



HAL
open science

Thermal stability of Co/C multilayers

Jingtao Zhu, Yuchun Tu, Yanyan Yuan, Zhixiang Feng, Haochuan Li, Yizhi Zhang, Philippe Jonnard, Christian Mény, Karine Le Guen, Jean-Michel André, et al.

► **To cite this version:**

Jingtao Zhu, Yuchun Tu, Yanyan Yuan, Zhixiang Feng, Haochuan Li, et al.. Thermal stability of Co/C multilayers . Materials Research Express, 2014, 1, pp.046503. 10.1088/2053-1591/1/4/046503 . hal-01238002

HAL Id: hal-01238002

<https://hal.science/hal-01238002>

Submitted on 8 Dec 2015

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Thermal stability of Co/C multilayers

Jingtao Zhu^{1*}, Yuchun Tu^{1,2,3}, Yanyan Yuan^{2,3}, Zhixiang Feng¹, Haochuan Li¹, Yizhi Zhang¹, Philippe Jonnard^{2,3}, Christian Mény⁴, Karine Le Guen^{2,3}, Jean-Michel André^{2,3}, Zhanshan Wang^{1*}

1 MOE Key Laboratory of Advanced Micro-structured Materials, School of Physics Science and Engineering, Tongji University, Shanghai 200092, China

2 Sorbonne Universités, UPMC Univ Paris 06, Laboratoire de Chimie Physique-Matière et Rayonnement, 11 rue Pierre et Marie Curie, F-75231 France

3 CNRS UMR 7614, Laboratoire de Chimie Physique-Matière et Rayonnement, 11 rue Pierre et Marie Curie, F-75231, France

4 Institut de Physique et Chimie des Matériaux de Strasbourg, UMR 7504 CNRS-Université De Strasbourg, 23 rue du Loess, 67034 Strasbourg, France

memey

E-mail address : jtzhu@tongji.edu.cn and wangzs@tongji.edu.cn

Abstract

The structural and interface changes induced by thermal annealing in Co/C multilayers were investigated. Co/C multilayers with period thickness of 4.1 nm and bi-layer number of 20 were deposited by direct current magnetron sputtering. We characterized all samples by using X-ray reflectivity, X-ray diffuse scattering, zero-field nuclear magnetic resonance spectroscopy and X-ray diffraction. The results indicate that Co and C atoms mixed during deposition and then after annealing both atoms separated from their mixed region. The annealing process also causes a sharp increase of roughness at interfaces, which can be attributed to the crystallization of Co layers.

Keywords: Multilayer, X-ray optics, interface, thin film structure, NMR

1 Introduction

Multilayer mirrors are widely used as reflective optical elements for applications such as extreme ultraviolet (EUV) lithography [1], solar astrophysics imaging [2], synchrotron radiation [3] and x-ray spectrometry [4]. Near the “carbon window” region ($\lambda \sim 4.5$ nm) where the absorption of carbon materials is low, Co/C multilayers have the rather high theoretical reflectivity [5] and have been produced for Schwarzschild objective [6]. The peak reflectivity of Co/C multilayers was measured to be 14.8% at incident angle of 5° . In x-ray optics of synchrotron radiation beamlines and telescopes for astronomical observations, multilayers are used as monochromators and focusing elements. Co/C multilayers are promising near Co K-edges because of their fine optical properties [7].

In order to improve the optical performance, it is necessary to deposit multilayer films that give rise to smooth and sharp interfaces, as the interface imperfections (i.e., roughness and interdiffusion) will reduce the reflectance and increase non-specular scattering as well [7]. Furthermore, multilayer mirrors are usually exposed to high flux of incident photons or endure high heat loads in practical applications such as solar observation or synchrotron radiation, where they might reach temperatures and heat load in excess of 500°C [8] and 100 W/mm² [9]. It is known that the structure and interfaces of multilayers may change, e.g. period expansion or contraction, interdiffusion, crystallization, which could reduce the optical performance and accelerate the aging of the multilayer [10]. Thus, it is important to investigate the thermal stability and structure evolution of the multilayers.

In this paper, we combined X-ray reflectivity (XRR), X-ray diffuse scattering (XDS), zero-field nuclear magnetic resonance (NMR) spectroscopy and X-ray diffraction (XRD) techniques to investigate the evolution of structure and interfaces of Co/C multilayers upon annealing.

2 Experiments

The Co/C multilayers were deposited onto polished Si wafer by ultra-high vacuum direct current (DC) magnetron sputtering system with targets of Co (purity 99.95%), C (purity 99.99%). The working gas is argon (99.999%). The base pressure was 1×10^{-4} Pa and the sputtering gas pressure was 0.13 Pa. The deposited multilayer was designed with bilayer number $N=20$, period thickness $\Lambda=4.1$ nm, and the thickness of Co layer, $d_{Co}=1.5$ nm. The layer thickness was calibrated by using grazing incident X-ray reflectivity measurement. After deposition, the samples were mounted on a plate heated by a wire-wound furnace in a vacuum chamber with a base pressure of 3×10^{-4} Pa. The samples were heated from room temperature to 300 and 600°C keeping for 1 hour. A detailed description of the deposition and annealing setup can be found in Ref. [11].

The structure of the multilayers was analyzed by using grazing incident XRR on a X-ray diffractometer (D1 system, Bede Inc.) at Cu K α line (0.154 nm) working in the θ - 2θ mode. The angular resolution is 5/1000°. Bragg law corrected for refraction was used to determine the multilayer period. The fitting of the XRR curves performed with Bede Refs software was used to determine thickness, roughness and density of each layer. Rocking curves were measured by using the same diffractometer with the detector fixed at the angle of first order Bragg peak. XRD measurements in the symmetric (θ - 2θ) geometry were performed on a Rigaku-Dmax-2550V powder diffractometer.

In order to probe the chemical state of the Co atoms within the multilayer, the samples are analyzed by NMR spectroscopy. The NMR spectra represent the distribution of the Co atoms as a function of their resonance

frequency, *i.e.* the hyperfine field experienced by the Co nuclei [12-13]. The NMR resonance frequency is sensitive to the local environment of the probed atoms: nearest neighbor local structure and/or local chemical environment. To enhance the sensitivity, the testing temperature is 2 K for all the samples. All spectra have been recorded for different values of radio frequency field strengths allowing for correcting the NMR intensities for a frequency dependent enhancement factor.

3 Results and discussion

3.1 Grazing incident X-ray reflectivity

The grazing incident X-ray reflectivity curves of the Co/C multilayers are presented in Figure 1. All the XRR curves were fitted to obtain the roughness, thickness and density of individual layers. The fitted values are listed in Table.1. For the sample annealed at 300°C, the Bragg peaks slightly shift to lower grazing incident angle with respect to those of as-deposited sample. This means a slight increase of period thickness. When the sample was annealed at 600°C, we observe an expansion of 17.5% in period thickness (from 4.09 nm to 4.81nm).

The fitting results reveal that the carbon layer plays a crucial role in the period expansion. After 600°C annealing, the thickness of C layer increases from 2.58nm to 3.37nm. Observation of period expansion in carbon-based multilayers after annealing was reported in Cr/C [14], Pt/C [15] and W/C [16] systems. This phenomenon is attributed to the graphitization of the amorphous carbon layers by annealing, which is confirmed by Raman scattering measurements [14, 16]. There is a conversion of sp³ bond to sp² bond and amorphous carbon structure to nanocrystalline graphite in carbon layers during annealing [14]. The density of carbon changes linearly with sp³ fraction [17]. That is to say, the density of carbon should decrease and the thickness of the carbon layers should increase upon annealing. The thickness of Co layers decrease from 1.51 nm to 1.44nm. This may be due to the demixing of Co and C atoms in the Co layers after annealing which will be mentioned below.

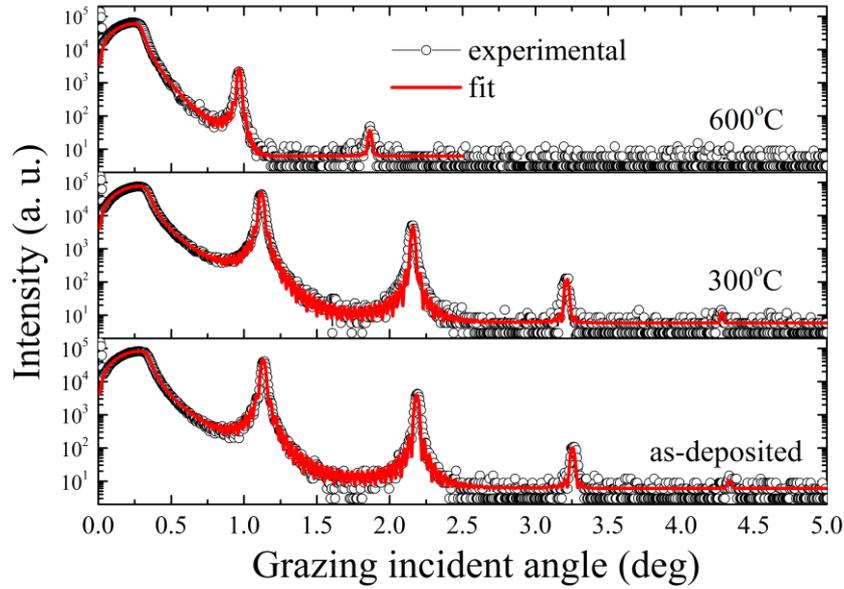


Fig. 1. Measured (black circle) and fitted (red solid line) XRR curves of as-deposited and annealed Co/C multilayers.

Table.1. Parameters of the Co/C multilayers deduced from fitting of the XRR curves. (The density ratio is the fitted density divided by the density of the bulk.)

Sample	Period Λ (nm)	d_{Co} (nm)	d_C (nm)	σ_{Co} (nm)	σ_C (nm)	Density ratio: Co (%), C (%)
as-deposited	4.09	1.51	2.58	0.41	0.37	89 \pm 5, 93 \pm 5
300°C annealing	4.14	1.53	2.61	0.40	0.35	91 \pm 5, 90 \pm 5
600°C annealing	4.81	1.44	3.37	1.16	1.02	98 \pm 5, 80 \pm 5

In Figure 1, three well-defined peaks are observed for the as-deposited and 300°C annealed samples up to 3.5°. In the case of the 600°C annealed sample, only first and second Bragg peaks are observed and the reflectance decreased. The intensity of Bragg peaks increases slightly after 300°C, meaning that there is an interface smoothing effect in Co/C multilayers. The comparison of the reflectivity curves shows that after 600°C annealing, the roughness of interfaces increases dramatically, from 0.4 nm to about 1.0 nm. The roughness deduced from the fitting of XRR (σ) is an overall imperfection of interfaces, including the contributions from both geometrical roughness (σ_r) and interdiffusion (σ_d). Possible reasons for thermally induced roughness change in Co/C multilayers are investigated in the following.

3.2 Zero-field nuclear magnetic resonance (NMR) spectroscopy

NMR spectra for the Co/C multilayers are presented in Figure 2. All spectra in Fig.2 (a) are normalized to the surface area of each sample because the intensity is proportional to the size of samples. The spectrum of the

Co/C as-deposited multilayer shows a weak signal without any defined feature in the frequency range of pure Co. This indicates that the Co layers are not pure but that alien carbon atoms are mixed with Co over the total Co thickness. The as-deposited multilayers are actually CoC_x/C multilayer with probably some concentration gradient at the interface with the C layers. In addition some Co atoms are most probably also situated in non-ferromagnetic phases (and therefore give no NMR signal) with a large content of C. The metal-containing layer is a Co-C alloy with the density of $6.2\text{-}6.5\text{ g/cm}^3$ that is less than density of massive Co and carbon enriched Co_2C layers [18]. As a result, Co/C multilayer mirrors consist of cobalt-carbon alloy and amorphous carbon layers.

The NMR spectrum of the Co/C 300°C annealed sample shows no defined peak either, meaning that Co and C atoms are still strongly mixed in CoC_x layers. There is a broad structure at 110MHz showing that some atomic motion occurred during annealing but the exact origin of this signal is difficult to identify. However, compared to the result of as-deposited samples, Co and C has a tendency of demixing at a temperature of 300°C . Indeed the demixing process between the Co and C atoms increases the x-ray optical contrast of the Co/C multilayers. That is why the X-ray reflectivity is improved at temperature of 300°C .

The spectrum of the Co/C 600°C annealed sample shows a well-defined peak at about 220MHz which corresponds to bulk *hcp* / *fcc* like Co [12, 13]. This means that the pure Co regions appear and the diffusion decreases at the interfaces. We infer from these results that Co and C layers in the Co/C stack are strongly mixed during deposition and then demixing occurs upon annealing.

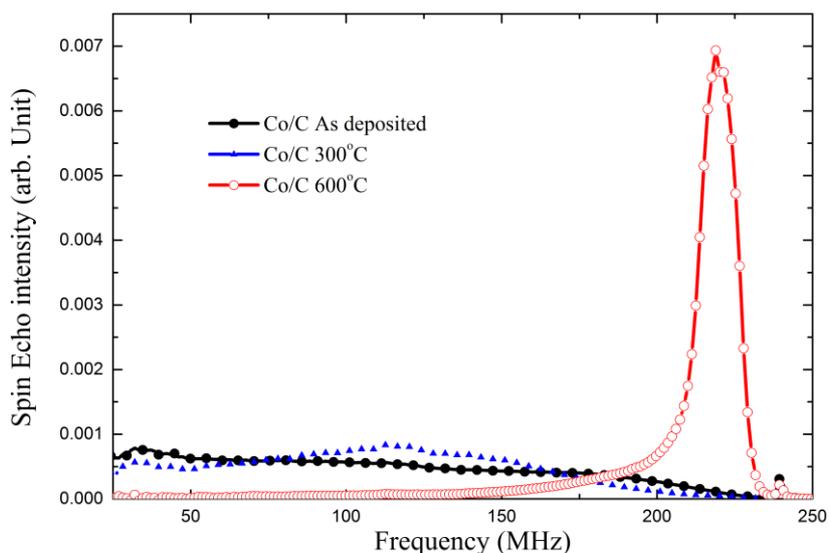


Fig. 2. Zero-field NMR spectra of as-deposited and annealed Co/C multilayers.

Based on the Miedema's macroscopic atom model [19], the mixing enthalpy of Co-C system is calculated and

the results are shown in Fig.3. It can be seen that the value of mixing enthalpy is positive at any carbon concentration. This indicates that the Co-C system is easy to separate into two phases from the view of thermodynamics. This is in agreement with the NMR results. On the other hand, the carbon atoms separating out from CoC_x layers may be an additional reason for the expansion of carbon layers.

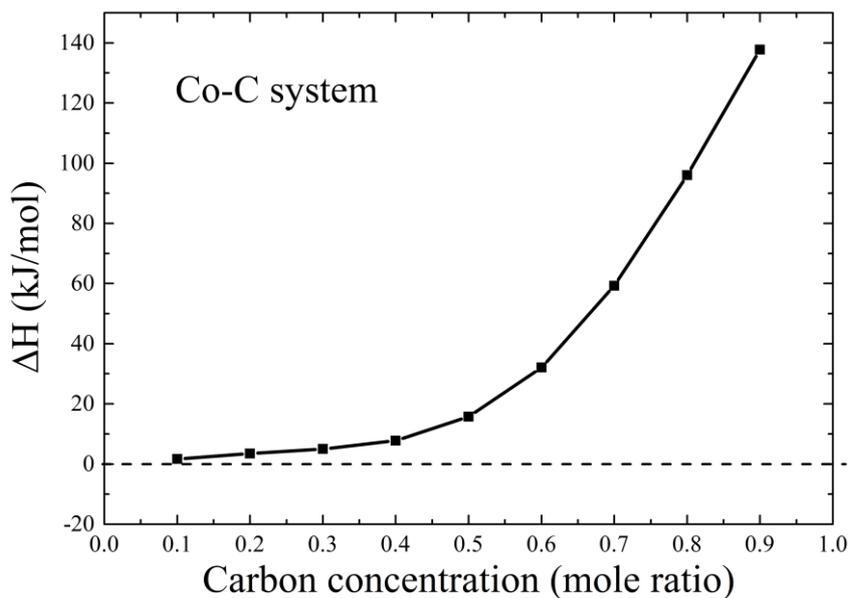


Fig.3.Theoretical calculated mixing enthalpy of the Co-C system.

3.3 X-ray diffuse scattering

The NMR results confirm the decrease of intermixing after annealing. Thus we attribute the deterioration of the interfaces to the increase of geometrical roughness. Therefore, X-ray diffuse scattering measurement was performed. Figure 4 shows the rocking curves measured around the first Bragg peak for the three samples. For the as-deposited and 300°C annealed sample there is no significant change of the intensity except a slight shift of peak position. After annealed at 600°C, a high intensity of diffuse scattered x-rays is observed, indicating significant increase of the interfaces roughness.

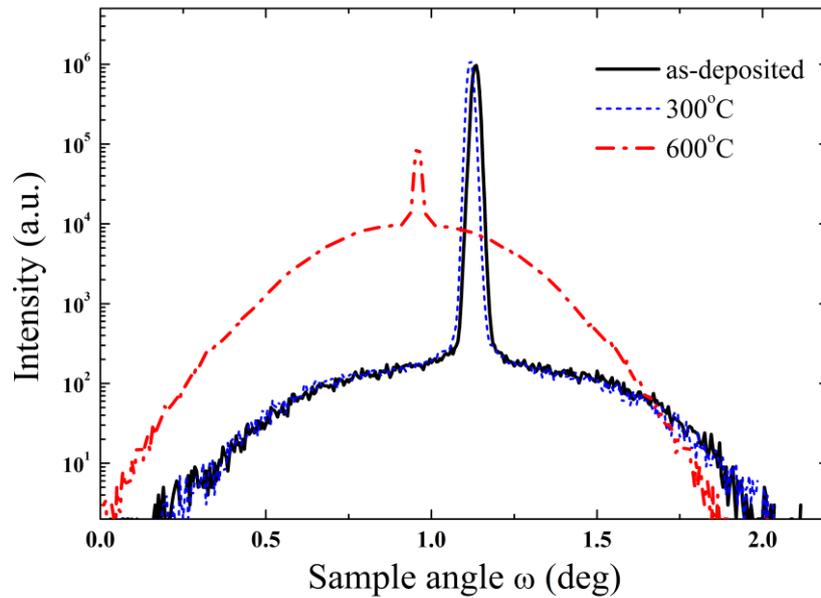


Fig.4. Rocking curves around the first Bragg peak of as-deposited and annealed Co/C multilayers.

3.4 X-ray diffraction

The x-ray diffraction patterns of Co/C as-deposited and annealed at 300°C and 600°C samples are presented in Fig.5. A broad intensity can be observed around 44.5° around the *hcp*(0002)/*fcc* (111) [20] peak position for the sample annealed at 600°C. Compared with the amorphous layers of as-deposited and 300°C annealed sample, this peak indicates a significant structural change: the amount of pure Co increases upon annealing. This is in good agreement with results of NMR spectra. Co and C atoms may not separate completely because the XRD peak is weak and its width is much broader than reported for Co/Cu multilayers with 1.5 nm thick Co layers [21]. That is to say, the Co layers still contain a certain amount of C upon 600°C annealing.

The reduction in reflectivity induced by interface roughness becomes more significant as the multilayer period thickness decreases, because the ratio of the interface roughness to the multilayer period thickness directly affects the reflectivity according to the Debye-Waller factor [22]. Crystallization of metal layers in multilayers can cause an increase of geometrical roughness [23]. Crystallites can nucleate at some points during annealing. They have a size limited to the metal layer thickness in the growth direction and are also small in the in-plane direction. The spatial distribution of crystallites in the metal layer is replicated as a modulation of the surface height. Since the metal layer becomes rougher, the nonmetal layer on top of the metal layer also becomes rougher. For the Co/C multilayers annealed up to 600°C, the crystallization of Co layers increases the geometrical roughness and aggravates the overall imperfection of the interfaces.

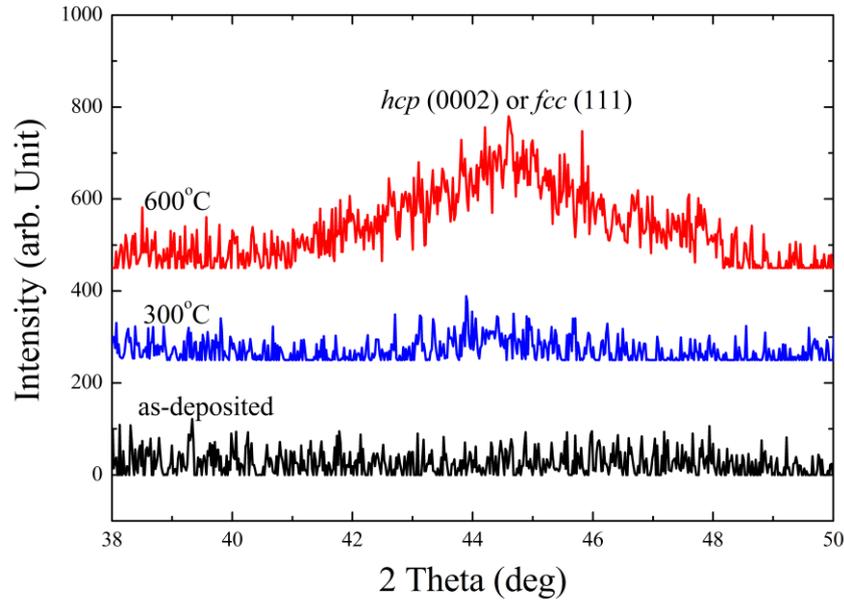


Fig.5. Diffraction patterns of as-deposited and annealed Co/C multilayers. The curves were shifted vertically for the sake of clarity.

4 Conclusion

Sputter-deposited Co/C multilayers annealed up to 600°C (2.6 nm C /1.5 nm Co)₂₀ are investigated by using XRR, XRD, XDS and NMR techniques. The multilayer is stable up to 300°C and there is a slight increase in the period and reflectivity. We demonstrate through the NMR spectroscopy that the strong demixing between Co and C atoms occurs after annealing at 600°C. This phenomenon is also demonstrated by the Miedema's model which shows the phase separation of the Co-C system. The XDS and XRD results show that when the annealing temperature increases up to 600°C, although the demixing of Co and C atoms increases the x-ray optical contrast of the Co/C multilayers, the formation of small Co crystalline grain causes the interfaces rough. The demixing and graphitization of the amorphous carbon layers induce an expansion of period thickness.

Acknowledgement:

This work was supported by Cai Yuanpei Project (PHC N° 30248NF), National Basic Research Program of China (No.2011CB922203), and National Natural Science Foundation of China (Nos. 11375131 and 11305104).

References

- [1] D. L. Windt and W. K. Waskiewicz 1994 J. Vac. Sci. Technol. B, 12 3826-3832
- [2] J. F. Seely, C. M. Brown, D. L. Windt, S. Donguy, B. Kjornrattanawanich 2004 App. Opt. 43 1463-1471
- [3] C. Morawe, J-C. Peffen, E. Ziegler, A. K Freund 2001 Proc. SPIE 4501 61-71

- [4] C. Hombourger, P. Jonnard, J.-M. André, J. P. Chauvineau 1999 X-Ray Spectrom. 28 163-167
- [5] H. Takenaka, K. Nagai, H. Ito, Y. Muramatsu, T. Kawamura, E. Gullikson, R.C.C. Perera 2001 Nucl. Instrum. Methods Phys. Res. A 467–468 337–340
- [6] I. Artyukov, Y. Bugayev, O. Devizenko, E. Gullikson, V. Kondratenko, and A. Vinogradov 2009 Opt. Lett. 34(19) 2930-2932
- [7] J. A. Bellotti and D. L. Windt 2009 Proc. SPIE 7437 15, 1-7
- [8] E. Ziegler, Y. Lepetre, I. K. Schuller, E. Spiller 1986 Appl. Phys. Lett. 48 1354-1356
- [9] J. A. Trail and R. L. Byer 1989 Opt. Lett. 14 539-541
- [10] T. Bottger, D. C. Meyer, P. Paufler, S. Braun, M. Moss, H. Mai, E. Beyer 2003 Thin Solid Films 444 165-173
- [11] J. Zhu, S. Zhou, H. Li, Q. Huang, Z. Wang, K. Le Guen, M.-H. Hu, J.-M. André, and P. Jonnard 2010 Appl. Opt. 49 3922–3925
- [12] P. Panissod and C. Mény 2000 Appl. Magn. Reson. 19 447–460
- [13] M. Malinowska, C. Meny, E. Jedryka, P. Panissod 1998 J Phys-Condens. Mat. 10 4919-4928
- [14] Y. Tu, J. Zhu, H. Li, P. Jonnard, K. Le Guen, J.-M. André, H. Chen, Z. Wang 2014 Appl. Surf. Sci. 313 341-345
- [15] G. S. Lodha, S. Pandita, A. Gupta, R. V. Nandedkar, K. Yamashita 1996 Appl. Phys. A 62 29-32
- [16] Z. Jiang, B. Vidal, G. Desrousseaux, V. Dupuis, M. Piecuch 1993 J. Appl. Phys. 74 249-254
- [17] A. C. Ferrari, J. Robertson, 2000 Phys. Rev. B 61(20) 14 095-107
- [18] I. A. Artyukov et al 2005 Proc. SPIE 5919, 59190E
- [19] N. Das et al 2013 J. Alloys Compd. 550 483–495
- [20] The diffraction information for Co is obtained from ICDD-PDF No. 05-2727 and No. 15-0806
- [21] Kubota, H., S. Ishio, T. Miyazaki, and Z. M. Stadnik 1994 J. Magn. Magn. Mater. 129(2) 383-388
- [22] D. K. G. De Boer, A. J. G. Leenaers, and W. W. Van den Hoogenhof 1994 Appl. Phys. A 58 169-172
- [23] S. Bajt, D. G. Stearns, P. A. Kearney 2001 J. Appl. Phys. 90(2) 1017-1025