

# X-ray absorption spectroscopy study of buried Co layers in the Co/Mo<sub>2</sub>C multilayer mirrors

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X-ray absorption spectroscopy at the Co K edge was applied to investigate the chemical environment of Co atoms inside Co/Mo<sub>2</sub>C periodic multilayers. The results show a mixing between Co and Mo<sub>2</sub>C layers prior to any annealing process, whereas following annealing from 300 °C pure Co layers are observed. X-ray absorption spectroscopy results are in agreement with previous nuclear magnetic resonance spectroscopy results. They indicate that the pure Co content increases upon annealing, while it is absent in the as-deposited samples. The comparison of the results, based on the analysis of the data obtained on the multilayer samples and some reference materials, reveals that the ordering of Co atoms inside the Co layers increases upon annealing. Copyright © 2016 John Wiley & Sons, Ltd.

**Keywords:** XANES; EXAFS; interface analysis; periodic multilayer; buried Co layers; annealing

## Introduction

Multilayer structures consisting of a periodic alternation of thin films show a variety of interesting properties and applications. They provide not only the potential applications as X-ray and neutron optical elements but also convenient tools for studying the interfaces between different materials. The accurate characterization of interfaces in multilayer structures is still a challenging task and is very important for the improvement of their application properties<sup>[1,2]</sup>.

X-ray absorption spectroscopy (XAS) is well known for probing the local atomic structure around a specific element in thin films and other structures<sup>[3–8]</sup>. In the case of buried interfaces, the phases are often formed in a narrow region, are highly disordered, or present a short-range order. Thus, the XAS technique with short-range order sensitivity provides a powerful tool for the study of interface phases, also called interphases. Examples of XAS investigation of multilayered samples can be found in<sup>[9–14]</sup>.

The interfacial properties of the Co/Mo<sub>2</sub>C multilayer have been studied in a previously published paper<sup>[15]</sup>. It reported that the Co and C atoms mix together during deposition and then, following annealing from 300 °C, Co and C demix from their mixed regions. In order to interpret the chemical bond environment of Co layers upon annealing, XAS was measured by detecting the fluorescence radiation. Both X-ray absorption near edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) spectra were used.

## Experiment

The Co/Mo<sub>2</sub>C multilayer samples were prepared by magnetron sputtering. Three different samples are considered: as-deposited, annealed at 300 and 600 °C in a furnace for 1 h with a pressure of

$3.0 \times 10^{-4}$  Pa, respectively. The details of sample preparation were given previously<sup>[16]</sup>. Here, we recall only the structure of the samples: the thickness of Co and Mo<sub>2</sub>C layer in one period is 2.6 and 1.5 nm, respectively; the number of period is 30; the substrates are sliced and polished Si (100) wafers. A 3.5-nm-thick B<sub>4</sub>C capping layer is deposited onto the multilayer top to prevent oxidation. Table 1 lists the structural parameters of these samples derived from the X-ray reflectivity data measured at 0.154 nm<sup>[16]</sup>. Those values will be used in the following sections. Different characterization methods have been carried out such as X-ray reflectometry in the hard and soft X-ray ranges, X-ray emission spectroscopy,

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**Table 1.** Structural parameters of the three multilayers derived from X-ray reflectivity data measured at 0.154 nm

Sample	Period $d$ (nm) prior annealing	Period $d$ (nm) following annealing	Thickness/Roughness (nm) ( $\pm 0.05$ nm)		
			B <sub>4</sub> C	Co	Mo <sub>2</sub> C
As-deposited	4.20	—	3.60/0.56	2.65/0.32	1.55/0.26
300 °C	4.17	4.18	3.31/0.56	2.93/0.82	1.25/0.26
600 °C	4.17	4.13	2.89/0.54	2.47/0.38	1.66/0.22

nuclear magnetic resonance spectroscopy whose results were given elsewhere<sup>[15,17]</sup>.

The XAS experiments were carried out at beam line BL14W1 at the Shanghai synchrotron radiation facility<sup>[18]</sup>. Two types of double crystal monochromators are used for covering photon energy range from 4.5 to 50 keV. The photon energy Resolution ( $\Delta E/E$ ) is around  $10^{-4}$ . The multilayers deposition onto thick substrates leads to the impossibility of absorption measurements in transmission; fluorescence detection was used in this study. The XAS experiment is made in the partial fluorescence yield mode, where the integrated intensity of the Co K $\alpha$  characteristic emission is measured as a function of the energy of the incident radiation scanned through the Co K edge (7709 eV). A 32-element Canberra/XIA Ge detector system was used to detect the fluorescence radiation.

For the sake of comparison, the XAS spectra of some reference samples (CoMo (1 at %), Co<sub>3</sub>Mo, Co<sub>3</sub>Mo<sub>3</sub>C, and Co<sub>6</sub>Mo<sub>6</sub>C solid solutions and a Co foil) were also obtained. Here, the spectra of the reference samples CoMo (1 at %), Co<sub>3</sub>Mo, Co<sub>3</sub>Mo<sub>3</sub>C, and Co<sub>6</sub>Mo<sub>6</sub>C solid solutions were obtained in fluorescence mode and that of the Co foil in transmission mode. We should keep in mind

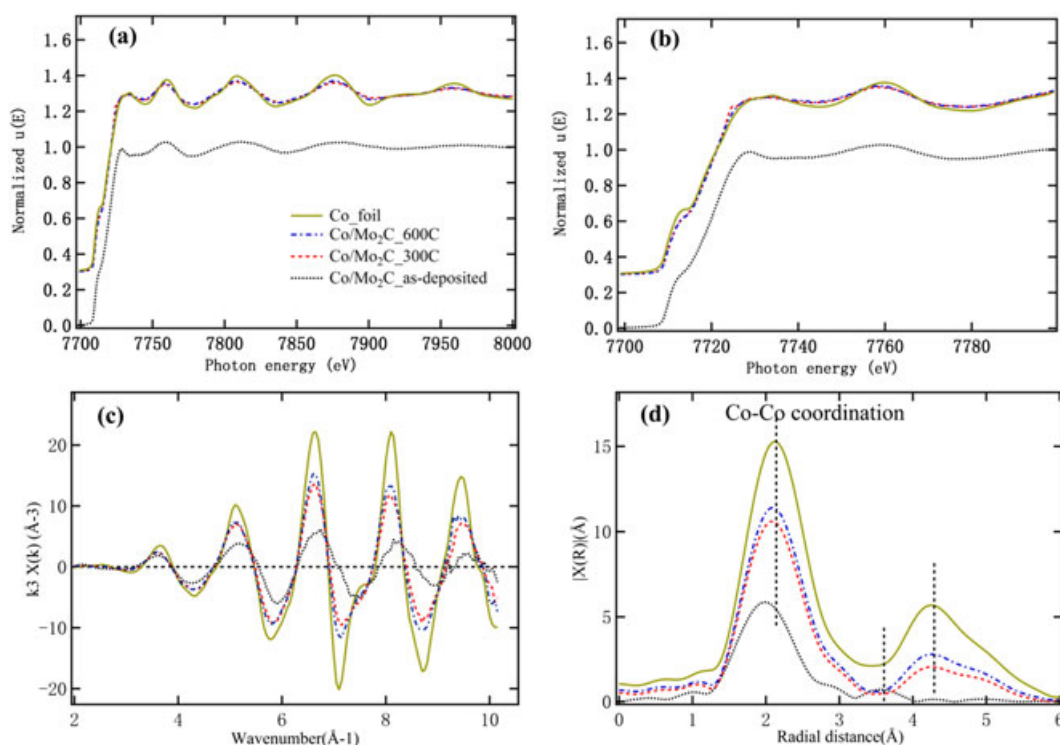
that the direct comparison of the intensity of the features of the multilayers and the reference samples is difficult as the self-absorption conditions are not the same in thin films and bulk materials.

All the XAS spectra were normalized after a background subtraction taking into account the low and high photon energy parts of the spectra far from the threshold. This was done with the IFEFFIT software<sup>[19]</sup>. The background toward the high energy side can be difficult to determine owing to the presence of the first EXAFS oscillations, leading to an uncertainty on the intensity near the threshold.

## Results and discussion

Figure 1a and b respectively shows the EXAFS and XANES spectra in the vicinity of the Co K edge of the three Co/Mo<sub>2</sub>C multilayer samples and the Co foil reference. All the spectra present a shoulder at about 7713 eV, whose value is determined by the minimum of the first derivative. The spectra of the annealed multilayers exhibit higher-contrasted oscillations and are close to those of the Co reference. This indicates that the local environment of the Co atoms in the annealed multilayer is similar to that of Co atoms in the Co foil. In the case of the as-deposited sample, the oscillations are attenuated, especially above 7850 eV.

Figure 1c and d respectively shows, for the three multilayers and the reference, the  $k^3$ -weighted  $k$ -space spectra (data have been multiplied by  $k^3$  to enhance the oscillations at high  $k$ ) and Fourier transform R-space spectra (the Fourier transform of an EXAFS spectrum would give a similar radial distribution function) of the EXAFS data. In all spectra, the highest contrast is obtained for the Co foil. The  $k^3$ -weighted  $k$ -space spectra of the multilayer present



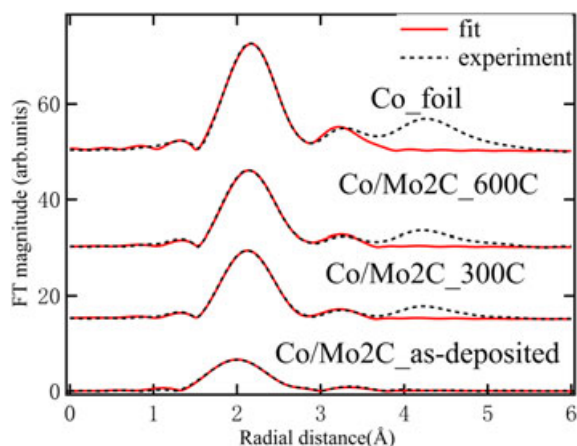
**Figure 1.** Co K edge X-ray absorption measurement of the Co/Mo<sub>2</sub>C multilayers (as-deposited, annealed at 300 and 600 °C) and the Co foil reference: (a) normalized X-ray absorption fine structure spectra; (b) normalized X-ray absorption near edge spectroscopy spectra; (c)  $k^3$ -weighted  $k$ -space spectra; and (d) Fourier transform R-space spectra of X-ray absorption fine structure. For the sake of clarity, curves are vertically shifted in (a) and (b). [Colour figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

well-contrasted oscillations for high  $k$  values. The amplitude of the oscillations increases as a function of the annealing temperature. The same trend can be seen on the Fourier transform R-space spectra, Fig. 1d.

Quantitative analysis of EXAFS spectra is performed to determine the local environment information of Co atoms: coordination number and atoms bond length. A hexagonal Co<sub>3</sub>Mo phase (space group P63/mmc, lattice parameters  $a = 5.1245$  nm,  $b = 5.1245$  nm, and  $c = 4.1125$  nm<sup>[20]</sup>) were used. In the fit procedure, we introduced the parameters: amplitude reduction factor  $S_0^2$ , zero energy shift  $\Delta E_0$ , atoms bond length  $R$ , and Debye–Waller factors  $\sigma^2$ . Four single-scattering paths of Co atoms were used and yield an excellent fit for the region from 1.0 to 5.0 Å. In four single-scattering paths, the amplitude reduction factor  $S_0^2$  and zero energy shift  $\Delta E_0$  are defined to be consistent for each scattering path; the bond length  $R$  is defined independent; the Debye–Waller factors  $\sigma^2$  of the first path are independent; and others are consistent.

The best fit is obtained with the hexagonal Co<sub>3</sub>Mo phase theoretical model for the Co/Mo<sub>2</sub>C multilayers (as-deposited, annealed at 300 and 600 °C), shown in Fig. 2. A good fit is obtained in the R range of [1.0, 5.0] Å for the Co/Mo<sub>2</sub>C as-deposited sample and that of the other samples are in the interval of [1.0, 3.5] Å. This indicates that the local structure of Co atoms in the multilayers sample is close to that of the hexagonal Co<sub>3</sub>Mo phase. The Co–Co coordination number of the first shell is obtained using four single-scattering paths. Best fit values of the parameters are listed in Table 2 for the first shell. The results show that the coordination number of the first shell increases with the annealing temperature. The Debye–Waller factors  $\sigma^2$  are decreasing, indicating the strong ordering of Co atoms upon annealing. The same results were reported by Chernov *et al.* in the Co/C multilayer<sup>[10]</sup>. From the structural parameters of the EXAFS fit, however, it is not possible to determine if the Co<sub>3</sub>Mo phase is fully formed or if only subscale crystallites are formed at the interfaces of the multilayer. We can only say that the local structure around the Co atoms is similar but not equal to the one in the Co<sub>3</sub>Mo *hcp* phase.

In order to better understand the structure of the multilayer samples, the XAS spectra of the references, namely, the CoMo (1 at. %), Co<sub>3</sub>Mo, Co<sub>3</sub>Mo<sub>3</sub>C, and Co<sub>6</sub>Mo<sub>6</sub>C solid solutions, are



**Figure 2.** The  $k^3$ -weighted Fourier transforms of the Co K edge X-ray absorption fine structure spectra ( $k = 3$  to  $10.15 \text{ \AA}^{-1}$ ) measured on the Co/Mo<sub>2</sub>C multilayers (as-deposited, annealed at 300 and 600 °C) and the Co foil reference. The fits were carried out in R-space in the interval of [1.0, 5.0] Å. For the sake of clarity, curves are vertically shifted. [Colour figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

**Table 2.** Parameters of the first coordination shell in Co/Mo<sub>2</sub>C multilayers (as-deposited, annealed at 300 and 600 °C) and the Co foil

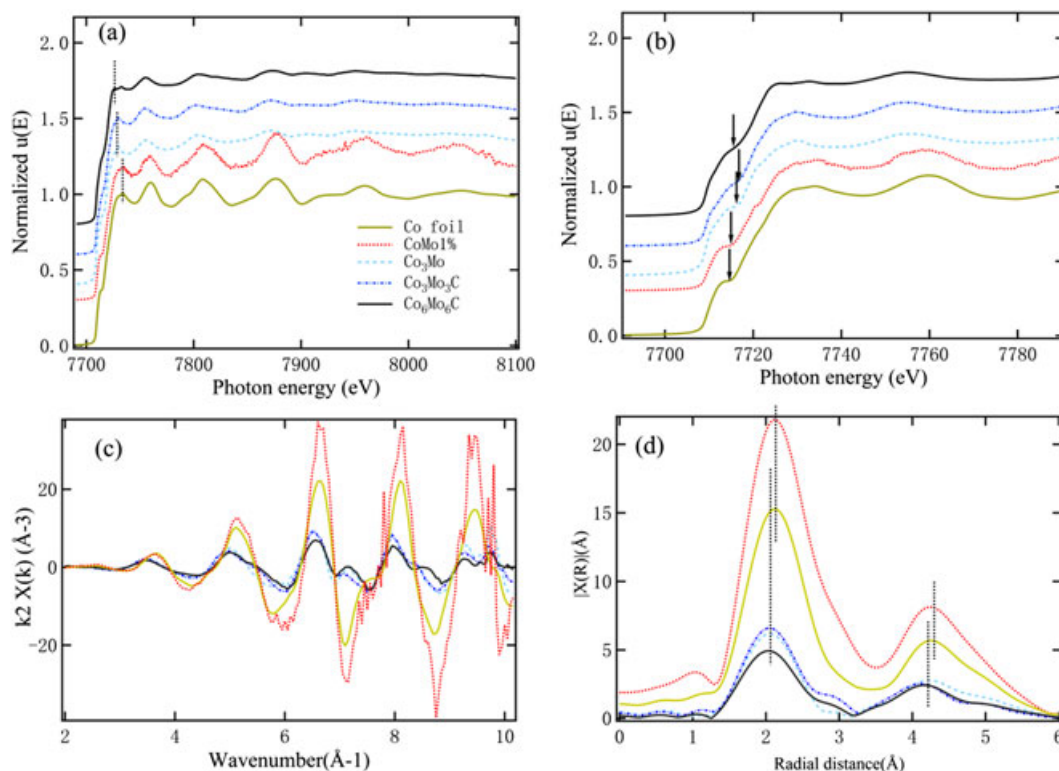
Sample	The first shell (Co–Co)		
	$N$	$R(\text{\AA})$	$\sigma^2(\text{\AA}^2)$
As-deposited	4(1)	2.41(9)	0.0125(3)
300 °C	5(2)	2.46(4)	0.0084(4)
600 °C	6(2)	2.49(2)	0.0089(7)
Co foil	6(2)	2.47(4)	0.0038(2)

$N$ : coordination number,  $R$ : neighbor atoms distance,  $\sigma^2$ : Debye–Waller factor for individual shells. Uncertainty of the last digit is given in parentheses.

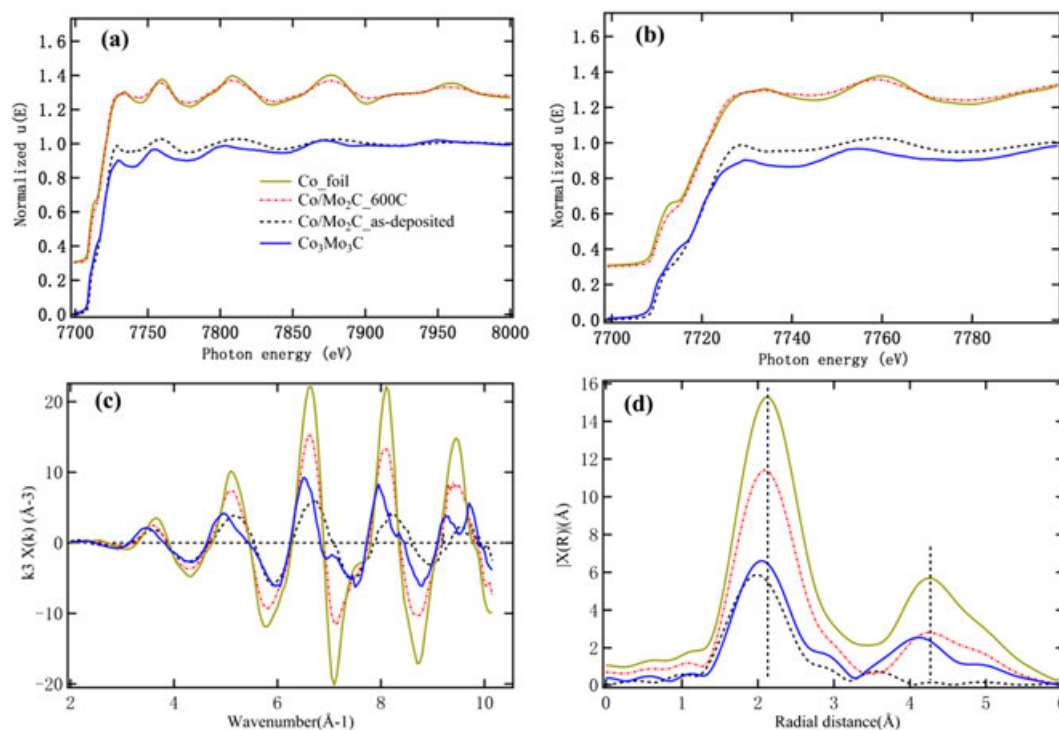
presented in Fig. 3 compared with the one of the Co foil. Here, self-absorption correction of XAS spectra has been performed for the thick samples. In Fig. 3a and b, the oscillations in the spectra of the solid solutions are poorly contrasted with respect to those of the pure Co foil reference, except that of the CoMo (1 at. %). The first maximum is reported at 7730 eV for the Co<sub>3</sub>Mo, Co<sub>3</sub>Mo<sub>3</sub>C, and Co<sub>6</sub>Mo<sub>6</sub>C solid solutions and 7734 eV for the Co foil and CoMo (1 at. %). The second and third ones are located at 7754 and 7803 eV respectively for the Co<sub>3</sub>Mo, Co<sub>3</sub>Mo<sub>3</sub>C, and Co<sub>6</sub>Mo<sub>6</sub>C solid solution samples, while they are located at 7760 and 7808 eV respectively for bulk Co and CoMo (1 at. %). Near the edge, all spectra present a shoulder, whose intensity and positions vary depending on the sample (and on the self-absorption conditions). The shoulder position of the Co foil and CoMo (1 at. %) is located at around 7715 eV and around 7716 eV for the other samples. The shift is due to the change of Co oxidation state.

In Fig. 3c, the spatial frequency in the  $k^3$ -weighted  $k$ -space spectra slightly differs from one sample to another. In Fig. 3d, the Co<sub>3</sub>Mo, Co<sub>3</sub>Mo<sub>3</sub>C, and Co<sub>6</sub>Mo<sub>6</sub>C show a weak coordination sphere peak corresponding to that of the Co foil. A closer examination of the R-space spectra of the Co<sub>3</sub>Mo<sub>3</sub>C and Co<sub>6</sub>Mo<sub>6</sub>C samples shows a shoulder toward the high radial distances, close to the first coordination sphere, which is located in between the first and second Co–Co coordination spheres of the Co foil. This indicates a local ordering trend of Co atoms inside the Co<sub>3</sub>Mo<sub>3</sub>C and Co<sub>6</sub>Mo<sub>6</sub>C samples.

In order to obtain further details on the chemical bond of the Co atoms within the multilayers, we compared in Fig. 4 the Co K edge XAS spectra of two references (Co foil and Co<sub>3</sub>Mo<sub>3</sub>C) and two multilayers (as-deposited and annealed at 600 °C). In Fig. 4a, the positions of the observed features for the as-deposited sample correspond to those of the Co foil but with different relative intensities. It is clear that for the as-deposited sample, there is no pure Co in the stack<sup>[15]</sup>. Compared with Co<sub>3</sub>Mo<sub>3</sub>C, the as-deposited multilayer exhibits close EXAFS features, similar amplitudes but with different frequencies in the  $k^3$ -weighted  $k$ -space spectrum and similar low coordination numbers in the Fourier transform R-space spectra. This suggests that only the local atomic structure of the Co layer inside the as-deposited sample is similar to that of the solid solution Co<sub>3</sub>Mo<sub>3</sub>C. It can be deduced that in the as-deposited sample, the Co layers are mixed with C and Mo atoms. Concerning the Co/Mo<sub>2</sub>C multilayer annealed at 600 °C, the great similarities in the EXAFS and XANES spectra with respect to the Co foil point out a similar local environment of the Co atoms. This confirms our previous results demonstrating that annealing leads to the ordering of the Co layer and the inherent increase of pure Co content.



**Figure 3.** Co K edge X-ray absorption measurement of the solid solution references, CoMo (1 at. %),  $\text{Co}_3\text{Mo}$ ,  $\text{Co}_3\text{Mo}_3\text{C}$ , and  $\text{Co}_6\text{Mo}_6\text{C}$ , compared with the Co foil: (a) normalized X-ray absorption fine structure spectra; (b) normalized X-ray absorption near edge spectroscopy spectra; (c)  $k^3$ -weighted  $k$ -space spectra; and (d) Fourier transform R-space spectra of X-ray absorption fine structure data. For the sake of clarity, curves are vertically shifted in (a) and (b). [Colour figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]



**Figure 4.** Co K edge X-ray absorption measurement of two solid solution references,  $\text{Co}_3\text{Mo}_3\text{C}$  and  $\text{Co}_6\text{Mo}_6\text{C}$ , and of two  $\text{Co}/\text{Mo}_2\text{C}$  multilayers, as-deposited and annealed at  $600^\circ\text{C}$ : (a) normalized X-ray absorption fine structure spectra; (b) normalized X-ray absorption near edge spectroscopy spectra; (c)  $k^3$ -weighted  $k$ -space spectra; and (d) Fourier transform R-space spectra of X-ray absorption fine structure data. For the sake of clarity, curves are vertically shifted in (a) and (b). [Colour figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

## Conclusion

The XAS spectra of Co/Mo<sub>2</sub>C multilayer samples measured in the partial fluorescence mode were carried out at the Co K edge. The chemical environment of the Co atoms was studied by collecting the Co K $\alpha$  fluorescence signal. In light of all the aforementioned results, some significant spectra have been obtained for the differently annealed samples and for the reference materials. There is a clear distinction between the as-deposited and the annealed Co/Mo<sub>2</sub>C multilayer samples from the XAS spectra. This behavior is in agreement with the one measured through nuclear magnetic resonance experiments<sup>[15]</sup>, where the mixing of the Co layers occurs for the as-deposited sample, whereas pure Co is observed upon annealing from 300°C. In addition, we show that both Mo and C atoms of the Mo<sub>2</sub>C layers are involved in the mixing with the Co atoms. Moreover, the quantitative analysis of the EXAFS data indicates a stronger local ordering of the Co layers following annealing. In conclusion, with the annealing process, demixing takes place in the Co and C mixing region, and the layers become ordered, which results in the existence of pure Co region in the annealed samples.

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