are sandwiched between Na^+-reversible Na/Hg electrodes, the observed impedance response of the cryptand-modified electrolyte is similar to that of the parent electrolyte but shifted to higher frequency as illustrated by the Bode plots (Figure 4). The interfacial behavior of the polyelectrolyte–cryptand complex studied here against Na/Hg electrodes is in sharp contrast to the observations of Chen in our laboratory.[23] When [2.2.2] is added to a poly(phosphazenesulfonates), a small low-frequency second arc was found in the impedance spectrum. This arc was ascribed to a slow charge-transfer process between electrolyte and electrode involving the release of Na^+ from the cryptand. (No arc was observed for the cryptand-modified aluminate polyelectrolyte in the same frequency range.) Apparently the release of the cation from the cryptand is faster relative to ion migration in the aluminate networks than in the polyphosphazene sulfonates. NMR studies of Na^+ release from [2.2.2] in several solvents have shown that the rate of cation release is highly solvent dependent but does not correlate with the dielectric properties of the solvent.[24] The difference in the observed interfacial behavior for the aluminate networks and the poly(phosphazenesulfonates) may be due to the different nature of the solvent properties of the polymers or perhaps to the different concentrations of cation within the polymers. Further studies with these and related polyelectrolytes should yield insight into how the nature of the polymer affects the degree of conductivity enhancement and the interfacial kinetics when cryptands are added to polymer electrolytes.

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Interfacial Interactions of Titanium-Coated Polyester Films

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The chemical composition of the interfacial region between sputter-coated titanium metal and both plasma-pretreated and nonpretreated poly(ethylene terephthalate) (PET) film is presented. Upon application of a gaseous (nitrous oxide/argon) plasma, titanium/polyester adhesion increased dramatically following metallization compared to the nonpretreated analogue. To relate this phenomenon to a physical and/or chemical change, X-ray photoelectron spectroscopy, Auger electron spectroscopy, and transmission electron microscopy have been used to characterize both the surface and interfacial regions of these films.

Introduction

Although a number of techniques have been discovered to improve metal adhesion to plastics, two distinct methodologies have progressed and been commercially applied. The first method concerns the application of a thin polymeric coating to the polymer that acts as a binding agent between the film and subsequently vacuum sputtered metal.[1,2] The second method used to increase sputtered metal-to-polymer adhesion is to chemically modify or clean the surface of the polymer substrate prior to metal deposition.[3-5]

In the case of polyesters, a limited number of authors have described the effects of plasma processing on poly(ethylene terephthalate).[3,6] Yasuda et al. exposed PET to both argon and nitrogen plasmas.[7] Following treatment with either plasma, plasma-induced surface oxygen species were detected; however, no functional assignments were made. Dunn et al. have studied the effects of oxygen and argon plasma on the surface properties of poly(ethylene terephthalate) by both photoelectron[8] and infrared[9] spectroscopic techniques. Oxygen plasma treatment incorporated additional carbonyl functionality into the polyester; however, argon plasma treatment resulted in a decrease of both C=O and C—O. These results suggested that the surface of the PET film was oxidized by O_2 plasma treatment but carbonized by the Ar plasma.

One of the most important aftereffects of PET plasma treatment with a nitrous oxide/argon gas mixture is a substantial increase in adhesion to sputter-deposited titanium. In a previous study,[10] the chemical alterations in PET that were induced by N_2O/Ar plasma treatment prior to metallization were determined by application of a variety of analytical methods. Surface functionalization was achieved via photochemical dissociation of the ester moiety arising from short-term plasma exposure. The purpose of

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this paper is to probe both chemically and physically the interfacial PET/Ti composition in order to determine how the plasma treatment of the polymer induces additional PET/Ti adhesion. Hopefully, one will ascertain whether a mechanical interlocking or chemical interaction dominates.

Experimental Section

The poly(ethylene terephthalate) film used as a substrate was obtained from ICI Ltd. Technical grade (99.0%) nitrous oxide and ultrapure carrier grade (99.999%) argon used to sustain an rf plasma were purchased from Air Products, Inc.

An rf plasma was generated by a 0.30-kW automatically controlled and tuned supply. The commercial apparatus was evacuated to 2×10^{-5} Torr followed by introduction of the pretreatment gas(es) through a variable-leak valve to attain a system pressure of $(3-15) \times 10^{-3}$ Torr. Following discharge initiation, the PET substrate was exposed to the plasma for times of up to 1 min. The same chamber was used for sputtering titanium in order to eliminate exposure to air. A titanium cathode (99.9% purity, grade 2) obtained from Astro Metallurigical Co. was used as the source for sputter-coated process. A planar magnetron sputtering system operating at a pressure of 0.2 Pa in argon was used to metallize the polyester substrate. Sputtering power was varied between 3.0 and 8.0 kW.

Auger electron spectra and depth profiles via argon ion etching were recorded with a Perkin-Elmer Phi Model 610 scanning Auger microprobe system. Typical auger electron beam voltage was 1.5 kV with a beam current of 30 μA. The ion beam used for concurrent Ar sputter etching was operated with an accelerating voltage of 4 kV and an ion current of 5 $\mu A/cm^2$.

X-ray photoelectron spectra were obtained with a Perkin-Elmer Phi Model 5300 ESCA system using a magnesium anode ($K\alpha$ = 1253.6 eV) at 250 W (14 keV, 18 mA). Operating pressures were in the range $(0.5-5.0) \times 10^{-7}$ Torr. Samples were attached onto aluminum mounts with double-sided transparent tape. The binding energies were referenced to the aromatic C(1s) photopeak maximum at 284.6 eV.

Scanning and transmission electron micrographs were taken with either a Philips Model 420 scanning transmission microscope (STEM) or a JEOL 100 CX-II transmission electron microscope. Samples prepared for TEM analysis were embedded in Polyscience ultralow-viscosity resin and cured for 8 h at 70 °C. Samples were then sectioned to between 500 and 800 Å with a Reichert-Jung ultramicrotome using a Microstar diamond knife. The thin sections were then placed on 200-mesh copper grids prior to analysis.

Results and Discussion

Previously[10] we studied via XPS the modifications to the surface of PET film brought about by plasma treatment with a mixture of nitrous oxide and argon. Both surface cleansing and surface functionalization occurred at low-to-moderate plasma exposure. A Norrish type I mechanism was shown to dominate wherein a new carbonyl species was created through the dissociation of the carboxyl carbon and the ester oxygen concurrrent with removal of hydrocarbon contamination. With greater exposure polymer chain scission resulted followed by loss of carbon monoxide rather than relaxation to the aldehyde species. Titanium–polyester adhesion was optimized when plasma exposure was brief, suggesting that at the interphase titanium and the new functionality may chemically interact. The experiments to be discussed address this issue.

To understand the adhesion of titanium to both the nontreated and pretreated polyester, it is extremely important to know the composition of the substrate surface as close to the interface as possible to thereby determine the primary bonding mechanism. An Auger depth profile of every titanium-coated polyester film (Figure 1) exhibits three distinct regions within the deposited layer (i.e., a metallic layer sandwiched between two titanium oxide layers). It was expected that the outermost surface of the titanium metal would oxidize at room temperature. Typically, titanium has a native oxide layer of approximately 30 Å in air at room temperature. This is verified by the high titanium and even higher oxygen atomic percent seen during the initial stages of argon ion sputtering (Figure 1). Approximately 15% carbon is also detected, which quickly decreases to near zero within 1 min of sputter time. After 2 min the titanium atomic percent has risen to greater than 70%, while oxygen has diminished to around 20%. This observation suggests a much greater enriched titanium phase than existed at the surface. Further into the film oxygen atomic percent rises such that the titanium-to-oxygen ratio is nearly 1:1.

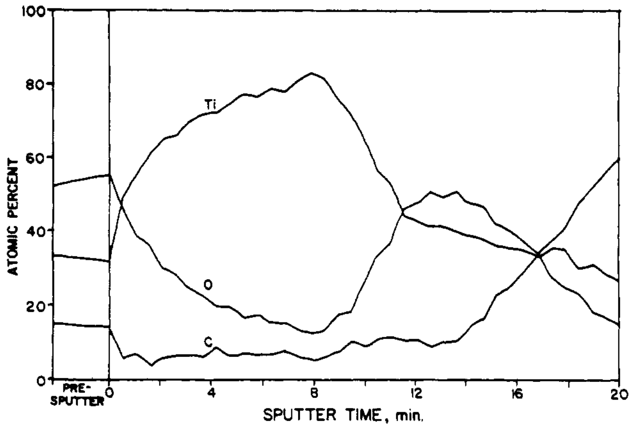

Figure 1. AES depth profile of a typical titanium-coated ICI-442 polyester film.

The appearance of a titanium oxide species near the polyester/titanium interface was unexpected. This observation may be explained in several ways. First, it has been shown[11] that atmospheric water and oxygen may travel along titanium grain boundaries and react with components present in these regions. However, precautions taken to prevent this occurrence (i.e., dry conditions) as well as the time of film exposure to the atmosphere do not seem to affect the size of the interfacial oxide. Another possibility is that the oxidation may occur through some chemical interaction between the titanium and polyester present at the interface, such as coordination of an ester oxygen with titanium. Some reactivity can be anticipated with the plasma-treated polymer surface since a new aldehydic functionality has been shown to be produced on the polymer surface. Bonding directly to the aldehydic oxygen or abstraction of a carbonyl oxygen by the titanium are two envisioned possibilities. For the non-plasma-treated surface, this reactivity is not possible. Again, this does not seem likely, at least on a large scale, because the amount of titanium in direct contact with the polyester could not produce enough oxygen (if all were abstracted by the metal) to account for the expansiveness of this oxide region even taking into account smearing by ion beam "knock-in" artifact effects. The most probable cause of this titanium/oxygen enriched region is probably the interaction of off-gassed water from the polymer with the adjacent layer of sputtered titanium atoms. In support of this notion, residual gas analysis of the polymer off-gases has shown that a significant amount of water exists in the plasma pretreatment chamber both prior to and during plasma treatment. The highly reactive metal atoms nearest the polymer would react with the water released by the polymer to form an oxide-like moiety near the

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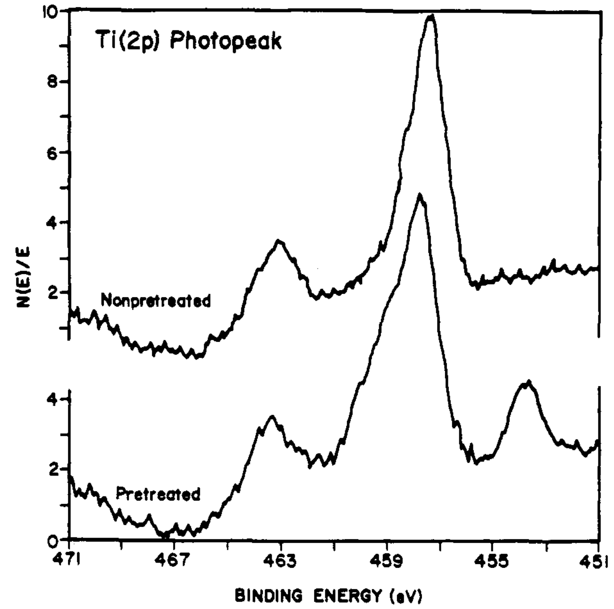

Figure 2. XPS Ti_{2p} spectrum of both plasma (N_2O/Ar) pretreated and nontreated 800-Å titanium-coated ICI-442 polyester film following argon ion etching to within approximately 50 Å of the interphase region.

interfacial region. This notion seems reasonable in that the time the film is in the plasma chamber and the time required to move the film from the plasma chamber to the sputter chamber is <5 s. In other words, the film probably would not have sufficient time to allow removal of all water in the on-line continuous commercial process (feet per minute) before deposition of titanium. In evidence of this proposed reactivity, titanium is used commercially to getter oxygen and moisture in a large number of instruments where a high vacuum is required.

To inspect the interfacial composition of the metallized PET films, several studies that revolve around the use of X-ray photoelectron spectroscopy (XPS) have been undertaken. In the first series of experiments, titanium-coated PET films, both plasma (N_2O/Ar) pretreated and nontreated, with a titanium thickness (determined by transmission electron microscopy) of approximately 800 Å, were first rapidly argon ion sputtered in the Auger spectrometer, immediately removed from the instrument, and placed into an XPS for analysis. Maximum raster size (10 mm^2) was used in order to produce a spot large enough for X-ray photoelectron analysis. The film was sputtered to within 50 Å of the titanium/polyester interface to minimize disturbance of the interphase region. XPS was then conducted on this surface at a 90° takeoff angle in order to minimize edge effects from the crater produced via the etching process.

Analysis of the titanium $2p_{3/2,1/2}$ photopeak region indicated that at least two distinct species were present at or near the interface (Figure 2). A peak assignable to carbidic titanium ($2p_{3/2}$) appeared at 454.7 eV in agreement with reported results.[12] A second peak ($2p_{3/2}$) attributable to TiO_2 appeared at 458.7 eV; however, the full width at half-maximum (fwhm) for this peak was significantly greater (2.1 eV) than that for a TiO_2 standard (1.4 eV). The Ti $2p_{1/2}$ photopeak from the carbidic titanium species could not wholly account for this broadening since its intensity would be even lower than that of the Ti $2p_{3/2}$ photopeak at 454.7 eV. A variety of oxytitanium species may therefore be present to account for the peak breadth.

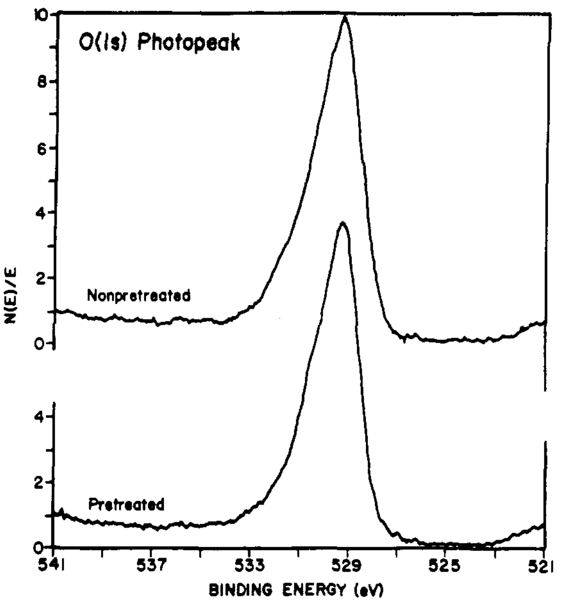

Figure 3. XPS O_{1s} spectrum of both plasma-pretreated and nontreated titanium-coated ICI-442 polyester film following argon ion etching as in Figure 2.

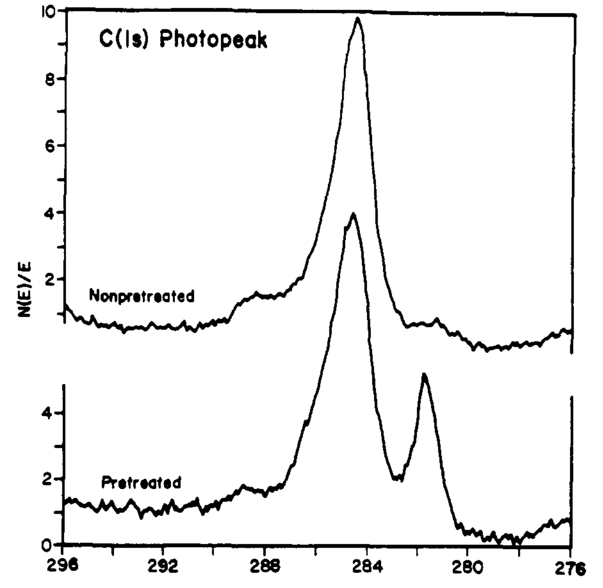

Figure 4. XPS C_{1s} spectrum of both plasma-pretreated and nontreated titanium coated ICI-442 polyester film following argon ion etching as in Figure 2.

Baba and Sasaki[13] have reported chemical reduction of a TiO_2 surface to both Ti^{2+} and Ti^{3+} upon He^+ ion bombardment. It has also been found that Ar^+ bombardment preferentially removes oxygen from a TiO_2 surface resulting in different oxide forms.[14] Alternatively, titanium alkoxide or carboxylate linkages to the polymer backbone may exist. For example [TiO(acac)] (acac = acetylacetonate) has a reported binding energy of 458.4 eV.[12] Species of this type are probable through reactions of titanium with the activated species produced in the polymer by plasma pretreatment. Neither the carbidic titanium photopeak nor the increase in fwhm (1.7 eV) observed for the TiO_2 was exhibited in the Ti_{2p} XPS of an etched metallized nonplasma treated PET film. Therefore, the appearance of carbidic titanium and/or

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additional oxy(hydroxy)titanium species must result from the effect of preliminary plasma treatment. The likelihood of differential charging was considered but ruled out.

Further elucidation of the titanium species at the interphase occurred when the O_{1s} and C_{1s} photopeaks were evaluated after argon ion etching (Figures 3 and 4). The largest peak present in the O_{1s} spectrum for both the nonpretreated and pretreated films has a corrected binding energy of 530.2 eV, indicating the presence of oxide oxygen, in agreement with Auger depth profiling. Less intense, but unresolved, photopeaks appeared at higher binding energies, and they could be considered due to either polyester oxygens or various nonstoichiometric oxide oxygen. In the C_{1s} XPS a peak assignable to carbidic carbon appeared at 281.6 eV in the pretreated film. This peak did not appear in the C_{1s} photoelectron spectrum of the etched nontreated metallized PET film. A weak signal at slightly higher binding energy was detected in both films indicative of the carbonyl carbons in the polyester substrate. In support of these assignments, Suzuki et al. have studied the effect of reactivity ion plating PET films with TiO_2.[15] TiC and carbidelike species were suggested to be in the interfacial region.

Another route used to obtain information about the interfacial region of metallized PET films was to study via XPS the fracture specimens obtained from peel tests. A manual peel procedure was used in order to produce freshly fractured samples that could be placed directly into the XPS. Samples were first prepared by application of a proprietary polymeric coating to the metallized surface of the polyester film so that the titanium layer could be peeled away. A cross-hatch over the metal layer was made with a razor blade. To this prepared fracture, Scotch tape was applied and pulled by hand to manually delaminate the film. Cohesive failure occurred within the polyester substrate for the plasma (N_2O/Ar) treated/metallized films. XPS analysis of either fracture surface provided C_{1s} and O_{1s} photopeaks identical with that of raw polyester film. No titanium signal was observed on either surface. On the other hand, nontreated/metallized polyester films exhibited mixed-mode failure. Significant concentrations of both oxide oxygen and polyester oxygen were present on the surface of both fracture surfaces. The Ti_{2p} photopeaks region also suggested that only TiO_2 was present on the fracture surface as opposed to carbidic titanium, in accord with that observed earlier following argon ion etching of nontreated metallize PET.

Information regarding the interfacial composition of metallized polyester films via XPS with either argon ion etching or fracture analysis was limited due to the inherent destructive nature of the test in the first case and the cohesive rather than adhesive failure encountered when plasma processing was applied in the second. A third method then was used to probe the interface. A graded titanium thickness on both nontreated and plasma (N_2O/Ar) pretreated polyester film was prepared. Graded thicknesses were produced by simply turning off the sputtering source power while the film was moving at a constant rate through the sputtering chamber. It was estimated by optical measurements that the thickest titanium deposit at one end of the 8 in. × 11 in. graded sample was nearly 150 Å.

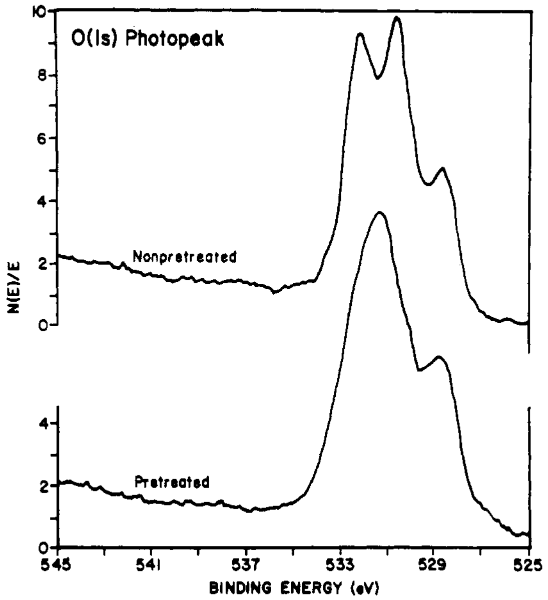

Figure 5. XPS O_{1s} spectrum (15° takeoff) of both plasma (N_2O/Ar) pretreated and nontreated ICI-442 polyester film sputter coated with a thin layer of titanium.

Selected sections from the length of the sheet were then analyzed by XPS at both 15° and 90° takeoff angles. Examination of the thickest deposit revealed a continuous coating of titanium dioxide on the polyester substrate. Significant concentrations of polyester were not detected until the upper third of the graded metallized sheet was reached. The detection of polyester oxygen and carbon photoelectron signals in this region of the sheet indicated that either the titanium coating was thin enough for the polyester photoelectrons to escape or that discontinuities were present in the titanium coating, thereby exposing polyester. The initial nucleation and growth of a sputtered titanium film is acknowledged to occur through the formation of islands of the deposited materials.[16] It, therefore, is most likely that discontinuities exist in the coating.

With the presence of a discontinuous titanium layer, observation of the interface was difficult. The "island" deposited metal was so thick that it interfered with XPS acquisition at a 15° takeoff angle. Under these data acquisition conditions, the C_{1s} photopeak spectrum was typical of solely PET. No carbidic carbon was observed. The O_{1s} photopeak spectrum at 15° takeoff angle exhibited a mixture of polyester oxygen and oxide oxygen probably arising from both the metallized and nonmetallized regions (Figure 5). Resolution of the two polyester oxygen types was considerably better in the metallized nonpretreated case. However, with improved depth resolution (90° takeoff angle) the interface was detected, albeit not strongly. For example, a slight amount of carbidic-type carbon was detected for the plasma-pretreated metallized substrate (Figure 6). The Ti_{2p} XPS spectrum, however, did not correspondingly exhibit a photopeak at 454.7 eV. Since the sensitivity of XPS toward carbon is greater than toward titanium, the small amount of carbide detected in the C_{1s} region would probably not be noticable in the corresponding carbide region of the Ti_{2p} spectrum. The observation of carbidic carbon in this experiment also gave credence to its presence following argon ion etching of fully metallized PET and was not an artifact of that process and also that it was indeed located in the interfacial region. The C_{1s} photopeak region of the nontreated titanium graded PET film did not display a carbide carbon signal. The O_{1s} photoelectron spectrum at 90°, for both treated and nontreated metallized PET, was consistant with that

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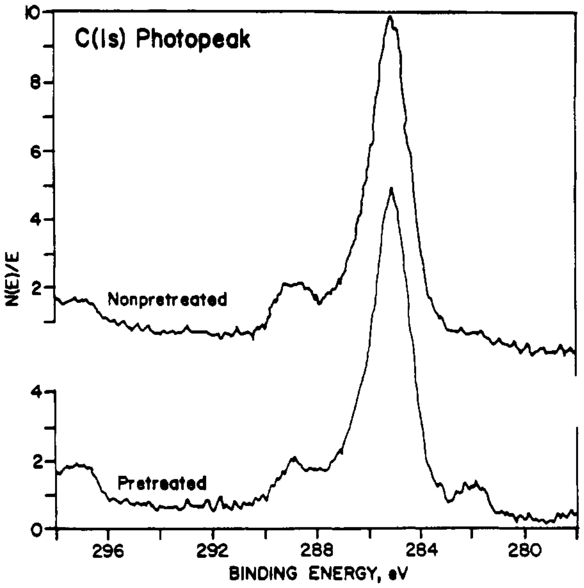

Figure 6. XPS CC_{1s} spectrum (90° takeoff) of both plasma (N_2O/Ar) pretreated and nontreated ICI-442 polyester film sputter coated with a thin layer of titanium.

Table I. Deposition Characteristics of Titanium-Coated Polyester Films[a]

sample	plasma exposure, s	metal thickness, Å AES	TEM	profilometry
ICI-442	28.0	610	1480	850
ICI-442	22.0	580	1160	750

[a] Obtained through Auger electron spectroscopy with ion milling.

observed at a 15° takeoff angle.

Transmission electron microscopy (TEM) was used to analyze the metallized polyester film structure. This particular technique, when the sample is prepared by ultramicrotomy, yields a micrograph of the cross section of the sample in which both the air interface and titanium–polyester interface as well as the bulk material can be examined. Micrographs of both nontreated and pretreated metallized samples exhibited continuous titanium deposits. The thickness of the titanium layer in both the nontreated and treated films obtained from TEM is given in Table I. It can be seen that TEM provides thickness significantly greater than those obtained by either profilometry or Auger depth profiling. TEM micrographs showed the titanium to be slightly embedded into the polyester substrate. Yet, profilometry would ignore any titanium located below the original plane of the uncoated polyester film. The resulting difference may then account for the low thickness values obtained by using profilometry. The deviation between TEM and Auger depth profiling data may have resulted from an error in the assumed sputter rate. It was originally assumed that titanium sputters at a rate similar to that of tantalum oxide, which is used as an instrumental standard. Normalization to the titanium thickness obtained from TEM yields an average sputter rate of approximately 103 Å/min (i.e., more than triple the rate assumed) for the titanium/titanium dioxide composition.

Table II. UV Spectral Characteristics of Gaseous Plasmas

gas	wavelength,[a] Å	photon energy, kcal/mol
argon	1048	273
nitrous oxide	1093	261

[a] Most intense resonance line.

Finally, whether 100% Ar, 100% N_2O, or a 50:50 mixture was used in the plasma pretreatment process, titanium adhesion is not affected. In fact, XPS analysis determined that each gaseous treatment produced the same surface functionality. This is an important result considering that N_2O is a reactive gas whereas Ar is inert. A possible explanation for this phenomenon is that excited gaseous species (metastables, ions, free radicals) play far less of a significant role in the observed surface chemistry. It has been reported[17] that the use of N_2O in plasma processing produced a highly functionalized surface incorporating substantial amounts of both nitrogen and oxygen. But in our study, although small amounts of nitrogen were added, surface oxygen is relatively constant. This may be in part due to the orientation of the sample during plasma processing. In many studies,[18-20] the sample is treated in the primary glow region, where the number of excited gas molecules is in highest concentration. Samples produced in our study, however, are in contact with the secondary glow discharge. In this region, the number of excited gaseous species as well as the averge energy per molecule is less, since the molecules or atoms undergo numerous collisions before arriving at the surface. Therefore, plasma species such as free electrons and photons, which are capable of interacting with surface atoms, may play a more important role. At this time we are, however, not able to confidently say the common impurity such as water in both gases is activated by the discharge.

Processes such as photoexcitation, photoionization, and photoradicalization are all known to occur by vacuum UV radiation, and they have also been confirmed to exist in glow discharges.[21-23] UV radiation is strongly absorbed by polymers producing polymer free radicals. The polymer free radicals are active sites that can then react with gas components or other polymer chains or relax to some stable form. The effects of UV exposure would also be deemed more selective than surface interaction with excited particles since the ester functionality alone would absorb radiation of these wavelengths, while direct energy transfer (particle interaction) would be nonselective in effect. It could account for the predominance of a single surface change (e.g., aldehyde functionality through Norrish type I cleavage) during plasma treatment as has been described in a previous report.[10]

Liston[24] has tabulated the vacuum-UV spectral characteristics as well as photon energies for rf plasmas excited in a number of gases, including argon and nitrous oxide. Table II provides a partial listing of these results. The predominant Ar and N_2O resonance lines appear at similar wavelengths and have comparable photon energies. In both cases, the energies are more than sufficient to disrupt organic bonds. The similar ultraviolet character of argon and nitrous oxide plasmas may account for their similarity in surface modification. If UV photolysis is responsible for the surface changes wrought by the plasma, indeed the chemical nature of the gas would not be of importance, in

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accord with the results of our experimental design.

In conclusion examination of the titanium/polyester interfacial region with Auger electron spectroscopy revealed that a titanium oxide existed between the sputtered titanium metal and polyester film. TiO_x formation most likely resulted from the interaction of the sputtered atoms with film off-gassing products such as water and oxygen. Further analysis by XPS indicated that a titanium carbide like moiety resides at the interface. However, it was not determined whether this species existed as discrete units or was acting to covalently couple the titanium to the polyester substrate. Titanium-polyester oxygen interaction was also suggested by an increase in the fwhm of the Ti_{2p} photopeak following plasma treatment and metallization, which may result in alkoxide or carboxylate linkages. Therefore, a chemical bond and not a mechanical effect must be responsible for the observed increase in adhesion relative to nontreated metallized poly(ethylene terephthalate) films.

Registry No. PET, 25038-59-9; Ti, 7440-32-6; Ar, 7440-37-1; N_2O, 10024-97-2.

Cadmium Substitution in $YBa_2Cu_3O_{7-\delta}$ and $Bi_2Sr_2CaCu_2O_{8+\delta}$

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The chemical interactions of CdO with $YBa_2Cu_3O_{7-\delta}$, $Bi_2Sr_2CaCu_2O_{8+\delta}$, and related oxides are examined. Mixtures of CdO with other oxides (Y-Ba-Cu-O, BaO_2, CuO, Y_2O_3, Bi-Sr-Ca-Cu-O, CeO_2, and CaO) were heated to 800-900 °C under N_2, O_2, air, and 1.5 GPa quasi-hydrostatic pressure. The reacted samples were characterized by powder X-ray diffractometry, thermogravimetric analysis, and dc resistivity and ac magnetic susceptibility measurements. CdO was found to be chemically inert under most of these conditions. When CaO is present, the cubic $CaCdO_2$ is formed. Cadmium(II) can be partially substituted for yttrium(III) (up to 30 mol %) in $YBa_2Cu_3O_{7-\delta}$ without detriment to superconducting properties. Although Cd^{2+} is aliovalent to Y^{3+}, charge compensation is achieved by the formation of additional oxygen vacancies, as evidenced by TGA measurements. This oxygen vacancy formation occurs rather than the expected change in hole concentration in the CuO chains and planes. Also, investigations of CdO substitution by other groups are reviewed.

Introduction

Cadmium(II) is a good candidate for inclusion in the superconducting ceramic compounds for several reasons. It is divalent, has an ionic radius[1] (1.09 Å) similar to those of Ca^{2+} (1.14 Å), Cu^{2+} (0.87 Å), and Y^{3+} (1.04 Å) and lies in the periodic table on a diagonal between copper and thallium. The presence of a filled 4d subshell in cadmium provokes comparison of cadmium compounds with analogous compounds formed by alkaline-earth metals. We have performed a broad search for cadmium-containing compounds related to the familiar high-temperature superconductors. In addition to reactions in air, nitrogen, and oxygen, some samples were heated under high pressure. Since cadmium ions are smaller than barium ions, reaction under high pressure might facilitate the substitution of cadmium for barium. To give a more complete description of the chemistry within these systems, we also summarize for the first time the results of several studies of cadmium substitution.

Table I. Batches, Processing Conditions, and Results for Cadmium Substitution Experiments[a]

batch	proc conds	products	T_c, K
CdO + BaO_2	air, hi-p, N_2	CdO, BaO_2 (BaO in N_2)	
CdO + CaO	air, hi-p	$CaCdO_2$	
CdO + CuO	air, hi-p	CdO, CuO	
CdO + CeO_2	air, hi-p, N_2	CdO, CeO_2	
2CdO + Y_2O_3	air, hi-p, N_2	CdO, Y_2O_3	
$YBa_2Cu_3O_{7-\delta}$	air, O_2, hi-p	$YBa_2Cu_3O_{7-\delta}$, $BaCuO_2$	92
$Y_{0.9}Cd_{0.1}Ba_2Cu_3O_{7-\delta}$	O_2	$Y_{0.9}Cd_{0.1}Ba_2Cu_3O_{7-\delta}$, $BaCuO_2$	92
$Y_{0.7}Cd_{0.3}Ba_2Cu_3O_{7-\delta}$	O_2	$Y_{\sim 0.8}Cd_{\sim 0.2}Ba_2Cu_3O_{7-\delta}$, $BaCuO_2$, CdO	92
$Y_{0.5}Cd_{0.5}Ba_2Cu_3O_{7-\delta}$	O_2	$Y_{\sim 0.7}Cd_{\sim 0.3}Ba_2Cu_3O_{7-\delta}$, $BaCuO_2$, CdO	90
$YBa_{2-y}Cd_yCu_3O_{7-\delta}$	air, hi-p	$Y_2Cu_2O_5$, CuO, CdO for all y; + $BaCuO_2$, Y_2BaCuO_5 for $y < 2.0$	
$Bi_2Sr_2CaCu_2O_{8+\delta}$	air	$Bi_2Sr_2CaCu_2O_{8+\delta}$, minor phases	80
$Bi_2Sr_2Ca_{0.5}Cd_{0.5}Cu_2O_{8+\delta}$	air	$CaCdO_2$, $Bi_2Sr_2CuO_6$, CaO, CuO, CdO, Bi_2O_3	
$Bi_2Sr_2CdCu_2O_{8+\delta}$	air	$Bi_2Sr_2CuO_6$, CdO, CuO, Bi_2O_3, SrO	

[a] The reaction conditions were: "air" = 850 °C, air, 8 h; "hi-p" = 850 °C, 1.4 GPa, 2.5 h; "N_2" = 900 °C, flowing N_2, 8 h; "O_2" = 900 °C, air, 24 h followed by 500 °C, O_2, 12 h. Products listed are those identified by X-ray diffraction. T_c values are onset temperatures for resistive transitions. Several batches in the $Bi_2Sr_2Ca_{1-z}Cd_zCu_2O_{8+\delta}$ system were made, with slightly different starting compositions but similar results.

Experimental Section

CdO powder was ground by mortar and pestle in equimolar ratios with CuO, Y_2O_3, CaO, CeO_2, and BaO_2. Stoichiometric amounts of CdO and other oxides were ground to form mixtures with the following nominal compositions: $Y_{1-x}Cd_xBa_2Cu_3O_{7-\delta}$, where x = 0.1, 0.3, 0.5; $YBa_{2-y}Cd_yCu_3O_{7-\delta}$, where y = 0.5, 1.0, 1.5, 2.0; $Bi_2Sr_2Ca_{1-z}Cd_zCu_2O_{8+\delta}$, where z = 0.5, 1.0. For comparison, undoped $YBa_2Cu_3O_{7-\delta}$ and $Bi_2Sr_2CaCu_2O_{8+\delta}$ were also prepared. The samples were heated in air, nitrogen, and oxygen and under ~1.5 GPa quasihydrostatic pressure to temperatures between 800 and 900 °C. The exact reaction conditions for each composition are given in Table I. For the samples reacted under high pressure, the following method was used: 2-3-g samples of these powders were packed into silver tubes 6 mm in diameter and ~30 mm

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[1] Ionic radii given are for 6-fold coordination, from: Shannon, R. D. *Acta Crystallogr.* 1976, *A32*, 751.

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