

Tuesday Afternoon, October 29, 2013

Synchrotron Analysis Focus Topic

Room: 203 C - Session SA+AS+MG+SS-TuA

HAXPES Studies on Interfaces and Buried Layers

Moderator: A. Rossi, University of Cagliari

2:00pm SA+AS+MG+SS-TuA1 **Past and Present of Synchrotron Radiation, from Hard X-ray Photoemission to Soft X-ray and Back, P. Pianetta**, Stanford University **INVITED**

Synchrotron radiation has proven to be a very important tool for the study of materials in applications including earth sciences, energy and semiconductors. Most of the early applications focused on the study of surface phenomena using valence and core level spectroscopies using soft x-rays. Although one of the first studies at a multi-GeV synchrotron used hard x-rays, its practical use was limited by low counting rates. With the advent of high brightness synchrotron sources along with highly efficient electron energy analyzers, x-ray photoelectron spectroscopy using multi-keV x-rays has seen a rebirth for the study of buried interfaces and bulk materials properties. This talk will discuss the evolution of synchrotron radiation photoelectron spectroscopy from the early experiments to the present day.

2:40pm SA+AS+MG+SS-TuA3 **Practical use of Photoemission with Synchrotron Radiation in Nanotechnology: From Soft to Hard X-rays, O.J. Renault, E. Martinez**, CEA-LETI, France, *N. Barrett*, Cea Dsm Iramis Spcsi, France

Over the past 15 years, due to intrinsic limitations of laboratory X-ray sources, photoemission using synchrotron radiation has played an increasing role in solving issues of technologically-relevant materials and systems. With narrow spectral widths, synchrotron sources enable photoemission at uncomparable effective energy resolutions for refined assessment of chemical states at interfaces [1]. The broad energy range offers ultimate surface sensitivities with soft x-rays [2], and also much deeper photoelectron escape depths in the hard x-ray range which is crucial to investigate buried interfaces intrinsically found in devices. This contribution will highlight the advantages and achievements of hard x-ray photoemission (HAXPES) compared to soft x-ray photoemission, through a selection of recent studies performed on nanotechnological materials and devices (CMOS high-k/metal gate stacks, memory devices) [3]. Finally, we will briefly mention new developments: first, the extension of photoelectron spectroscopy (XPEEM) from chemical state and band structure imaging, to hard x-rays excitation (HAXPEEM) [4]. Second, the application of inelastic background analysis of HAXPES spectra.

[1] O. Renault *et al.*, Appl. Phys. Lett. 81 (2002), 3627; 90 (2007), 052112; J. Appl. Phys. 96 (2004) 6362; E. Martinez *et al.*, Appl. Surf. Sci. 285 (2012), 2107.

[2] K. Huang, P. Reiss, O. Renault *et al.*, ACS Nano 4 (2010), 4799; O. Renault *et al.*, Appl. Phys. Lett. 87 (2005), 163119.

[3] R. Boujama *et al.*, J. Appl. Phys. 111 (2012), 054110; P. Calka *et al.*, J. Appl. Phys. 109 (2011) 124507.

[4] C. Wiemann *et al.*, Appl. Phys. Lett. 100 (2012), 223106.

3:00pm SA+AS+MG+SS-TuA4 **Effective Attenuation Length for Titanium Nitride, Hafnium Oxide, Silicon, Silicon Dioxide, Lanthanum Lutetium Oxide, Lanthanum Calcium Manganite, and Gold from 1 keV up to 15 keV, J. Rubio-Zuazo, G.R. Castro**, SpLine Spanisch CRG beamline at the European Synchrotron Radiation Facility, France

Material composites, which combine different materials mostly multilayer hetero-structure, with specific and defined properties, are a promising way to create products with specific properties. In these materials the interfaces define many of their properties. The surfaces and interfaces play a fundamental role, and are the source of a great variety of new, and even unexpected, physical phenomena due to the existence of step changes in the structure and the electronic coordination. Third generation synchrotron radiation sources enables the extension of photoemission spectroscopy to higher electron kinetic energies (HAXPES, Hard X-ray Photoelectron Spectroscopy) compensating the decrease of the photoionization cross-section for excitation energies in the hard X-ray region. HAXPES allows the accessibility to buried interfaces and bulk materials due to the dramatic increase of the effective attenuation length (EAL). Electronic, compositional and chemical depth profiles can be then performed in a non-destructive way over the tens-of nanometers scale with nanometer depth resolution. Such an important application of HAXPES is crucial for many condensed matter experiments and requires reliable EALs for high kinetic

energy. EALs are well established for electrons with kinetic energies up to 2 keV. Even if EALs can be obtained by extrapolating well-known formulae, there is a lack of experimental data in the energy range between 1 and 15 keV. In the present study we have determined the EAL dependency on kinetic energy for titanium nitride (TiN), hafnium oxide (HfO₂), silicon (Si), silicon dioxide (SiO₂), lanthanum lutetium oxide (LaLuO₃), lanthanum calcium manganite (La_{0.66}Ca_{0.33}MnO₃), and gold (Au) from 1 keV up to 15 keV. A correlation between the EAL energy dependence and the material density is established. The EALs have been obtained by following either core level peak intensity dependence for a fixed kinetic energy as a function of the overlayer thickness or the core level peak intensity dependence with the photoelectron kinetic energy (i.e. photon energy) for a fixed overlayer thickness. The experimental set-up used is devoted to the combination of X-ray Diffraction (XRD) and HAXPES. Hence, we are able to determine the exact thickness and roughness of the layer from a fit of the X-ray reflectivity (Kiessig fringes) and simultaneously to obtain the EALs from the HAXPES signal evolution. It is important to stress that due to the simultaneous detection of the diffracted and photoemitted signal, the EALs, thickness and roughness determination correspond exactly to the same sample region.

4:00pm SA+AS+MG+SS-TuA7 **Hard X-ray Photoelectron Spectroscopy (HAXPES) Investigations of Electronic Materials and Interfaces, J.C. Woicik**, National Institute of Standards and Technology (NIST) **INVITED**

Photoelectron spectroscopy is a widely used technique that can uniquely measure the chemical and electronic structure of solids. Owing, however, to the historical use of low-energy photons and the resulting limited photoelectron inelastic mean-free path, the technique has found only general application to surfaces and shallow interfaces. With advances in both photon-source and electron-spectrometer instrumentation, hard x-ray photoelectron spectroscopy (HAXPES), where the photon energy is typically in the 2.1 – 10 keV range, has consequently emerged as a powerful tool for studying the bulk and interfacial properties of complex materials systems.

In this talk, we will discuss developments of the HAXPES technique at the NIST beamline X24A at the National Synchrotron Light Source for the study of electronic materials. Examples will include nitrogen treatment of HfO₂ gate stacks on Si, depth profiling of the HfO₂/SiO₂ interfaces, Ga and As “out-diffusion” at semiconductor/oxide interfaces, band offsets and Schottky barrier heights at semiconductor/oxide and diamond/metal interfaces, and oxygen vacancies in N doped TiO₂ and solid-oxide fuel cells. In all cases, the increased probing depth of HAXPES over traditional lab based XPS is crucial to study the electronic structure of entire overlayers and/or buried interfaces with thicknesses of industrial significance.

4:40pm SA+AS+MG+SS-TuA9 **HAXPES Study of Full High-κ/Metal Gate Stacks Deposited on Ge Substrates, C. Fleischmann, I. Kalpyris, T. Conard, C. Adelman, S. Sioncke**, IMEC, Belgium, *J.P. Rueff, J. Ablett*, Synchrotron SOLEIL, France, *W. Vandervorst*, IMEC, KU Leuven, Belgium

The introduction of Ge in CMOS devices beyond the 14 nm technology node requires effective passivation of the Ge gate stack. Besides the interface passivation, a highly scaled gate stack is needed for the next generation of CMOS devices. Scaling of the gate stack can be achieved by several means, for instance by changing process conditions. In this work, we investigate the influence of both the high-κ stack and the metal gate on the properties of a GeO_xS_y interfacial passivation layer by Hard X-ray Photoelectron Spectroscopy (HAXPES). Using high energy x-rays (4 to 8 keV), we are able to probe the buried interface between the high-κ layer and the Ge substrate, and hence to reveal direct information on the chemistry and the thickness of the GeO_xS_y passivation layer. Note that such a buried interface is not accessible using a “standard” XPS tool relying on Al K_α x-ray radiation.

In this study, we considered three high-κ materials (Al₂O₃, HfO₂ and an Al₂O₃/HfO₂ bi-layer) and three metal gates (TiN, TiW and Pt). Samples have been measured both directly after atomic layer deposition and after forming gas anneal, to investigate the effect of a thermal treatment on the interfacial properties. To disentangle the impact of the particular metal gate, comparison is made to a high-κ stack sample without metal gate.

We first demonstrate the importance of analyzing full stacks, as no effect of annealing was observed on the stacks without metal gates, while clear modification of the Ge/high-κ interfacial layer thickness is observed when a gate is present. We then show that this effect on interfacial layer thickness depends on both the high-κ and the metal gate material used. This can lead

for example to an increase (i.e. HfO_2/TiN) or to a decrease (i.e. $\text{Al}_2\text{O}_3/\text{TiN}$) of the interfacial layer thickness after annealing. As a global trend, the thinnest interfacial layers are obtained for pure Al_2O_3 . However, the interfacial layer thickness appears to be more sensitive to variations in the metal gate rather than the high- κ material. We also show that the introduction of a very thin Al_2O_3 layer ($\sim 2 \text{ \AA}$) between the Ge substrate and the HfO_2 layer strongly influences this observed sensitivity of the interfacial layer properties to the metal gate and forming gas anneal. Aside from quantifying the interfacial layer thickness, we will also analyze changes in the interfacial layer from a chemical point of view. As a conclusion, the final layer structure (hence, the Equivalent Oxide Thickness of the gate stack) is thus a complex interplay between the initial GeO_xS_y thickness before forming gas anneal and the chemistry of the high- κ and metal gate materials.

5:00pm **SA+AS+MG+SS-TuA10 X-ray Absorption Spectroscopy of Magnetic/Ferroelectric Complex Oxide Interfaces**, *M.B. Holcomb, J. Zhou, D. Chen*, West Virginia University, *C. Jenkins, M.A. Marcus*, Lawrence Berkeley National Laboratory, *Y.-H. Chu*, National Chiao Tung University, Taiwan, Republic of China

Magnetoelectric coupling (the electrical control of magnetic properties or vice versa) has promising applications in computer memory and logic, magnetic sensing and energy scavenging. Magnetoelectric interfaces are a potential new method to improving magnetoelectric coupling strength and controllability. We utilize x-ray absorption spectroscopy, photoemission electron microscopy, and second harmonic generation to understand both the order parameters of the individual layers and the resulting interface. This talk will focus on bilayers composed of ferromagnetic $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO) and ferroelectric $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ (PZT). Through photoemission electron microscopy imaging, ME coupling was confirmed at the interface. X-ray absorption spectroscopy of Mn was taken across wedged samples of varying ferroelectric and ferromagnetic thicknesses. The change of Mn valences at different thicknesses of LSMO and PZT helps to understand ME coupling and impact of thickness on the ME properties. This work suggests a strategy for improving not only magnetoelectric devices, but also magnetic systems. This work is supported by West Virginia's Higher Education Policy Commission.

5:20pm **SA+AS+MG+SS-TuA11 Local-Structure Determination Using Combined Fitting of EXAFS and Neutron Total Scattering Data**, *I. Levin*, National Institute of Standards and Technology **INVITED**

The functional responses of many industrially-relevant materials are controlled by their *local structure* – a term that refers to the atomic arrangements on a scale ranging from atomic (sub-nanometer) to several nanometers. Today, multiple experimental techniques exist for probing the local atomic order. Nonetheless, finding accurate comprehensive structural solutions still remains a challenge, because any one of the existing methods yields only a partial view of the structure. In this talk, we will discuss recent advances in local-structure determination using simultaneous fitting of EXAFS, X-ray/neutron total scattering, and electron diffuse scattering data. Examples will include several representative perovskite systems that find use as dielectrics and ferroelectrics.

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