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Effect of interfacial iron oxidation on the exchange bias in CoO/Fe bilayers

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ABSTRACT

The relation between the interface structure and the exchange bias was studied in the epitaxial CoO/Fe(0 0 1) bilayers that were grown on MgO(0 0 1) using molecular beam epitaxy. Three samples with different interface structures were prepared. The CoO/Fe bilayer, which was prepared using the reactive evaporation of CoO, served as the reference sample. In the other two samples, the CoO/Fe interfaces were modified prior to the CoO growth using either (i) the deposition of a 2 Å thick Co layer or (ii) an exposure to molecular oxygen, which resulted in under- and over-oxidized CoO/Fe interfaces, respectively. The actual structures of the resulting interfaces were revealed using conversion electron Mössbauer spectroscopy. For each sample, an iron oxide was found at the interface, and its amount depended on the sample preparation recipe. The exchange bias effect (EB), as a function of the temperature, was experimentally studied in detail using VSM magnetometry. The coercivity showed a distinct peak near the blocking temperature for all samples; however, the peak's location and its width were diverse. The obtained EB values depended on the interface structure. The largest hysteresis loop shift (H_{EB} = 180 Oe at 4 K) was obtained for the sample with the thickest interfacial iron oxide layer.

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1. Introduction

Magnetic multilayer systems are important constituents of magnetic memories, sensors, spin valves and reading heads [1,2]. Despite their wide applicability, these systems are the subjects of great scientific study [3,4] to fully understand the physics involved in their performance. One of the interesting effects for basic research is the exchange bias (EB), which occurs in the ferromagnetic (FM)–antiferromagnetic (AFM) systems [5]. EB manifests itself from the horizontal shift of the magnetic hysteresis loop, which is accompanied by increased coercivity. Although EB was discovered a few decades ago [6] and many theoretical models have been developed to describe it [7–10], there is no general model to explain all of the experimental findings. Therefore, detailed investigations on the model FM–AFM systems are required to generate conclusions of the more universal character.

To observe EB, the sample must be either grown in an external magnetic field or subjected to the field-cooling procedure (FC), during which the system is cooled down through the Néel temperature of the AFM layer in the presence of a static magnetic field [5]. The magnetic ordering of the AFM layer, which is established at the interface with the FM layer, affects the magnetization reversal of the FM layer. The true interfacial character of this effect is proposed in a simple phenomenological description and supported by the inverse proportionality of the loop shift as a function of the FM layer thickness [5]. Furthermore, EB depends on the details of the interface structure, such as the atomic-scale roughness [11,12] and the magnetic (un-)compensation of the AFM surface [13]. Chemical reactions and intermixing at the FM/AFM interfaces [14] are also expected to influence EB; however, the systematic studies that are focused on this issue are scarce [15].

In this study, we investigated the interplay between the interface composition and the magnetic properties of the CoO/Fe bilayers, which were grown on MgO(0 0 1). Fe–CoO bilayers are good candidates for the model EB systems because their crystallographic match results in a reasonable structural quality of the epitaxial bilayers. Moreover, CoO has a high magnetocrystalline anisotropy, which enhances the EB; an easily accessible Néel temperature (T_N = 293 K); and a simple NaCl-type crystal structure.

The Fe–CoO bilayers were formed using epitaxial Fe(0 0 1) films on MgO(0 0 1). Three different preparation recipes were used to obtain the interfaces with various Fe oxidation levels. The CoO layer in the reference bilayer (REF) was prepared using the standard reactive evaporation of Co in an oxygen atmosphere, which followed

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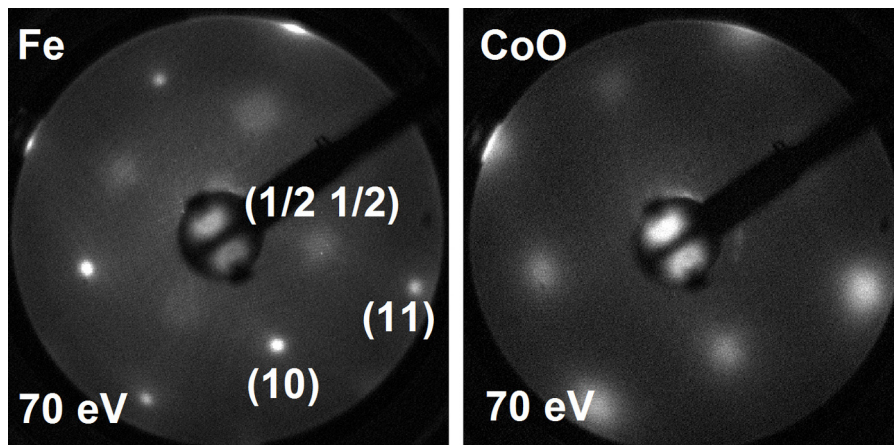*E-mail address:* mlynczak@agh.edu.pl (E. Młyńczak).

Fig. 1. LEED patterns for Fe (left) and CoO (right) for the sample REF.

the procedure described in our previous paper [16]. In the other two samples, the interface between Fe and CoO was modified by: (i) preventing Fe oxidation using an interfacial ultra-thin buffer layer of metallic Co (sample Ox⁻) or (ii) additional oxygen exposure of the Fe film surface before the CoO deposition (sample Ox⁺). The structure and the composition of the CoO/Fe interfaces were characterized using conversion electron Mössbauer spectroscopy (CEMS), and they were related to the magnetic properties studied using a vibrating sample magnetometer (VSM).

2. Experimental procedure

The samples were prepared in a multi-chamber ultra-high vacuum (UHV) system using molecular beam epitaxy (MBE). The metals (^{56}Fe, ^{57}Fe and Co) were evaporated from the thermally heated BeO crucibles. The MgO(0 0 1) substrates were cleaved in air, degassed under UHV conditions and annealed at 600 °C for 1 h. The ^{56}Fe films, which were 190 Å thick, were deposited on MgO(0 0 1) at room temperature and annealed at 530 °C for 30 min to obtain atomically flat surface. Next, a 10 Å layer of ^{57}Fe was deposited at 180 °C to serve as the Mössbauer probe. For the reference sample (REF), the 20 Å CoO layer was prepared using the reactive evaporation of Co under an oxygen partial pressure of 1×10^{-6} mbar at 180 °C. The structures of the other two samples were modified before the CoO deposition. For the under-oxidized sample (Ox⁻), a 2 Å layer of metallic Co was deposited; for the over-oxidized sample, the surface of the ^{57}Fe probe layer was exposed to 30 L of molecular oxygen at 180 °C. All of the CoO layers in the Fe–CoO bilayers were epitaxial with Fe(0 0 1), as verified using low-energy electron diffraction (LEED). The exemplary LEED patterns, which were obtained from the surfaces of the Fe and CoO layers for the sample REF, are shown in Fig. 1. For the Fe layer, the LEED spots were sharp, which proved a good crystalline quality. However, the additional spots of the $(\sqrt{2} \times \sqrt{2})$R45° reconstruction were visible for all samples, which we interpreted as the carbon segregation from the MgO substrate [17]. The spots of the CoO LEED pattern were slightly diffused, which indicates that CoO has a lower structural quality than the Fe film. This result is analogous to the CoO/Fe(0 0 1) bilayer structure that was reported by Brambilla et al. [18]. All of the samples were capped with 50 Å of MgO to allow *ex situ* measurements.

The *ex situ* CEMS experiments were performed at room temperature (RT) using a 100 mCi ^{57}Co(Rh) source, a standard Mössbauer spectrometer and a He/CH₄ flow proportional detector. The spectra were collected under the normal-incidence geometry and numerically analyzed using a commercial software, where the hyperfine magnetic field distribution was approximated using a sum of the

Gaussian components [19]. The number of Gaussian components was gradually increased to a minimum number of fitting parameters, which ensured a statistically good fit.

The dc magnetization was measured using the VSM option of the Quantum Design Physical Property Measurement System (PPMS). The magnetic hysteresis loops were measured *ex situ* at selected temperatures in the 4–320 K range with the magnetic field (up to ±20 kOe) applied along the Fe[1 1 0] direction after field cooling (FC). To exclude the reduction of the exchange bias field H_{EB} due to the training effects, after taking the hysteresis loop for each temperature, the sample was heated to $T = 320$ K, which is approximately 30 K above the Néel temperature of the bulk CoO; then, the sample was field-cooled at −20 kOe to a chosen temperature. The hysteresis loops were analyzed using the coercive field $H_C = (|H_{C1}| + |H_{C2}|)/2$ and the exchange bias field $H_{EB} = (|H_{C1}| - |H_{C2}|)/2$, where H_{C1} and H_{C2} were the coercive fields of the ascending and descending branches of the hysteresis loop, respectively.

3. Results and discussion

To verify the actual structure of the formed interfaces, the CEMS measurements were performed. The CEMS spectra were deconvoluted into sextets, which were grouped into sites (M, O₁, O₂) according to the values of the isomer shift (IS) and hyperfine magnetic field (B_{hf}). The fitted spectra that present the identified sites are shown in Fig. 2, whereas the average hyperfine parameters (weighted on the relative weights of each sextet) are listed in Table 1.

The isomer shift values (reported relative to α-Fe), indicate the oxidation state of the probe atoms. The components with IS values that were equal to or approximately zero corresponded to the metallic atoms, whereas the positive IS values indicated the oxidation of the corresponding atoms. The relative weight of each component directly reflects the relative contribution of the probe atoms in the given state. Thus, an iron oxide detected at the CoO/Fe interfaces constituted 60%, 37% and 86% of the probe layers for the REF, Ox⁻ and Ox⁺ samples, respectively. These values demonstrate that the applied preparation recipes resulted in the expected variations in the amount of interfacial iron oxide.

The spectra that contained a relatively strong metallic Fe signal (REF and Ox⁻) required the application of two metallic components, which are listed separately in Table 1. For both cases, one metallic component reflected the Fe atoms with the hyperfine magnetic field (B_{hf}) that corresponded to the bulk value for α-Fe ($B_{hf} = 33$ T at RT [20]), which suggested that the corresponding atoms were far from the interface with CoO, i.e., near the ^{57}Fe/^{56}Fe interface. The other metallic component was characterized by the