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Observation of an asymmetrical effect when introducing Zr in Mg/Co multilayers

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We have developed Mg/Co, Mg/Zr/Co, Mg/Co/Zr, and Mg/Zr/Co/Zr periodic multilayers and measured at 25.1 nm a reflectivity (R) highly sensitive to the material order within the period. To understand why Mg/Co/Zr is a more efficient mirror (R=50%) than Mg/Zr/Co and Mg/Zr/Co/Zr (~40%), we have probed the interface quality through time-of-flight secondary ion mass spectrometry and nuclear magnetic resonance measurements. The Zr-on-Co interface is found quite sharp while a strong intermixing process is evidenced between the upper Co and lower Zr layers, responsible for the decrease in optical contrast and subsequent R loss. © 2011 American Institute of Physics. [doi:10.1063/1.3601859]

We have developed Mg/Co, Mg/Zr/Co, Mg/Co/Zr, and Mg/Zr/Co/Zr nanometric periodic multilayers to build efficient mirrors for applications in the extreme ultraviolet (EUV) range.^{1,2} For *s*-polarized light, the experimental peak reflectivity at 25.1 nm and 45° of grazing incidence for Mg/Co, Mg/Zr/Co, Mg/Co/Zr, and Mg/Zr/Co/Zr is equal to 42.4%, 41.4%, 50.0%, and 40.6%, respectively. Introducing a Zr layer at one or at the other interface or at both interfaces of Mg/Co does not induce an equivalent effect on the optical performances.² We are interested in understanding this asymmetrical “behavior” by correlating the mirror reflectivity to the quality of its interfaces. Sharp interfaces are required to ensure the highest reflectance, but the choice of the material combination is highly important as well as the order of the sequence within a period, for multilayers made of more than two materials.³

To describe the interface composition and structure, we have performed time-of-flight secondary ion mass spectrometry (ToF-SIMS) to get information about the chemical and elemental distribution, and nuclear magnetic resonance (NMR) spectroscopy to probe the chemical state of the magnetic Co atoms. To check the reliability of the stack structure reconstructed from ToF-SIMS and NMR analysis, we compare, for a given multilayer, the simulated EUV reflectivity curve to that measured at the ELETTRA synchrotron.² In a previous work based on X-ray emission spectroscopy (XES),¹ the chemical state of the Mg atoms within Mg/Co was found to be the same as in Mg metal: no noticeable interaction between the Mg and Co layers was evidenced. We have checked that the same result remains valid for Mg/Zr/Co, Mg/Co/Zr, and Mg/Zr/Co/Zr.

All multilayers were deposited using magnetron sputtering.² Each sample consists of 30 periods and exhibits a 3.5-nm-thick B₄C capping layer to prevent oxidation. In the following list, the first mention concerns the first layer deposited onto the Si substrate and the thickness is expressed in nm: Mg (14.45)/Co (2.55); Mg (13.20)/Zr (1.50)/Co (2.50); Mg (13.20)/Co (2.50)/Zr (1.50); Mg (12.00)/Zr (1.50)/Co (2.00)/Zr (1.50).

Depth elemental distributions are measured using ToF-SIMS working in the dual beam mode: both Bi⁺ primary and Cs⁺ sputtering ion beams are aligned to analyze secondary ions from the center of the sputtered crater. Here, we present only the Co⁻ ion depth profile since the Mg⁻ ion yield is very low and the Zr layers are too thin to provide Zr⁻ profiles exhibiting clear periodic oscillations. As a consequence, in the following we will not discuss the quality of the Mg-on-Zr and Zr-on-Mg interfaces. However, our XES analysis concluded that there was no significant interaction between Mg and Zr layers (unpublished). As sputtering yields can vary drastically, the sputtering time scale is not converted into a thickness scale and the profile intensity is not related to the number of atoms. The sample is analyzed from the surface down to the substrate.

The multilayers are analyzed using zero field NMR spectroscopy operating a broadband spectrometer working at 4.2 K. The NMR spectra depict the Co atom distribution as a function of their resonance frequency.^{4,5} Since the presence of alien atoms as nearest neighbor of Co atoms shifts the resonance frequency, this technique is powerful to probe the Co local environment. All spectra are normalized to the sample surface area. The NMR intensity is therefore proportional to the thickness of ferromagnetic Co atoms in each frequency range.

Figure 1 presents the comparison of the Co⁻ profile for the four samples from period five to period ten as counted from the surface. It is striking that the shape of the Co⁻ profile is nearly symmetrical for Mg/Co and Mg/Co/Zr while

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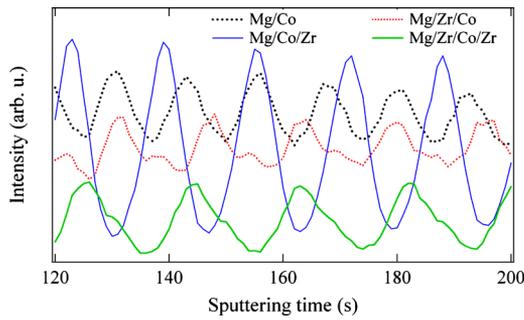


FIG. 1. (Color online) Evolution over five periods of the Co^- ToF-SIMS depth profile.

it is asymmetrical for Mg/Co/Zr and Mg/Zr/Co/Zr where it exhibits a main peak and an intense shoulder toward higher sputtering times.

For a given period, we define the contrast as the profile amplitude divided by the profile minimum. On the 130–150 s region, the contrast values are 0.34, 0.35, 2.10, and 0.87 for Mg/Co, Mg/Zr/Co, Mg/Co/Zr, and Mg/Zr/Co/Zr, respectively. By compiling the qualitative (symmetry) and quantitative (contrast) information on the Co^- profile shape, we can draw some conclusions about the interfaces. In Mg/Co, the symmetrical profile and our previous results¹ allow us to exclude intermixing between layers. The low value of the contrast could be due to a 0.5–0.6 nm interfacial roughness. Mg/Co/Zr presents the best profiles in terms of both symmetry and contrast. This indicates well-defined Co-on-Mg and Zr-on-Co interfaces. For Mg/Zr/Co, the splitting of the profile could reveal intermixing at the Co-on-Zr interface only. As a consequence, the interfaces in Mg/Zr/Co/Zr are asymmetrical: no intermixing at the Zr-on-Co interface (as in Mg/Co/Zr) while intermixing occurs at the Co-on-Zr interface (as in Mg/Zr/Co).

The NMR spectra of all samples are presented in Fig. 2. On one hand, the Mg/Co and Mg/Co/Zr spectra are both characterized by a well-defined and intense line at 226 MHz due to bulk hcp Co and a shoulder at 156 MHz related to the Co/Mg interface. In the spectrum of Mg/Co/Zr, we note the additional presence of a shoulder at 180 MHz corresponding to the Co/Zr interface. On the other hand, the 226 MHz line is no more observed in the spectra of Mg/Zr/Co and Mg/Zr/Co/Zr: they are solely made of a wide and flat feature covering the whole frequency domain.

From this distinction, we can deduce that (i) the Co layers and related interfaces are well-defined in Mg/Co and Mg/Co/Zr, giving evidence in this latter case that the Zr-on-Co interface is sharp in agreement with ToF-SIMS results and (ii) no more pure Co layers remain within Mg/Zr/Co and

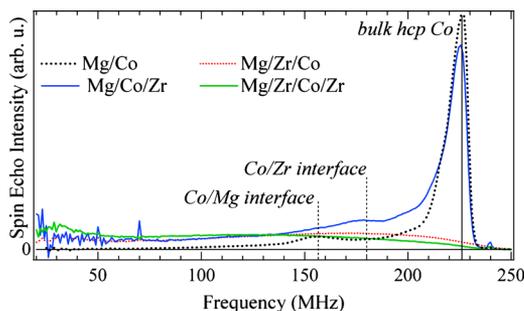


FIG. 2. (Color online) NMR spectra of the Mg/Co, Mg/Zr/Co, Mg/Co/Zr, and Mg/Zr/Co/Zr multilayers.

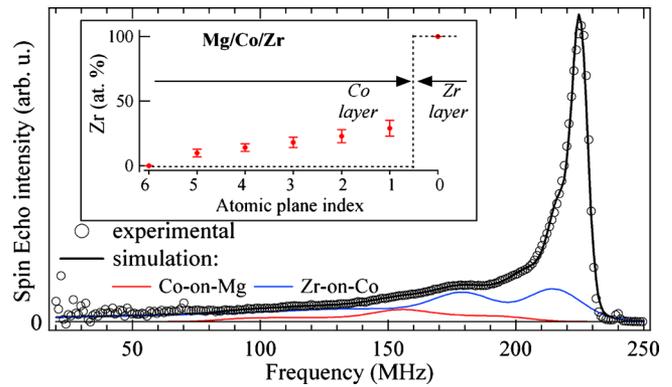


FIG. 3. (Color online) For Mg/Co/Zr, comparison of the experimental and simulated NMR spectra, the simulated spectrum being divided into the respective contributions of Co-on-Mg and Zr-on-Co interfaces. The Zr concentration profile at the Zr-on-Co interface is shown in inset compared to an “ideal” interface (dotted line).

Mg/Zr/Co/Zr as a consequence of an intermixing between upper Co and lower Zr layers at the Co-on-Zr interface.

However, a careful look at the Mg/Co/Zr and Mg/Co spectra shows significant differences: lower amplitude and broadening of the hcp Co bulk line and larger intensity in the low-frequency range. This suggests that the Zr-on-Co interface in Mg/Co/Zr is not as sharp as the Co-on-Mg interface in Mg/Co. Thus we have simulated the Mg/Co/Zr NMR spectrum. Two interface models are available: the step model which considers a perfectly flat interface with only step defects of monoatomic heights and the diffuse model where the interface is a succession of two dimensional random alloys, the fitting parameter being the concentration profile at the interface.⁴

The step interface model used for Mg/Co¹ cannot be implemented for Mg/Co/Zr as its intensity for frequencies lower than 200 MHz is significantly larger. However, since a feature similar to the one observed for the Co/Mg multilayer can still be observed (156 MHz), we assumed that the Mg/Co interfaces are similar to the interfaces of the Co/Mg multilayers and that the additional interfacial mixing that is observed arises solely from the Co/Zr interfaces. The simulated spectrum in Fig. 3, assuming a Co-on-Mg step interface and a Zr-on-Co diffuse interface, reproduces the experimental one. In the inset, the interfacial concentration profile at the Zr-on-Co interface shows that the intermixing region extends over five atomic planes with a concentration of Zr atoms into the Co layer limited to (29 ± 6) at. %. To give an order of magnitude, a 2.55-nm-thick hcp Co layer corresponds to ~ 12 atomic planes.

Given the drastic differences between the NMR spectra of Mg/Co/Zr and Mg/Zr/Co in Fig. 2, we assume that the Zr-on-Co interface in Mg/Co/Zr is sharp. The distinctions between the two sets of samples (on one hand Mg/Co and Mg/Co/Zr and on the other hand, Mg/Zr/Co and Mg/Zr/Co/Zr) are in agreement with ToF-SIMS results and with our recent studies.^{1,2} From the point of view of thermodynamics, this asymmetrical behavior could be explained by a surfactant effect, i.e., an atomic exchange at the frontier induced by the minimization of the surface energy leading to the formation of the Co_xZr_y compound, rather than by a chemical effect accounting for a strong chemical affinity between Co and Zr.⁹ In their study of a series of Au/Si bilayers exhibiting different period values but a constant thickness ratio, Labat

TABLE I. Structural parameters used to build the Mg/Co/Zr and Mg/Zr/Co systems and simulate their respective EUV reflectivity curves.

| Sample | Mg/Co/Zr | Mg/Zr/Co |
|-------------------------------------|--|--|
| Period (nm) | 17.1 | 17.2 |
| Intermixing Structure | — | At the Co-on-Zr interface |
| Structure | Trilayered stack | Bilayered stack |
| Layer thickness (nm) | Mg/Co/Zr Mg: 13.2 Zr: 1.5 Co: 2.4 | Mg/(Co _{0.78} Zr _{0.22}) Mg: 13.2 Co _{0.78} Zr _{0.22} : 4.0 |
| Layer density (g cm ⁻³) | Mg: 1.6 Zr: 6.5 Co: 8.8 | Mg: 1.6 Zr _{0.22} Co _{0.78} : 8.4 |
| Interfacial roughness (nm) | Co-on-Zr=0.6 Mg-on-Co=0.6 Zr-on-Mg=0.7 | Mg-on-(Co _{0.78} Zr _{0.22})=1.4 |

*et al.*⁶ reported a large asymmetry between the Au-on-Ni and Ni-on-Au interfaces. They correlated the intermixing evidenced at the Ni-on-Au interface to the surfactant effect of Au atoms leading to a subsequent accommodation of the lattice parameters. In our case, this “dynamic segregation” mechanism⁷ relies on vertical exchanges on a microscopic scale between lower Zr and upper Co atoms, responsible for the formation of a diffuse Co-on-Zr interface as a consequence of the surfactant effect of Zr atoms.

We are now able to propose a reliable description of each multilayer. As a test of validity, the simulated EUV reflectivity curve is compared to the experimental one. We simulate the EUV reflectivity curves at 50° of grazing angle.² We restrict our simulations to the Mg/Co/Zr and Mg/Zr/Co trilayered systems.

In Mg/Co/Zr, all layers and interfaces are well-defined. The corresponding structural parameters (thickness, roughness, and density of all layers) are those extracted from the fit of the x-ray reflectivity curve measured at 0.154 nm.²

As a consequence of the intermixing taking place at the Co-on-Zr interface, Mg/Zr/Co cannot be considered as a trilayered system anymore. But, given the high peak reflectivity of this sample, a sufficiently high optical contrast and thus a layered structure still exist between the materials present in this sample. For these reasons, we model Mg/Zr/Co as a Mg/(Co_xZr_y) bilayered stack where x and y are the relative number of Co and Zr atoms, respectively. The values of x and y , estimated from the number of Co and Zr atoms within the Co and Zr layers in Mg/Zr/Co, are found equal to 0.78 and 0.22, respectively. This compound could be ascribed to Co₄Zr (Co₂₃Zr₆ in the literature) present in the Zr–Co binary phase diagram.⁸ Its density, calculated as the weighted sum of the Co and Zr densities, is estimated to 8.4 g cm⁻³. In addition to the structural parameters describing the stack, we also take into account the fact that, in the EUV range, the available refractive indices⁹ are not known with high accuracy. Therefore, in a second step, we introduce the possibility of varying the indices (directly or indirectly through the density). All simulation parameters are collected in Table I. The corresponding simulated reflectivity curves are presented in Fig. 4, in comparison with the one measured.

In the case of Mg/Co/Zr, the agreement between measurement and simulation becomes reasonable provided that the values of the refractive indices are slightly changed

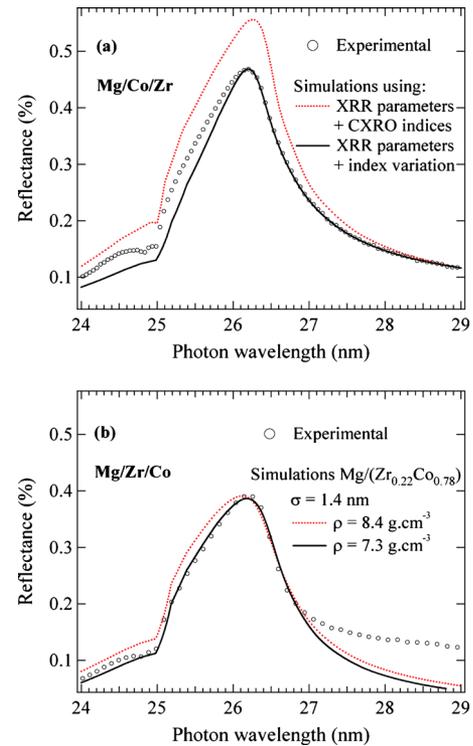


FIG. 4. (Color online) Comparison of the experimental and simulated reflectivity curves at 50° of grazing incidence of Mg/Co/Zr (a) and Mg/Zr/Co (b). Simulations are performed without (dotted line) and with (plain line) modification of the CXRO refractive indices.

(±15% maximum).² For Mg/Zr/Co, taking also into account an indirect variation in the EUV indices through a decrease of 13% of the Co_{0.78}Zr_{0.22} density while keeping constant that of Mg, the simulated curve satisfactorily reproduces the experimental one up to 27 nm.

In conclusion, we have found a correlation between the optical performances of Mg/Co/Zr and the high structural quality of the interfaces within this stack. On the contrary, at the Co-on-Zr interface within Mg/Zr/Co, we have observed an intermixing process leading to the formation of Co_{0.78}Zr_{0.22} and hence ruled out the preservation of the trilayered structure.

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⁹CXRO database <http://www-cxro.lbl.gov>.