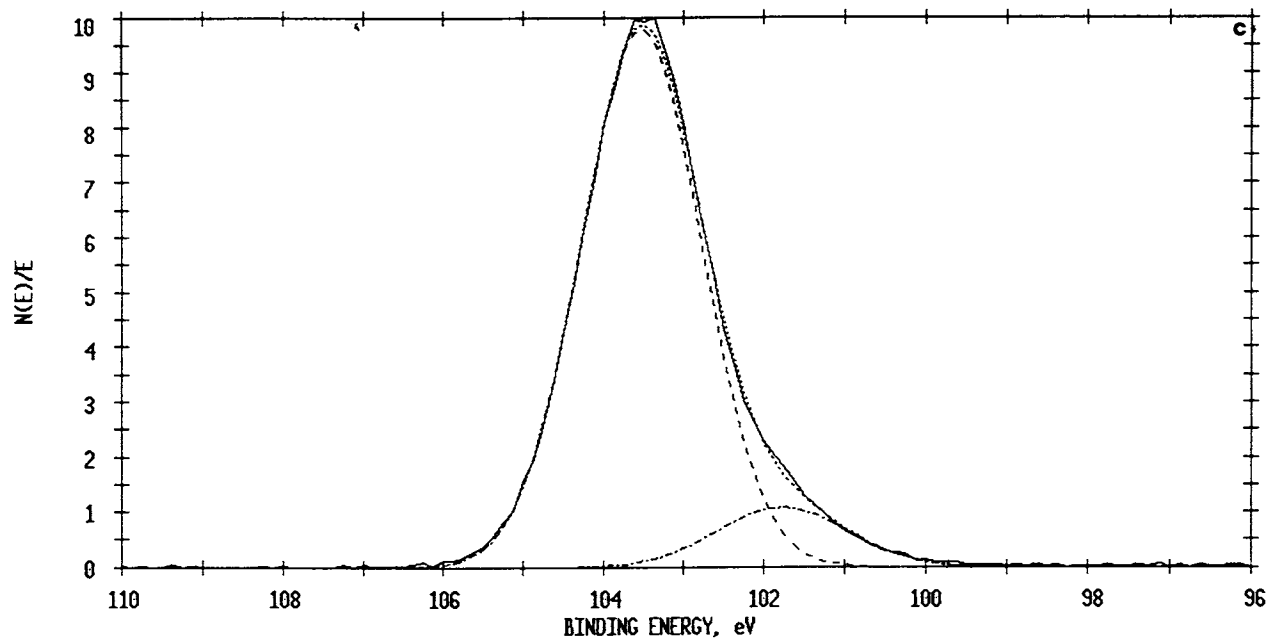


Figure 2 (continued from the previous page)

by plasma with radicals formed in the plasma-induced fragmentation of the monomer molecules.

### Effect of O<sub>2</sub> Plasma Treatment on Siloxane Films

#### XPS Core Level Studies

To better evaluate the effect of the O<sub>2</sub> plasma treatment on the siloxane films, XPS core level spectra were measured in the variable-angle mode. Results at three different takeoff angles are shown as a function of plasma treatment time in Figure 1. Data refer to the film deposited at 40 W power.

Considering the less surface sensitive data (70° takeoff angle), the O-to-Si ratio increases with treatment time, whereas the carbon content is greatly reduced. Thus, the effect of O<sub>2</sub> plasma is to etch away the organic carbon-containing portion, as already observed in the case of conventional (i.e., nonplasma-deposited) siloxane polymers.<sup>16-21</sup> The same effect is clearly observable also at 45° takeoff angle [Fig. 1(b)] and in the high-resolution Si<sub>2p</sub> peak, shown in Figure 2 (takeoff angle 45°). In fact, two components are detected: a lower binding energy component, whose energy is typical of organic siloxanes,<sup>24</sup> and a higher-binding energy one, falling in the region of silica and suggesting the presence of high number of Si—O bonds.

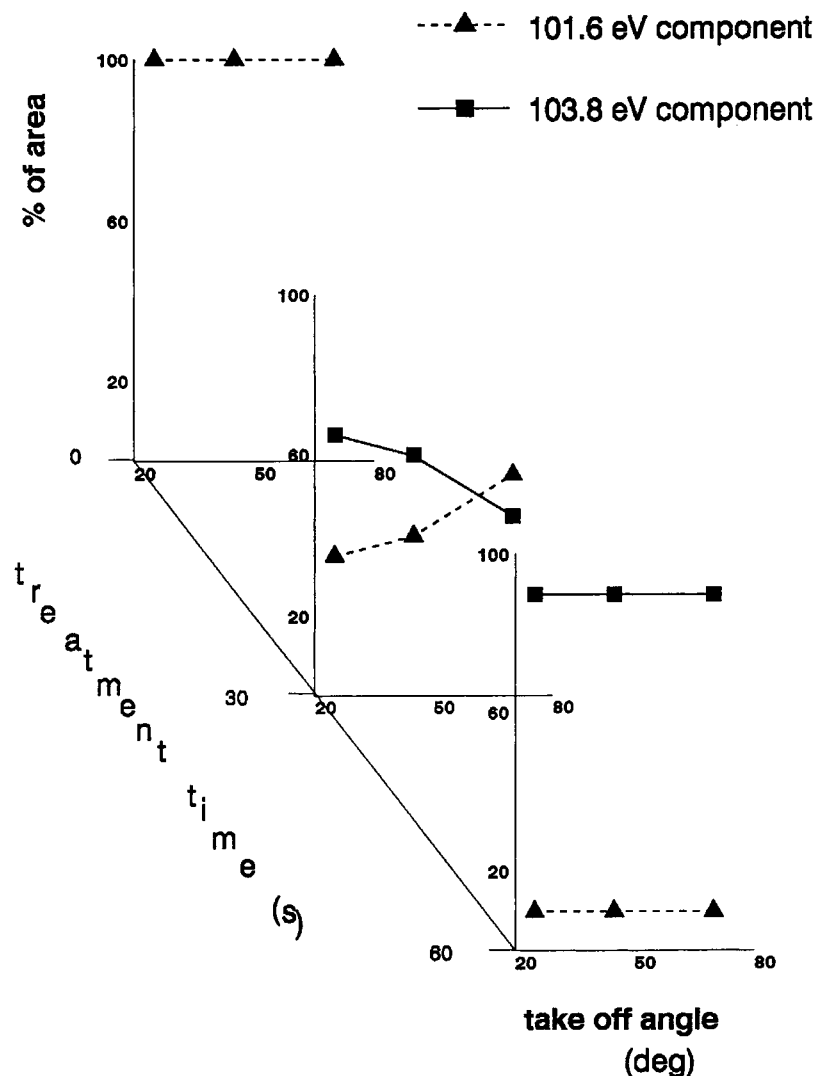
Increasing treatment time, the latter component

prevails (Fig. 2). The fraction of total Si<sub>2p</sub> area occupied by the two components as a function of treatment time and takeoff angle is shown in Figure 3.

Coming back to Figure 1, it is interesting to note that measurements performed with a high surface sensitivity [25° takeoff angle, Fig. 1(c)] show a peculiar trend: Contrary to diagrams of Figure 1(a) and (b), in fact, after an initial decrease, the surface concentration of C rises again. The most likely explanation of this behavior is the adsorption of organic contaminants from the atmosphere: The treated siloxane surface is, like inorganic oxides, a high-energy surface, prone to adsorb contaminants from the atmosphere in order to lower its surface energy.<sup>25,26</sup> The adsorbed layer of organic contaminants from the atmosphere is too thin to be detected at high takeoff angles, but is readily observed in conditions of high surface sensitivity. To test this hypothesis, measurements were performed on a clean coverglass slide, and the same behavior (i.e., a marked increase of C at 25° takeoff angle) was observed. Thus, it is safe to conclude that the observed trend of the carbon concentration is a side effect of the O<sub>2</sub> plasma-induced modification of the siloxane surface.

#### XPS Valence Band (VB) Studies

XPS VB spectra (0–30 eV) represent the photoelectrons emitted from the delocalized or bonding



**Figure 3** Effect of O<sub>2</sub> plasma treatment on the two components of the Si<sub>2p</sub> peak of TDMSO deposited at 40 W.

molecular orbitals within the polymer. The band structure of VB spectra contains potentially much information on the nature of the polymer,<sup>27</sup> but theoretical and experimental difficulties make VB studies still scarce within the literature.

The interpretation of VB spectra requires accurate quantum mechanical calculations, as done by Pireaux and co-workers.<sup>27-30</sup> As recently shown by Briggs and co-workers, however, it is possible to make useful identification of specific structures using a fingerprint approach.<sup>31</sup> In the present case, Figure 4 shows VB spectra of the TDMSO film deposited at 40 W discharge power [Fig. 4(a)] and

the same after 10 min, 100 W O<sub>2</sub> plasma treatment [Fig. 4(b)], compared to VB spectra of an organic siloxane [PDMS, Silastic, Dow Corning, Fig. 4(c)] and an inorganic siloxane [a coverglass slide, Fig. 4(d)]. The close resemblance between TDMSO and PDMS from one side and O<sub>2</sub>-treated TDMSO and glass from the other side is readily observed. A definite assignment of the observed features require state-density calculations, which are presently being performed. However, assigning the sharpest band of the organic siloxanes [Fig. 4(a) and (c)], centered at about 16 eV, to the methyl pendent groups is likely (incidentally, the methyl side chain gives rise to a

similar sharp feature at about the same binding energy in the VB spectrum of polypropylene<sup>27,31</sup>), which are removed after O<sub>2</sub> plasma treatment [Fig. 4(b)] and are, of course, not present on glass [Fig. 4(d)]. Thus, the modification of the polymer as a consequence of the plasma treatment is carefully reflected in VB spectra.

### Permeability Measurements

Results of permeability measurements are shown in Table III. Plasma deposition alone does not produce significant effects, whatever the discharge power. On the other hand, when the TMDSO coating is subjected to O<sub>2</sub> plasma treatment, a decrease of the O<sub>2</sub> permeability is observed for the 40 W and the 60 W deposited TMDSO. This effect is likely due to the creation of the inorganiclike coating, as shown by the previous results. The lack of any improvement when the 80 W-deposited TMDSO is subjected to O<sub>2</sub> plasma treatment agrees with the hypothesis that at this power it is not possible to obtain a homogeneous coating, as suggested by the XPS results.

## DISCUSSION

Previous results clearly show that siloxane polymer deposited from plasma does not affect the permeability to O<sub>2</sub> of HDPE, whereas some change is obtained after O<sub>2</sub> plasma treatment of the coatings. A few points, however, deserve some further discussion. First of all, the strong dependence of the deposition rate on the details of the molecular structure (Table I) is somehow in disagreement with general theories on plasma polymerization, which claim that, due to the peculiar "atomic" mechanism of polymerization from plasma, deposition rates are not deeply affected by the chemical features considered important in conventional or "molecular" polymerization.<sup>1</sup> It must be considered that, due to the experimental setup, deposition from plasma was carried on with a very high flow rate, which means a low-power (W)-to-flow rate (F) ratio. For instance, as compared with the quoted work of Park and Kim,<sup>15</sup> we used a flow rate about two orders of magnitude greater and about the same discharge power. In these conditions, the energy imparted to the single molecule (expressed by the combined parameter  $W/F^1$ ) is not enough to extensively fragment the molecule, as also confirmed by XPS, so that a depen-

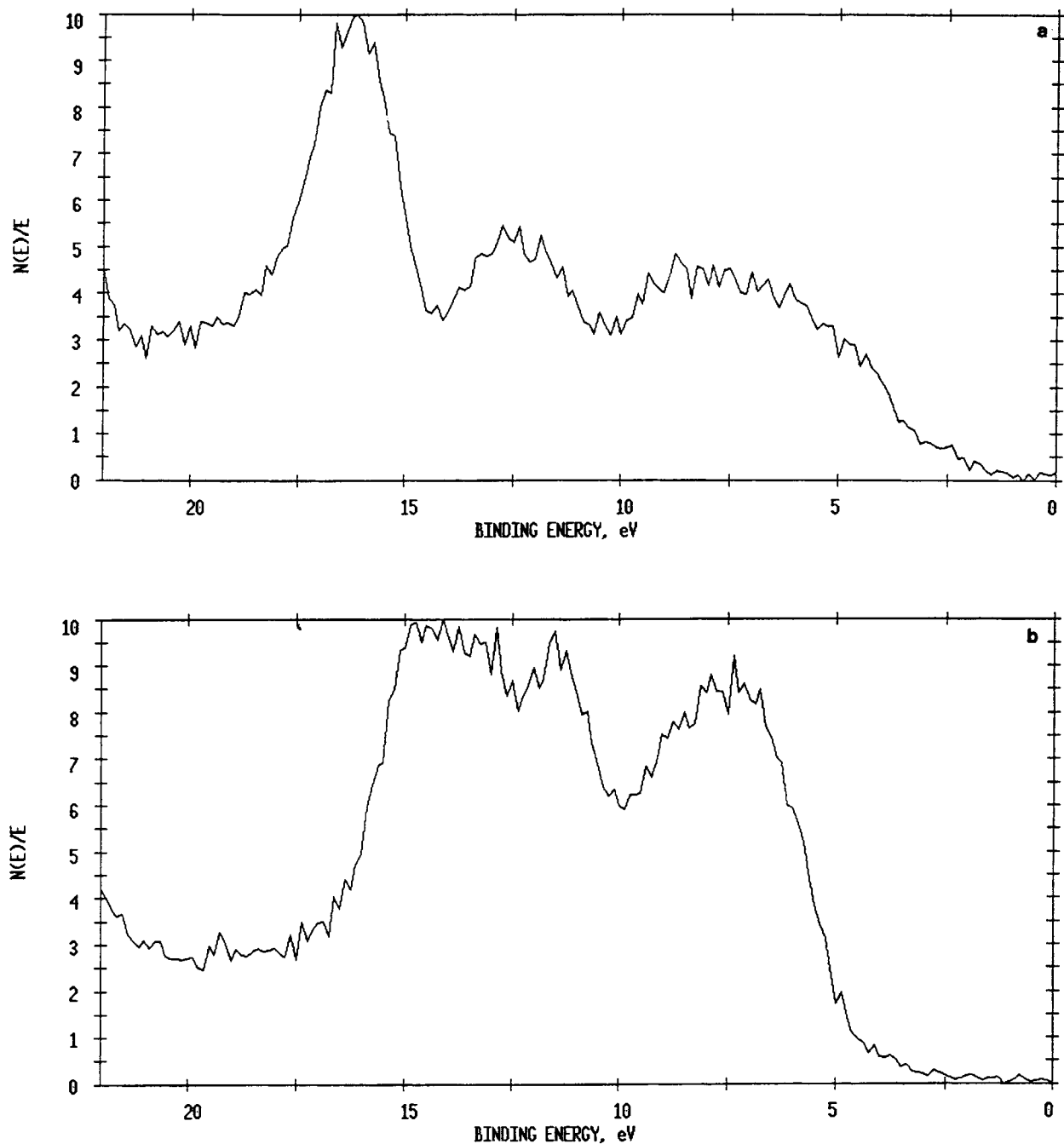
dence of the deposition rate on the chemical details of the molecule is likely.

As to the effects of the O<sub>2</sub> plasma treatments on the surface composition of the TMDSO films, the organic pendent groups are removed and an inorganiclike structure is produced. Permeability results, however, show that the inorganiclike coating is less effective as a barrier to oxygen than are silica coatings deposited, for instance, by evaporation. Several explanations to this behavior exist: First of all, our analysis evaluated only the first few nanometers of the coating, and the effect of the O<sub>2</sub> plasma at greater depth is not known. In other words, we ignore the effective thickness of the inorganiclike layer. More important, the transformation from an organic siloxane to an inorganic one involves a more than double increase in density,<sup>15</sup> which, on a substrate of fixed dimensions, can be accomplished only through the formation of cracks, as shown schematically in Figure 5. In this respect, better results could be obtained by monomers that do not contain oxygen, on which the oxygen atoms coming from plasma could compensate for the etching away of the organic part.

Finally, VB XPS spectra clearly show how carefully the details of the polymer backbone are re-

**Table III** Effect of Deposition Parameters and Postdeposition O<sub>2</sub> Plasma Treatment on the Barrier Properties of TMDSO-Coated HDPE

Power (W)	Posttreatment	Permeability (cm <sup>3</sup> m <sup>-2</sup> d <sup>-1</sup> bar <sup>-1</sup> )
	untreated	52
	600 s 100 W O <sub>2</sub>	50
40	—	48
40	30 s 100 W O <sub>2</sub>	35
40	60 s 100 W O <sub>2</sub>	18
40	120 s 100 W O <sub>2</sub>	19
40	600 s 100 W O <sub>2</sub>	20
60	—	46
60	30 s 100 W O <sub>2</sub>	40
60	60 s 100 W O <sub>2</sub>	19
60	120 s 100 W O <sub>2</sub>	18
60	600 s 100 W O <sub>2</sub>	20
80	—	56
80	30 s 100 W O <sub>2</sub>	48
80	60 s 100 W O <sub>2</sub>	46
80	120 s 100 W O <sub>2</sub>	45
80	600 s 100 W O <sub>2</sub>	43



**Figure 4** VB XPS spectra of (a) TDMSO deposited from plasma at 40 W, (b) the same after 10 min  $O_2$  plasma treatment, (c) PDMS, and (d) coverglass slide.

flected in the band structure. With the help of quantum mechanical calculations, which are presently being performed, it is expected that a more complete understanding of the effects of plasma treatment on polymers will be obtained.

## CONCLUSION

Organic siloxane coatings deposited from plasma do not create a barrier to  $O_2$  on HDPE.  $O_2$  plasma treatments of the coating, however, etch away the



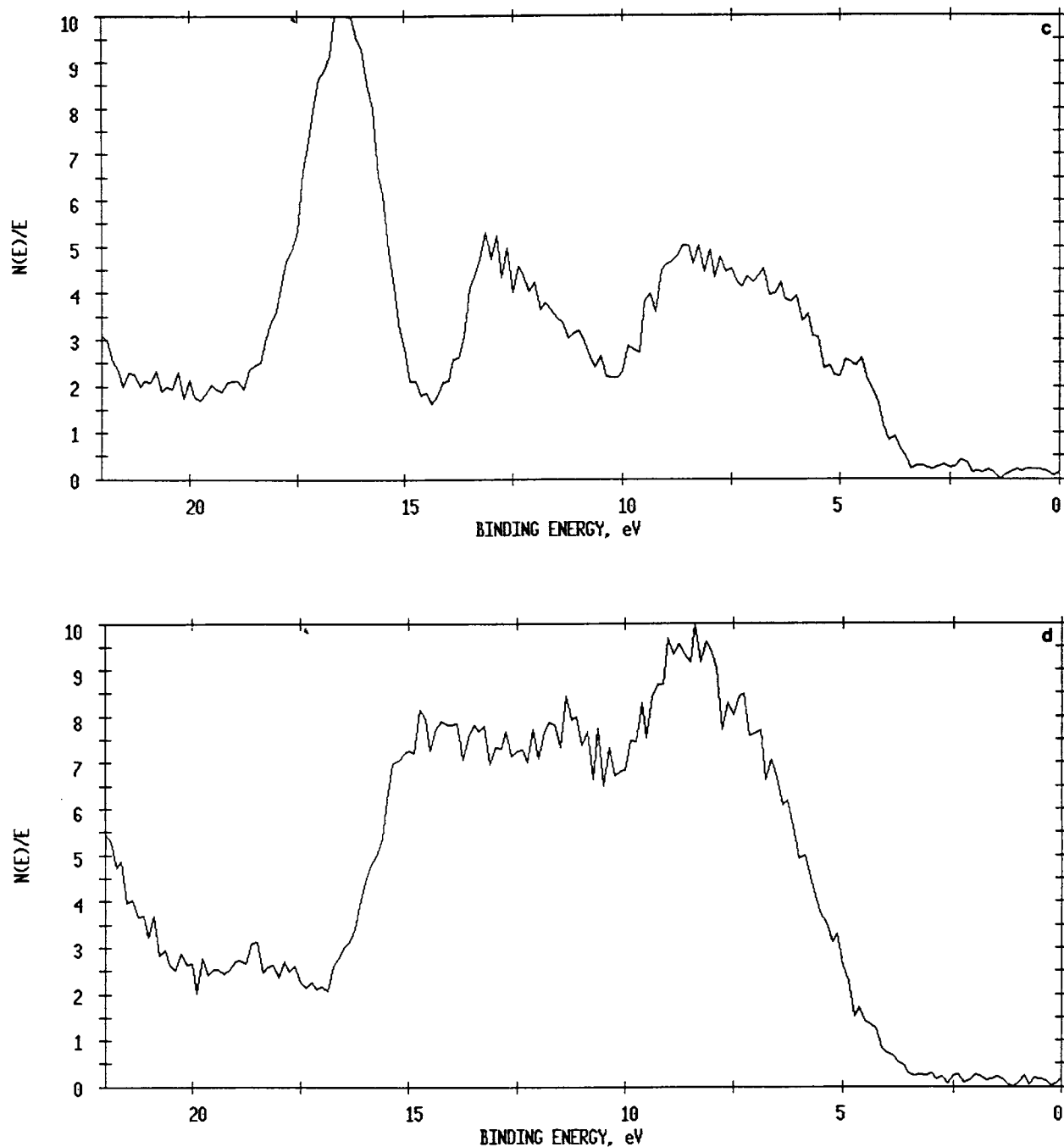
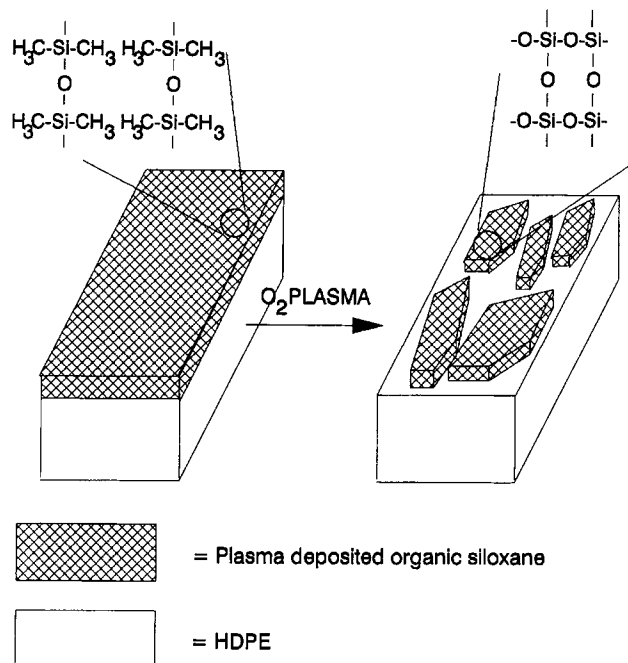


Figure 4 (continued from the previous page)

organic portion of the coating and create an inorganiclike Si/O layer. After this treatment, a decrease of about three times of the permeability to  $O_2$  is observed. The effectiveness of the treatment is

probably limited by the formation of cracks, due to the shrinkage of the backbone. Etching away of methyl groups of the organic siloxane is clearly observable in the VB XPS spectrum.



**Figure 5** Scheme of cracks formation as a consequence of  $\text{O}_2$  plasma treatment of organic siloxanes.

We thank Mr. L. Pozzi and Mr. L. Torelli for experimental assistance.

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Received June 24, 1992

Accepted August 7, 1992