J. Chem. Chem. Eng. 7 (2013) 601-605

Hard X-ray Photoelectron Spectroscopy Study of Electron Spectral Structure beyond the Known Signal Electron Peak

Alon Givon[1], Eitan Tiferet[2], German R. Castro[3, 4], Juan Rubio-Zuazo[3, 4], Erez Golan[5], Ilan Yaar[2] and Itzhak Orion[1*]

1. Department of Nuclear Engineering, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel

2. Nuclear Research Center-Negev (NRCN), Beer Sheva 84190, Israel

3. Spanish CRG BM25-SpLine at the European Synchrotron Radiation Facility, Grenoble 38043, France

4. Instituto de Ciencia de Materiales de Madrid, Madrid 28049, Spain

5. The Nano-Fabrication Center, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel

Received: May 08, 2013 / Accepted: May 31, 2013 / Published: July 25, 2013.

Abstract: HAXPES (hard X-ray photoelectron spectroscopy) is a powerful emerging instrument in surface analysis. It extended the photoelectron energy range up to 15,000 eV and opened the possibility to study much thicker films, buried layers and bulk electronic properties. In order to study these features, data for the electron IMFP (inelastic mean free path) at these energies is needed. To date, only calculated IMFP are available at energies above 5,000 eV and therefore experimental validation of these calculations are essential. In this paper, a new approach for using the HAXPES spectra is presented. This approach, treats the attenuated part of the electron spectrum as a whole to calculating the average electron energy loss. This average electron energy loss is the result of inelastic collisions in the material and hence, carry with it information about the electron transport poses. Carbon layers with thicknesses between 20 and 75 nanometer deposited over copper substrate were used to test this approach at the Spanish beam-line (Spline) in the ESRF (European synchrotron radiation facility). The measured results showed good agreement with the predictions of the multiple inelastic scattering theory. In addition, an algorithm for the experimental evaluation of electron IMFP, using the measured energy loss, is proposed.

Key words: HAXPES, IMFP, carbon, synchrotron.

1. Introduction

Photoelectron spectroscopy is a powerful tool for analyzing surface composition and film thickness of materials. Combined with the improved capabilities of third generation synchrotrons, to generate photoelectrons at intermediate energies (5,000-20,000 eV) enables the study of bulk electronic properties in matter. In XPS (X-ray photoelectron spectroscopy) technique, an incident photon beam interacts with the sample and emits photoelectrons, i.e., signal electron [1]. By analyzing its energy, the signal electron is used to determine the surface composition. It can also be used as an electron beam to analyze thin layers on the surface of the material. When analyzing thin layers, the signal electron is attenuated in the material. Electrons that lost energy in the attenuation process are no longer a part of the signal electron. However, these electrons still appear in the lower part of the spectrum and can screen the desired signal electron.

The main process that gives rise to attenuated electrons at the measured spectrum is the MIC (multiple inelastic collisions) in the bulk material. For the analysis of the electron spectrum, in traditional electron spectroscopy, the electron peak needs to be separated from these attenuated electrons. Extensive

*Corresponding author: Itzhak Orion, Ph.D., research field: nuclear physics. E-mail: iorion@bgu.ac.il.

work was carried out over the years in order to strip the attenuated signal, caused by multiple inelastic collisions, from the signal electron peak [2-8]. The practical electron energy for common XPS ranges from a few eV up to 2,000 eV [9]. The use of HAXPES (hard X-ray photoelectron spectroscopy) at third generation synchrotron's [10, 11] extended the photoelectron energy range up to 15,000 eV and opened the possibility to study much thicker films, buried layers, and bulk electronic properties.

Using HAXPES to study the bulk material requires data for the electron IMFP (inelastic mean free path) at these energies. Theoretical predictions and experimentally determined IMFP's in traditional electron spectroscopy are well established for electron energies up to 2,000 eV [12]. Only recently, calculated IMFP's for energies up to 30,000 eV have been published [13] and experimental values to validate these calculations for a given material are generally available only in a limited energy range. Although the HAXPES extended the photoelectron energy to 15,000 eV, there are still many limitations on the depth from which the electron probe can provide useful information. Electron MIC in the bulk material is one of the main contributors to the reduction of the signal electron energy and intensity. This gives rise to noise at the detected spectrum. As the electrons are emitted deeper in the material, this effect intensifies to a point where no signal electron can be recognized. Using this approach, only the signal electron is analyzed.

In this paper, a study of the electron spectral structure beyond the known signal electron peak is examined. Experimental measurements, using HAXPES, of the broad electron spectrum at signal electron energies between 8,000 eV and 10,000 eV are presented. Electrons that have been attenuated in the bulk material create a convolution of peaks that are measured at the lower part of the spectrum, as depicted in Fig. 1. A comparison between these attenuated electrons, measured at the experiment, and theoretical calculations is performed. In addition, a mathematical

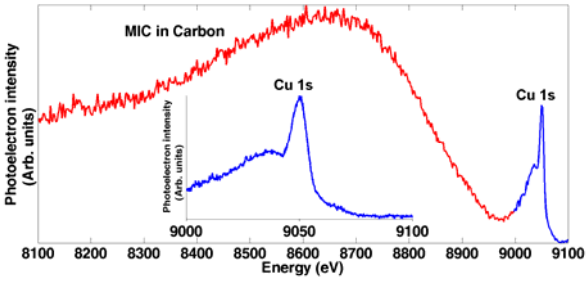

Fig. 1 Normalized photoelectron intensity plotted as a function of energy for Cu 1-s photoelectrons induced by 18 keV photon beam generated using HAXPES in the GRC-spline, ESRF; the photoelectrons are collected after passing through a 74.7 nm layer of carbon.

algorithm that enables the measurement of IMFP using this approach is presented.

The spectrum in Fig. 1 shows the signal electron at the right end followed by a large tail. The tail in the spectrum is a convolution of electron peaks. These peaks are created when the photoelectron undergo MIC (multiple inelastic collisions) in the layer. The inserted spectrum is a standard HAXPES spectrum of the same measurement in which only the signal electron peak is shown. The tail energy range can extend to 1,500 eV down from the signal electron peak. This broadening of the spectrum depends on the initial electron energy, the energy loss probability per collision and the electron path length. From these properties, the MIC energy shift can be calculated [14] and vice versa, the MIC energy shift can be used to calculate a property of the electron transport if other electron transport properties are known.

2. Experiments

The sample substrate is a 10 × 10 × 0.5 mm^3 copper plate with one face polished to surface RMS smaller than 3 nm [15]. Using sputtering deposition technique, three spots (3 × 3 mm^2) of pure (99.99%) carbon graphite were sputtered on the polished copper surface. The thickness measurement (±1 nm) showed the samples to be 19.2 nm, 34.4 nm and 74.7 nm. In the setup of the HAXPES, the electrons of the copper 1-s shell substrate were used to generate the photoelectron beam. The HAXPES is located at the Spanish

beam-line (spline) in the ESRF (European synchrotron radiation facility). More details on the experimental setup are available in Refs. [16, 17].

Electrons from the copper 1-s shell were generated using three different setups of the photon energy. The energy collimation for the photons coming from the synchrotron was set to 19, 18 and 17 keV. Each setup requires a new calibration of the system. In every calibration the photoelectron spectra was measured for the pure copper substrate and the 19.2, 34.4 and 74.7 nm carbon over-layer samples. The measured spectrum was normalized according to the total photon flux measurement; background correction using the Tougaard's algorithm [18] was applied, and finally the intensity of each spectrum was normalized to one.

3. Results and Discussion

The spectra collected from the pure copper substrate and from the 19.2, 34.4 and 74.7 nm carbon over-layer are depicted in Fig. 2, for photon energies of 19, 18 and 17 keV, respectively. Two types of low energy electron buildup can be observed in the spectra presented in Fig. 2. When the electron path length is extended, the electron undergoes more interactions in the material, resulting in higher energy loses. This correlates to the spectra results of the different samples in Fig. 2. At the other hand, if the photoelectron energy is decreased, the electron undergoes more interactions because the probability for an interaction increases as the energy decreases. This correlates to the spectra results of the different energies in Fig. 2. These two types of low energy electron buildup in the spectrum can be used to obtain different properties of the examined material.

To validate the wide energy spectrum approach, theoretical calculations of the average energy loss are compared to the experimental results. This comparison is shown in Fig. 3. The theoretical calculation were performed using the approach presented by Werner [2, 3], and the measured average energy loss was obtained from the spectra depicted in Fig. 2. From Fig. 3, authors

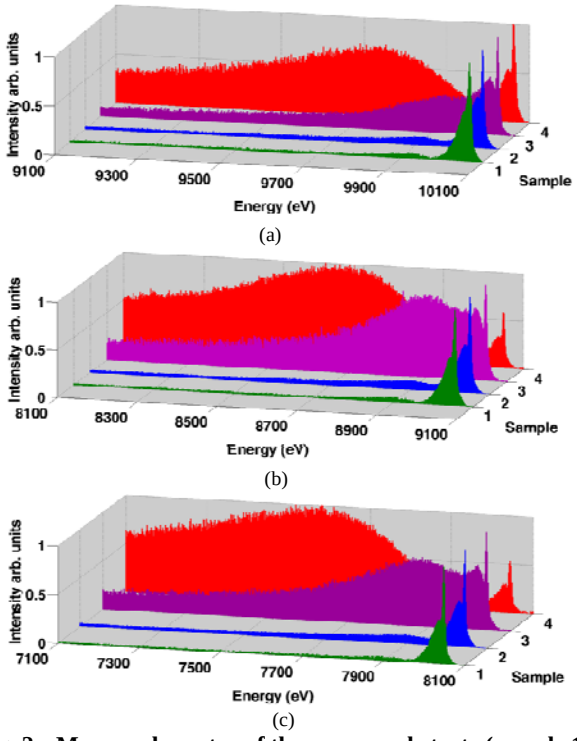

Fig. 2 Measured spectra of the copper substrate (sample 1), the 19.2 nm carbon over-layer (sample 2), the 34.4 nm carbon over-layer (sample 3) and the 74.7 nm carbon over-layer (sample 4); the peak observed at the right side of the spectra originates from the contribution of the copper 1 s electrons; the photon energies in (a), (b) and (c) are 19, 18 and 17 keV, respectively.

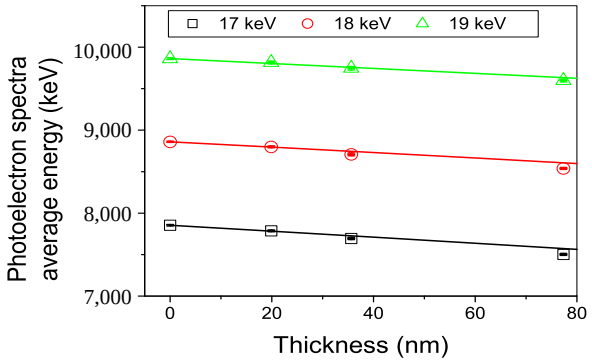

Fig. 3 Theoretical and experimental photoelectron average energy, plotted as a function of carbon layer thickness for the 19, 18 and 17 keV photon beam energy; the lines are the theoretical calculated results obtained according to the method described in Ref. [14].

can see that the average electron energy is proportional to the electron path length. This proportionality arises from the electron inelastic interaction characteristics. As an impinging electron interacts with the field of the

material electrons it experience energy loss. However, the average electron energy loss probability in an individual collision is almost independent from the electron initial energy [2]. Therefore, regardless of the electron initial energy the number of interactions are what determine the average energy loss.

The difference between the electron projection length and the real electron path length is expressed in the small discrepancy between the measurements and the model results observed in Fig. 3. While the sample thickness represents the projection length, the electron path length is elongated due to elastic interactions. This effect is more dominate for thicker samples and it intensifies as the electron energy decreases.

Exploiting the fact that in an individual collision the electron energy loss is almost independent of its initial energy [2], the average energy loss can be written by Eq. (1).

$$E_{Av} = \overline{n} \times \overline{T} \tag{1}$$

where, $\overline{n}$ is the average number of inelastic interactions and $\overline{T}$ is the average energy loss per collision. The IMFP depends on the electron energy and hence changes after every interaction. The average electron IMFP is defined as Eq. (2) [3].

$$\Lambda_{(n)} = \frac{\sum_{k=0}^{n} \lambda_k}{(n+1)} \tag{2}$$

where, λ_k is the IMFP for each collision and $\Lambda_{(n)}$ is the average IMFP after *n* collisions. The average IMFP can also be defined as the average traveled path length divided by the average number of inelastic collisions in Eq. (3).

$$\Lambda = \frac{x}{\overline{n}} \tag{3}$$

where, *x* is the average path length. From Eq. (2), it is easy to see that for $n = 0 \rightarrow \Lambda_{(0)} = \lambda_{(0)}$. In order to find $\Lambda_{(0)}$, several samples with known thicknesses are needed to be measured using the same electron beam energy. Using Eq. (1) to calculate the average number of interactions from the measured MIC and inserting it into Eq. (3) will resolve in a trend line of the average IMFP as a function of the number of interactions. By extrapolating this trend line to *n* = 0, the IMFP for the electron initial energy can be obtained.

4. Conclusions

The average photoelectron energies as measured in Fig. 2 are in very good agreement with the theoretical calculations, depicted in Fig. 3. These results substantiate the approach of using a wide electron energy spectrum. In addition, an algorithm for the experimental evaluation of electron IMFP was presented. Although insufficient data in this experiment prevented IMFP calculations, it demonstrates the validity of this approach. The authors are confident that future experiments will provide the necessary data for electron mean free path measurements beyond 5,000 eV.

Acknowledgments

The authors thank D. Kotlyar for his computational assistant. The authors acknowledge the European Synchrotron Radiation Facility for approving the use of the synchrotron radiation facilities and would like to thank the SpLine staff for technical and scientific assistance in using beam-line BM25. The authors also thank the nano fabrication facility staff at Ben-Gurion University of the Negev for providing technical support with the sample preparation.

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