Korea Polymer Journal, Vol. 2, No. 1, pp 66-70 (1994)

Biased Referencing for the XPS Analysis of Polymers

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Received March 16, 1994

ABSTRACT: Biased referencing, which involves the combination of gold decoration and electron charge neutralization by an electron flood gun, was investigated for the XPS analysis of nonconducting polymers. Biased referencing provided calibration of sample core level ionizations to the Fermi level of Au $4f_{7/2}$ set at a conductive value of 84.0 eV. Reproducible high resolution spectra of various polymers were obtained and the measured binding energies were compared with the literature values.

Introduction

X-ray photoelectron spectroscopy (XPS) or ESCA (Electron Spectroscopy for Chemical Applications) accurately measures the core level electron binding energies of the atoms in the species. Thus it can provide chemical information concerning the surface and immediate subsurface of solid samples.[1] When the surface is typical of the bulk, XPS also provides information pertaining to the bulk. However, XPS has met with limited success when applied to nonconducting materials mainly due to the charging problem.[2] The bombardment of a nonconducting materials with x-rays can cause charging of the specimen which alters the kinetic energies of the ejected photoelectrons, thereby causing arbitrary shifts in the measured binding energies of the photoemission peaks. When the standard polychromatic sources are used, the charging shifts are often in the 1 to 10 eV range. Differential charging at the surfaces of the nonconducting materials can also occur and it obscures the details of the peak shape by broadening the peak significantly.

A number of methods have been used to address the charging problem of nonconducting materials. One of the earlier methods was to use adventitious carbon as an energy reference.[3] Here, the observed spectra are adjusted so that the C 1s peak, that is present due to the hydrocarbon contamination, is assumed to be at 284.8 eV. This technique has been quite successful for much of the XPS analyses on insulators. However, since it is based on the assumption that all contaminating carbon is of the same species, errors will be introduced if this criterion fails. Moreover, it becomes increasingly complicated to analyze the spectra of the insulating samples containing various types of carbons, such as polymers. Other methods may be used to utilize some type of internal standard to which measurements can be referenced. These include deposition of gold,[4] and the use of charge independent Auger parameters, which was developed by Wagner and his coworkers.[5] The results, however, can be ambiguous in many instances.[6] In addition to the use of internal standards, there has been an attempt to minimize the influence of charging. Huchital and McKeon[7] used low energy electron flood guns to compensate for charge build-up on the specimen. However, Barn[8] indicated that the use of an electron flood gun is not sufficient for attaining the accurate information on chemical states of the specimen.

In 1976, Stevenson and Binkowski[9] introduced a potentially very useful method for the XPS analysis of insulators now called biased referencing. For this method a gold dot is applied to an insulating specimen which is then flooded with electrons at a potential of a few eV. Biased referencing technique was successfully applied to the studies on glasses by Tasker,[10] on mineral standards of biological

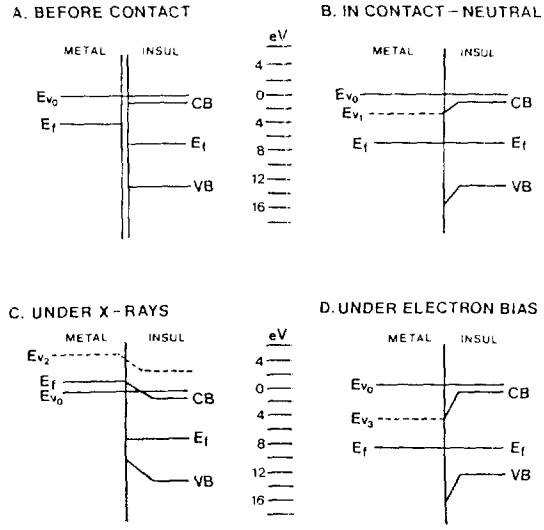

Figure 1. Schematic band structures for the metal (Au)-insulator system (after Ref. 11). Ev_1 represents the contact potential, Ev_2 and Ev_3 represent induced surface potentials. The original vacumm level Ev_0 is assumed to be constant at a position above the surface. E_f represents the respective Fermi levels.

interest by Landis and Martin,[11] and on sapphire and yttrium aluminum garnet crystals by Mullins and Averbach.[12] Edgell and coworkers[13] applied the biased referencing for the XPS analysis of silica and zeolite with various arrangements of metal dots and reported that this method allowed highly reproducible binding energy measurements.

Biased Referencing

When a conducting sample is in electrical contact with the spectrometer, electrical conductivity between the sample and the spectrometer prevents surface charge from building up during photoionization. Referencing may then be accomplished by adjusting the spectrometer work function so that an appropriate peak of a chosen reference standard appears at some established value.[14] For nonconducting sample such as polymers, there is no efficient conducting path from the spectrometer to the insulating sample surface. It precludes any possible equalization of the Fermi levels of the sample surface and the spectrometer during the analysis because there is a build-up of surface potential under x radiation.

In order to eliminate the binding energy shifts due to surface charge and to return the binding energy reference to the Fermi level of the conducting standard, the sample is decorated with a gold dot.[9] Figure 1A shows the band structure of the insulator-metal (gold) system shortly before there is any contact. As the gold is evaporated onto the insulator surface, equalization of the Fermi levels may occur (Figure 1B).[15] Under x radiation (Figure 1C) there will be previously described surface build-up which may reach a steady state value of a few eV.[15] Since the photoelectron cross sections, mean free paths and other fators are different for the gold and for the insulator, a potential difference will result on the sample surface in the neighborhood of the gold marker. Ev_2 indicates the x-ray induced positive potential on the insulator surface and this double potential is denoted by the dotted lines in Figure 1C. It should be noted that Ev_2 is larger in the region below the gold dot. Under the conditions where the lateral surface charge variation occurs, the use of the gold as a reference would be inapplicable since there will be a nonlinear shifting of peaks.[16] According to Stephenson and Binkowski[9] a flux of low energy electrons from a standard neutralizing filament with a high negative bias needs to be introduced to compensate for such surface charge differential and to equalize the Fermi levels. Now, Figure 1D shows that a uniform negative surface charge is established on the sample surface, so that the surface potential may be treated as an apparent, applied work function. Under these bias conditions it is difficult to know the exact bias potential on the insulator surface.[17] What has been used instead is a more appropriate method of determining the exact binding energy of the Au $4f_{7/2}$ peak from the gold marker under bias conditions and calculating a shift factor between the Au $4f_{7/2}$ peak under bias and its conducting value of 84.0 eV. This shift factor is then applied to sample peaks taken under the same bias conditions.[9]

This paper reports the high resolution XPS spectra of various polymers, which were obtained by utilizing the biased referencing technique.

Materials and Methods

Sample Preparation. Low-density polyethylene (LDPE), high-density polyethylene (HDPE), poly(methyl methacrylate) (PMMA), poly(vinylidene fluoride) (PVDF), and polytetrafluoroethylene (PTFE) were analyzed by XPS. They were purchased in powder form from Scientific Polymer Prod-

ucts and used as obtained. With the exception of PTFE, polymers were dissolved in proper solvents and uniform films were cast and vacuum dried for several days. The thickness of the films was 70± 5 μm. PTFE was hot pressed to produce films 0.5 mm thick. Each film was covered by a 15×20 mm stainless steel mask having a circular 2 mm diameter cutout. Then a 2 mm gold dot was vapor-deposited onto each film as a charge-referencing marker by conventional vacuum deposition.

Analytical Procedure. Gold-decorated polymer samples were examined in a Vacuum Science multitechnique ESCA/AES/SIMS surface analysis system with a polychromatic Al Kα x-rays (10 KV source potential, 25 mA emission current) as the excitation source. High resolution spectra were scanned with a pass energy of 22 eV. A low energy flood gun (Vacuum Generator, model LEG-41) was installed facing the x-ray gun with an emission current of 0.3 mA. The spectrometer was maintained at high vacuum ($2\times10^{-9}\sim6\times10^{-8}$ Torr) and was energy-calibrated with respect to the Au $4f_{7/2}$ at 84.0 eV.[14] Spectra were taken at a constant take-off angle of 83°. When the sample was positioned properly, a survey scan was taken to determine the gross composition. The bias voltage was then applied and the precalibration data were collected by taking high resolution scan of Au $4f_{7/2}$ of the gold marker. After the sample was moved a few mm away from the gold so that the analysis region did not encompass the gold dot, high resolution multiplex scans of the sample surface of the elemental region observed in initial surveys were generated. Finally, another scan of the Au $4f_{7/2}$ (postcalibration) of the gold dot was taken by realigning the sample. An extreme care was taken to make certain that the alignment of the analysis region could be duplicated as closely as possible. Charge correction was accomplished by computing a shift factor for each sample and shifting the raw data. The shift factor was calculated by averaging the binding energies of the precalibration and the postcalibration of the gold reference and subtracting this average from the Au $4f_{7/2}$ standard binding energy, 84.0 eV.

Results and Discussion

Overall composition of each of the polymer samples was confirmed by taking the survey scans before applying the bias voltage. Negligible amount of oxygen was detected only on the surface of LDPE specimen due to the oxidation. Detailed analysis of the oxygen peak was not attempted.

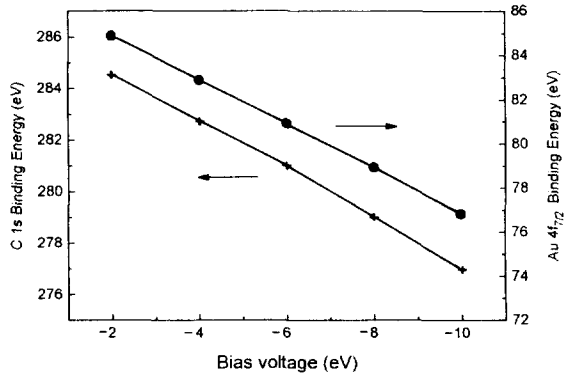

Figure 2. Corrected binding energies of the core level peaks as a function of flood gun bias voltage.

We first investigated the effect of the magnitude of the bias voltage on the change in the surface potential developed on the HDPE surface. Emission current of the electron flood gun was kept constant at 0.3 mA. High resolution multiplex scans for the Au $4f_{7/2}$ and the C 1s of the gold-decorated HDPE sample were obtained. Figure 2 plots the measured binding energies of the C 1s and the Au $4f_{7/2}$ peaks as a function of the bias voltage of the electron flood gun. The binding energies of both the C 1s and the Au $4f_{7/2}$ peaks decreased almost linearly with the bias voltage and the slopes were almost identical. This indicates that the surface potential of the gold dot and the polymer was changed by the applied bias voltage and that a relatively uniform surface potential was generated by the electron flood gun. Therefore, we assumed that the electron flood gun of our system was working properly.[11,13,17] However, it should be noted that in Figure 2 the magnitude of the change in the negative surface potential formed on the sample surface as a result of the biasing was not same as the magnitude of the applied bias voltage. Table I summarizes the measured full width at half maximum (FWHM) of the C 1s and the Au $4f_{7/2}$ peaks and the binding energies of the C 1s peak of HDPE corrected by the procedure described earlier. The charge-corrected binding energies of the C 1s peak of HDPE were almost constant when the negative bias voltage was higher than 6 eV. Lower bias voltages produced inconsistent results. This agrees well with what was reported in the literature[13] that under the low bias voltages the flood gun energy was not adequate to provide a uniform surface potential on the sample surface. In fact, Stephenson and Bin-

Table I. The Effect of Bias Voltage for HDPE

	Flood-gun bias voltage (eV)					
	0	−2	−4	−6	−8	−10
FWHM of Au $4f_{7/2}$ (eV)	1.20	1.21	1.21	1.20	1.20	1.18
FWHM of C 1s (eV)	1.58	1.56	1.78	1.96	2.23	2.35
C 1s corrected (eV)	282.4	283.6	283.8	284.2	284.1	284.2

Table II. Summary of Corrected Binding Energies

Sample	C 1s (eV)	O 1s (eV)	F 1s (eV)	Δ C 1s[a] (eV)
HDPE	284.2	−	−	0
LDPE	284.3	−	−	0.1
PVDF	$-CH_2-$ 285.6	−	688.2	1.4
	$-CF_2-$ 209.1			5.9
PTFE	292.1	−	689.4	7.9
PMMA	$-\underset{\diagdown}{\overset{}{C}}-C-$ 284.2	$=C=O$ 531.1		0
	$-\underset{\diagup}{\overset{}{C}}-O-$ 285.8	$-\underset{\diagup}{\overset{}{C}}-O-$ 532.6	−	1.6
	$=C=O$ 288.0			3.8

[a]In reference to the C 1s binding energy of HDPE.

kowski[9] suggested that a flux of low energy electrons should be introduced onto the sample surface by way of a standard neutralizing filament with a high negative bias of about −10 eV. While the full width at half maximum of the Au $4f_{7/2}$ peak was nearly constant, that of the C 1s peak slightly decreased initially and then increased as the bias voltage increased. There are conflicting reports in the literature on the effect of the bias voltage on the FWHM of the core level peaks.[9] Since the optimum value of the bias voltage for accurate charge compensation is dependent on many parameters including the geometry of the sample and the spectrometer, and the nature of the sample, we decided to operate the flood gun at −6 eV bias voltage. In Table I it is worth noting that when measured by using the gold as the internal standard and without the use of the flood gun, the binding energy of the C 1s peak of HDPE was quite inaccurate in comparison with the literature values.[18] Under the same condition (with flood gun off) core level binding energies of LDPE, PTFE, PVDF and PMMA were not in agreement with the literature values.[19]

Table II shows the corrected binding energies of core level peaks for the polymers studied by the biased referencing method with a bias voltage of −6 eV. The C 1s binding energy of HDPE and LDPE was 284.2 eV and 284.3 eV, respectively. These values are slightly lower than those reported for aliphatic carbons in polymers (284.6~285.0 eV).[20] However, the literature values were obtained by utilizing a high focusing monochromatic x-ray source. Although LDPE and HDPE have different degrees of branching, no significant difference in the C 1s binding energy was observed. Clark and coworkers[21] also obtained the same C 1s binding energies for both LDPE and HDPE. In poly(methyl methacrylate) there are three different types of carbons, namely from carbonyl linkage, ether linkage and from backbone carbon-carbon linkage. Also, there are ether and carbonyl oxygens in PMMA. The binding energies of the C 1s and the O 1s peaks of PMMA are tabulated in Table II.

When the XPS was initially applied to the characterization of polymers, fluoropolymer systems were studied extensively. They are among the most technologically important systems of interest and are often difficult to study by other spectroscopic techniques. More importantly they showed the large chemical shift in the core level peaks induced by the fluorine atoms. We analyzed the gold-decorated poly(vinylidene fluoride) by the biased referencing method. High resolution C 1s spectrum was deconvoluted into two distinct peaks at 285.6 eV and at 290.1 eV, corresponding to the carbons of $-CH_2-$ and $-CF_2-$ linkage, respectively (Figure 3). These values are slightly lower than the values obtained by Clark.[22] The binding energy of the F 1s peak was determined to be 688.2 eV. Briggs[1] studied the

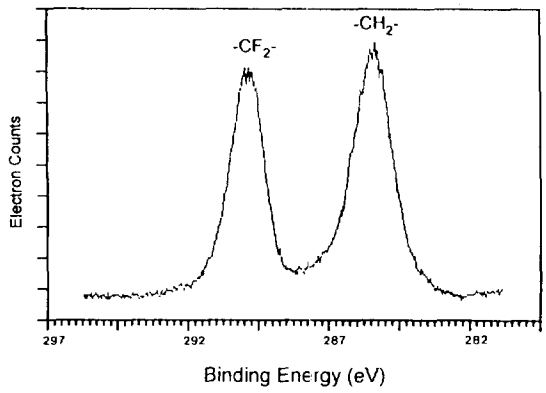

Figure 3. Corrected C 1s core level spectrum of poly(vinylidene fluoride).

effect of the fluorine substitution on the chemical shifts of the C 1s peak in polymer. He found that the primary shift of the C 1s peak (which is directly bonded to the fluorine atom) was about 2.9 eV and the secondary shift was about 0.7 eV with respect to the binding energy of the C 1s peak of C−C bonds or C−H bonds. The results of the charge correction for our PVDF sample were in good agreement with the reported findings. However, during the analysis the intensities of the core level peaks were drastically reduced, indicating that the surface of PVDF was degrading as a result of the x radiation. The degradation of the PVDF surface by the x radiation has been documented in the literature.[1] In general, the positive surface charge of the fluorine containing polymers is known to be relatively large, since the photoionization cross section of fluorine is greater than other atoms.[18] We analyzed the surface of polytetrafluoroethylene and found that a positive charge of about 8.4 eV was formed on the surface. The corrected binding energies of the C 1s and the F 1s peaks were 292.1 eV and 689.4 eV, respectively.

Summary

Charge correction for nonconducting polymers was studied by utilizing the biased referencing method. Reproducible binding energies of the core level photoemission peaks of interest were obtained under a bias voltage of −6 eV. Measured binding energies in general agreed reasonably well with the literature values. It is suggested that biased referencing would provide a means to effectively correct charging problem in XPS analysis of polymers.

Acknowledgment. I. Chin and D. S. Kim appreciate the financial support of Inha University (June 1992~May 1993). Helpful discussions with Dr. Young Man Kim at Korea Institute of Science and Technology is greatly acknowledged.

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