Optical and structural characterization of the Co/Mo2C/Y system

To cite this version:
Optical and structural characterization of the Co/Mo$_2$C/Y system

Yanyan Yuan$^{1,2, *}$, Karine Le Guen$^{1,2}$, Jean-Michel André$^{1,2}$, Zhanshan Wang$^3$, Jingtao Zhu$^3$, Christian Mény$^4$, Philippe Jonnard$^{1,2}$

$^1$ Sorbonne Universités, UPMC Univ Paris 06, Laboratoire de Chimie Physique-Matière et Rayonnement, 11 rue Pierre et Marie Curie, F-75231 Paris cedex 05, France
$^2$ CNRS UMR 7614, Laboratoire de Chimie Physique-Matière et Rayonnement, 11 rue Pierre et Marie Curie, F-75231 Paris cedex 05, France
$^3$ Institute of Precision Optical Engineering, Department of Physics, Tongji University, Shanghai 200092, China
$^4$ Institut de Physique et Chimie des Matériaux de Strasbourg, UMR 7504 CNRS-Université De Strasbourg, UMR 7504 CNRS-Université De Strasbourg, 23 rue du Loess, 67034 Strasbourg, France

Abstract

We study the thermal behaviour of a tri-layer multilayer, designed by inserting a third material, yttrium, into the previously studied Co/Mo$_2$C system. The system is designed to work at near-normal incidence at the wavelength of 14.1 nm. The theoretical reflectivity of Co-based multilayer (Co/Mo$_2$C/Y system) is improved up to 54% after the addition of yttrium. Two types of multilayers with different orders of yttrium layer are deposited: Co/Mo$_2$C/Y and Co/Y/Mo$_2$C. The samples are annealed up to 600°C. The multilayers were characterized using hard x-ray and extreme ultraviolet reflectivity, nuclear magnetic resonance (NMR) spectroscopy and x-ray diffraction (XRD). The results show that the reflectivity of the Co/Mo$_2$C/Y multilayer is 27.5% at near normal incidence around 14.6 nm for as-deposited sample, and then it decreases gradually after annealing up to 600°C. A significant period compression is observed from 300°C annealing and above. The Co/Y/Mo$_2$C multilayer shows low reflectivity, less than 2.5%. NMR spectra reveal that the pure Co layers are completely mixed with other elements since there is no signal from ferromagnetic Co in the annealing samples of the Co/Mo$_2$C/Y multilayer and all Co/Y/Mo$_2$C samples. Based on the NMR and XRD results, we fit the EUV data for both multilayers with two different models in one period taking into account the formation of the interfacial compounds.

Keywords: Co/Mo$_2$C/Y multilayer, interface analysis, thermal behaviour, optical properties, nuclear magnetic resonance spectroscopy, X-ray reflectivity, X-ray diffraction

*Corresponding author, e-mail: yanyan.yuan@upmc.fr. Tel: +33(0)1 44 27 62 22. Fax: +33(0)1 44 27 62 26.
Introduction

Multilayer mirrors for the soft x-ray and extreme ultraviolet ranges consisting of two materials with high and low optical constants are studied since a long time. The potential applications include telescope [1], projection lithography [2,3], synchrotron beamline [4] and x-ray microprobe [5]. Bi-layer multilayers have been studied for many years and some of them have achieved high optical performance and good thermal stability. Tri-layer multilayers, resulting from the addition of a third layer into bi-layer [6–9], are proposed with the aim of improving the optical performance and thermal stability.

The optical performance of Co/Mo\textsubscript{2}C multilayer has been recently studied in our group [10] (experimental reflectivity is 25% @ 11° and 1.59 nm). The optical performance is related to the chemical and physical environments at the interfaces. In the bi-layer system, it is not possible to know clearly which interface, Co-on-Mo\textsubscript{2}C or Mo\textsubscript{2}C-on-Co, has more influence on the optical performance. Thus in order to distinguish these two interfaces contributions and improve the optical performance of multilayer, we inserted a third layer, yttrium, into Co/Mo\textsubscript{2}C multilayer stack. Two types of multilayers are formed: \textit{one is} Co/Mo\textsubscript{2}C/Y multilayer with interfaces Mo\textsubscript{2}C-on-Co, Y-on-Mo\textsubscript{2}C and Co-on-Y; \textit{one is} Co/Y/Mo\textsubscript{2}C multilayer with interfaces Co-on-Mo\textsubscript{2}C, Y-on-Co and Mo\textsubscript{2}C-on-Y.

Yttrium is a promising material for application in the multilayer and can provide good thermal stability. Indeed, Bosgra has reported that 0.2 nm thick Y layer significantly reduced the silicon diffusion towards Mo in the B\textsubscript{4}C/Mo/Y/Si system [11]. A theoretical study about the Y-based multilayers, for example, Pd/Y, Ag/Y, Mo/Y, Nb/Y, has shown that the combination of yttrium and these materials could give normal incidence peak reflectivity ranging from 50% to 65% in the range of 8-13 nm [12]. The study of Mo/Y multilayer demonstrated that this stack is stable up to 400°C [13].

In the present work we study the optical performance of the Co/Mo\textsubscript{2}C/Y tri-layer multilayer with different interface orders. The order of the Y layer in the system is supposed that it cannot only significantly affect the reflectivity but also the interfacial diffusion, as reported in the Co/Mg system with an insertion of Zr layer [9]. We observed that the addition of the third layer of yttrium improves the optical performance of the Co/Mo\textsubscript{2}C multilayer (45% theoretical reflectivity). The two designed systems Co/Mo\textsubscript{2}C/Y and Co/Y/Mo\textsubscript{2}C with different interface orders present the theoretical reflectivity of 54% and 11% at near normal
incidence, respectively. The reason for the significant difference of theoretical reflectivity of these two systems is the difference of the optical path of the incident beam into the multilayer stacks. In order to assess how the two sets of interfaces affect the optical performance and the interfacial diffusion, we fit the reflectivity curves performed in the EUV range to provide the structural parameters and the interface width of the multilayer. Results are complemented by nuclear magnetic resonance (NMR) spectra and x-ray diffraction (XRD) experiments.

1 Experiments method

1.1 Sample fabrication

The Co/Mo\textsubscript{2}C/Y and Co/Y/Mo\textsubscript{2}C systems were deposited by direct current magnetron sputtering. The substrates were sliced and polished Si (100) wafers, with surface roughness of 0.4 nm (\textit{rms}) determined by atomic force microscopy in the range of 10\textsuperscript{-2} to 10 \textmu m\textsuperscript{-1} spatial frequencies. The designed period is 7.71 nm and the thickness of Co, Mo\textsubscript{2}C and Y layer was 1.00 nm, 2.67 nm and 4.04 nm, respectively. The base pressure was 10\textsuperscript{-5} Pa before deposition. The working gas was argon (99.999% purity) at a constant working pressure 0.1 Pa. The number of periods is 30. There were six 10\times10 mm\textsuperscript{2} substrate sections cleaved from a single wafer for each system. Then six multilayers were deposited separately in the same conditions. The first layer on the substrate was the Co one. With our notation, the layers are indicated from the substrate toward the surface. A 3.5 nm thick B\textsubscript{4}C capping layer was deposited to prevent oxidation. Five as-deposited samples of each system were annealed at 200, 300, 400, 500 and 600°C during 1 h under high vacuum to study their thermal behaviour.

1.2 Sample characterization

The quality of the multilayer was checked through grazing incidence x-ray reflectometry (GIXR) using Cu K\alpha wavelength (0.154 nm) in the \(\theta-2\theta\) mode. The angular resolution is 5/1000°. The fit of GIXR data allowed the determination of the thickness and roughness of the different layers in each structure and also the estimation of the density of the Co, Mo\textsubscript{2}C and Y layers.

In the extreme ultraviolet range, the reflectivity measurements were performed with \(s\)-polarized radiation at the application wavelength of 14.6 nm on the BEAR beamline in the Elettra synchrotron radiation facility.
The photon energy is calibrated by the Si 2p\textsubscript{3/2} binding energy at 99.2 eV. The reflectivity curves were obtained at the angle of 4° off-normal incidence. The fits of reflectivity data were performed with IMD software [15] and provided information about interdiffusion.

In order to probe the chemical state of the Co atoms within the multilayer, we analyzed the samples by using zero field NMR spectroscopy. To enhance the sensitivity, the testing temperature was set at 4.2 K. The NMR spectra represent the distribution of the Co atoms as a function of their resonance frequency, that is to say the hyperfine field experienced by the Co nuclei. The NMR resonance frequency is sensitive to the local environment of the probed atoms: the number, nature and symmetry of atoms in its neighbourhood [16,17].

X-ray diffraction is a well-established technique for determining the crystal structure of thin films. To identify the phase present in our systems as a function of the annealing temperatures, we performed x-ray diffraction of the Co/Mo\textsubscript{2}C/Y (as-deposited, 300 and 600°C) and Co/Y/Mo\textsubscript{2}C (as-deposited) samples.

## Results and discussion

### 2.1 Grazing incidence x-ray reflectometry at 0.154 nm

We show in Fig.1 the GIXR curves of the Co/Mo\textsubscript{2}C/Y and Co/Y/Mo\textsubscript{2}C systems prior and following annealing. Six well-defined peaks are observed for both systems, indicating that these multilayers possess a well-defined periodic structure. After 400°C annealing the peak positions of the Co/Mo\textsubscript{2}C/Y multilayers shift toward high angle, which implies a period decrease according to the Bragg law. Concerning the Co/Y/Mo\textsubscript{2}C systems, it is observed that the Bragg peak positions of the 600°C annealed sample generate a significant shift toward high angle. This is due to the variation of period upon annealing.

We performed the fit of the GIXR data with Bede Refs software (genetic algorithm) [18] to estimate the structural parameters (thickness, roughness and density of each layer) using a tri-layer model (no interlayer is taken into account). A good agreement between fitted and experimental curves is obtained. As an example, we show in Fig.2 the results for the Co/Mo\textsubscript{2}C/Y multilayer as-deposited and annealed at 600°C. The structural parameters are listed in Table 1, except density. The density ratio, which is the density of the layer with respect to the bulk value, is determined with a 15% uncertainty and within this uncertainty there is no significant density change as a function of annealing. The period variation of each sample with annealing temperature is plotted in Fig.3. \( \Delta d \) represents the period change before and after annealing. It can be seen
that the period change of the Co/Mo$_2$C/Y system decreases quickly with temperature and then increases gently from 400°C. The period of the Co/Y/Mo$_2$C system decreases gradually upon annealing. Both systems show compressed periods after annealing. This phenomenon can be explained by the interdiffusion between two layers with the formation of compounds upon annealing.

![Reflectivity curves at 0.154 nm of the Co/Mo$_2$C/Y and Co/Y/Mo$_2$C systems before and after annealing as a function of the grazing angle.](image)

**Fig 1** Reflectivity curves at 0.154 nm of the Co/Mo$_2$C/Y and Co/Y/Mo$_2$C systems before and after annealing as a function of the grazing angle. For the sake of clarity, spectra of the sample annealed at 200, 300, 400, 500 and 600°C as well as corresponding as-deposited samples are shifted vertically.

**Table 1.** Structural parameters extracted from the fit of the GIXR curves measured at 0.154 nm.

<table>
<thead>
<tr>
<th>T/°C</th>
<th>Sample</th>
<th>Period / nm Before /after annealing</th>
<th>Thickness / roughness nm</th>
<th>B$_2$C</th>
<th>Co</th>
<th>Mo$_3$C</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>200°C</td>
<td>Co/Mo$_2$C/Y</td>
<td>7.56 / 7.55</td>
<td></td>
<td>3.02</td>
<td>2.00/1.00</td>
<td>1.32/0.33</td>
<td>4.23/0.29</td>
</tr>
<tr>
<td></td>
<td>Co/Y/Mo$_2$C</td>
<td>7.52 / 7.55</td>
<td></td>
<td>3.96</td>
<td>0.89/0.55</td>
<td>2.91/1.03</td>
<td>3.75/0.30</td>
</tr>
<tr>
<td>300°C</td>
<td>Co/Mo$_2$C/Y</td>
<td>7.52 / 7.48</td>
<td></td>
<td>3.46</td>
<td>1.21/0.33</td>
<td>2.06/0.31</td>
<td>4.21/0.31</td>
</tr>
<tr>
<td></td>
<td>Co/Y/Mo$_2$C</td>
<td>7.55 / 7.55</td>
<td></td>
<td>3.60</td>
<td>1.99/0.62</td>
<td>1.39/1.30</td>
<td>4.17/0.30</td>
</tr>
<tr>
<td>400°C</td>
<td>Co/Mo$_2$C/Y</td>
<td>7.59 / 7.39</td>
<td></td>
<td>3.77</td>
<td>0.90/0.12</td>
<td>2.22/0.26</td>
<td>4.27/0.72</td>
</tr>
<tr>
<td></td>
<td>Co/Y/Mo$_2$C</td>
<td>7.41 / 7.41</td>
<td></td>
<td>3.37</td>
<td>1.91/0.44</td>
<td>1.31/0.97</td>
<td>4.19/0.38</td>
</tr>
<tr>
<td>500°C</td>
<td>Co/Mo$_2$C/Y</td>
<td>7.55 / 7.37</td>
<td></td>
<td>3.55</td>
<td>1.05/0.04</td>
<td>2.15/0.28</td>
<td>4.17/0.68</td>
</tr>
<tr>
<td></td>
<td>Co/Y/Mo$_2$C</td>
<td>7.52 / 7.49</td>
<td></td>
<td>3.76</td>
<td>1.26/0.41</td>
<td>2.04/0.94</td>
<td>4.19/0.30</td>
</tr>
<tr>
<td>600°C</td>
<td>Co/Mo$_2$C/Y</td>
<td>7.59 / 7.46</td>
<td></td>
<td>3.10</td>
<td>1.94/0.96</td>
<td>1.38/0.33</td>
<td>4.14/0.36</td>
</tr>
<tr>
<td></td>
<td>Co/Y/Mo$_2$C</td>
<td>7.46 / 7.37</td>
<td></td>
<td>3.90</td>
<td>1.70/0.31</td>
<td>1.71/0.12</td>
<td>3.96/0.67</td>
</tr>
</tbody>
</table>
Fig 2 Comparison of experimental and fitted data of the as-deposited and 600°C annealed Co/Mo$_2$C/Y samples. Curves of 600°C annealed sample are shifted vertically for the sake of clarity.

Fig 3 Variation $\Delta d$ of the periods of the Co/Mo$_2$C/Y and Co/Y/Mo$_2$C systems upon annealing with respect to the value of the as-deposited sample.

2.2 Extreme ultra-violet reflectivity with synchrotron radiation

Shown in Fig. 4 (a) and (c) are the reflectivity measurements of the two systems performed at the application wavelength of 14.6 nm for as-deposited and annealed at 300 and 600°C samples. In Fig. 4(b) and (d) we present the evolution of the reflectivity values as a function of the annealing temperature. As can be seen the Co/Mo$_2$C/Y multilayer achieves a reflectivity of 27.5% with as-deposited sample and after annealing the reflectivity linearly decreased down to 17% at 600°C. The reflectivity of the Co/Y/Mo$_2$C system is low, less than 2.5%. This value is about 4 times smaller than its theoretical reflectivity (about 11%). One reason for the decreasing of reflectivity might be the high sensitivity of Y to atomic oxygen: oxygen contamination of the Y layer could cause the low measured reflectivity because of the impurities present in the vacuum system during deposition. Montcalm pointed that when the base pressure is above 10$^{-6}$ Pa,
oxygen contamination of Y layer leads to a decrease of reflectivity of about 3.2% with respect to the value in the $10^{-8}$ Pa [19]. On the other hand the deposition order of the Y layer is an important factor, which could cause the asymmetrical interface width. It should be noted that the reflectivity of the Co/Y/Mo$_2$C sample increases slightly after 400°C. This could be related to the creation of compound or mixtures which changes the optical contrast in the stack.

To estimate the interface widths, we first use a tri-layer model to fit the EUV experimental data for both systems, meaning that are considered only Co, Mo$_2$C, Y layers in one period. The resulting fitted reflectivity curves of the as-deposited, 300°C and 600°C annealed samples for both systems are presented in Fig.5. Table 2 lists the interface widths ($\delta$) and periods, as well as the interface widths derived from the GIXR data. Let us note that $\delta$ represents the total interface widths with contributions from both local interdiffusion and interface roughness.

Comparing the parameters extracted from the GIXR and EUV data, it is found that the periods derived from EUV data are larger than those from the GIXR data (for all samples, fluctuation of 0.2 to 0.3 nm). In addition, the interface widths derived from the EUV data are much larger than those derived from
GIXR data. This can be explained by considering that photons with different wavelengths respond to different effective roughnesses on the respective spatial frequency scales. Moreover the availability of accurate optical constant in the EUV spectral range is limited, so it is difficult to obtain precise values for these structural parameters.

**Fig 5** Comparison of experimental and fitted data for as-deposited, annealed at 300 and 600°C of the Co/Mo2C/Y and Co/Y/Mo2C systems. The incident angle is at 4° from normal.

**Table 2.** Interface widths (δ), period and thicknesses of the Co/Mo2C/Y and Co/Y/Mo2C systems (as-deposited and annealed at 300 and 600°C) fitted with tri-layer model.

<table>
<thead>
<tr>
<th>T /°C</th>
<th>Sample</th>
<th>Period / nm</th>
<th>δ_{Co-on-Mo2C} / nm</th>
<th>δ_{Mo2C-on-Co} / nm</th>
<th>δ_{Mo2C-on-Y} / nm</th>
<th>d_{Co} / nm</th>
<th>d_{Mo2C} / nm</th>
<th>d_{Y} / nm</th>
<th>EUV / GIXR</th>
<th>EUV / GIXR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As-deposited</td>
<td>Co/Mo2C/Y</td>
<td>7.76</td>
<td>--</td>
<td>0.94 / 0.33</td>
<td>--</td>
<td>1.00 / 1.30</td>
<td>2.00 / 0.36</td>
<td>1.00 / 0.96</td>
<td>1.00 / 1.20</td>
<td>1.00 / 1.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.65 / 0.30</td>
<td>1.30 / 0.31</td>
<td>1.27 / 0.62</td>
<td>1.27 / 0.30</td>
<td>1.30 / 0.31</td>
<td>1.23 / 1.33</td>
<td>1.23 / 2.38</td>
<td>1.23 / 3.67</td>
</tr>
<tr>
<td>300°C</td>
<td></td>
<td></td>
<td>1.26 / 0.39</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Co/Y/Mo2C</td>
<td>7.97</td>
<td>1.15 / 0.95</td>
<td>--</td>
<td>--</td>
<td>1.20</td>
<td>2.61</td>
<td>3.95</td>
<td>1.20</td>
<td>2.53</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.30 / 0.57</td>
<td>--</td>
<td>--</td>
<td>1.30</td>
<td>2.67</td>
<td>4.00</td>
<td>1.30</td>
<td>2.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.27 / 0.30</td>
<td>--</td>
<td>--</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>600°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Co/Mo2C/Y</td>
<td>7.74</td>
<td>1.00 / 1.30</td>
<td>--</td>
<td>--</td>
<td>1.00 / 1.20</td>
<td>1.20</td>
<td>2.59</td>
<td>3.95</td>
<td>1.00 / 1.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.00 / 0.36</td>
<td>--</td>
<td>--</td>
<td>1.30 / 0.33</td>
<td>1.23</td>
<td>2.38</td>
<td>3.95</td>
<td>1.33 / 0.67</td>
</tr>
<tr>
<td></td>
<td>Co/Y/Mo2C</td>
<td>7.56</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


The evolution of interface widths upon annealing allows assessing the thermal stability of multilayer. The interface widths of the Mo$_2$C-on-Co and Co-on-Mo$_2$C interfaces derived from GIXR data and EUV data for all samples are close to the thickness of the Co layers (designed as 1.0 nm), and those values are larger than that of the Y-on-Co, Co-on-Y, Mo$_2$C-on-Y and Y-on-Mo$_2$C interfaces. This implies that the Co layers are probably mixed completely with other layers to form compounds in the stack. In addition, based on fitted parameters from the EUV data for the Co/Mo$_2$C/Y multilayer, the $\delta_{\text{Mo}_2\text{C-on-Co}}$ value stays close to 1.0 nm while $\delta_{\text{Co-on-Y}}$ value increases upon annealing and $\delta_{\text{Y-on-Mo}_2\text{C}}$ value slightly decreases upon annealing. At the opposite, in the Co/Y/Mo$_2$C multilayer, the three values of interface width $\delta$ do not significantly depend on annealing; this indicates that the interdiffusion strongly takes place at the deposition time and thus there is no more evolution of interdiffusion as a function of temperature. This also illustrates that the diffusion at the Y-on-Co and Mo$_2$C-on-Y interfaces in the Co/Y/Mo$_2$C multilayer is easier than at the Co-on-Y and Y-on-Mo$_2$C interfaces in the Co/Mo$_2$C/Y multilayer.

2.3 Zero-field nuclear magnetic resonance spectroscopy

NMR spectra of the Co/Mo$_2$C/Y as-deposited sample and two references, Co$_3$Mo and CoMo1% (atomic ratio) disordered alloy, are presented in Fig.6. All spectra are normalized to their integrated area. The spectra of the samples annealed from 200 to 600°C for the Co/Mo$_2$C/Y and Co/Y/Mo$_2$C systems show no signal (and thus, not are shown here). The multilayer NMR spectrum shows no bulk Co peak (intense peak at 217MHz for fcc Co) but only a low frequency signal (<200 MHz). This demonstrates that the Co layers are strongly mixed with the other atoms of the multilayer stack. In order to probe the influence of the vicinity of Mo atoms on the resonance frequency of Co we have measured the reference sample CoMo1%. As in references [20,21] the peak at 176 MHz is attributed to the presence of one Mo atom within the 12 first neighbors of a fcc Co sample. This shows that the frequency shift due to the presence of Mo atoms is very strong and explains why the NMR signal obtained for the multilayer is mainly found at rather low frequencies. It can be seen that the spectrum of the Co/Mo$_2$C/Y as-deposited sample is very close to the one of bulk Co$_3$Mo disordered alloy. These observations strongly suggest that the Co layers are fully mixed with Mo and that the Mo concentration in Co is of the order of 25% at. But we cannot get a conclusive result: indeed if the Co
atoms were totally surrounded by other atoms such as Y atoms, no ferromagnetic signal would also be measured. At the present time the NMR spectra of Co$_x$Y$_y$ compounds are unavailable.

![NMR spectra](image)

**Fig 6** NMR spectra of the Co/Mo$_2$C/Y as-deposited sample and two reference samples Co$_3$Mo disordered alloy and CoMo1% (atomic ratio). Ne faudrait-il pas mettre le zéro des ordonnées?

### 2.4 X-ray diffraction

The XRD patterns of the Co/Mo$_2$C/Y as-deposited, 300 and 600°C and the Co/Y/Mo$_2$C as-deposited samples are presented in Fig.7. A series of weak peaks are detected in the 2θ=10-80° range for the Co/Mo$_2$C/Y multilayer. The peak at 30° probably corresponds to Y (002) [13,22,23] and/or Co$_3$Mo (101). It is found that the intensity of this peak decreases upon annealing while no peak position shifts can be observed, which indicates that the pure Y layers react upon annealing with atoms from the others layers. Another possible reason for the decrease of the pure Y intensity is the interfacial diffusion during the annealing or amorphous phase formation. The peak at 44° may be the combination of several phases, *i.e.* Co$_3$Mo (002) or Co$_2$Y (222) or Co$_3$Y (111) phase. The peak at 49° may correspond to the MoC (101). The compounds produced from Mo and Y are not easy to form because of their positive heat of mixing being +26 kJ/mol [24] and consequently we exclude this possibility. From the NMR spectra, we know that there is no pure Co layer left in the stack and the NMR spectra of the Co/Mo$_2$C/Y as-deposited sample is the same as that of Co$_3$Mo reference. Hence we assume that the Co$_3$Mo solid solution is formed at the interface. However, the combination of the Co and Y atoms is also possible. The peaks around at 40° and 48° are unidentified. The Co/Y/Mo$_2$C as-deposited sample does not show intense peaks: this sample is mainly amorphous.
Fig 7 X-ray diffraction patterns of the Co/Mo$_2$C/Y as-deposited, 300 and 600°C samples and the Co/Y/Mo$_2$C as-deposited sample.

From the XRD and NMR experimental results, a four-layer model is now proposed to fit the EUV reflectivity data. An interfacial reaction is considered and the model structure is designed as Si/[Co$_3$Mo/MoC/Y/Co$_2$Y]$_{30}$/Y$_2$O$_3$/YC$_2$/B$_4$C and Si/[Co$_2$Y/Y/MoC/Co$_3$Mo]$_{30}$/B$_4$C for the Co/Mo$_2$C/Y and Co/Y/Mo$_2$C multilayers respectively. The fitting procedure is performed using the Levenberg-Marquardt (MINPACK-1) algorithm within IMD software [15]. The thickness of the Y$_2$O$_3$ and YC$_2$ layers is assumed to be 1.0 nm. We used the density of bulk Co$_3$Mo, Co$_2$Y, Y$_2$O$_3$ and YC$_2$ in the fits. Original Mo$_2$C layers are modified as MoC layers due to the Co$_3$Mo formation. The parameters (thickness and interface width) derived from these fits are collected in Table 3 for the Co/Mo$_2$C/Y system. Fig8(a) shows the resulting fitted spectra compared to those measured for the Co/Mo$_2$C/Y (as-deposited and annealed samples at 300 and 600°C).

With respect to tri-layer model, this new set of fitted reflectivity curves including oxidation layer and interlayer exhibits a slight improvement in the agreement with experimental spectra, especially for as-deposited sample.

The interface widths are large with respect to the thickness of the Co$_3$Mo and Co$_2$Y layer. Considering the atomic numbers per mole $N_i$

$$ N_i = N_0 \frac{\rho_i \cdot s_i \cdot d_i}{M_i} \quad (1.1) $$
where $N_0$ is the Avogadro constant, $\rho_i$ the layer density, $s_i$ the area of each layer, $d_i$ the thickness of each layer and $M_i$ the atomic weight and subscript $i$ represents the type of the atom. Here we can obtain the atomic ratio $n$ following the equation

$$n = \frac{N_i}{N_j}$$

(1.2)

Taking the Co/Mo$_2$C/Y 600°C annealed sample as an example, the thickness of Co, Mo$_2$C and Y layer being 1.94 nm, 1.38 nm and 4.14 nm, respectively (see Table 1), the atomic ratios of Co to Mo and Co to Y are 2.4 and 1.4, respectively. This means that only a small amount of the Co$_3$Mo and Co$_2$Y compounds can be formed by consuming the whole Co layers in one period.

In the case of the Co/Y/Mo$_2$C multilayer, the fitted spectra with the four-layer model are worse than that obtained from the tri-layer model (not shown here). In addition it is mentioned that there is no peak to be found in the XRD pattern. This means that there is no or few crystalline phase in the stack. However one possibility could exist: the formation of different compounds. Thus a new model, Si/[Co$_2$Y/Y$_2$C/MoC]$_{30}$/B$_4$C, is proposed for fitting the EUV reflectivity data of the Co/Y/Mo$_2$C multilayer. The results of the comparison of experimental and fitted (tri-layer and a new model) reflectivity curves of the Co/Y/Mo$_2$C multilayer (as-deposited and annealed at 300 and 600°C) are shown in the Fig.8(b). One can see that the fitted curves obtained by using both models are close to the experimental curves. The parameters of each layer are listed in the Table 3. The results show that the thickness of the MoC and Y$_2$C layer are stable and that of the Co$_2$Y varies upon the annealing. Furthermore, the interface width of the MoC-on-Y$_2$C is very close the value of Y$_2$C thickness. This indicates that a strong interdiffusion takes place at the interfaces.

The two different fitting models of the Co/Mo$_2$C/Y and Co/Y/Mo$_2$C systems obtain a good agreement with respect to the experimental data. This indicates that the formation of compound is dependent on the deposition order of the layers and also shows that the formation of Co$_3$Mo is located at the Mo$_2$C-on-Co interface rather than at the Co-on-Mo$_2$C interface.
Fig 8 (a) Comparison of experimental and fitted (tri- and four-layer models) reflectivity curves of the Co/Mo$_2$C/Y multilayer (as-deposited and annealed at 300 and 600°C) and (b) comparison of experimental and fitted (tri-layer and the new model) reflectivity curves of the Co/Y/Mo$_2$C multilayer (as-deposited and annealed at 300 and 600°C).

Table 3. Parameters of four-layer model to fit the Co/Mo$_2$C/Y multilayer and of tri-layer model to fit the Co/Y/Mo$_2$C multilayer.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness / interface width (nm)</th>
<th>Co$_3$Mo</th>
<th>MoC</th>
<th>Y</th>
<th>Co$_2$Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-deposited</td>
<td>1.50 / 0.60</td>
<td>2.10 / 0.84</td>
<td>3.05 / 0.70</td>
<td>1.10 / 0.50</td>
<td></td>
</tr>
<tr>
<td>Co/Mo$_2$C/Y</td>
<td>300°C</td>
<td>1.50 / 0.80</td>
<td>2.10 / 1.02</td>
<td>3.12 / 0.85</td>
<td>1.01 / 0.50</td>
</tr>
<tr>
<td></td>
<td>600°C</td>
<td>1.50 / 0.85</td>
<td>2.06 / 1.62</td>
<td>3.05 / 1.00</td>
<td>1.10 / 0.50</td>
</tr>
<tr>
<td>MoC</td>
<td></td>
<td></td>
<td></td>
<td>Y$_2$C</td>
<td>Co$_2$Y</td>
</tr>
<tr>
<td>As-deposited</td>
<td>2.00 / 0.30</td>
<td>2.25 / 0.30</td>
<td>3.72 / 0.38</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co/Y/Mo$_2$C</td>
<td>300°C</td>
<td>2.00 / 0.30</td>
<td>2.25 / 2.00</td>
<td>3.52 / 1.15</td>
<td></td>
</tr>
<tr>
<td></td>
<td>600°C</td>
<td>2.00 / 0.30</td>
<td>2.00 / 2.00</td>
<td>3.57 / 0.30</td>
<td></td>
</tr>
</tbody>
</table>

3 Conclusion

The Co/Mo$_2$C/Y and Co/Y/Mo$_2$C systems were deposited by direct current magnetron sputtering technology in high vacuum and then annealed up to 600°C with an interval of 100°C. These two systems are designed with different interface orders. The optical and interfacial properties of both systems are obtained by a combination of the reflectivity, XRD and NMR spectra. GIXR experiments showed that the Co/Mo$_2$C/Y multilayers present a well-defined periodic structure. In the extreme ultraviolet, a peak reflectivity of 27.5% at 14.6 nm at near normal incidence for as-deposited sample is obtained, while the Co/Y/Mo$_2$C multilayer showed a poor reflectivity. NMR spectra results showed that there is no pure Co layer left in the stack since the Co layers are strongly mixed with other layers in both systems. XRD patterns indicated that the crystalline phases in the Co/Mo$_2$C/Y multilayer are different from that in the Co/Y/Mo$_2$C multilayer. Based
on the NMR and XRD results, we fitted the EUV data using different models for two systems which take into account the formation of the Co$_3$Mo, Co$_2$Y and Y$_2$C compounds. The Si/[Co$_3$Mo/MoC/Y/Co$_2$Y]$_{10}$/Y$_2$O$_3$/YC$_2$/B$_4$C model to fit the Co/Mo$_2$C/Y multilayer and the Si/[Co$_2$Y/Y$_2$C/MoC]$_{10}$/B$_4$C model to fit the Co/Y/Mo$_2$C multilayer obtained a better improvement in the agreement with the experiment spectra. Comparison of those fitted results showed that the interdiffusion accompanied with the formation of compounds is responsible for the degradation of the reflectivity. These two systems with different interfaces orders probably show the different compounds formation. The formation of Co$_3$Mo is probably located at the Mo$_2$C-on-Co interface rather than the Co-on-Mo$_2$C interface. Further experiments, such as transmission electron microscopy, are in progress to provide more detailed interface information.

Acknowledgments

We are gratefully thankful to S. Nannarone and A. Giglia of the BEAR line in the ELETTRA synchrotron radiation for their help to perform the extreme ultraviolet reflectivity experiments. This work is done under the framework of the international ANR-NSFC COBMUL project (ANR #10-INTB-902-01 and NSFC #11061130549).

References