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X-ray photoelectron spectroscopy analysis as a tool to assess factors influencing magnetic anisotropy type in Co/MgO system with gold interlayer

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ABSTRACT

X-ray photoelectron spectroscopy (XPS) studies of Au/Co/Au(0.3 nm)/MgO and Au/Co/MgO systems were conducted in order to monitor the electronic structure modification at Co/MgO interface with/without gold interlayer. A detailed analysis of Co 2*p* states revealed that the amount of minor oxygen contribution at Co/MgO interface decreased after the Au interlayer was added. The obtained XPS results together with density functional theory (DFT) allowed explanation of the increase of surface anisotropy energy in the sample with the gold interlayer in terms of (i) noble and transitional metal *d*-*d* orbital hybridization; (ii) interfacial Co 3*d* and O 2*p*; and (iii) interface imperfection.

A phenomenon of perpendicular magnetic anisotropy (PMA) in Co films combined with Pd, Pt, Au multilayers [1] has opened an exciting field of research inquiring the fundamental origin of PMA and a role of interfacial orbital hybridization [2,3]. Other systems where PMA is noticed are systems based on F/MO_x interfaces, where F represents a ferromagnetic metal, M stands for a diamagnetic metal, and MO_x marks a nonmagnetic oxide (i.e., isolator). The PMA appears when the interface anisotropy energy overcomes the magnetostatic and volume energy contributions to the free energy of the magnetic layer. This type of magnetic anisotropy, a so-called interface or surface anisotropy, was predicted already in 1954 by Néel and is a result of lowering symmetry at the surface or interface. Up to now, many PMA materials have been advanced and implemented in magnetic tunnel junctions (MTJs) [4,5]. However, the development of PMA in materials based on F/MO_x interfaces is still problematic due to incomplete understanding of its causes. Some researchers declare that PMA can be created only through a hybridization of F 3*d* and O 2*p* orbitals at the F/MO_x interface, while others show that placing an appropriate underlying nonmagnetic material is critical for developing PMA [6–10]. Studies of the electronic structures of F/MO_x linked together with magnetic measurements and theoretical studies should, hopefully, lead to a full understanding of PMA in such systems.

XPS is one of the primary tools used to analyze the interfaces utilizing either conventional X-ray tubes or complex synchrotron sources. These studies are frequently accompanied by sputtering to investigate depth dependence of XPS signals. That, however, may lead to unambiguous results due to the fact that an interpretation of XPS data for buried interfaces recorded in combination with ion sputtering procedure should be performed with special care as sputtering itself can seriously affect the interlayer structure [11]. One should remember that ion sputtering, even when using noble gas ions, generates a large number of artifacts in subsurface region, as for instance, atomic mixing and knock-on implantation, preferential sputtering, bond breaking, phase formation, segregation, radiation-enhanced diffusion, roughness formation, etc. Such effects have been studied over the last decades and critical reviews of their influences on surface analytical techniques were published [12–16]. Taking into account the knowledge gathered within experimental observation of electronic structure modification due to sputtering procedure, it was decided to abandon it and study potential electronic structure modification at Co/MgO interface after addition of the thin layer of Au without sputtering procedure.

The samples containing Co/MgO interface with and without a thin gold interlayer in-between were grown onto a-plane sapphire substrate at room temperature by molecular beam epitaxy (MBE). Complete

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details of their growth procedure can be found in [6]. The thicknesses of each layer in the samples were identified as Mo(20 nm)/Au(20 nm)/Co(1.8 nm)/Au(0.3 nm)/MgO(2 nm) (Sample 1) and Mo(20 nm)/Au(20 nm)/Co(1.8 nm)/MgO(5 nm) (Sample 2).

Ferromagnetic resonance (FMR) measurements were performed at room temperature with a conventional X-band ($f = 9.38$ GHz) Bruker EMX spectrometer. A quartz rod was used as a sample holder and the FMR resonance field (H_{res}) was recorded as a function of the angle (θ_H) between the direction of the external magnetic field (H_{ext}) and normal to the sample's surface. In case of Sample 2 (with Co/MgO interface) a maximum ($\mu_0 H_{res} = 0.73$ T) and minimum ($\mu_0 H_{res} = 0.17$ T) of H_{res} were observed for perpendicular and parallel orientations of the external magnetic field, respectively. These values indicate an easy axis of magnetization in the plane of the magnetic layer, i.e. in-plane magnetic anisotropy (IMA), see Fig. 1(d). However, the structure with the gold incorporated at Co/MgO interface (Sample 1) has a maximum ($\mu_0 H_{res} = 0.41$ T) and minimum ($\mu_0 H_{res} = 0.13$ T) of H_{res} for parallel and perpendicular orientations of the H_{ext}, respectively: easy axis of magnetization is perpendicular to the plane now, see Fig. 1(c). A significant enhancement of the surface anisotropy energy of cobalt layer ($d_{Co} \sim 1.8$ nm) occurs due to insertion of a gold monolayer between Co and MgO, such that it overcomes the shape and magnetocrystalline magnetic anisotropy leading to PMA.

In order to understand the origins of this effect, the samples were studied by XPS using a Scienta/Prevac spectrometer system with monochromatic Al Kα radiation ($h\nu = 1486.6$ eV) from an X-ray source (ScientaVG, MX650) irradiating a spot size of 6×2 mm^2 while operating at 300 W. The high resolution (HR) XPS spectra were collected with the hemispherical analyzer (ScientaVG R4000) at two different take-off angles (0°, and 60° to the surface's normal) with a pass energy of 100 eV and an energy step size of 0.15 eV. Let us note that for the used spectrometer set-up the FWHM of Ag 3*d* line is about 0.6 eV. The slit of the analyzer has a curved shape with the dimension 0.5×25 mm^2 (width vs. length), whereas angular aperture had 2 mm diameter which sets the acceptance angle to ±7°. Only the surface of the reference sample (Co film) was cleaned from carbon contamination and native cobalt oxides using the Ar ion source (Prevac IS40E) at 0.8–1.4 kV. The incident angle of the Ar ion beam is 69° from sample normal and the sputter area was 10×10 mm^2. A charge compensation for the investigated multilayers was achieved using a low energy electron flood gun (at ~1.1–6.7 eV). Binding energies of the photoelectrons were calibrated using gold $4f_{7/2}$ line (84 eV). The CasaXPS software (version 2.3.17) [17] was used to evaluate the XPS data. Simulation of Electron Spectra for Surface Analysis (SESSA) software [18] was used to estimate thicknesses and composition of examined layers. The details of such analysis could be found in [16].

The HR XPS spectra for Sample 1 (with the gold interlayer) are shown in Fig. 1(a, b). As it was mentioned above, the Au $4f_{7/2}$ photopeak maximum, located at 84 eV, was taken for calibration of energy scale (see Fig. 1(a)). The Au $4f_{5/2}$ peak is overlapped with the Mg 2*s* states corresponding to various oxides of magnesium (marked as “3” and “4”) with binding energies (BE) of 88.6 and 89.3 eV. The obtained values agree well with the data presented in the literature [19], in which the Mg 2*s* peak positions of $Mg(OH)_2$, $MgCO_3$, and MgO are listed at the energies 89.2 eV, 89.3 eV, and 88.6 eV, respectively. Motivated by the uniqueness of peak shapes and positions within Auger spectra, which is useful for both elemental identification and chemical state analyses, a detailed analysis of Auger Mg KLL line in conjunction with Mg 1*s* XPS peak was performed (XPS spectra in the BE ranges 300–360 and 1300–1310 eV are not shown here). So-called Auger parameters (α) that can be used without interference of surface charging were identified. For each of the samples two Auger parameters for magnesium were found to be 998.6 and 997.7 eV. According to [20] the estimated values represent MgO and $Mg(OH)_2$&$MgCO_3$ species, respectively. Consequently, the electronic states corresponding to the mentioned above species reflect interaction of originally pure MgO phase (in the top layer) with atmosphere and following carbon contamination. According to SESSA calculations the thicknesses of that sub-layer and the following MgO one are ~20 ± 2 Å. The estimated thickness agrees well with the nominal one predicted from the growth process.

As our interest focuses on the top Co/MgO interface let us discuss the results for Co 2*p* line represented in Fig. 1(b). The parameters of deconvolution of Co $2p_{3/2}$ lines for Samples 1 and 2 are summarized in Table 1. The presented in Fig. 1(b) data are background subtracted and normalized to the maximum of Co^0 $2p_{3/2}$ peak intensity for clarity. They are compared to metallic cobalt film (reference sample) before and after surface cleaning. On the pristine reference sample one can distinguish two distinctive components corresponding to the metallic cobalt (Co^0, BE of $2p_{3/2}$: 778.0 ± 0.15 eV) and cobalt monoxide (Co(II)O, BE of $2p_{3/2}$: 780.2 ± 0.15 eV). The observed ‘chemical shift’ is an effective indicator of the charge transfer between O 2*p* and Co 3*d* states. Furthermore, one observes an Auger peak (Co LMM: 777 ± 0.15 eV) and satellite structures (marked “S” in Fig. 1(b)) at higher binding energy for the reference sample before and after sputtering. An explanation of Co 2*p* XPS spectral shape of cobalt dihalides and CoO was developed in [21,22] taking into account the 3*d*-multiplet coupling and the covalency hybridization among $3d^7$, $3d^8\underline{L}$, and $3d^9\underline{L}^2$ configurations (here $\underline{L}$ denotes a hole in the ligand orbital). According to such interpretation,

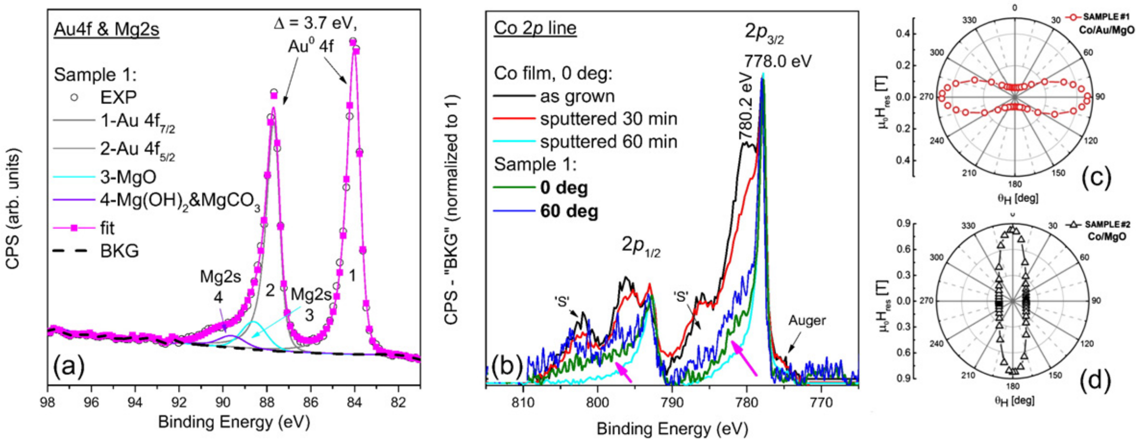

Fig. 1. XPS spectra for Sample 1 (Co/MgO interface with the gold interlayer): (a) split of Au 4*f* and Mg 2*s* states; (b) Co 2*p* states compared to metallic cobalt (after and before surface cleaning, see text for details); (c) Auger Mg KLL; (d) Mg 1*s* line. The polar angle dependence of the resonant field as a function of the angle between the direction of external magnetic field H_{ext}, and the normal to the sample surface for (c) Sample 1: Au(20 nm)/Co (1.8 nm)/Au(0.3 nm)/MgO(2 nm) and (d) Sample 2: Au(20 nm)/Co(1.8 nm)/MgO(5 nm).