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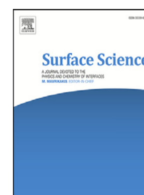

Modeling and parameterization of photoelectrons emitted in condensed matter by linearly polarized synchrotron radiation

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A R T I C L E I N F O

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A B S T R A C T

Growing availability of synchrotron facilities stimulates an interest in quantitative applications of hard X-ray photoemission spectroscopy (HAXPES) using linearly polarized radiation. An advantage of this approach is the possibility of continuous variation of radiation energy that makes it possible to control the sampling depth for a measurement. Quantitative applications are based on accurate and reliable theory relating the measured spectral features to needed characteristics of the surface region of solids. A major complication in the case of polarized radiation is an involved structure of the photoemission cross-section for hard X-rays. In the present work, details of the relevant formalism are described and algorithms implementing this formalism for different experimental configurations are proposed. The photoelectron signal intensity may be considerably affected by variation in the positioning of the polarization vector with respect to the surface plane. This information is critical for any quantitative application of HAXPES by polarized X-rays. Different quantitative applications based on photoelectrons with energies up to 10 keV are considered here: (i) determination of surface composition, (ii) estimation of sampling depth, and (iii) measurements of an overlayer thickness. Parameters facilitating these applications (mean escape depths, information depths, effective attenuation lengths) were calculated for a number of photoelectron lines in four elemental solids (Si, Cu, Ag and Au) in different experimental configurations and locations of the polarization vector. One of the considered configurations, with polarization vector located in a plane perpendicular to the surface, was recommended for quantitative applications of HAXPES. In this configurations, it was found that the considered parameters vary weakly in the range of photoelectron emission angles from normal emission to about 50° with respect to the surface normal. The averaged values of the mean escape depth and effective attenuation length were approximated with accurate predictive formulas. The predicted effective attenuation lengths were compared with published values; major discrepancies observed can be ascribed to a possibility of discontinuous structure of the deposited overlayer.

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1. Introduction

Quantitative applications of X-ray photoelectron spectroscopy are based on theoretical models relating the measured photoelectron signal intensity to different features of the surface region, e.g., the surface composition or the thickness of an overlayer. These models of acceptable accuracy were already proposed in the early 1970 s [1,2], and, after some modifications, are used until today [3,4]. The mathematical formalism is based on a number of assumptions among which two are of crucial importance. First, the radiation is assumed to be unpolarized which leads to a simple description of the photoemission cross sections and the photoelectron transport. Such radiation is emitted by the soft X-ray sources used in conventional spectrometers, e.g. laboratory Mg Kα and Al Kα radiation sources. Photoelectron kinetic energies then do not exceed the Al Kα radiation energy, i.e., $h\nu = 1486.6$ eV. Second, to simplify the formalism further, the elastic interactions of emitted photoelectrons are neglected. It is well know now that this assumption cannot be ignored in certain experimental configurations.

In recent years, we observe a growing interest in analytical applications of hard X-ray photoemission spectroscopy (HAXPES) [5,6]. This technique has important advantages as compared to conventional spectrometers. At radiation energies exceeding 1486.6 eV, the sampling depth of photoelectron spectroscopy increases, which reduces the disturbing effects of surface contaminations, and allows nondestructive characterization of deeper layers and interfaces. Furthermore, the spectral features due to Auger electrons can be shifted out of the energy window of analytical interest. The HAXPES potential applications have also stimulated construction of laboratory sources of unpolarized X-rays with energies exceeding 2 keV. In recent studies, attempts were made to extend the mathematical formalism of quantitative XPS to such energies [5-7]; however, general information on processing the HAXPES photoelectron signal intensities is rather limited. In recent studies, the

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parameterization of HAXPES formalism was analyzed [8-10]. The parameters needed for typical analytical applications of XPS and AES were determined, e.g., overlayer thickness measurements, estimation of sampling depth in a given geometry, etc. Nonetheless, the use of high-energy laboratory sources has limitations due to problems with fabrication. Although some constructions are available commercially (e.g. a source with a Zr Lα anode, $h\nu = 2042.4$ eV), generally the use of these sources is less frequent than the use of conventional laboratory sources.

The photoemission cross sections derived for unpolarized radiation are also expected to be valid for circularly polarized synchrotron radiation. Consequently, we can use the mathematical formalism derived for quantitative applications of conventional spectrometers. In fact, HAXPES studies in synchrotron facilities have an additional advantage of tuning the radiation energy in such a way that a desired thickness of the surface region or a desired depth of an interface is analyzed. The question arises as to what is the effect of linear polarization on photoelectron signal intensity and on typical parameters used for characterization of photoelectron transport. The signal intensity due to photoelectrons emitted by polarized radiation obviously depends on the direction of the X-ray beam and direction of the analyzer axis. Additionally, we must account for positioning the polarization vector with respect to the surface plane. The latter problem considerably complicates the formalism since more parameters are required to describe the experimental configuration of a given measurement. Tanuma et al. [11] recently analyzed the sampling depth of photoelectrons emitted by a polarized X-ray radiation; however a simplified theoretical approach was used in that study. In the present work, an attempt is made to develop an advanced theoretical model that is applicable to a number of quantitative applications of HAXPES using polarized radiation. This theoretical model is a tool that can be used for determination of typical parameters needed for quantitative analysis such as mean escape depths, information depths, and effective attenuation lengths. Finally, an extensive database of escape depths and effective attenuation lengths was created, and tests were performed to find predictive formulas for these parameters that would be useful for practical analysis.

2. Theory

The main difference between the frequency of photoemission events by polarized and unpolarized X-rays is visualized by the theoretical description of the photoemission cross section (PCS). In fact, the difference between these cross sections in a given configuration may be dramatic. The angular distribution of photoemission from a given atom is determined by location of the polarization vector in space. In a synchrotron facility, the polarization vector is parallel to the plane of the synchrotron ring. To describe the position of the polarization vector, we need to specify the laboratory Cartesian coordinates. It is convenient to locate this coordinate system in such a way that the x-z plane is parallel to the plane of the synchrotron ring, as shown in Fig. 1. Additionally, we fix the z-axis in the direction of the X-ray radiation beam. In that case, the radiation polarization vector is parallel to the x-axis. Finally, we assume that the Cartesian system follows the right-hand rule. In that case, the y-axis is directed upward with respect to the ring plane. To identify this coordinate system, the relevant vector components will be annotated with the subscript *lab*. For simplicity, no X-ray monochromator is shown in Fig. 1. While the elements in the monochromator and beam-transport optics will modify the polarization of the beam from the synchrotron, we ignore this complication here.

In the laboratory coordinate system, the directions of photoelectrons emitted in a sample irradiated by an X-ray beam can be described by two angles, θ and φ. The angle θ describes photoelectron direction with respect to the polarization vector, while φ is the angle between the plane containing the photoelectron direction vector and the polarization vector, and the x_{lab} - z_{lab} plane. This notation is illustrated in Fig. 2.

The photoemission event initiates a photoelectron trajectory in the solid. We assume that the distribution of photoemission directions is fully described in the laboratory coordinates and is independent of the position of the sample surface. Thus, quantification of the HAXPES signal intensity requires knowledge of the distribution of angles, θ and φ. The latter parameter can be derived from the photoemission cross section.

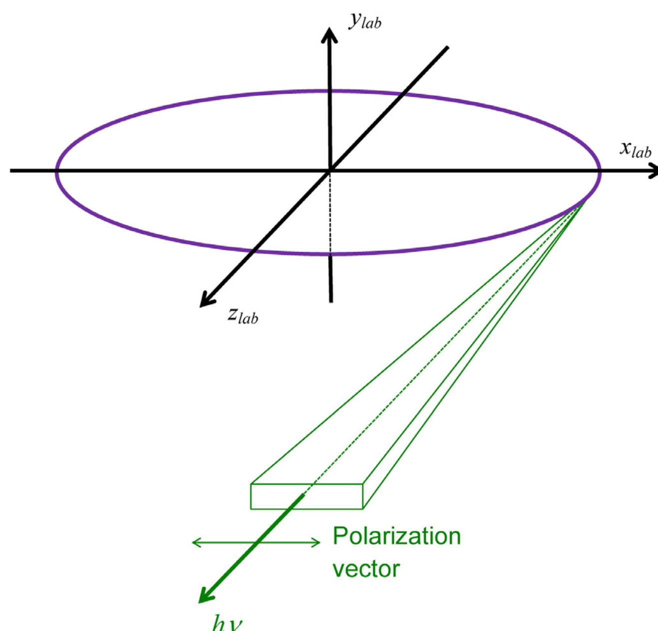

Fig. 1. Location of the laboratory system of coordinates with respect to the plane of a synchrotron ring, and the beam of polarized radiation.

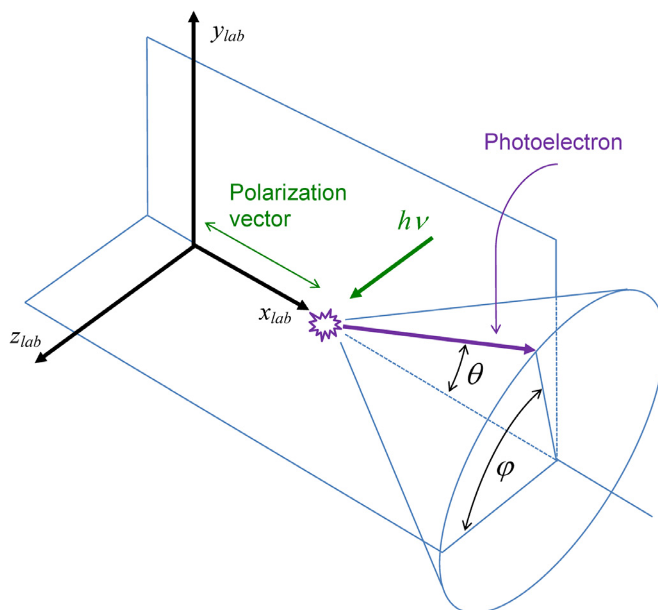

Fig. 2. Outline of the photoemission event and the notation used.

2.1. Photoemission cross section

The photoelectron emission event is characterized by the PCS, $d\sigma_x/d\Omega$, which is related to the probability of photoemission in a given direction. Analytical expressions describing the PCS of varying accuracy have been known since the 1960s. Cooper and Zare [12] and Cooper and Manson [13] derived a simple analytical formula describing the photoemission cross section for polarized radiation. Within the so-called dipole approximation (DA), this cross section can be expressed in terms of a

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