# Electrodeposited Multilayer Metal Nanowires

Subjects: Nanoscience & Nanotechnology
Contributor: Aiman Mukhtar

Because of having high aspect ratio nanowires(NWs) structures offer great advantages in many sensing and biological systems. Magnetic/non-magnetic multilayered NWs were fabricated by electrochemical deposition, usually by using potentiostatic, galvanostatic techniques, and they were seen to be kinetic or diffusion control. By using optimized deposition parameters i.e presence of additives, potential, solution concentration, hydrogen evolution and confinement effect of nanopore wall, one can successfully fabricate NWs with well-defined segmented structures for single, bilayer or even tri layer thickness. Structural and chemical compositional of the multilayer NWs was observed by using various characterization techniques i.e electron microscopy, spectroscopy, and x-ray diffraction. Studying the kinetics of the phase transformation of NWs between stable or metastable phases reveals basic thermodynamical information and essential for future various applications.

Keywords: electochemical deposition ; multisegmented nanowires ; transmission electron microscopy

## 1. Introduction

It is clear from the previous research work that the deposition parameters affects the growth mechanism of metal NWs, and it has technological and fundamental interests. The studies of Tian et al. [1]showed two important points: (1) At low deposition potential Cu, Ag and Au are single crystalline with preferred orientation[2], having an fcc structure, and using high deposition potential polycrystalline structure was obtained; (2) the Ni NWs have a polycrystalline nature and are rather insensitive to deposition potential. They explained that, at lower deposition potential larger critical nuclei are formed, which helped in formation of single crystalline NWs. However, Pan et al.[3]formed single crystalline Ni NWs using high deposition potential, with preferred orientation along[4] direction, they explained that the adsorption of H adatoms on cathode favors[4]growth orientation. Likewise, some other research groups claimed that the electrolyte pH (i.e., from 2 to 6) has no effect on orientation of Ni NWs[5][6]. The formation of fcc Ni, and Ag NWs along[4] was also observed by other researchers[7][8][9]. The growth of single crystalline metal NWs was very well demonstrated by Tan Ming and Xinqi Chen[10]; according to them, the growth of single crystalline NWs occurs on atomically rough planes like hcp [1010] and fcc[2] rather than smooth planes like hcp [0001] and fcc[11]. The reason for this is because the sites for dehydration on atomically rough planes are larger in number than smooth planes[10]. The change in phase transformation of Co NWs was seen (i.e., from hcp to fcc) by changing the deposition parameters[12][13][14], and a group of studies by Mukhtar et al.[15][16][17][18][19] showed that the smaller grain size of Co favors the formation of fcc Co NWs, and larger grain size favors the formation of hcp Co NWs. Similarly, the mixture of hcp and fcc phases was observed in Co NWs, which seems to crystallize in early stage of deposition, and later with the increase in deposition time as the length of Co NWs increases, they crystallize into the hcp phase[20]. Wang et al. [21]studied the expansion behavior of hcp Co NWs arrays along the (1010) plane and fcc Co NWs arrays along the (220) plane. The amount of change in the interplanar spacing of the hcp Co NWs array was found to be larger than the variation in the interplanar spacing of the fcc Co NWs array. The ability to control the thermal expansion of Co NWs is expected to provide new opportunities for the design of magnetic nano-devices.

## 2. Structure

By having the knowledge of growth of single NWs, as explained in the paragraph above, one can likely understand the growth of multilayer nanostructure. As mentioned in Table 2, the current density, potential and pulse time are the important parameters to form the distinct interface of multilayer NWs, and by controlling these parameters a distinct interface of multilayers could be formed. XRD is a significant tool to study the coherence in multilayers, because if they are coherent there are a lot of them to produce a strong Bragg diffraction peak. Satellites should appear on both sides of Bragg diffraction in the case if the structures are supper-lattice as shown in Figure 1a[22]. The angular shift between the satellites and the Bragg diffraction peak can be explained by , where λ is the wave length of X-ray photon, and $\Delta\theta$ is the angular shift, and Λ is the periodicity of superlattice structure. The main peak was seen as intermediate between the diffraction peaks for Ni and Cu, and satellites can specify that the thickenss of the layers are nearly equal, and they are reproduced by repeating the same experimental conditions cycle by cycle[22]. A lot of work has been done recently on Ni, Co, Fe, Pt and their alloys with Au, Ag, Cu segments[23][24][25][26]. High resolution TEM images allow us to study the cross sectional shape of NWs, which is absoultely cylindrical, but in some studies it deviate from the original shape due to defects in the porous template (Figure 1b,c). Advanced SEM intruments like the Zeiss ULTRA 55[27] are able to detect the interface defects of multi-segments very clearly, as shown in Figure 6d,e. Both energy-dispersive X-ray spectroscopy (EDS) and energy loss spectroscopy (EELS) gives the chemical composition NWs. The EDS mapping in TEM provides better and higher spatial resolution than the EDS in SEM, and EELS technique even gives more detailed chemical mapping about nanostructure[28][29]. Scanning transmission electron microscopy(STEM) with high angle annual dark field detector depends on material atomic number under study, as the atomic number of magnetic segment (Co) is lower than non-magnetic segment (Au), the magnetic segment appears darker and non-magnetic layer appear as a bright segment (see Figure 2a of[30]). Further analysis of High resolution transmission electron microscopy (HRTEM) showed the polycrystalline nature of Co-Au multilayers, and the growth orientation of Co was interestingly different on [011] and [002] at both sides between Au [210] plane[30]. Figure 2a show the SEM image of CoFe/Au/CoFe NWs, and Figure 2b,c,d show the EDX mapping of Co, Fe and Au NWs. Similarly, the phase change occurred in NiFe-Au multilayers NWs in NiFe segment from fcc to bcc as the concentration of Fe ions in solution increases[31][32], and for $Ni_{30}Fe_{70}$/Cu NWs the increase in Cu thickness from 4 nm to 12 nm and the phase change from bcc (110) to fcc (111) was observed[33].

Co-Cu is the most studied system among the tailored multilayerd nanostructures. According to previous studies[34] [35]the direct-current deposition of Co-Cu alloy results in to mixture of fcc and hcp phase, while pulse deposition of multilayered CoCu/Cu films the dominant fcc phase was obtained with little hcp crystals(>2%). Cziraki et al.[36] studied the structural evolution in CoCu/Cu films, study show that at the initial time of deposition nano-size small hcp and fcc crystallites was formed with high internal stress, after this initial polycrystalline region the size of crystals increases, and finally a fcc super-lattice columnar structure was formed. During the deposition process the bending of layer was observed[37], this bending of layers was also observed by the Co/Au and Co/Pd multilayers[38]. While studying NiCo-Cu NWs same phenomena was observed by S. Zsurzsa et al.[39], authors suggested that the bending may occur because of the restricted growth of NWs inside the pore wall, which may act as the grain boundaries, as the interface do in the columnar growth, which results in convex curvature. Meanwhile, depositing the multilayer Co-Cu NWs, the control over deposition parameters, the fcc phase of multilayer NWs was formed[40][41][42][43], which is highly desirable for magnetic applications.

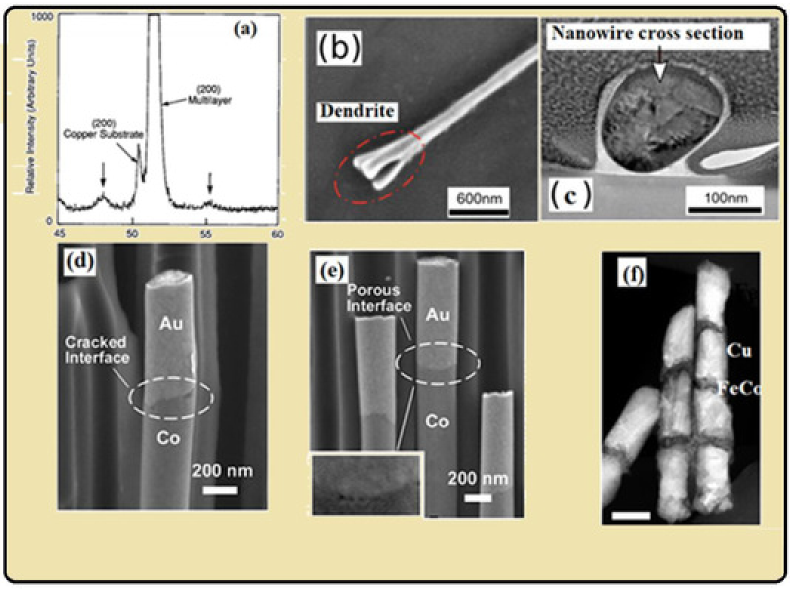


**Figure 1.** (**a**) X-ray diffraction image of Ni-Cu multilayer composite and two downward arrows with the main central peak show the typical satellites of Ni-Cu multilayer. Reprinted with permission from[22] Copyright "Elsevier", (**b**) SEM image of NW with dendrite structure, (**c**) Transmission electron microscopy (TEM) image show the cross section of NW. Reproduced from Reference[44] used in accordance with the Creative Commons Attribution (CC BY 4.0) license, (**d**,**e**) SEM of Co-Au NWs shows the defected interface of Co and Au, indicated the porous and cracked interface. Reprinted with the permission from[27] Copyright (2014) "American Chemical Society", (**f**) Scanning transmission electron microscopy (STEM) image of FeCo-Cu. Reprinted with the permission from[45] Copyright (2015) "American Chemical Society".

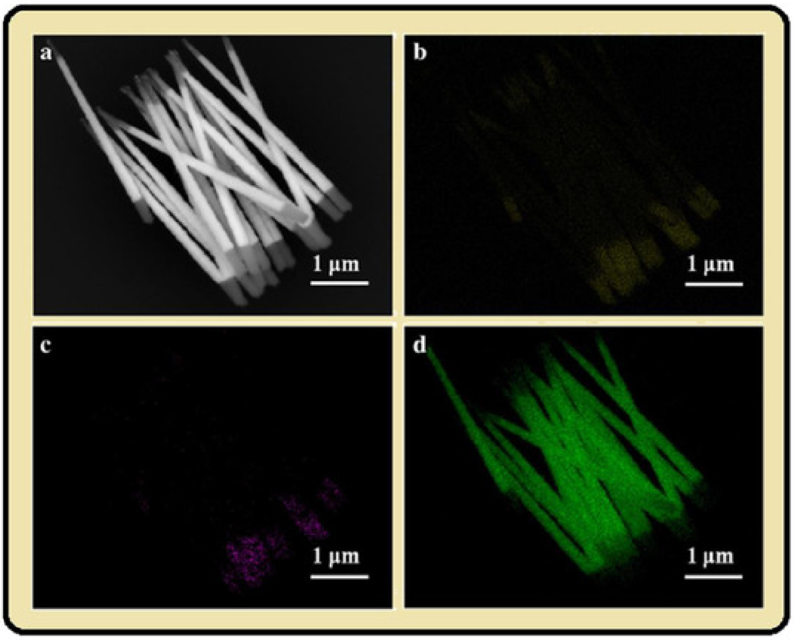


**Figure 2.** (**a**) SEM image of CoFe/Au/CoFe NWs, EDX mapping of (**b**) Co, (**c**) Fe, and (**d**) Au concentration. Reprinted with permission from[46]Copyright (2013) “Elsevier”.

This entry is from:https://www.mdpi.com/1996-1944/12/23/3908

## References


1. Mingliang Tian; Jinguo Wang; James Kurtz; Thomas E. Mallouk; M. H. W. Chan; Electrochemical Growth of Single-Crystal Metal Nanowires via a Two-Dimensional Nucleation and Growth Mechanism. *Nano Letters* **2003**, *3*, 919-923, 10.1021/nl034217d.
2. Yi-Kun Su; Dong-Huan Qin; Hao-Li Zhang; Hua Li; Hu-Lin Li; Microstructure and magnetic properties of bamboo-like CoPt/Pt multilayered nanowire arrays. *Chemical Physics Letters* **2004**, *388*, 406-410, 10.1016/j.cplett.2004.03.041.
3. Hui Pan; Han Sun; Chee Kok Poh; Yuanping Feng; Jianyi Lin; Single-crystal growth of metallic nanowires with preferred orientation. *Nanotechnology* **2005**, *16*, 1559-1564, 10.1088/0957-4484/16/9/025.
4. Joon-Rak Choi; Sang Jun Oh; Honglyoul Ju; Jinwoo Cheon; Massive Fabrication of Free-Standing One-Dimensional Co/Pt Nanostructures and Modulation of Ferromagnetism via a Programmable Barcode Layer Effect. *Nano Letters* **2005**, *5*, 2179-2183, 10.1021/nl051190k.
5. I.Z Rahman; K.M Razeeb; M.A Rahman; Kamruzzaman; Fabrication and characterization of nickel nanowires deposited on metal substrate. *Journal of Magnetism and Magnetic Materials* **2003**, *262*, 166-169, 10.1016/s0304-8853(03)00043-x.
6. Hui Pan; Binghai Liu; Jiabao Yi; Chee Kok Poh; Sanhua Lim; Jun Ding; Yuanping Feng; C. H. A. Huan; Jianyi Lin; Growth of Single-Crystalline Ni and Co Nanowires via Electrochemical Deposition and Their Magnetic Properties. *The Journal of Physical Chemistry B* **2005**, *109*, 3094-3098, 10.1021/jp0451997.
7. Xue Wei Wang; Guang Tao Fei; Xi Jin Xu; Zhen Jin; Li De Zhang; Size-Dependent Orientation Growth of Large-Area Ordered Ni Nanowire Arrays. *The Journal of Physical Chemistry B* **2005**, *109*, 24326-24330, 10.1021/jp053627i.
8. Xue Wei Wang; Guang Tao Fei; Li Chen; Xi Jin Xu; Li De Zhang; Orientation-Controllable Growth of Ni Nanowire Arrays with Different Diameters. *Electrochemical and Solid-State Letters* **2007**, *10*, E1-E3, 10.1149/1.2436642.
9. Xi Jin Xu; Guang Tao Fei; Wen Hui Yu; Li Chen; Li De Zhang; Xin Ju; Xiao Peng Hao; Bao Yi Wang; In situ x-ray diffraction study of the thermal expansion of the ordered arrays of silver nanowires embedded in anodic alumina membranes. *Applied Physics Letters* **2006**, *88*, 211902, 10.1063/1.2206136.
10. Ming Tan; Xinqi Chen; Growth Mechanism of Single Crystal Nanowires of fcc Metals (Ag, Cu, Ni) and hcp Metal (Co) Electrodeposited. *Journal of The Electrochemical Society* **2011**, *159*, K15-K20, 10.1149/2.034201jes.
11. Kotha Sai Madhukar Reddy; Jung Jin Park; Suok-Min Na; Mazin M. Maqableh; Alison B. Flatau; Bethanie J. H. Stadler; Electrochemical Synthesis of Magnetostrictive Fe-Ga/Cu Multilayered Nanowire Arrays with Tailored Magnetic Response. *Advanced Functional Materials* **2011**, *21*, 4677-4683, 10.1002/adfm.201101390.

12. K. R. Pirota; M. Vazquez; Arrays of Electroplated Multilayered Co/Cu Nanowires with Controlled Magnetic Anisotropy. *Advanced Engineering Materials* **2005**, *7*, 1111-1113, 10.1002/adem.200500162.

13. M. I. Irshad; M. S. M. Saheed; A. Mumtaz; M. Yasar; A. Yar; M. A. Zeeshan; N. M. Mohamed; M. Z. Abdullah; Jordi Sort; Influence of the electrodeposition potential on the crystallographic structure and effective magnetic easy axis of cobalt nanowires. *RSC Advances* **2016**, *6*, 14266-14272, 10.1039/C6RA01311B.

14. Daljit Kaur; Sujeet Chaudhary; D. K. Pandya; Manifestations in the magnetization of the hcp-Co nanowires due to interdependence of aspect ratio and c-axis orientation. *Journal of Applied Physics* **2013**, *114*, 43909, 10.1063/1.4816558.

15. Aiman Mukhtar; Tahir Mehmood; Babar Shahzad Khan; Ming Tan; Effect of Co2+ concentration on the crystal structure of electrodeposited Co nanowires. *Journal of Crystal Growth* **2016**, *441*, 26-32, 10.1016/j.jcrysgro.2016.02.009.

16. Tahir Mehmood; Babar Shahzad Khan; Aiman Mukhtar; Xinqi Chen; Ping Yi; Ming Tan; Mechanism for formation of fcc-cobalt nanowires in electrodeposition at ambient temperature. *Materials Letters* **2014**, *130*, 256-258, 10.1016/j.matlet.2014.05.130.

17. Tahir Mehmood; Babar Shahzad Khan; Aiman Mukhtar; Ming Tan; Influence of bath temperature and pH on the structure of electrodeposited cobalt nanowires. *International Journal of Materials Research* **2015**, *106*, 961, 10.3139/146.111269.

18. Aiman Mukhtar; Tahir Mehmood; Kaiming Wu; Babar S. Khan; Humaira Latif; Zahida Parveen; Syeda Ruqaya Kazmi; Study of phase transformation and crystal structure of Co nanowires. *International Journal of Materials Research* **2017**, *108*, 710-714, 10.3139/146.111535.

19. Aiman Mukhtar; Xiao-Ming Cao; Tahir Mehmood; Da-Shuang Wang; Kai-Ming Wu; Structural characterization of self-assembled chain like Fe-FeOx Core shell nanostructure.. *Nanoscale Research Letters* **2019**, *14*, 308-12, 10.1186/s11671-019-3128-2.

20. K. R. Pirota; Fanny Béron; Daniela Zanchet; T. C. R. Rocha; David Navas; Jacob Torrejon; M. Vazquez; Marcelo Knobel; Magnetic and structural properties of fcc/hcp bi-crystalline multilayer Co nanowire arrays prepared by controlled electroplating. *Journal of Applied Physics* **2011**, *109*, 83919, 10.1063/1.3553865.

21. Xue Wei Wang; Zhi Hao Yuan; Shao Qing Sun; Yue Qin Duan; Li Jian Bie; Thermal expansion behaviors of hcp and fcc Co nanowire arrays. *Physics Letters A* **2009**, *373*, 2887-2889, 10.1016/j.physleta.2009.06.009.

22. Keith D. Bird; Giant Magnetoresistance in Electrodeposited Ni/Cu and Co/Cu Multilayers. *Journal of The Electrochemical Society* **1995**, *142*, L65, 10.1149/1.2044185.

23. Enrique Vilanova Vidal; Yurii P. Ivanov; Hanan Mohammed; Jürgen Kosel; A detailed study of magnetization reversal in individual Ni nanowires. *Applied Physics Letters* **2015**, *106*, 032403, 10.1063/1.4906108.

24. Bong Gun Kim; Seung Jae Yoon; In Tak Jeon; Ki Ha Kim; Jun Hua Wu; Young Keun Kim; Dimensional Dependence of Magnetic Properties in Arrays of CoFe/Au Barcode Nanowire. *IEEE Transactions on Magnetics* **2012**, *48*, 3929-3932, 10.1109/TMAG.2012.2202101.

25. Ju Hun Lee; Jun Hua Wu; Hong Ling Liu; Ji Ung Cho; Moon Kyu Cho; Boo Hyun An; Ji Hyun Min; Su Jung Noh; Young Keun Kim; Iron–Gold Barcode Nanowires. *Angewandte Chemie International Edition* **2007**, *46*, 3663-3667, 10.1002/anie.200605136.

26. Bum Chul Park; Bong Gun Kim; Hyo Won Seo; Young Keun Kim; Magnetic Anisotropy Evolution in CoFe/Au Barcode Nanowire Arrays. *IEEE Transactions on Magnetics* **2013**, *50*, 1-4, 10.1109/TMAG.2013.2279278.

27. Bumjin Jang; Eva Pellicer; Miguel Guerrero; Xiangzhong Chen; Hongsoo Choi; Bradley J. Nelson; Jordi Sort; Salvador Pané; Fabrication of Segmented Au/Co/Au Nanowires: Insights in the Quality of Co/Au Junctions. *ACS Applied Materials & Interfaces* **2014**, *6*, 14583-14589, 10.1021/am5038998.

28. Junwei Zhang; HongBin Ma; Senfu Zhang; Hong Zhang; Xia Deng; Qianqian Lan; Desheng Xue; Feiming Bai; Nigel J. Mellors; Yong Peng; et al. Nanoscale characterisation and magnetic properties of Co81Cu19/Cu multilayer nanowires. *Journal of Materials Chemistry C* **2015**, *3*, 85-93, 10.1039/C4TC01510J.

29. Seung Jae Yoon; Bong Gun Kim; In Tak Jeon; Jun Hua Wu; Young Keun Kim; Compositional Dependence of Magnetic Properties in CoFe/Au Nanobarcodes. *Applied Physics Express* **2012**, *5*, 103003, 10.1143/apex.5.103003.

30. Egerton, R.F. Electron Energy-Loss Spectroscopy in the Electron Microscope; Springer Science & Business Media: Berlin, Germany, 2011.

31. Bum Chul Park; Bong Gun Kim; Hyo Won Seo; Young Keun Kim; Magnetic Anisotropy Evolution in CoFe/Au Barcode Nanowire Arrays. *IEEE Transactions on Magnetics* **2013**, *50*, 1-4, 10.1109/TMAG.2013.2279278.

32. Cristina Bran; Yurii Ivanov; Jürgen Kosel; O Chubykalo-Fesenko; M Vazquez; Co/Au multisegmented nanowires: a 3D array of magnetostatically coupled nanopillars. *Nanotechnology* **2017**, *28*, 95709, 10.1088/1361-6528/aa585f.
33. In Tak Jeon; Seung Jae Yoon; Bong Gun Kim; Ji Sung Lee; Boo Hyun An; Jae-Seon Ju; Jun Hua Wu; Young Keun Kim; Magnetic NiFe/Au barcode nanowires with self-powered motion. *Journal of Applied Physics* **2012**, *111*, 7, 10.1063/1.3676062.
34. F. Hakkens; W. Coene; F.J.A. Den Broeder; Micro- and Nanostructure of Co/Pd and Co/Au Multilayers Studied with Transmission Electron Microscopy. *MRS Proceedings* **1991**, *231*, 397-404, 10.1557/proc-231-397.
35. Á. Cziráki; L. Peter; B. Arnold; J. Thomas; H.D. Bauer; K. Wetzig; I. Bakonyi; Structural evolution during growth of electrodeposited Co–Cu/Cu multilayers with giant magnetoresistance. *Thin Solid Films* **2003**, *424*, 229-238, 10.1016/s0040-6090(02)01126-4.
36. Á. Cziráki; L. Peter; B. Arnold; J. Thomas; H.D. Bauer; K. Wetzig; I. Bakonyi; Structural evolution during growth of electrodeposited Co–Cu/Cu multilayers with giant magnetoresistance. *Thin Solid Films* **2003**, *424*, 229-238, 10.1016/s0040-6090(02)01126-4.
37. L. Péter; A. Cziráki; L. Pogány; Z. Kupay; I. Bakonyi; M. Uhlemann; M. Herrich; B. Arnold; T. Bauer; K. Wetzig; et al. Microstructure and Giant Magnetoresistance of Electrodeposited Co-Cu/Cu Multilayers. *Journal of The Electrochemical Society* **2001**, *148*, C168-C176, 10.1149/1.1346606.
38. F. Hakkens; W. Coene; F.J.A. Den Broeder; Micro- and Nanostructure of Co/Pd and Co/Au Multilayers Studied with Transmission Electron Microscopy. *MRS Proceedings* **1991**, *231*, 397-404, 10.1557/proc-231-397.
39. S. Zsurzsa; E. Pellicer; J. Sort; L. Péter; I. Bakonyi; Electron Microscopy Characterization of Electrodeposited Homogeneous and Multilayered Nanowires in the Ni-Co-Cu System. *Journal of The Electrochemical Society* **2018**, *165*, D536-D542, 10.1149/2.0571811jes.
40. K. R. Pirota; M. Vazquez; Arrays of Electroplated Multilayered Co/Cu Nanowires with Controlled Magnetic Anisotropy. *Advanced Engineering Materials* **2005**, *7*, 1111-1113, 10.1002/adem.200500162.
41. Saba Shojaie Mehr; Abdolali Ramazani; Mohammad Almasi Kashi; Study on magnetic properties of NiFe/Cu multisegmented nanowire arrays with different Cu thicknesses via FORC analysis: coercivity, interaction, magnetic reversibility. *Journal of Materials Science: Materials in Medicine* **2018**, *29*, 18771-18780, 10.1007/s10854-018-0002-4.
42. Xiaoxu Liu; Jianling Zhao; Yangxian Li; Shifeng Xu; Zhiyong Zhu; Jinglan Chen; Guangheng Wu; The pH Rule for Fabricating Composite CoCu Nanowire Arrays. *Chemistry Letters* **2007**, *36*, 166-167, 10.1246/cl.2007.166.
43. Ren Yong; Wang Jian-Bo; Liu Qing-Fang; Han Xiang-Hua; Xue De-Sheng; The effect of substrate on magnetic properties of Co/Cu multilayer nanowire arrays. *Chinese Physics B* **2009**, *18*, 3573-3576, 10.1088/1674-1056/18/8/073.
44. D. Reyes; N. Biziere; Benedicte Warot-Fonrose; T. Wade; Christophe Gatel; Magnetic Configurations in Co/Cu Multilayered Nanowires: Evidence of Structural and Magnetic Interplay. *Nano Letters* **2016**, *16*, 1230-1236, 10.1021/acs.nanolett.5b04553.
45. Berna Özkale; Naveen Shamsudhin; George Chatzipirpiridis; Marcus Hoop; Fabian Gramm; Xiangzhong Chen; Xavi Martí; Jordi Sort; Eva Pellicer; Salvador Pané; et al. Multisegmented FeCo/Cu Nanowires: Electrosynthesis, Characterization, and Magnetic Control of Biomolecule Desorption. *ACS Applied Materials & Interfaces* **2015**, *7*, 7389-7396, 10.1021/acsami.5b01143.
46. T.S. Ramulu; R. Venu; Brajalal Sinha; B. Lim; S.S. Yoon; C.G. Kim; Synthesis and cysteamine functionalization of CoFe/Au/CoFe nanowires. *Thin Solid Films* **2013**, *546*, 255-258, 10.1016/j.tsf.2013.04.080.