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High energy photoelectron spectroscopy in basic and applied science: Bulk and interface electronic structure

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ABSTRACT

With the access of new high-performance electron spectrometers capable of analyzing electron energies up to the order of 10 keV, the interest for photoelectron spectroscopy has grown and many new applications of the technique in areas where electron spectroscopies were considered to have limited use have been demonstrated over the last few decades. The technique, often denoted hard X-ray photoelectron spectroscopy (HX-PES or HAXPES), to distinguish the experiment from X-ray photoelectron spectroscopy performed at lower energies, has resulted in an increasing interest in photoelectron spectroscopy in many areas. The much increased mean free path at higher kinetic energies, in combination with the elemental selectivity of the core level spectroscopies in general has led to this fact. It is thus now possible to investigate the electronic structure of materials with a substantially enhanced bulk sensitivity. In this review we provide examples from our own research using HAXPES which to date has been performed mainly at the HIKE facility at the KMC-1 beamline at HZB, Berlin. The review exemplifies the new opportunities using HAXPES to address both bulk and interface electronic properties in systems relevant for applications in magnetic storage, energy related research, but also in purely curiosity driven problems.

1. Introduction

The surface sensitivity of X-ray photoelectron spectroscopy (XPS, PES) when performed with photoelectrons having kinetic energies in the range of 50–1000 eV has been key to many important contributions in surface science (for example, see Ref. [1]). On the other hand, the surface sensitivity can also be problematic when bulk properties are sought or when properties of buried structures and interfaces are investigated. Often samples needs to be prepared *in situ* to minimize contributions from surface contamination, as the probing depth of ‘conventional’ photoelectron spectroscopy is in the range of $\lessapprox$1 nm. If the sample is sensitive to oxidation it needs a protective capping layer or the top layers will not be representative for the bulk properties. In either case, the top layers needs to be removed which is difficult without affecting the sample. To study structures which are buried deeper than a few nanometers is not possible using traditional XPS [2–7].

However, as the kinetic energy of the emitted photoelectron is increased the inelastic mean free path is also increased and can approach tens of nanometers for kinetic energies in the range of 4 keV and higher. During the last decade there has been a large increase in the use of hard X-ray photoelectron spectroscopy (HAXPES; HX-PES, HIKE are common synonyms). With the availability of new bright synchrotron sources and monochromators with a resolving power in the range of 10^5 combined with electron analyzers capable of analyzing electron energies in the range of 10 keV with meV resolution, technology has finally reached the necessary level of perfection to fully enable the potential pointed out by Lindau et al. already in the seventies [8]. Since the first report of HAXPES using contemporary instrumentation [9,10], the method has rapidly developed into a promising tool to address electronic properties of buried interfaces and bulk layers [3–5,11–35], as it is one of the few methods that enable non-destructive bulk sensitive studies. The great advantage of HAXPES is the accurate measurement of shifts in core-level binding energies of bulk atoms, which reflect changes in chemical environment and give us information about the intermixing of interface atoms and alloying of the multilayers.

In this article we review some of our work on analyzing bulk and interface properties in several systems using photoelectron spectroscopy at excitation energies in excess of 2 keV. Regarding interface studies, we will provide examples from metallic multilayers relevant for magnetic sensors, and from interfaces in molecular solar cells. To exemplify how HAXPES can be used to address bulk-like electronic properties we have again chosen examples from both spin-based electronics and energy relevant materials, but also

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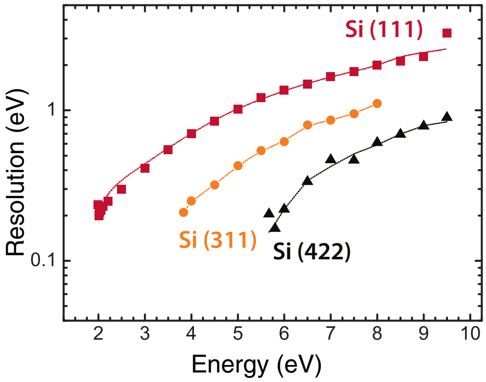

Fig. 1. The three sets of crystals available at the KMC-1 beamline covers a large energy range with good resolution.

Adapted from Ref. [28].

some of the early data on correlation effects in transition metals and metal oxides. We will also discuss how electronic properties may provide a better handle on nanoscale inhomogeneities than structural characterization. The paper is organized as follows. We begin by briefly describing some of the essential features of the HIKE facility at the KMC-1 beamline at HZB (BESSY-II) in Berlin. We will then continue to discuss the use of HAXPES to address properties of buried interfaces and conclude with studies of bulk electronic structure.

2. Experimental

The HAXPES experiments were carried out on the HIKE experimental station at the KMC-1 bending magnet beamline at HZB (BESSY-II), Berlin. The beamline is equipped with a high resolution double crystal monochromator which consists of three sets of crystals, Si(1 1 1), Si(3 1 1) and Si(4 2 2). The resolution as a function of energy is given in Fig. 1. Despite the fact that the source is a dipole on the BESSY-II storage ring operating at 1.7 GeV, it is possible to obtain good working conditions in terms of resolution and flux between 2 and 12 keV, where there is of course always a tradeoff between these quantities. We note in particular that we have been able to record Ni core level spectra from Ni metal at 12 keV excitation energy. In Ref. [4], we used this possibility to show how differences in the screening of the core hole lead to differences in the satellite structure at the 1*s* and 2*p* levels respectively. In that study, the total experimental resolution was limited by the Si(4 2 2) crystals which is approximately 1.2 eV at 12.6 keV photon energy.

The HIKE end-station at KMC-1 is equipped with a VG Scienta R4000 hemispherical electron analyzer modified for high transmission and high resolution at electron kinetic energies up to 10 keV. The R4000 analyzer is positioned at 90° with respect to the beam. The experimental chamber comprises a five-axis Omniax manipulator with a He cryostat. The sample stage is also equipped with a boron nitride heater which allows for sample heating up to 850 °C. More detailed information on the experimental set up can be found in Refs. [5,28].

3. Interface properties from hard X-ray photoelectron spectroscopy

Thin film structures like multilayers and superlattices are key ingredients in many applications and provide excellent opportunities to tune physical properties of the devices. The properties often arise from the introduction of interfaces and finite size effects. Multilayers have attracted interest in many fields because of their numerous practical applications and interesting properties. Nowadays, the development of technology is strongly coupled to the advance of nanodevices, built from thin films and multilayers or superlattices. The thickness, composition and interface structure of the layers are used to tailor magnetic, mechanical and optical properties of the devices. Due to the intrinsic properties of HAXPES this is a new tool to obtain information about buried multilayered structures including metallic multilayers and multilayers of semimetal alloys [2,6,36]. In the following section, we specifically exemplify new insights obtained with HAXPES on multilayer structures by presenting results on interface alloying processes in all-Heusler multilayer structures.

Conducting molecular materials offer an additional variety of interfacial design. Examples include possibilities in fine-tuning optical and electronic matching, wetting properties for control over interfacial structures as well as solution based processing and the use of flexible substrates. These advantages are currently exploited in devices for conversion between light energy and electrical energy including molecular light emitting devices and solar cells. One example is dye-sensitized solar cells (DSSC) based on dye-sensitization of inorganic mesoscopic materials [37]. Here we give examples on how HAXPES investigations on molecular interfaces can be used to understand depth composition variations and molecular orientations on surfaces.

3.1. *Multilayer interfaces: full-Heusler alloys for giant magnetoresistance applications*

The ever-increasing demand for high-density storage of data has been made possible by several enabling technologies like the discovery of the giant magnetoresistance (GMR) effect that gave us much increased sensitivity in the read heads used in magnetic storage devices [38,39]. Today's standard is however based on the tunneling magnetoresistance effect (TMR) due to the much superior change in magnetoresistance found for TMR. The TMR effect is typically an order of magnitude larger than the GMR. There are, however, some problems with TMR-based devices when the quest for further increases in storage density will lead to further reductions on the dimensions of the read head sensor. As the bit density is increased toward 1 Tbit/in^2 and beyond, it has been predicted that current-perpendicular-to-plane (CPP) GMR heads will have a better performance than read heads based on TMR [40]. Due to the theoretically predicted half-metallic character of Heusler alloys, i.e. majority band is metallic while the minority band exhibits a gap at the Fermi level, these materials are highly interesting for magnetoresistance (MR) studies [41,42]. Over the past few years there has been a number of reports on the use of full-Heusler alloys as magnetic layer(s) in metallic CPP structures [43,44], including some read heads applications [45–47].

Heusler alloys are ternary alloys with the composition X_2YZ, where X and Y in general are two different transition metal atoms and Z is group 3 or 4, non-metallic element. Nikolaev et al., have shown that CPP-GMR heads based on all-Heusler structures are interesting alternatives to achieve a CPP-GMR based read head exhibiting a MR of 7% and a resistance-area product (ΔRA) of $4\,\mathrm{m}\Omega\,\mu\mathrm{m}^2$ [46,48]. These performance parameters are achieved within the temperature constrains of the actual reader manufacturing. Even more encouraging results were presented in Ref. [49], where a MR of almost 75% where reported for a Heusler/Ag/Heusler trilayer.

One of the critical factors for the performance of an all-Heusler GMR structure is sufficiently high spin polarization which is in reality limited due to defects and specific details of the interface structure regarding roughness and intermixing. It is therefore central to characterize the degree of disorder at the interfaces and investigate its effect on spin polarization and ultimately spin current asymmetry. Ambrose and Mryasov [50,51] proposed a