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Electronic and electrical properties of functional interfaces studied by hard X-ray photoemission

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ABSTRACT

As the device downscaling in nanoelectronics has reached the 10 nm range, the functionality of materials employed in multilayered structures to be used in future logic and memory devices is largely defined by their interface properties. In particular, the electrical properties of the functional stacks are directly related to the electronic band line-up which is affected by the electric dipoles building up at the interface(s). In this work, hard X-ray photoelectron spectroscopy is applied to probe the electronic conditions at the interfaces of several relevant multilayered functional structures and to correlate the results with their electrical (transport) properties.

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1. Introduction

The study of complex heterostructures comprising oxide layers has attracted much attention because of their intriguing properties which are not only fundamentally interesting but also often very promising for potential device applications [1]. As the thickness of oxide materials employed in such multilayered structures drops beyond the 10 nm scale, new functionalities emerge giving rise to novel concepts of logic and memory devices. In particular, a range of phenomena referred to as “resistive switching” effects in metal oxide based metal-insulator-metal (MIM) multilayers has been identified and is currently being investigated targeting the development of the novel non-volatile memory applications. Hard X-ray photoelectron spectroscopy (HAXPES) combining brilliant X-ray undulator radiation from 3rd generation sources with commercially available optimized high-energy electron spectrometers has recently emerged as an excellent tool providing information on the chemical and electronic structure of prototype functional oxide based multilayered stacks thereby enabling new insight into the physical mechanisms behind the resistance switching effects in ultrathin metal oxide films [2–4]. The use of hard X-rays in an energy range of about 2.5–12 keV is particularly beneficial since it produces photoelectrons with variable high kinetic energies yielding large electron inelastic mean free paths which results in electron escape depths up to about 20 nm. This technique is therefore ideally suited to non-destructively probe both the chemical composition and the electronic structure of multilayered structures as well as buried interfaces at some 10 nm depths [5]. Functional structures often comprise top metal layers (serving as electrodes), and it is worth noting that continuous metal layers can only reliably be produced with thicknesses larger than 7–10 nm. It is therefore not possible to use soft X-ray electron spectroscopy methods or laboratory XPS instruments for such studies. In addition, HAXPES provides a unique opportunity to monitor the spatial redistribution of charges across the functional structures upon *ex situ* or *in situ* voltage biasing conditions, modeling the devices under operation. In this work, we report on the application of HAXPES instruments at DORIS III and PETRA III (DESY, Hamburg) to investigate the electronic and electrical properties at the interfaces of several relevant functional structures having potential for applications in nanoelectronics and spintronics.

The materials under investigation here are prototypical functional multilayers representing alternative emerging non-volatile memory concepts. In particular, a promising concept challenging currently dominating Flash technology exploits reversible switching under external voltage between the conducting and insulating states in ultrathin films of various materials embedded in a metal-insulator-metal (MIM) structure (see review [6] and refs. therein). The challenge is to elucidate the microscopic physical mechanism(s) behind the observed switching phenomena which will enable to optimize the operation of future memory devices based on resistive switching which have entered the commercialization stage. Among the materials exhibiting resistive switching behavior are transition metal oxides, particularly hafnium oxide. However, devices constructed using HfO_2 often suffer from nonuniformity

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of resistive switching parameters such as the on-/off-state resistance values and V_{set}/V_{reset} switching voltages; this nonuniformity leads to false programming and gives rise to readout hazards. Earlier, it has been shown that the introduction of an additional ZrO_x layer leads to a tight distribution of switching parameters, good switching endurance, and good data retention [7]. Furthermore, the bilayer HfO_{2-x}/ZrO_x structure shows lower reset current and operating voltage than a HfO_x single layer under dc sweep voltage. In this paper, HAXPES is used to probe functional MIM structures based on p^{++}-Si/HfO_{2-x}/ZrO_x/Pt upon *in situ* biasing ("under operation"). By observing small changes of the core level lines position following the assumed (charged) oxygen vacancies drift we get insight into the processes accompanying the effect of resistive switching in dielectrics based on the transition metal oxides. HAXPES technique has been previously employed to investigate the origin of the resistivity change in thin films, particularly, in NiO [8].

In an alternative memory concept employing ultrathin ferroelectric (FE) layers in metal/FE/metal heterostructures, the predicted effect of ferroelectric polarization orientation on the electron transport properties in the so-called ferroelectric tunnel junctions (FTJ) [9] has recently been directly established [10,11]. The results clearly indicate that the tunneling electroresistance which depends on the electrostatic potential barriers at both FE/metal electrode interfaces is controlled by the direction of the FE polarization. One of the promising though rather unexplored material systems is Pt/$BaTiO_3$ because due to the favorable lattice mismatch $[(a_{BTO} - a_{Pt})/a_{Pt} \approx 1.8\%]$ an ultrathin heteroepitaxial $BaTiO_3$ layer on Pt is under biaxial compressive strain, which produces tetragonal distortion and ensures that the ferroelectric polarization is aligned in the direction perpendicular to the surface [12]. In this work, HAXPES is employed to directly determine the electronic band line-up in the functional FTJ based on the Pt/$BaTiO_3$/Cr heterostructure and eventually to reconstruct the electrostatic potential barrier profile to correlate their electronic and transport properties. We also investigate the expected effect of oxygen vacancies in $BaTiO_3$ on the band alignment at the Pt/$BaTiO_3$ interface.

Further extension of an FTJ concept is to use ferromagnetic electrodes to exploit the so-called "interfacial magnetoelectricity", *i.e.* magnetoelectric coupling arising at a ferromagnetic metal/dielectric (ferroelectric) interface [13]. Such heterointerfaces have proven to be ideal for controlling and manipulating electrical charges and spins in multifunctional solid state devices, and recently the successful implementation of ferroelectric control of spin polarization has been convincingly demonstrated [14]. To elucidate the effect of FE polarization on the magnetic and transport properties, it is important to obtain detailed information on the interfacial electronic structure. Here, using HAXPES we experimentally determine the electronic band alignment at the $La_{0.67}Sr_{0.33}MnO_3$(LSMO)/$BaTiO_3$ interface which is a model ferromagnetic/FE system.

2. Experimental

2.1. HAXPES instruments

The HAXPES data presented here were measured using two different instruments at DESY (Hamburg, Germany) synchrotron photon sources. At the DORIS III storage ring, the X-ray photoemission setup at wiggler beamline BW2 was used which provides a high-flux X-ray beam in an energy range from 2.4 to 8 keV. For this experiment, an X-ray energy of 4.5 keV was chosen at this beamline. Photoelectrons were recorded using a SCIENTA SES-200 analyzer. This facility allows to obtain high quality data with medium energy resolution around 0.5 eV with a Si(1 1 1) double-crystal monochromator which is sufficient for most core level studies. The size of the focused X-ray beam at the sample is rather large ($\sim 0.4 \times 2\ mm^2$).

The second instrument used in this study is the HAXPES endstation at X-ray undulator beamline P09 of the new 3rd generation X-ray storage ring PETRA III [15]. Typical spot sizes on the sample are 0.1 mm × 0.3 mm. Here, the spectrometer is a SPECS Phoibos 225 allowing to acquire electron spectra up to 15 keV kinetic energy. The data shown here were measured using the Si(311) high-heatload double-crystal monochromator tuned to 6 keV resulting in an overall energy resolution of about 0.2 eV.

At either instrument, the spectrometer energy scale was calibrated using the Au 4*f* line at $BE_{Au4f} = 84.0$ eV. The UNIFIT software was used to fit the experimental data [16].

For the 5-axis precision manipulator of the P09 HAXPES system, a specialized ultra-high vacuum (UHV) compatible sample holder with 4 electrical contacts has been designed to allow *in situ* voltage biasing of the samples, enabling also to acquire spectra from the biased samples. This option provides an opportunity to monitor the changes in the chemical and electronic structure of the functional structures modeling devices under operation. The constant voltage as well as the bias sweeps to the samples were applied using an Agilent B2912A precision source/measure unit.

2.2. HAXPES methodology of band line-up determination at the metal/FE interface

The value of the electric potential barrier height φ (also known as a conduction band offset, CBO) at the metal/FE interface(s) is an important characteristics, particularly to predict the transport properties of the respective ferroelectric tunnel junction. It is defined as $\varphi = E_g - VBO_{Me/BTO}$ where E_g is the band gap of the FE and $VBO_{Me/BTO}$ is the valence band offset, *i.e.* the energy separation between the FE valence band maximum (*VBM*) and the Fermi level of the metal in contact. In order to determine the band line-up at the metal/$BaTiO_3$ interface we employ the well-known methodology described previously [17,18]. In particular, the VBO at the Pt/$BaTiO_3$ interface is calculated according to the formula (1):

$$\mathrm{VBO} = (E_{\mathrm{Ti}2p3/2} - E_{\mathrm{Pt}4f7/2})_{\mathrm{BTO/Pt}} + (E_{\mathrm{Pt}4f7/2} - E_{\mathrm{F}})_{\mathrm{Pt}} - (E_{\mathrm{Ti}2p3/2} - \mathrm{VBM})\mathrm{BTO} \quad (1)$$

where the quantities $(E_{Pt4f7/2}-E_F)$, $(E_{Ti2p3/2}-VBM)_{BTO}$ and $(E_{Pt4f7/2}-E_{Ti2p3/2})$ are measured by HAXPES on clean bulk Pt, $BaTiO_3$ and Pt/$BaTiO_3$ bi-layers, respectively. Similar measurements can be performed for the Fe/$BaTiO_3$ bi-layers. Once the band gap E_g of $BaTiO_3$ films is determined independently, the value of the potential barrier height φ is obtained.

2.3. Sample preparation

p^{++}-Si/HfO_{2-x}/ZrO_x/Pt multilayered stacks were grown by the combination of Atomic Layer Deposition (ALD) and Pulsed Laser Deposition (PLD) techniques. Details of the deposition procedure are described elsewhere [19]. Briefly, HfO_2 layers were grown by ALD on highly doped ($\rho = 0.01$ Ohm cm) p^{++}-Si substrates ($T_{subst.} = 300\,^\circ C$), while ultrathin Zr and Pt layers were separately deposited on top by PLD in a single vacuum cycle at room temperature. The thickness of the Zr interlayer $d \approx 4$ nm was optimized in terms of the resistive switching effect by separately performing *I–V* measurements on standard size ($\sim 10^{-4}\ mm^2$) MIM stacks (results will be reported elsewhere). The thickness of the Pt capping layer serving as the top electrode also has to be carefully chosen to ensure both a continuous film coverage and a sufficiently high yield of photoelectrons from the buried HfO_{2-x}/ZrO_x/Pt

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