

CONF-861019--4

SYNCHROTRON RADIATION AS A SOURCE FOR QUANTITATIVE XPS:
ADVANTAGES AND CONSEQUENCES

T. M. Rosseel and T. A. Carlson
Oak Ridge National Laboratory, Oak Ridge, TN 37831

CONF-861019--4

DE87 000389

R. E. Negri
Physical Electronics Division
Perkin Elmer Corporation, Eden Prairie, MN 55344

C. E. Beall and J. W. Taylor
Department of Chemistry
University of Wisconsin, Madison, WI 53706

Synchrotron radiation (SR) has a variety of properties which make it an attractive source for quantitative X-ray photoelectron spectroscopy (XPS). Among the most significant are high intensity and tunability. For example, because it is a continuous source (10 eV-20 keV) selected wavelengths may be utilized to exploit the physical properties (e.g. cross section and absorption edge) of the material or element under study. In addition, the intensity of the dispersed radiation is comparable to laboratory line sources (1). Synchrotron radiation is also a clean source, i.e. it will not contaminate the sample, because it operates under ultra-high vacuum conditions. We have used these properties to demonstrate the advantages of SR as a source for quantitative XPS. We have also found several consequences associated with this source which can either limit it's use or provide unique opportunities for analysis and research.

Using the tunability of SR, we have measured the energy dependence of the 3p photoionization cross sections of Ti, Cr, and Mn from 50 to 150 eV above threshold at the University of Wisconsin's Tantalus electron-storage ring (2). In agreement with theory, maxima were observed \sim 100 eV above threshold.

By acceptance of this article, the publisher or recipient acknowledges the U.S. Government's right to retain a non-exclusive, royalty-free license in and to any copyright covering the article.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER
me

Taking advantage of the nearly one hundred-fold increase in atomic sensitivity, we quantitatively measured the oxidation states of Ti and Mn in TiO_2 -TiO and MnO_2 -MnO mixtures, respectively, over a mole-ratio range of 0.33 to 3.0 with an RSD of $\leq 4\%$ (3).

Tuning the photon energy to increase the atomic sensitivity also produces a set of consequences associated with the relatively low kinetic energy of the photoelectrons. We have found, for example, that angular distribution effects are important near threshold for amorphous solids. The functional relationship between θ , the angle between the non-polarized photon beam and the detected electrons and the differential cross section is described by:

$$\frac{d\sigma}{d\Omega}(\theta, h\nu) = \frac{\sigma_T}{4\pi} \left[1 - \frac{\beta_{n,1}(E_k)}{4} (3 \cos^2\theta - 1) \right] \quad (1)$$

where $d\sigma/d\Omega(\theta, h\nu)$ differential cross section as a function of θ and photon energy, σ_T is the total subshell cross section and β is the asymmetry parameter as a function of kinetic energy of the ejected electron. Although it is well known that the angular distribution of photoelectrons differs for different orbitals (4), it is often assumed that β is nearly zero for amorphous materials because elastic scattering is believed to produce an almost isotropic distribution ($\beta=0$) of photoelectrons (5,6). In addition, if β is 90° , then from equation 1 it can be seen that the angular distribution effect is reduced to $\beta/4$. The assumption that the angular distribution effect is negligible

means that a cross section ratio or relative sensitivity factor is the ratio of the angular independent total cross section.

We have shown that this assumption is invalid for the 3p relative cross sections of Ti, Cr and Mn ratioed to the oxygen 2s level over the range of 50 to 100 eV above the 3p threshold (2). Unless corrections were made for the rapid change of β over the 50 eV energy interval, disagreement with theory ranged from 30-70%. This compares to a 10% error for NaF over the 233 eV range between Mg and Al K X-ray sources (7). Recent measurements of the angular distribution of the scandium 2p photoelectron line near threshold confirm these results (8).

The consequences of these studies are two-fold. First, sensitivity factors calculated using theoretical total subshell cross sections near threshold will produce systematic errors in quantitative XPS results. Quantitative analysis using SR must therefore use standards, relative sensitivity factors corrected for angular distribution effects or rely upon empirical sensitivity factor data from a system with identical source-sample-analyzer geometry. Second, depth profiling studies, taking advantage of the variable energy photon source to change the kinetic energy and thus the mean-free-path (mfp) of ejected electrons, will also be erroneous unless corrections are made for the rapid change in β . The alternative method for depth profiling would be to maintain the angle of detection with respect to the plane of polarization while varying the take-off angle. The advantage of using SR for these studies is that the

cross section or sensitivity can be enhanced by the appropriate choice of photon energy and angular effects do not change if θ is unchanged.

Another consequence of using photons near the ionization threshold is that the mfp of the ejected electrons is small. The advantage is an enhanced sensitivity to the top-most surface layer. The disadvantage is the proportionately larger effect of surface inhomogeneities and contamination. These problems can be managed by improving the vacuum and sample preparation methods and by using sample cleaning techniques that do not modify the surface in an unknown or unpredictable fashion.

The variable energy source has two additional advantages for quantitative XPS. The mfp in a single sample can be studied over a large range of kinetic energies. Comparison of different types of materials (e.g. metallic, semiconductors, insulators and organics) can thus be examined for similarities and discrepancies from the universal curve. Finally, the ability to tune the photon energy also provides a convenient way to identify and remove any overlapping Auger electrons.

Acknowledgments: Support for this research was provided in part by Office of Energy Research, U. S. Department of Energy, under contract DE-AC0584OR21400 with Martin Marietta Energy Systems, Inc., NASA under NS6-7215, NSF Grant CHE-8121205 and the Chevron Corp. The Synchrotron Radiation Center is operated under NSF Grant DMR-8020164.

1. T. A. Carlson, Surf. Interface Anal. **4**, 125 (1982).
2. T. M. Rosseel, J. W. Taylor and R. E. Negri, Anal. Chem. **57**, 2685 (1985).
3. R. E. Negri, J. W. Taylor, C. E. Beall and T. M. Rosseel, Anal. Chem. **58**, (1986) (in press).
4. See for example: R. F. Reilman, A. Msezane and S. T. Manson, J. Electron Spectrosc. **8**, 389 (1976).
5. W. J. Carter, G. K. Schweitzer, T. A. Carlson, J. Electron Spectrosc. **5**, 827 (1974).
6. C. D. Wagner, Anal. Chem. **49**, 1282 (1977).
7. M. Vulli, Surf. Interface Anal. **3**, 67 (1981).
8. T. M. Rosseel and T. A. Carlson, unpublished results 1986.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.