Electron spectroscopic investigation of polymers and glasses

Şefik Süzer

Department of Chemistry, Bilkent University,
06533 Bilkent, Ankara, Turkey.

Abstract: X-ray induced photo and Auger electron spectroscopic techniques have been applied to investigate conducting polymers, their blends and some glasses. In the N1s region of the spectra of films containing polypyrrole the peak corresponding to N^+ at 402.0 eV is separated from the neutral N. Intensity of the N^+ peak can be correlated with electrical conductivity of the films and the spectroscopically derived ratio of F/N^+ is close to 4 indicating that one BF_4^- dopant ion is incorporated for every oxidized nitrogen center. In the spectra of the films of polythiophene and its blends peaks corresponding to S and S^+ can not be resolved, but again F/C ratio correlates with the electrical conductivity. On the basis of measured XPS chemical shifts in the binding energies the chemical state of Sn (+2 or +4) incorporated on to the float glasses could not be assigned. Use of the Auger parameter lets one separate relaxation and chemical contributions. The derived true chemical shifts of Sn on float-glasses are larger than those of SnO and/or SnO_2 due to the larger ionic environment of the glass matrix.

INTRODUCTION

Over the last three decades electron spectroscopic techniques (both X-Ray Photoelectron Spectroscopy, XPS, and Auger Electron Spectroscopy, AES) have become one of the most important tools of chemist for any type of material characterization. Their surface sensitivity, applicability to any element (except for hydrogen), and capability to distinguish between various valence states through the chemical shifts are the most important assets of these techniques. Application of the electron spectroscopic techniques to electrically conducting polymeric materials in their unblended forms have been extensively reported [1-3]. Preparation of electroactive polymers with improved chemical and/or mechanical properties is still a scientifically and technologically important issue. Blending is one of the ways to achieve this goal. Blends of polypyrrole and polythiophene with polyamide has proved to be quite successful for some applications [4-6]. We have already reported an x-ray photoelectron spectroscopic investigation of polypyrrole and its blends with polyamide [7]. We have extended this study to polthiophene and its blends with polyamide.

Coating of Sn and its oxides have technological importance in applications like float-glass production, solar energy cells, protective and conductive coatings etc.. For many applications quantitative data of Sn, like surface coverage or depth profiling, are important parameters sought after. In some applications, however, further information like oxidation state, coordination number etc. are needed. XPS and/or AES studies attempting to distinguish between the two oxides of tin, SnO and SnO_2, have found either absence or only a small difference in the core

level binding energies [8-11]. In a different investigation it was demonstrated that although the core level shifts were not significant, XPS of the valence band region could unambiguously distinguish between the two oxides [12]. Another parameter which can de derived from the x-ray induced electron spectra is the Auger parameter, introduced by Wagner [13] and further developed by others [14,15], can be very informative. In a recent study [16], we have reported the Auger parameters of the tin metal, tin oxides and chlorides. Here, we report our study to float glasses with different thickness and a tin oxide coated conducting glass. Tin is incorporated on to both surfaces of glasses produced by the float technique (float glasses). Incorporation of tin on to the tin-bath surface of the glass is through contact with liquid tin and is homogeneous while in the atmospheric surface it is known to be through precipitation of tin vapors and in forms of islands

EXPERIMENTAL

The electron spectrometer is a KRATOS ES300 with AlKα source. Quantitative data from the XPS data is obtained using the standard procedures [17].

Conducting polymer blend films were prepared by electrochemical polymerization of pyrrole or thiophene onto a polyamide dipcoated electrode at a constant predetermined potential. Electrochemical deposition of polypyrrole was carried out in a three compartment cell equipped with Pt foils (1.0 cm^2 each) as working electrode (at +1.1V) and counter electrodes. A capillary (Ag/Ag+) was used as reference electrode and the solvent/electrolyte couple was acetonitrile/tetrabutylammonium tetrafluoroborate. For polythiophene working electrode was operated at +2.0V. Electrochemical reduction was achieved by reversing the polarity and discharging the prepared films. X-ray photoelectron spectra of the various films were recorded after thorough washing with the solvent and drying the films while intact on their platinum electrodes.

Float glasses with thicknesses of 3, 4, 5, 6 and 10 mm were provided by the local producer (Türkiye Şişe-Cam A.Ş.) while the conducting tin oxide glass was a commercial tin oxide glass. Surface of the samples of appropriate size were wiped by a clean tissue paper before introduction into the spectrometer. Pressure in the analyzer chamber is kept below $5x10^{-9}$ torr during analysis. Depth profiling was carried out using either (i) in-situ Ar^+ etching with 1keV ions or (ii) prior to introduction to the spectrometer with 2% HF solution.

RESULTS AND DISCUSSION

Conducting Polymers

Fig. 1 displays parts of the photoelectron spectra of polypyrrole-only (PPy), polyamide/polypyrrole (PA/PPY), polythiophene (PTh) and polyamide/polythiophene blends in their conducting forms and after electrochemical reduction. (PA/PTh). Spectra of polyamide after electrochemical oxidation (PA(oxidized)) and further reduction (PA(ox.+red.)) are also included to ensure that electrochemical treatment does not introduce additional features. The strong features are due to F1s, O1s, N1s and C1s and S2s and 2p. Since our x-ray source is not monochromatized the F1s, C1s, S2s and S2p peaks are observed as single peaks at around 686, 285, 228 and 164 eV respectively. The O1s peak around 532 is broad and can be deconvoluted into 2 or 3 components. The N1s peak in films containing polpyrrole has two components at 399.7 and 402.0 eV which can be assigned to the neutral (-N-) and the quaternized nitrogens ($-N^{+-}$) respectively. The relevant data are collected in Table 1. Examination of Figure 1 reveals that no additional features are introduced during electrochemical oxidation and/or reduction of the polyamide-only film. The N/C ratio determined from our result is not far from the stoichiometric ratio given by the supplier (0.05). Intensity of the

extra peak observed at the high binding energy side, assigned to N^+ moieties, correlates with electrical conductivity of the films. The atomic ratio of F to N^+ derived from our XPS data is close to 4 for these films, indicating that one BF_4^- dopant ion is introduced for every N^+ center. Both the N^+ and the F1s intensities decrease considerably after electrochemical reduction.
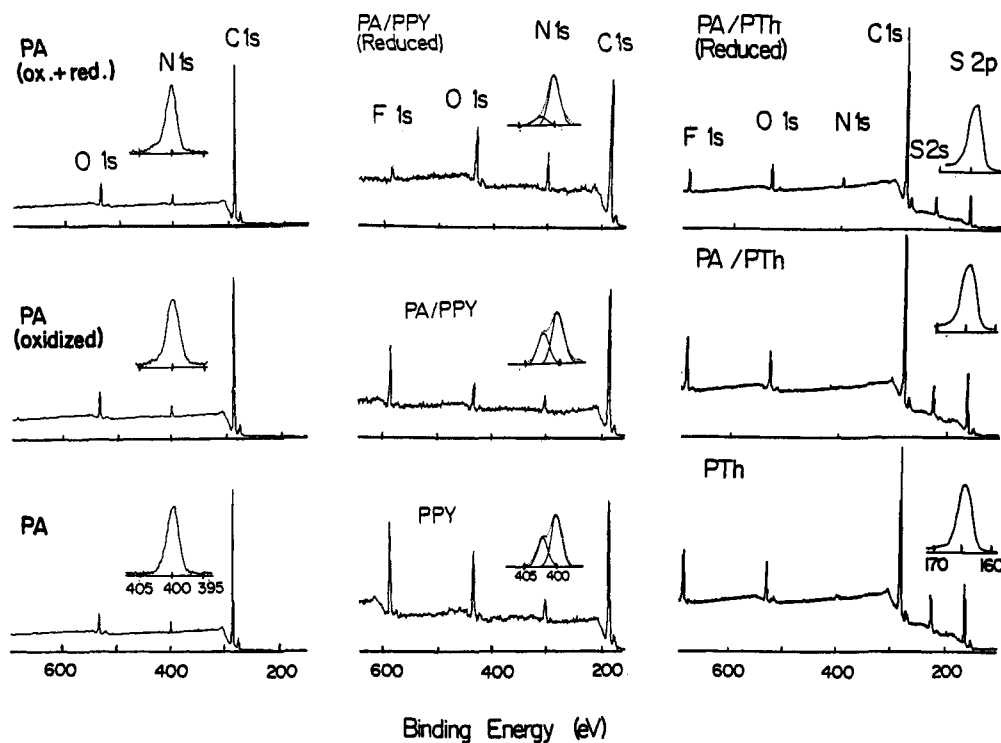

Fig.1. AlKα induced electron spectra of electrochemically prepared polypyrrole and polythiophene blended with polyamide. Spectra of the films after electrochemical oxidation and/or reduction are also included. Expanded N1s and S2p levels are also shown.

In the case of films of polythiophene, polyamide/polythiphene as prepared and after electrochemical reduction, our resolution does not permit to distinguish between the neutral S and its oxidized form S^+. Information about electrical conductivities of the films can still be derived from the atomic ratios of F/C. Again the F/C ratio in films of polythiophene and its blend with polyamide are very close to each other and this ratio is smaller in the less conducting electrochemically reduced blend.

Sn Coatings on Glasses

Fig. 2 displays electron spectra (induced by AlKα x-rays) of a 3mm float glass (bottom) and the tin oxide coated glass (top). Photoelectron lines corresponding to O1s, C1s, Si 2s and 2p, Ca 2s and 2p, Sn 4d, 3d and 3p lines as well as O, Na and Mg KLL and Sn MNN (shown in the left side of the figure) Auger lines are the prominent features. Na KLL Auger and Sn $3d_{3/2}$ lines overlap but can easily be separated by deconvolution. Intensity of Sn lines vary depending on the surface examined (i.e. tin-bath or atmospheric), the thickness of the glass and naturally the etching time. The relevant data are collected in Table 2. The table also contains data on SnO, SnO_2 as well as the tin-oxide conducting glass.

TABLE 1. XPS data of electrochemically prepared polypyrrole and polythiophene together with their blends with polyamide.

	C1s	N1s -N- -N⁺-	O1s	F1s	S2p	F/N⁺	F/C	Cond. (S/cm)
		Binding Energy(eV) (Atomic Percentage)				**At. Ratio**		
PA	285.0 (91)	399.8(3) -	532.4 (6)	-	-	-	-	-
PPy	285.0 (65)	399.7(5) 402.0(3)	532.3 (14)	686.3(13)	-	4.4	-	2
PA/PPY	285.0 (74)	399.7(5) 401.8(3)	532.3 (7)	686.3(11)	-	3.6	-	2
PA/PPY (Red)	285.0 (71)	399.7(10)401.8(1)	532.3 (15)	686.3 (3)	-	2.2	-	0.004
PTh	285.0 (68)	400.5 (2)	532.8 (10)	686.5 (7)	164.5 (14)	-	0.10	4
PA/PTh	285.0 (69)	400.6 (1)	532.9 (9)	686.7 (7)	164.6 (14)	-	0.10	3
PA/PTh (Red)	285.0 (74)	400.8 (3)	532.8 (9)	686.8 (4)	164.7 (10)	-	0.05	0.008

The measured binding energies of SnO, SnO_2 and Sn on glasses are very close to each other. On the basis of the raw binding energies of Sn one can not, unambiguously, decide on the chemical state of Sn. The measured binding energies contain contributions from relaxation effects besides the chemical ones. At this point we must refer to the Auger parameter or the true chemical shift. As can be seen from the insert of Fig. 2, the Sn MNN Auger peaks of SnO_2 and SnO exhibit a much larger (close to 1 eV) chemical shift. We can analyze the chemical shifts in binding energies, ΔE_{ch}, using Wagner's approach of identifying compounds on the basis of their Auger parameters:

$$\alpha = E_b + E_k$$

Where E_b is the binding energy of the photoelectron and E_k is the kinetic energy of the Auger electron emitted as a result of Auger process involving the same electron level. The Auger parameter exhibits a much larger shift in various Sn coatings and depends linearly on Sn/Si ratio (as plotted in the right hand side of Fig. 2). The shift in E_b can be regarded as the sum of (i) the chemical shift, ΔE_{ch}, which depends on the effective charge of the atom, (ii) the relaxation energy. The latter consists of two components, intra and extra atomic relaxations, E_{ir} and E_{er} determined by the interaction of other electrons within the same atom or the neighboring ones. One can roughly describe them as gas phase (intra-atomic) and solid-state (extra-atomic) contributions. Regarding E_{ir} constant one obtains the binding energy shift with respect to zero-valent bulk material (Sn metal): $\Delta E_b = \Delta E_{ch} + \Delta E_{er}$

TABLE 2. XPS/XAES Data of some float glasses, the tin oxide conducting glass together with some reference compounds (Referenced to Si2p=103.2 eV). [a]Referenced to C1s=285.0 eV

	BE (eV) Sn3d$_{5/2}$	KE(eV) Sn$_{MNN}$	α_{Sn} (eV)	ΔE_{er} (eV)	ΔE_{ch} (eV)	Atomic Ratio Sn/Si	O/Si
3mm	488.2	430.4	918.7	-1.8	0.8	0.283	4.12
3mm(surf.)	487.7	430.6	918.3	-2.0	0.1	0.026	3.12
4mm	488.1	430.7	918.8	-1.8	0.7	0.235	3.12
5mm	488.0	430.5	918.5	-1.9	0.5	0.193	4.68
6mm	488.1	430.2	918.3	-2.0	0.5	0.164	3.93
10mm	488.1	430.5	918.6	-1.8	0.7	0.222	3.22
Cond. Glass[a]	487.6	431.9	919.5	-1.4	0.6	-	2.58
Sn[a]	485.6	436.7	922.3	-	-	-	-
SnO[a]	487.1	432.5	919.6	-1.3	0.2	-	0.98
SnO_2[a]	487.5	431.7	919.1	-1.6	0.3	-	1.66

As can be seen from the table the chemical shift computed using this procedure is 0.15 eV for SnO and 0.35 eV for SnO_2. For Sn coated on glasses, however, the derived shifts vary between 0.5 and 0.8 and are larger than that of SnO_2. This can be rationalized if one considers that Sn atoms in the glass matrix are in stronger ionic environment compared to the oxides.

Contributions to the chemical and relaxation terms of the Auger electrons could be expressed as follows : $\Delta E_k = -\Delta E_{ch} + 3\Delta E_{er}$, $\Delta\alpha = -\Delta E_b + \Delta E_k$, $\Delta\alpha = 2\Delta E_{er}$

This procedure lets one separate chemical (the true chemical shift) and relaxation contributions from the measured binding energies and Auger parameters.
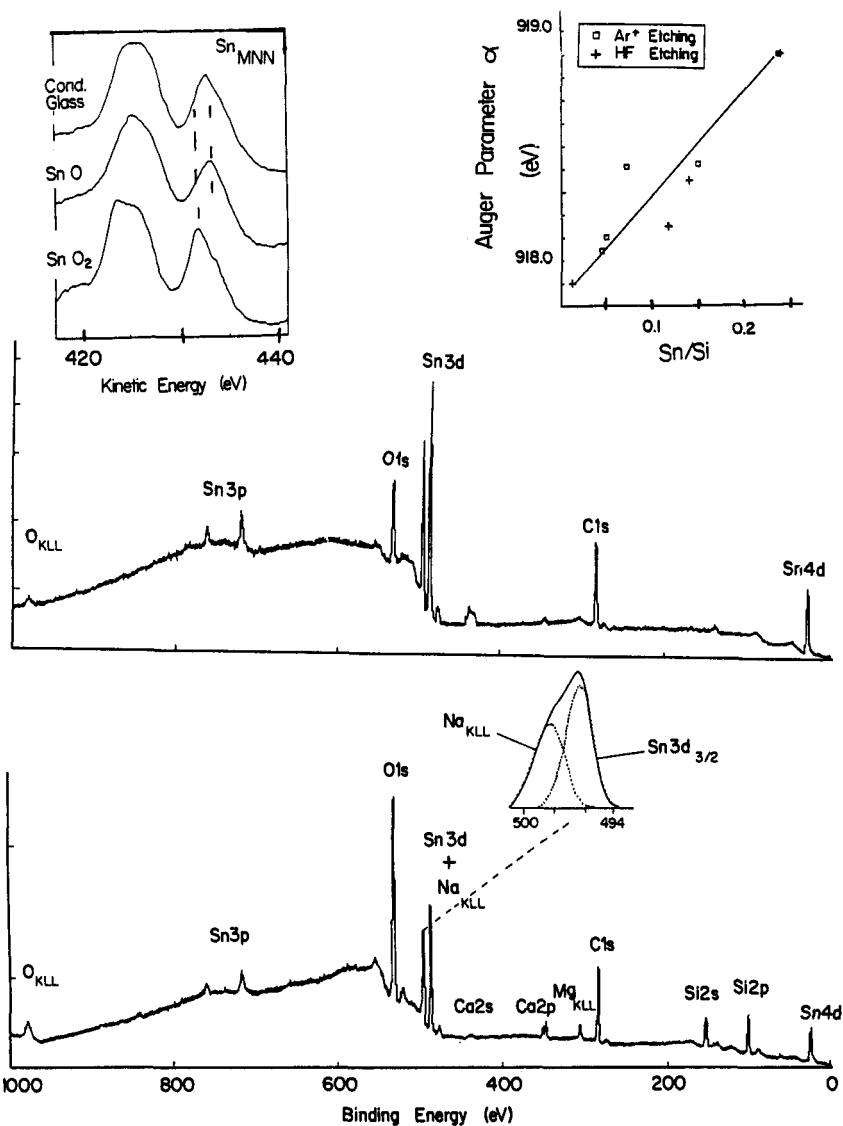

Fig.2. AlKα x-ray induced electron spectra of 3mm float glass (bottom), the tin oxide coated conducting glass (middle). Th Sn MNN Auger pekas of SnO, SnO2 and the conducting glass are shown as an insert in the left hand-side and change of the Auger parameter as a function of Sn/Si ratio in various float-glasses are shown on the right hand-side.

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