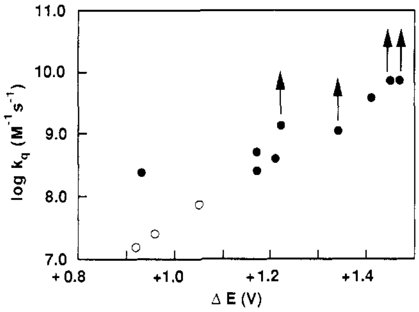

Figure 8. Plot of the observed rate constant for electron transfer quenching of phenothiazine singlet (●) and triplet states (○) as a function of ΔE; taken from the last columns of Tables I and III. Arrows indicate direction of possible movement of points which are minimum values.

(vide supra). Only in the cases of PH1, PH2, and PH3 were the measurements straightforward. Combination of the time-resolved and Stern–Volmer data allows the estimation of singlet quenching rate constants; these, along with the corresponding redox properties, have been included in Table III.

Interestingly, the singlet quenching data indicate that under typical conditions of photoresist applications most of the photosensitizing role of the phenothiazines may involve singlet processes. Indeed, the high efficiency of radical-cation formation from the singlet state (vide supra) supports this interpretation.

Conclusion

Clearly the mechanism for phenothiazine quenching by I involves electron transfer, which ultimately leads to photoacid generation. Interestingly, the rates of excited-state quenching for those molecules where the measurements were feasible correlate well in a single plot for both singlets and triplets (Figure 8). The points for those systems where we were able to determine only a lower limit to k_q as a result of the short singlet lifetime have been identified with an arrow and in general fit rather well; in the cases of PH0 and PH5 the values are sufficiently close to the diffusion limit that one should not anticipate much variation from the position displayed in Figure 8. The origin of the deviation for PH3 is unclear, although it is possible that the ketone substituent introduces enough of a perturbation in the chromophore to alter significantly its behavior.

The photochemistry of seven of the nine molecules examined in this work had not been reported before. Clearly, the basic behavior remains much the same throughout the group. Increased delocalization (as in PH1 and PH2), which makes these molecules better candidates for photoresist applications employing the mercury lamp g line (436 nm), also reduces the electron-donor ability of the triplet state toward molecules such as I. It is very likely that the ability of molecules such as PH1 and PH2 to act as photosensitizers is related more to their singlet than to their triplet state. Fluorescence quenching studies show that while these molecules are less reactive than PH0, the rate constants (see Table III) remain high enough for them to be useful. All the phenothiazine triplets are modest singlet oxygen sensitizers.

The overall complexities in these systems have led us to propose a new "differential" approach for the use of optoacoustic spectroscopy for the determination of intersystem crossing yields. This method proved readily applicable to PH0.

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Registry No. I, 52434-90-9; PHO, 92-84-2; PH1, 225-83-2; PH2, 226-06-2; PH3, 6631-94-3; PH4, 92-39-7; PH5, 1771-18-2; PH6, 1207-72-3; PH7, 258-08-2; PH8, 92-30-8; O_2, 7782-44-7.

X-ray Photoelectron Spectroscopic Depth Profiling of an Atomic Oxygen Resistant Poly(carborane–siloxane) Coating

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A novel, self-healing atomic oxygen resistant coating based on poly(carborane–siloxane) has been developed. Scanning electron microscopy studies of coated specimens after exposure to an atomic oxygen environment showed a distinct glassy layer on the surface. XPS depth profiles from such layers were processed by nonlinear curve-fitting methods to yield smooth, continuous atomic concentration curves. A depletion in the boron content was observed near the surface of the glassy layer. The glassy layer has a silica composition at the surface and approaches the borosilicate composition at deeper levels. High oxygen levels prevail beneath the glassy layer, indicating that the original polymer was oxygenated by atomic oxygen. The nonlinear smoothing of the depth profile curves is a powerful method to determine atomic ratios from the inherently noisy data.

Introduction

Atomic oxygen degradation of organic materials has been extensively studied in recent years.[1-4] According to these studies, most polymers and polymer matrix composites are not adequate for low earth orbit (LEO) space structures

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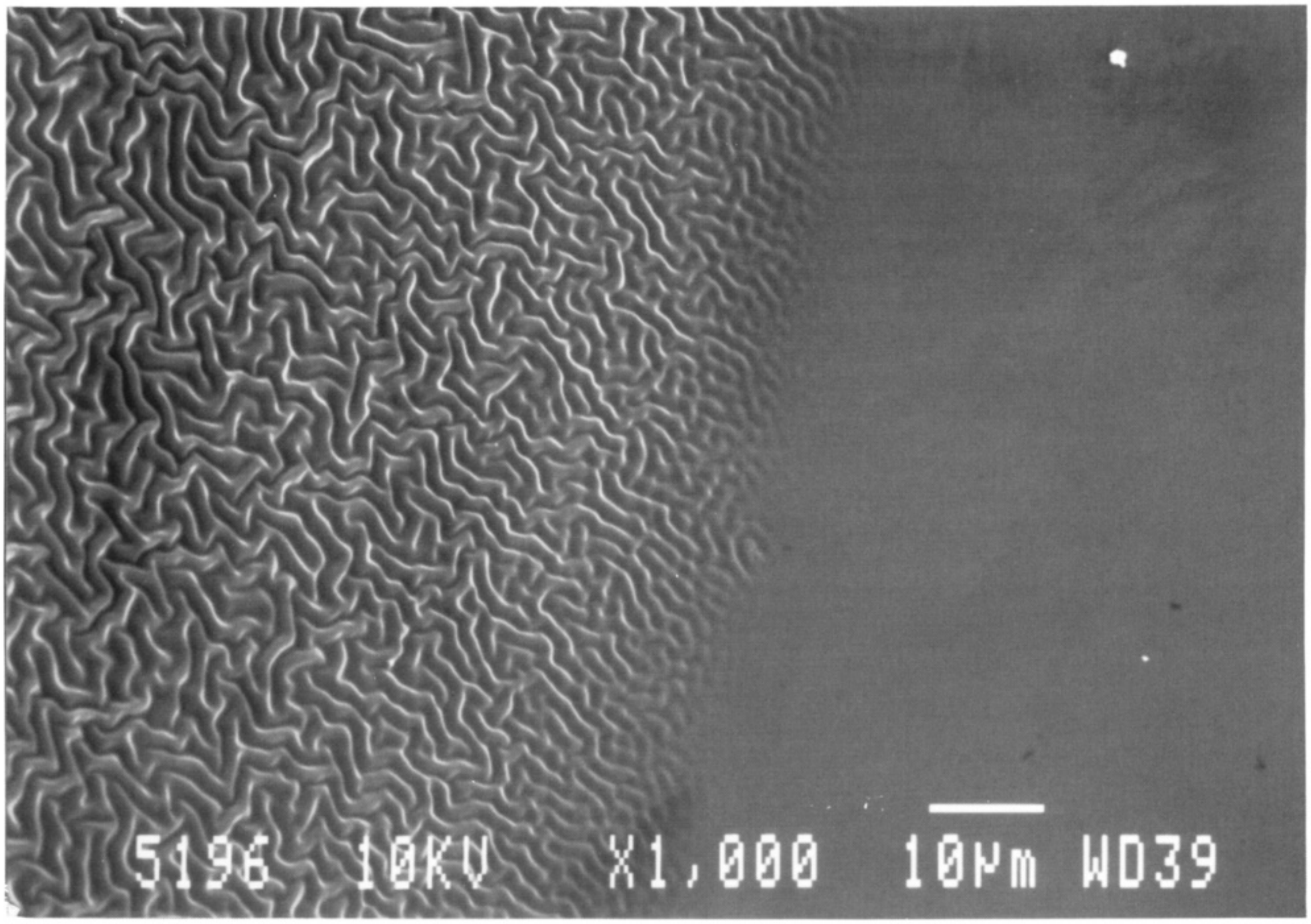

Figure 1. Waffling of thick P2 coatings.

without a suitable coating; they are readily attacked by atomic oxygen.

With the objective of an atomic oxygen resistant material in mind, a poly(carborane–siloxane) (P2) coating has been developed.[5] Coatings were tested in an air plasma asher. While we recognize that this is far from LEO conditions, it has been used extensively for preliminary screening of structural materials and coatings for space applications.[6] The coating demonstrated excellent protection of Kapton and silver substrates. Almost no weight loss was detected after 1 week of ashing, the equivalent of about 5 years of exposure to atomic oxygen in space.

The P2 coating forms a protective borosilicate glassy layer on oxidation. Concomitantly, incorporation of oxygen atoms by the carborane unit counteracts the shrinkage and cracking that would otherwise occur as the glassy layer forms. The remaining intermediate rubbery polymer has self-healing properties while also acting as a stress accommodator.

Formation of a silica layer on coatings of organosilicon polymers during exposure to oxygen plasma has been reported mainly in the photoresist literature.[7-11] Many investigators used RIE (reactive ion etching), which is not comparable to the very low energy conditions found in our asher.

To better understand the nature of the glassy layer and the interaction of P2 with atomic oxygen, a combined SEM/XPS study was undertaken.

Experimental Section

The synthesis and application procedure of the P2 coatings were described in a previous paper.[5] The coated specimens were exposed to atomic oxygen in a 13.56-MHz Plasma Prep II asher. SEM work was conducted on a JEOL 840A scanning electron microscope at 10 kV. XPS data were obtained on a Perkin-Elmer 5400 spectrometer. The survey and high-resolution spectra were collected by using a Mg ($K = 1253.6$ eV) anode at 400 W. The depth profiling of the glassy layer was performed using a 4-keV calibrated high-purity argon ion beam for sputtering. For this condition, a reproducible sputtering rate of approximately 33 Å/min was obtained.

Results and Discussion

After exposure of P2-coated kapton specimens to plasma, coatings thinner than ca. 1 μm stayed flat, whereas thicker ones became waffled (Figure 1). Similar patterns have been observed in thin carbon films, caused by buckling and delamination due to high compressive

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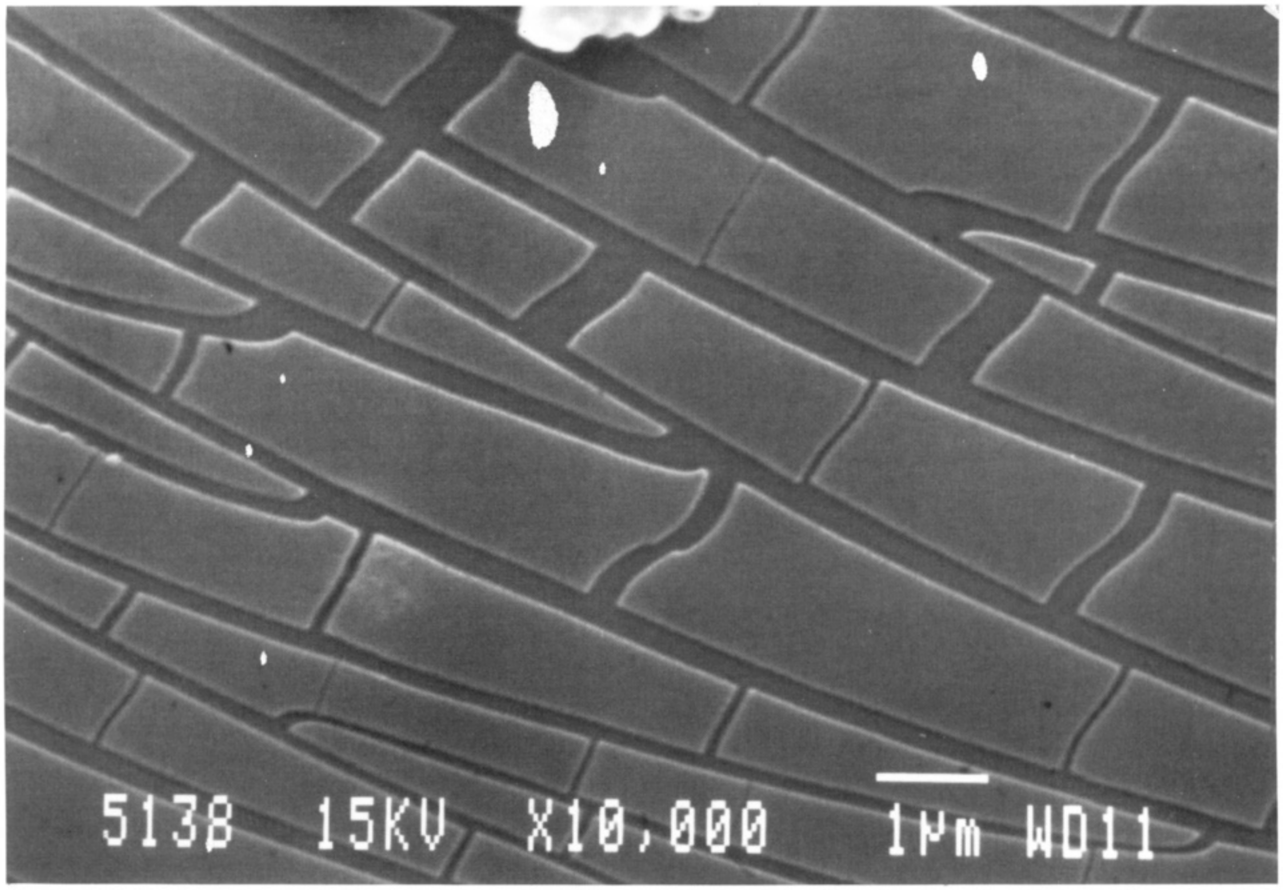

Figure 2. SEM micrograph of a broken glassy layer in a severely bent area of the P2 coating.

stresses.[12–14] In our case there is no evidence of delamination. The stress relief patterns indicate that compressive stresses are present in the film and above a certain thickness can lead to waffling. At higher magnifications, a smooth, crack-free, glassy layer is observed on SEM micrographs with an estimated thickness of 1500 Å. The rubbery coating can accommodate severe bending of the specimen, whereas the brittle glassy layer cracks extensively. The pattern of the cracks depends on the stress field. Tensile or bending uniaxial stresses tend to create bandlike crack patterns, perpendicular to the stress axis, and biaxial stresses form tilelike shapes (Figure 2).

The main scope of this investigation is the elucidation of the nature of the glassy layer and its interface using X-ray photoelectron spectroscopy (XPS). This surface characterization tool is gaining increased popularity for studying interactions of polymers with plasma.[15,16] This is due to the bonding information it can provide, based on measured shifts of the photoelectron lines. In combination with its depth profiling capability and excellent depth resolution it is a powerful method. The spectrum displayed in Figure 3a illustrates XPS data obtained from an "as-coated" P2 surface. Prior to the spectrum acquisition, 75 Å was sputtered from the coating to remove any adventitious contaminants. Sputtering generates other problems that will be discussed later. As expected on the basis of the polymer composition, the XPS survey spectrum shows the presence of silicon, boron, carbon, and oxygen. Note that for binding energies smaller than 200 eV the sensitivity scale was increased 4-fold in order to expand the relatively small peaks of boron and silicon.

Table I. Atomic Concentration of P2 Coating in the Unashed Condition and after 120 h of Ashing

condition, depth, Å	boron	carbon	oxygen	silicon
unashed	36.8	33.5	17.1	12.7
ashed, 600	4.1	1.8	68.0	26.2
ashed, 3000	28.2	18.4	43.6	9.8

XPS survey spectra from the P2 coating after ashing for 120 h are shown in Figure 3b–d in increasing depth order. At a depth of 600 Å the boron peak is very small. No carbon is present, leaving silicon and oxygen as the major constituents. Oxidation of the surface is evident from the very prominent O(1s) peak near 530 eV in the spectrum.

At 1600 Å the carbon peak appears in the spectrum and the boron peak gains height, although still not reaching the original value of the unashed polymer.

At 3000 Å one sees the same constituents. The oxygen peak is relatively high, still well above its level in the original polymer. This can be interpreted as an "oxygenated state" of the polymer. We propose that the major initial reaction of atomic oxygen is insertion in the C–Si bond, since this reaction generates the most energy. As this reaction increases the polymer weight and volume, it could lead to the waffling that is observed. However, the carbon peak is lower than in the unoxidized polymer. It may be assumed that if penetration of the atomic oxygen is much deeper than the glassy layer, some could also react with carbon and release volatile carbon species.

To obtain a more quantitative evaluation of the P2 coating's compositional changes, high-resolution scans were

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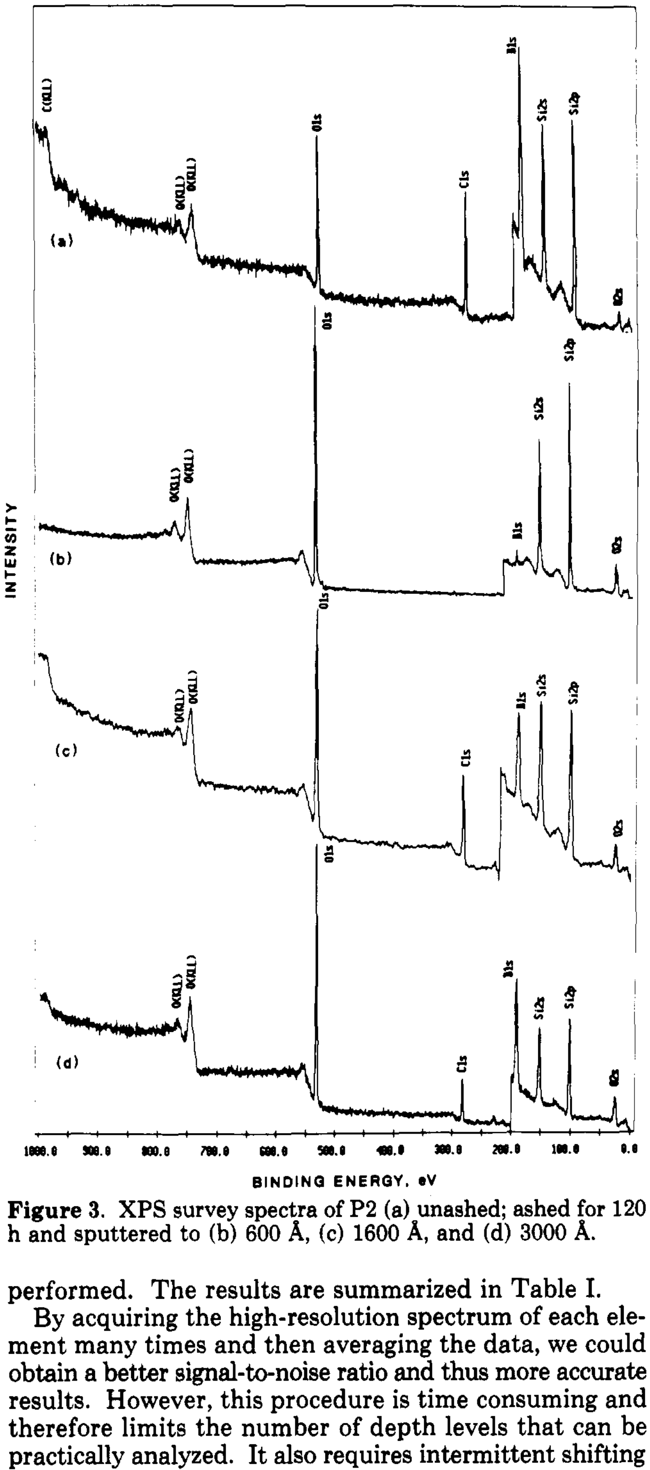

Figure 3. XPS survey spectra of P2 (a) unashed; ashed for 120 h and sputtered to (b) 600 Å, (c) 1600 Å, and (d) 3000 Å.

performed. The results are summarized in Table I.

By acquiring the high-resolution spectrum of each element many times and then averaging the data, we could obtain a better signal-to-noise ratio and thus more accurate results. However, this procedure is time consuming and therefore limits the number of depth levels that can be practically analyzed. It also requires intermittent shifting between acquisition and sputtering modes, which involves repositioning the detector. While not necessarily so, this operator intervention could lead to certain changes in acquisition parameters.

Conventional depth profiling on the other hand is normally done by averaging a smaller number of high-resolution spectra from each depth level, hence yielding "noisier" curves (see Figure 4). It has however the advantage of including a large number of experimentally acquired data counts from many depth levels. No operator-assisted changes are made, and thus the acquisition conditions are better preserved.

By applying nonlinear curve-fitting methods to the low count data, it is possible to obtain much smoother count depth profile curves. The following equation was used in our case for all elements:

$$y = a + b\exp(-x^2/c)$$

where

$$x = t - d, \quad x = 0 \quad \text{for } t < d$$

The parameters a–d were then optimized by using a nonlinear least-squares algorithm.

Such sigmoidal curves are often utilized to describe composition changes across an interface. The XPS depth-profiling experimental counts for oxygen along with the fitted curve are shown in Figure 5.

Finally, the atomic ratio with respect to silicon was separately determined for each element, as shown in Figure 6. Such continuous depth profile curves of the atomic ratios provide excellent insight into the possible interactions between P2 coatings and atomic oxygen.

The approximate 2:1 oxygen to silicon ratio at the surface and the very low values of boron indicate that the glassy layer's top surface is close to silica composition. Depletion of boron close to the surface of borosilicate glasses is not unusual and has been reported in the literature.[17,18] The mechanism of boron depletion is presumably related to exposure of the sample to humidity since boric oxide and its acids are water soluble. Boric and metaboric acid will volatilize under the high vacuum of the XPS chamber.

For this reason analysis of boron is usually done by in situ cleaving of bulk specimens inside the vacuum chamber of the testing instrument. Unfortunately this procedure is not applicable for thin coatings.

The oxygen curve rises to a maximum at about 1400 Å and then gradually drops while still remaining above the original polymer composition. The maximum can be attributed to the combined contribution of the silicon and boron oxides at this depth level. However, the oxygen concentration stays higher than its initial concentration in the polymer even at a depth of 3000 Å. This explains the increase in volume, which manifests itself as waffling in the thicker regions of the coating.

Jurgensen et al. also utilized XPS depth profiling to demonstrate that 15.3% silicon methacrylate forms a 210-Å silica layer on the surface during exposure to oxygen RIE.[10] The silica layer subsequently acted as a diffusion barrier, which prevented further penetration of oxygen. Since the conditions of RIE exposure are different, it is hard to conclude at this point whether the differences are material or exposure related.

Carbon is almost nil in the glassy layer and sharply increases across the interface. This is in fact the best indication of the interface location, since it is expected that practically no carbon would be present in the glassy layer. Note that the trends in the carbon profile do not coincide with the boron curve. This leads us to believe that the depletion of boron from the surface is a separate process, independent of the glassy layer formation. It is probably due to the subsequent exposure of the specimen to humidity and evaporation of boric acids in the vacuum chamber prior to the XPS analysis. Recent data in our laboratory confirms this hypothesis. Later spectra on carefully handled specimens show a much thinner boron-depleted layer.

UV photons originating from the plasma may also play a role in the process. To separate effects of atomic oxygen and UV radiation a sidearm or afterglow asher, experimental design is under evaluation.

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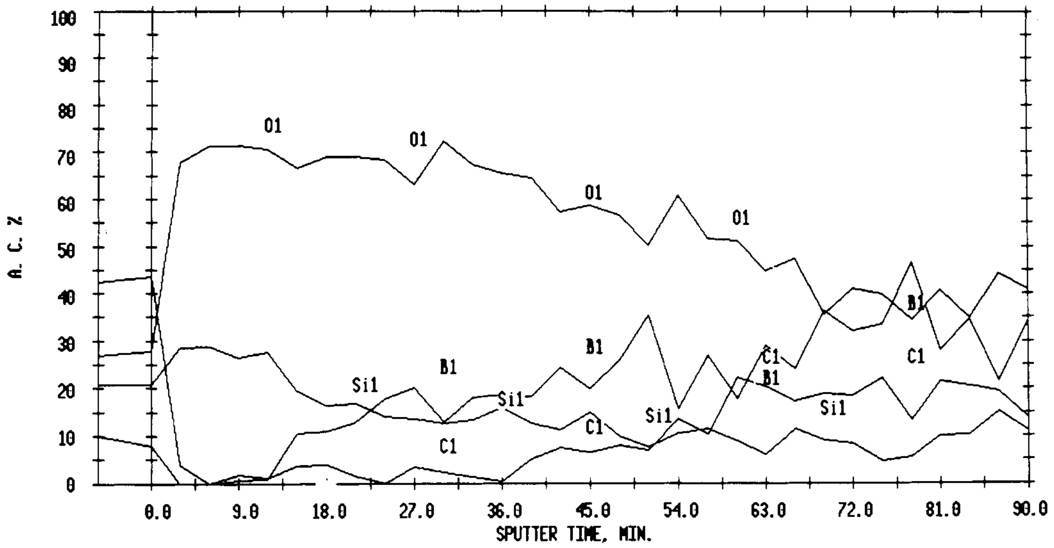

Figure 4. XPS atomic concentration depth profiles for ashed P2.

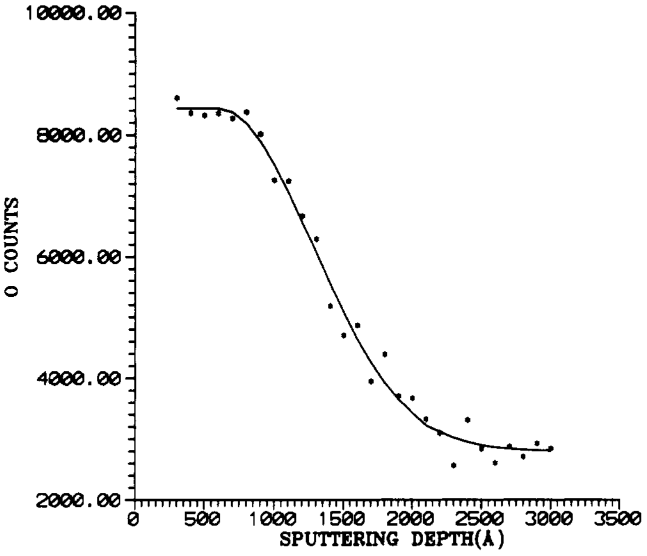

Figure 5. XPS depth profile of oxygen in ashed P2 shown as raw count data with fitted curve.

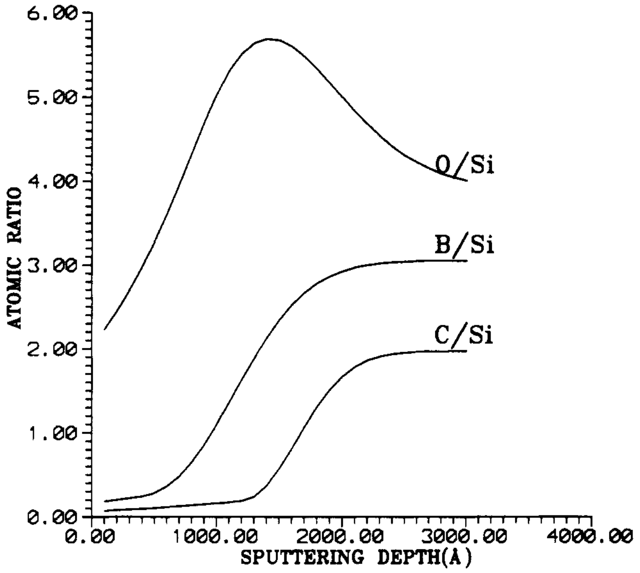

Figure 6. Atomic ratio depth profiles for a P2 coating (normalized to silicon) after 120 h of ashing.

The generally sigmoidal shape of the XPS atomic concentration profiles across an interface is often broader than the "true" profile because of instrumental factors, surface texture, roughness, and nonuniform sputtering. The combination of XPS volume of analysis and the crater wall effect of ion milling makes exact determination of the interface width difficult.

The ion beam sputtering used here to generate the depth profiles is a complex process. The rate of sputtering is a function of composition and may vary between different materials, especially across an interface. Preferential sputtering may occur if the specimen is not homogeneous. No preferencial sputtering was observed in our study. Reduction of oxygen has been also reported for some oxides, including silica.

Despite the above-mentioned concerns, there is presently no other efficient substitute for ion beam sputtering to reveal the elemental depth profiles in the study of a polymeric coating to a depth range of 3000–4000 Å and with light elements to consider.

Summary and Conclusions

XPS depth profiling of P2 [poly(carborane–siloxane)] coatings after air-reactive plasma treatment shows the formation of glassy borosilicate layer about 1500 Å thick.

The concentration of boron in the glassy layer is low at the surface and increases with depth. Rather than being related to the formation process, this is probably due to absorption of water during storage and handling and subsequent evaporation of boric and metaboric acids under high vacuum.

Oxygen levels are consistently higher than its concentration in the original polymer. This is true even below the glassy layer. Incorporation of atomic oxygen in the polymer is believed to be a dominant factor in the interaction of P2 with the air plasma. It also provides a plausible explanation of the waffling effect that occurs when coatings are thicker than 10 000 Å.

The nonlinear smoothing of the depth profile count curves is a powerful method to determine atomic ratios from such inherently noisy data. It may often provide valulable information that otherwise can be obtained only by averaging many high-resolution scans at different depth levels.

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