ULTRA-SOFT X-RAY ABSORPTION SPECTROSCOPY: A BULK AND SURFACE PROBE OF MATERIALS

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ABSTRACT

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Direct comparisons between the surface and bulk of diverse materials can be made by simultaneous electron yield (5 nm depth sensitivity) and fluorescence yield (200 nm) ultra soft x-ray absorption spectroscopy measurements utilizing a rapid sample interchange apparatus. For example the orientations of functional groups have been characterized at and near the surface of a series of model polymeric materials highlighting the chemical and molecular sensitivity of ultra soft x-ray absorption spectroscopy. In addition we discuss a bulk sensitive use of fluorescence yield to non destructively study a buried metal polymer interface. A second bulk sensitive example is the use of fluorescence yield oxygen K near edge x-ray spectroscopy as a method to determine the hole state density of high Tc materials.

INTRODUCTION

Ultra soft x-ray absorption spectroscopy (USXAS) is an important extension of a traditionally hard x-ray technique for structural determination of low Z elements (C,N,O,F) in materials. Until recently USXAS studies have been accomplished solely by electron yield methods which usually must be done under ultra high vacuum conditions [1]. Although the fluorescence yield for low Z elements is very small (e.g. .0012 for carbon) the technical challenge of the technique opens an opportunity for the development of an *in situ* photon-in photon-out structural probe. The technique is particularly useful in surface chemistry applications for *in situ* monitoring (kinetics) of transient surface species under real reaction conditions of temperature and pressure [2,3,4,5]. We have developed an ultra high vacuum compatible system for measuring low Z fluorescence USXAS over a broad pressure range; 10⁻¹⁰ mbar to several atmospheres [6]. Such a system allows the USXAS technique to address a range of materials problems from monolayers to bulk materials (including insulators such as polymers and diamond) even in the presence of a reactive gas atmosphere. Direct comparisons between the surface and bulk of diverse materials can be made by simultaneous electron yield (50 nm depth sensitivity) and fluorescence yield (200 nm) measurements utilizing a rapid sample interchange apparatus [6]. For example the orientation of phenyl rings in spin coated polystyrene has been characterized at and near the surface for a series of molecular weights (MW) and casting solvents highlighting the chemical and molecular sensitivity of USAXS [7]. The bulk sensitivity of fluorescence yield has been utilized to study a buried metal polymer interface, highlighting the use of USXAS to provide new detailed chemical information which will be useful in predicting and optimizing the adhesion in metal / polymer interfaces. A second bulk-sensitive example is the use of fluorescence-yield oxygen K near edge x-ray spectroscopy as a method to determine the hole state density of high Tc materials. A pre-edge peak occurs just above the Fermi level which can be assigned to holes in the oxygen 2p band. The intensity of this peak was determined as a function of composition in high Tc materials [8,9].

POLYMERS

I. Polystyrene: Surface Versus Bulk

The experiments described were performed on the U1 beam line at the National Synchrotron Light Source, Brookhaven National Laboratory. The estimated total photon flux was about 1x10¹⁰ per second at 300 eV photon energy with a resolution of 0.6 eV. Typical storage ring currents were in the 400 - 600 mA range during these experiments. The ultra soft x-ray absorption spectra were collected with a rapid sample interchange system equipped with

facilities for simultaneous fluorescence yield and partial electron yield detection described fully in reference 6. Thin polystyrene samples were spin cast from toluene or methylene chloride (HPLC grade) solvent solutions (approximately 0.3 weight percent) onto 200 nm gold films under coated with 5 nm of Ti on 15 x 15 mm squares of Si(100) wafers, 1.0 mm thick. Samples of various thicknesses were prepared by spin coating the polymer from different concentration solutions. The resulting polymer thickness was estimated using x-ray photoelectron spectroscopy (XPS) and should be considered to have absolute uncertainties on the order of the electron mean free path (5 nm in this case). Figure 1 shows a typical fluorescence yield (FY) carbon K near edge x-ray, absorption spectrum of a spin-cast film of 35,000 MW anionically polymerized polystyrene, 10 nm thick. The spectrum was fit to a combination of 5 Gaussian peaks and an edge step function to simulate the ionization threshold at 290 eV, after reference 10. There are three important pre-edge resonances in the spectrum of polystyrene, the C-C π^*_1 resonance at 285 eV, the C-H* resonance at 287 eV, and the C-C π^*_2 resonance at 288 eV [10]. The π^* resonances involve the excitation of a 1s electron to unfilled π^* antibonding orbitals on the aromatic ring. Higher in energy, above the ionization potential for the 1s electron, are the σ^*_1 and the σ^*_2 resonances. These resonances are excitations of the 1s electron to the higher unoccupied molecular orbitals characteristic of σ bonds. Included in the σ^*_1 resonance are also contributions from the main chain σ -bonds [11]. Since no resonant excitations are detected above the σ^*_2 peak, the excitations above 300 eV involve transitions to the continuum and will be independent of the chemical state of the carbon atoms which are under study. Thus the intensity at 325 eV is used below as a convenient measure of the total amount of carbon present in the probed volume.

Figure 1. Fluorescence yield spectrum of anionically polymerized 35 k MW polystyrene at normal photon incidence. The dashed line corresponds to the fitted spectrum which is a sum of the constituent peaks shown with the dotted lines. π^*_1 and π^*_2 are resonances to antibonding orbitals of the aromatic functional group characteristic of the double bonds. σ^*_1 and σ^*_2 are resonances of antibonding orbitals of the phenyl ring characteristic of the single bonds. σ^*_1 also has contributions from the main chain. The unmarked peak at 290 eV is a result of the overlap of the edge jump and the π^*_2 resonance.

A comparison of polystyrene FY carbon K near edge spectra taken with a normal (90 degree) and glancing (25 degree) incidence (with respect to the sample surface) photon beam are shown in figure 2. The π^* peak appears more intense for the normal geometry than in the glancing incidence case. At normal incidence the electric field vector of the incident radiation is parallel to the surface. Since the π^* orbitals in the phenyl rings of polystyrene are perpendicular to the ring this result indicates that the phenyl rings are preferentially tilted towards the surface normal. Both EY and FY near edge spectra of the spin coated films indicate that the plane of the phenyl rings were oriented towards the surface normal of these thin polymer films.

Figure 2. FY spectra of 35 K molecular weight polystyrene at both normal and glancing photon incidence. By comparing the intensity of the π^*_1 resonance, a preferential spatial orientation of the aromatic functional group toward the surface normal is apparent.

In figure 3 we plot the intensity ratio of the π^* peak (285 eV, polystyrene phenyl ring) to the intensity at 325 eV as a function of film thickness for EY and FY in normal and glancing incidence. Normalization by the intensity at 325 eV allows the spectra of all film thicknesses to be directly compared independent of total carbon content. For the FY data (shaded symbols), the ratios decrease with increasing thickness, but more quickly for normal incidence than glancing. For EY data (open symbols), the ratio appears to remain constant with thickness (unfortunately, for the thickest samples at normal incidence the EY spectrum suffered from surface charging effects and the data was unreliable). In both FY and EY, the ratios for normal incidence are always larger than that at glancing incidence. This anisotropy is indicative of a preferential orientation of the phenyl ring plane towards the surface normal for all film thicknesses. The decrease in anisotropy with thickness observed in FY is also consistent with what would be expected if the preferential orientation of the phenyl rings were due to a surface effect. But if the latter were the case, the ratios in FY for the extremely thin case should extrapolate back to the same value as for EY. In fact the FY ratios show more anisotropy for the thinnest case than is apparent in EY. This suggests that the film is slightly relaxed at the surface and less oriented. Vilar et al have suggested from HREELS results that the end groups of polystyrene molecules tend to segregate to the surface of spin coated films [12,13]. An increase in the number of end groups at the surface would also be consistent with our data. For these spin cast polystyrene thin films the pendant phenyl groups are found to be preferentially oriented toward the surface plane normal, independent of casting solvent, molecular weight, and film thickness.

DISCLAIMER

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Figure 3. Comparison of the ratio of the π^*_1 to the intensity at 325 eV at normal and glancing incidence angles and for EY and FY versus thickness. This graph illustrates an apparent preferential spatial orientation of the phenyl ring normal to the surface plane and illustrates the variation in relative intensities with film thickness.

In thin films, one may consider two possible reasons for the preferential orientation of the phenyl rings: Orientation may occur by either (1) the effect of surface forces directly on the aromatic rings, or (2) because of an effect on the overall polymer chain which is then transmitted to the aromatic rings (ie. the rings have a more or less defined orientation relative to the chain axis). We believe the latter is the case for the following reasons. If the orientation of the phenyl rings were exclusively a surface effect, there would be more anisotropy in the EY than the FY spectrum and this is not observed. If the polymer were randomly oriented relative to the surface, or if the phenyl rings were randomly oriented in the polymer, the π^* intensity would be independent of the angle of incidence of the x-ray beam. The fact that anisotropy is observed, is good evidence for both preferential orientation of the phenyl rings relative to the polymer axis and orientation of the polymer axes relative to the surface plane of the film. Preferential orientation of the phenyl rings with respect to the chain axis in polystyrene is consistent with what one surmises from examination of space-filling models of the polymer.

II. DVS bis-BCB (divinyl siloxane bis-benzocyclobutene): Buried Metal / Polymer Interface

DVS bis-BCB (divinyl siloxane bis-benzocyclobutene) is used for dielectric layers in new generation multilayer interconnect devices (multi-chip modules) [14]. For this application it is important to understand the nature of the bonding and complexing which occurs at the metal / polymer interface. The depth sensitivity (about 200 nm) and the non destructive nature of fluorescence yield are particularly useful in studying the buried interface between DVS bis-BCB coated with aluminium (10 to 100 nm)[15]. In contrast the relatively short depth sensitivity of traditional electron yield USXAS makes it useless for the buried interface study, since it would only probe the outer 5nm of the aluminium overlayer. We have collected FY carbon K near edge spectra for evaporated aluminum coated (50 nm thick) DVS bis-BCB (50 nm thick) as well as the identical bare polymer. Figure 4, upper and lower panels show these normalized spectra for normal and glancing incident x-rays respectively. In order to enhance the metal / polymer interface sensitivity each panel shows a difference plot (coated polymer minus bare polymer). The C-C π^* peak (286 eV) of the aromatic ring of DVS bis-BCB in the difference plots appears to undergo a dramatic enhancement in polarization dependance after the formation of the metal / polymer interface. This polarization enhancement at the interface region implies that the aromatic ring planes of DVS bis-BCB are highly oriented towards the surface normal. These preliminary results highlight the use of ultra soft x-ray absorption spectroscopy to provide new detailed chemical information which may be useful in predicting and optimizing the adhesion in metal / polymer interfaces.

Figure 4. FY carbon K near edge spectra for evaporated aluminum coated (50 nm thick) DVS bis-BCB (50 nm thick) as well as the identical bare polymer, upper and lower panels show spectra for normal and glancing incident x-rays respectively. In order to enhance the metal / polymer interface sensitivity each panel shows a difference plot (coated polymer minus bare polymer).

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