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Dehydrogenation at the Fe/Lu_2O_3 interface upon rapid thermal annealing

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ABSTRACT

The interfaces between ferromagnetic electrodes and tunnel oxides play a crucial role in determining the performances of spin-based electronic devices, such as magnetic tunnel junctions. Therefore, a deep knowledge of the structural, chemical, and magnetic properties of the buried interfaces is required. We study the influence of rapid thermal annealing treatments up to 500 °C on the interfacial properties of the Fe/Lu_2O_3 system. As-grown stacks reveal the presence of hydrogenated Fe–Lu–H intermetallic phases at the Fe/Lu_2O_3 interface most likely due to the H absorption on the Lu_2O_3 surface upon exposure to air and/or to the oxide growth. The annealing treatments induce remarkable changes of the structural, chemical, and magnetic properties at the interface, as evidenced at the atomic scale by the sub-monolayer sensitivity of conversion electron Mössbauer spectroscopy. The use of complementary techniques such as X-ray diffraction, time-of-flight secondary ion mass spectrometry, and *in situ* X-ray photoelectron spectroscopy, confirms that the main effect of the annealing is to gradually promote the dehydrogenation at the Fe/Lu_2O_3 interface.

1. Introduction

The study of the Fe/oxide interfaces properties at the atomic scale represents a fundamental step towards their efficient inclusion in novel spin-based electronic devices, such as magnetic tunnel junctions (MTJs) [1]. A MTJ stack includes two ferromagnetic (FM) layers separated by a tunnel barrier. The chemical bonding at the FM/oxide interfaces and the interfacial density of states dramatically influence the MTJ performances, while the presence of paramagnetic layers at the interface has a detrimental effect on the tunnel magnetoresistance (TMR) [2]. A deep knowledge of the structural and magnetic properties of the buried interfaces is, therefore, required for a better engineering of MTJ devices.

We have already reported the study of as-deposited interfaces between Fe and different oxides (Al_2O_3, ZrO_2, HfO_2, and Lu_2O_3) [3]. These interfaces have been compared by considering the Fe atoms reactivity at the interface (intermixing), as estimated by conversion electron Mössbauer spectroscopy (CEMS) [3]. We found that the largest intermixing occurs at the Fe/Lu_2O_3 interface, and we attributed this result to the formation of intermetallic phases and hydrogenated intermetallic compounds [2]. The rapid thermal annealing (RTA) processes are known to be beneficial for improving the TMR and the thermal stability of MTJs [4]. In this contribution, we use the sub-monolayer sensitivity of CEMS to investigate the structural, chemical, and magnetic changes at the Fe/Lu_2O_3 interface upon RTA. Complementary information is obtained by grazing incidence X-ray diffraction (XRD) and time-of-flight secondary ion mass spectrometry (ToF SIMS). The early stage of the Fe/Lu_2O_3 interface formation is investigated by *in situ* X-ray photoelectron spectroscopy (XPS). Our results show that RTA treatments induce a gradual desorption of hydrogen from the Fe/Lu_2O_3 interface, leaving the α-Fe and the intermetallic Fe–Lu phases in contact with Lu_2O_3.

2. Experimental

The Lu_2O_3 layers (nominal 20 nm thick) are deposited at 360 °C by atomic layer deposition (ALD) on a Si(1 0 0) substrate, by using the bis-cyclopentadienyl complex $\{[C_5H_4(SiM_3)]_2LuCl\}_2$ and H_2O as Lu and O sources, respectively [5]. The oxide surface roughness is around 2.4 nm, as measured by atomic force microscopy [3]. Pulsed laser deposition (PLD) at room temperature (RT) is used to

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deposit a thin ^{57}Fe tracer layer (~2 nm) in contact with Lu_2O_3, followed by the deposition of ^{54}Fe layer. CEMS is therefore sensitive to the Fe/Lu_2O_3 interface, being unaffected by the surface oxidation of Fe. Second sample, only containing the ^{54}Fe isotope (nominal 10 nm Fe), has been prepared for the XRD analyses. From here on, we indicate the sample used for CEMS as Fe(20 nm)/Lu_2O_3 and the sample with only ^{54}Fe as Fe(10 nm)/Lu_2O_3. A third Lu_2O_3 substrate is used for performing XPS *in situ* during the PLD of a 2 nm thick Fe layer. Following the Fe deposition, this sample has been vacuum annealed *in situ* at 500 °C for 3 min, and characterized by XPS with a XSAM-800 spectrometer (MgK_α source, $E = 1253.6$ eV) coupled with the PLD chamber.

The RTA has been performed in Ar ambient in two separate stages: 300 °C for 15 s and 500 °C for 15 s, followed by a 6 min cool down. The CEMS and XRD analyses have been performed *ex situ* on corresponding samples before and after each RTA. CEMS has been carried out at RT by using a ^{57}Co source embedded in a Rh matrix (activity ~30 mCi when the measurements were performed), which is moved by a standard constant acceleration drive. The samples are incorporated as electrodes in a parallel-plate avalanche counter, which is filled with 180 mbar of a He–CH_4 counting gas [6]. Operating voltages are around 700 V. The spectra are fitted with the least-squares fitting program NORMOS 90 [7]. The XRD data are taken with an ItalStructures HRD3000 diffractometer equipped with a position sensitive curve detector. The data are analysed by using the software package MAUD [8]. ToF SIMS analysis is performed after RTA at 500 °C on the Fe(20 nm)/Lu_2O_3 sample, with a IONTOF IV instrument using Ga^+ ions at 25 keV for analysis and Cs^+ ions at 0.5 keV for sputtering.

3. Results and discussion

Fig. 1 shows the CEM-spectra of the as-deposited Fe/Lu_2O_3 interface and after RTA at 300 and 500 °C. The CEM-spectra evidence the typical Mössbauer sextet of α-Fe, component *a* in Fig. 1(a), showing hyperfine field (B_{hf}) of 33 T due to non-interacting ^{57}Fe atoms, a distribution of magnetically split sextets *b*, and a paramagnetic doublet *c*. The distribution *b* has been attributed to the presence of the $LuFe_2$ intermetallic phase at the Fe/Lu_2O_3 interface, together with the existence of a hydrogenated intermetallic compound $LuFe_2H_x$ [3]. The incorporation of H at the interface has been attributed to the two-step process necessary to deposit the Fe layer by PLD on top of the Lu-oxide, which is exposed to air following the ALD and/or the ALD process itself [3]. The doublet *c* is possibly related to a small fraction (~2%) of a binary Fe–Lu amorphous alloy [3]. When compared with the CEM-spectrum reported in Ref. [3] for the same sample, we now use a larger velocity scale. Some additional contributions coming from sextets having $B_{hf} \geqslant 33$ T are now identified in the distribution *b*. Similar increase of B_{hf} for Fe atoms in contact with oxide layers has been previously observed [9]. To exclude the presence of any FeO_x magnetic oxides, spectra with an even larger velocity scale were recorded (not shown). In fact, the presence of Fe_2O_3 and/or Fe_3O_4 could be easily detected as the CEM-spectra of these phases are characterized by magnetically split sextets having B_{hf} around 50 T [10]. These phases are not detected at the Fe/Lu_2O_3 interface either on the as-deposited or on the annealed samples. According to CEMS results, the RTA at 300 °C is beneficial in reducing the relative fraction (of the total spectral area) of the distribution *b* from ~71% to 58%, Fig. 1(b). In particular, we observe a large decrease of the contribution from the components having the B_{hf} in the 25–30 T range, which are related to the hydrogenated $LuFe_2H_x$. Further, a drastic decrease of the intermixing at the Fe/Lu_2O_3 interface is observed after the RTA at

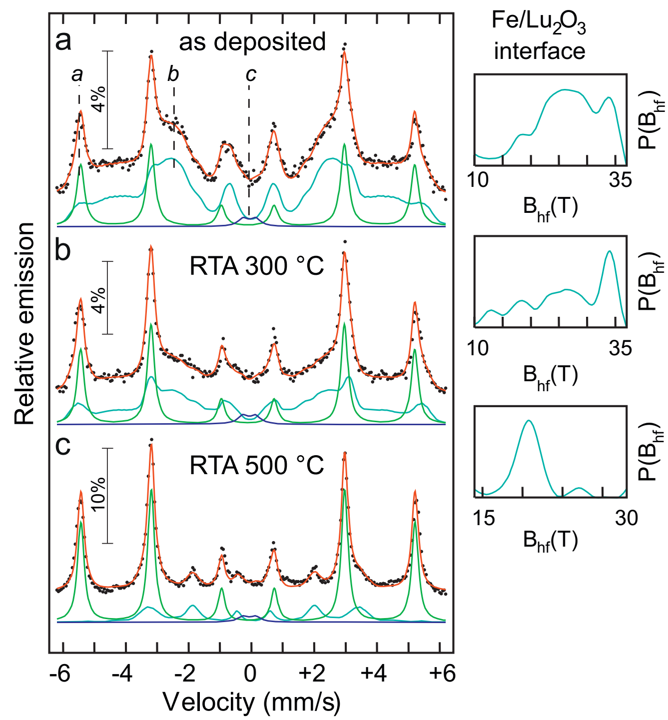

Fig. 1. (Colour online) (a) CEM-spectrum of the Fe/Lu_2O_3 interface as-deposited and after (b) RTA at 300 °C and (c) RTA at 500 °C. CEMS detects the presence of α-Fe, ($LuFe_2$+$LuFe_2H_x$), and a small fraction of Lu-rich Lu–Fe phase, as indicated in the figure with *a*, *b*, and *c*, respectively.

500 °C, when the spectral contribution from the distribution *b* is reduced to 22% of the total intensity, Fig. 1(c). This is attributed to the almost complete disappearance of the hydrogenated intermetallic contribution from the Fe/Lu_2O_3 interface. The CEMS results are substantiated by the XRD, ToF SIMS, and XPS analyses as discussed later. After RTA at 500 °C, the main peak in the B_{hf} distribution is around 20 T, which is very close to the B_{hf} observed by Mössbauer spectroscopy for the $LuFe_2$ crystalline compound at RT [11]. The spectral area of component *c* remains almost constant throughout the RTA treatments. The isomer shift and the quadrupole splitting values of the *a*, *b*, and *c* components in the CEM-spectra after RTA do not show any significant difference with respect to those observed for the as-deposited interface [3].

The XRD spectrum for the as-deposited Fe(10 nm)/Lu_2O_3 sample, shown in Fig. 2(a), reveals characteristic features of the diffraction patterns of Lu_2O_3, α-Fe, $LuFe_2$, LuO(OH), and $LuFe_2H_3$ further supporting the presence of hydrogenated compounds at the Fe/Lu_2O_3 interface [12]. Following the RTA at 300 and 500 °C, XRD shows a gradual decrease of the contributions from the hydrogenated compounds confirming the CEMS results, Fig. 2(b). Although a slight reduction of the Lu_2O_3 lattice parameter (within 0.2%) cannot be excluded, the main effect of the 500 °C annealing on the diffraction pattern is the reduction of the LuO(OH) and $LuFe_2H_3$ related components.

We performed ToF SIMS analysis on the Fe(20 nm)/Lu_2O_3 sample after RTA at 500 °C, and the results are reported in Fig. 3. The uniform distribution of the OH signal through the Fe and Lu_2O_3 layers, strongly supports the hypothesis for a dehydrogenation process taking place at the Fe/Lu_2O_3 interface, as suggested by CEMS. ToF SIMS evidences also a partial interdiffusion at the Fe/Lu_2O_3 interface. This aspect could be crucial in view of the inclusion of the Fe/Lu_2O_3 system in devices such as MTJs, and is currently under investigation.

To further investigate the structural modifications taking place at the Fe/Lu_2O_3 interface, we have performed *in situ* XPS during