Research Article Adv. Mater. Lett. 2016, **7**(3), 197-200 Advanced Materials *Letters*

www.vbripress.com/aml, DOI: 10.5185/amlett.2016.6150

Synthesis of Ni filled multiwalled carbon nanotubes and study of magnetic behaviour

Reetu Kumari, Anshika Singh, Rajesh Kumar, Lucky Krishnia, Vinay Kumar, Nitin K. Puri, Pawan K. Tyagi*

Department of Applied Physics, Delhi Technological University, Delhi 110042, India

*Corresponding author. Tel: (+91) 11-27852212; Fax: (+91) 11-27871023; E-mail: pawan.phy@dce.edu

Received: 09 September 2015, Revised: 21 September 2015 and Accepted: 03 January 2016

ABSTRACT

In this report, we have illustrated the synthesis of the Ni-filled multiwalled carbon nanotubes (MWCNTs) on both metallic and non-metallic substrates, by using thermal CVD technique. Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD) have been used to characterize the surface morphology and crystalline nature of the MWCNTs encapsulated with Ni nanorod. These filled MWCNTs have exhibited strong magnetic response due to encapsulation of pure phase of Ni. Magnetic Force Microscopy (MFM) study of such filled tubes reveals the pole formation in the Ni nanorod and confirms magnetization direction perpendicular to tube axis. Filling occurs in a fragmented manner confirmed by MFM and each fragment found to have north and south poles along the axis perpendicular to the tube i.e. radial direction of tube. Copyright © 2016 VBRI Press.

Keywords: Carbon nanotubes; thermal CVD; magnetic force microscopy (MFM); magnetization direction.

Introduction

Metal-filled multiwalled carbon nanotubes (MWCNTs) have potential industrial application in various fields of science and technology. The injection or filling of metal into the MWCNT may significantly amend their mechanical **[1]**, electrical **[2]** and magnetic properties **[3-7]**. The metal-filled MWCNTs have variety of industrial applications such as catalysts **[8]**, electronic devices **[9]**, magnetic tape **[10]**, and biosensors **[11]**. Filling of MWCNT can be accomplished either *in-situ* or *ex-situ* **[12]**. Among all, routes of *in-situ* filling have been preferred because of the easy way and filler exhibit high integrity in properties. *In-situ* filling can be made by various methods such as Arc discharge **[13]**, Laser ablation **[14]**, Plasma enhanced CVD **[15]** and Thermal CVD **[16, 17]**. Generally, in order to study the magnetic properties of ferromagnetic materials filled inside MWCNT, Fe, Co and Ni have selected as filler in the most of published reports **[17-22]**. Among all metals, which have been filled to the date, filling with Fe, or Fe_3C has been reported by most of the researchers **[20, 23-25]**. This happens due the high solubility of carbon in Fe. However, due to low binding energy of carbon with Fe, crystalline quality of MWCNT grown by using Fe as catalyst is low as compared to MWCNT grown by using Ni or Co as catalyst. Filling of the pure phase of Fe is very difficult because of the rapid formation of Fe_3C, which dominates over Fe phase formation. The carbide formation deteriorates the magnetic properties of the filled MWCNTs. MWCNTs filled with pure phase exhibit extraordinary magnetic properties. However, very few researchers have published the CVD method to grow pure Fe, Ni, Co; Ni/Pt filled MWCNTs **[20, 21, 22, 26]**. For the application of nanorod filled inside MWCNT as nanomagnet, it is important to first investigate magnetization behaviour and then pole formation in ferromagnetic nanorod filled inside the MWCNT. Another burning issue related to on-going research in area of MWCNT is to grow the MWCNT on conducting, non-conducting, magnetic or non-magnetic substrates. Among them MWCNTs grown on conducting substrate are of high importance. Reason is, if MWCNT follow root-growth mechanism depending on catalyst nature **[27]** then substrate-MWCNT interface has low contact resistance and substrate can used as a one contact for the devices. Objective of present study is two folds: (1) to grow pure Ni-filled MWCNTs on various substrates, and (2) to study the magnetization behaviour in confined nanorod by using MFM.

Experimental

Materials and synthesis method

Thermal chemical vapour deposition (Thermal CVD) technique was used to grow Ni- filled MWCNTs. In the technique quartz tube of inner diameter (ID) 3.5 cm and length of 60.0 cm was used as a reactor. The system has a 10.0 cm pre-heating zone (100 - 150 ^{o}C) and 15.0 cm heating zone (800 – 900 ^{o}C). To grow samples on quartz we have taken mixture of nickelocene and benzene of ratio 0.015 gm/ml. The mixture was first introduced in pre heating zone where solution vaporized and then vapour were introduced in to hot zone by using Ar/H_2 mixture as a carrier gases. Flow of Ar/H_2 gas mixture (Ar-100 sccm, H_2-50 sccm) was optimized for growth on all substrates. After the completion of reaction, system was set to cool down to room temperature in the presence of Ar. In order to grow MWCNTs on SiO_2/Si, Copper (Cu) and Stainless Steel (SS) temperature was set at 830 ^{o}C. When temperature of furnace reaches to reaction temperature, substrates were brought in to the hot zone in such a manner that the dense vapours immediately diffused on the substrates at set reaction temperature. After synthesis substrates were found to be fully covered by black thick layer of MWCNTs.

Characterization techniques

As-grown samples were characterized with Bruker D8 Advance X-Ray diffractometer and Hitachi S3100 Scanning Electron Microscopy. Very few amount of sample dispersed in Isopropyl alcohol (IPA) and then sonicated for 20 minutes to make a uniform dispersion. A single drop of dispersion of MWCNTs was used to make thin film on Si substrate. The thin film of MWCNTs on Si substrate was used in MFM study.

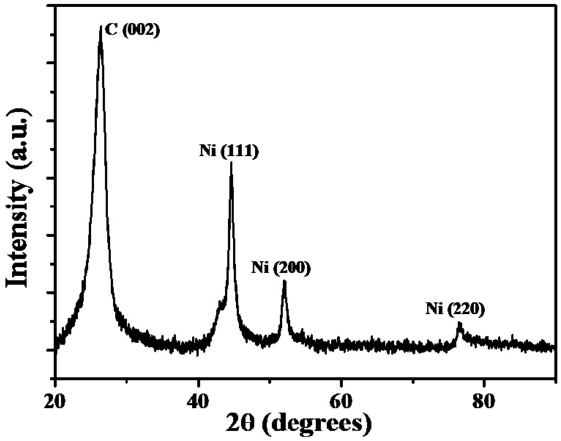

Fig. 1. XRD diffraction pattern of the as-grown Ni-filled MWCNTs, which grow on wall quartz reactor.

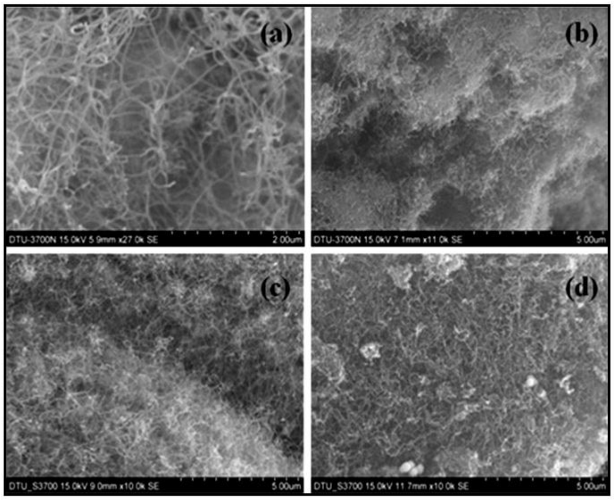

Fig. 2. SEM Images of Ni filled-MWCNTs grown on (a) Cu substrate, (b) SS substrate, (c) SiO_2/Si (300 nm/500 μm) substrate, (d) quartz.

Results and discussion

X-ray diffraction (XRD) measurement was performed on the as-grown filled MWCNTs scratched from the walls of quartz reactor. In **Fig. 1**, signature peak of MWCNT at 2θ =26.33° position, reflected from (002) plane of graphite (PCPDF 75-2078) was observed. Diffraction peaks at 2θ = 44.62°, 51.9° and 76.50° positions are indentified and found to be of (111), (200) and (220) planes of the fcc Ni (PCPDF 87-0712). Filling of fcc Ni having symmetry with intimate walls MWCNT have been also reported in Ref. **[26]** and reported results are matched with observed values. XRD profile confirmed that MWCNTs filled with fcc Ni have high crystalline quality. This is evident by FWHM (2°) and intensity of peak observed at (2θ =26.33°) position.

Growth possibility of MWCNTs on various substrates has been demonstrated and confirmed by SEM images as shown in **Fig. 2.** Variation in density of MWCNT with morphological change clearly depicts the influence of the substrates on MWCNT growth.

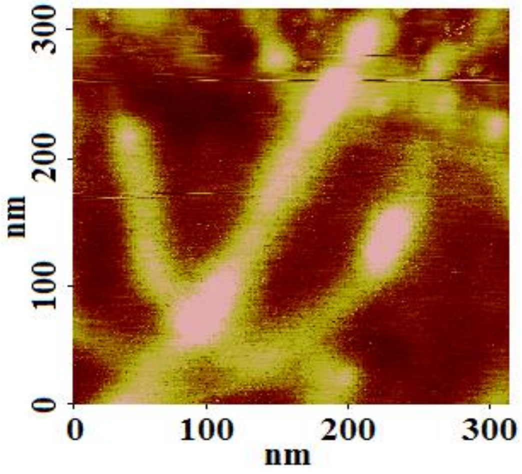

Fig. 3. MFM topography of Ni filled MWCNTs by using magnetic tip in taping mode.

MWCNTs grown on Cu (**Fig. 2(a)**) are less curly than that grown on other substrates. MWCNTs are well separated while CNTs on SS grown in bunches of high density. On SiO_2 coated Si substrate, MWCNTs are observed to be grown more vertical and have uniform morphology. In powder samples scratched from the walls of quartz reactor, MWCNTs are found to be grown randomly. As-grown MWCNTs have shown strong magnetic interaction when they are brought close to the bar magnet. This confirms the presence of Ni as either filler or catalytic impurities. Further, fragmented filling of Ni inside the core of MWCNT have been confirmed by MFM and shown in **Fig. 3**. Detailed MFM studies of Ni-filled MWCNT have shown in **Fig. 4**. In order to corroborate tip-sample interaction, MFM studies including amplitude and phase changes have been performed for hard disk also (shown in **Fig.5**). MFM measurement performed on Ni-filled MWCNT with the lift height of 50 nm.

Image in **Fig. 3** is the topographic image of Ni filled CNTs captured by using magnetic tip in taping mode. Bright contrast in topographic image, if captured by using the magnetic tip in taping mode, directly measures the dominating interaction between tip-Ni while other interaction like, between CNT and tip are minimized. So, intensity can be assumed as a direct measure of the interaction strength. Therefore, filled parts of MWCNT respond very strongly to the magnetized tip and have both vander waal and magnetic interaction. Consequently, filled parts of MWCNT can be identified by the contrast variation. Filling inside the MWCNT was found to be fragmented as confirmed by the intensity variation along tube axis (as shown in **Fig. 3**).

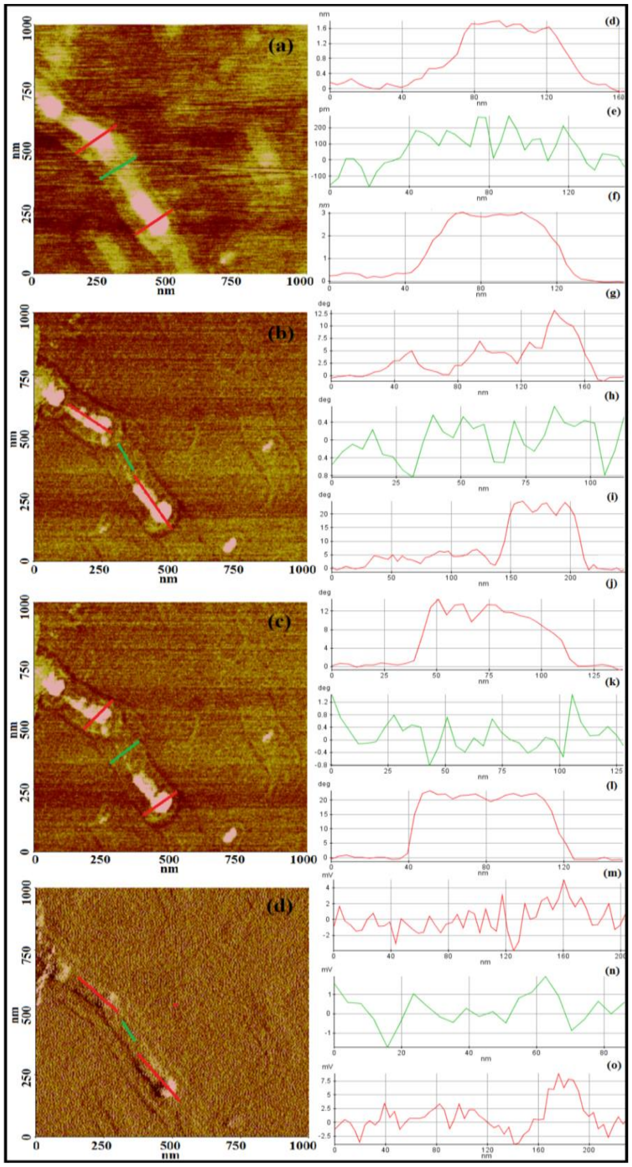

Fig. 4. MFM studies with lift height 50 nm (a) Topography, (b & C) Phase, and (d) amplitude images of Ni filled MWCNT. (e-o) corresponding profiles of filled and unfilled regions represented by lines in planes (a-c).

In the present study, MFM measurements were taken in two passes across each scan of the sample. In the first pass surface topography was scanned which is represented in (**Fig. 4(a)**). The topographical trace and retrace were performed in tapping mode of AFM. In second pass, the probe was lifted to the desirable height from the surface so that short-range forces (vander walls force) get minimize. At this height the tip was able to trace and retrace only magnetic responses. The magnetic interaction depends on the factors like: lift height, coercivity and the magnetic moment of the tip as well as magnetic stray field intensity of the sample **[28]**. In this scan mode, a force acts between magnetic tip and sample magnetic stray field and this force gradient results in change in phase as well as amplitude with which cantilever vibrates **[28]**. The shift in phase and amplitude are exceedingly informative in analyzing magnetic response. In **Fig. 4** (**b**, **c** and **d**) these shifts are explained along with their corresponding line profiles.

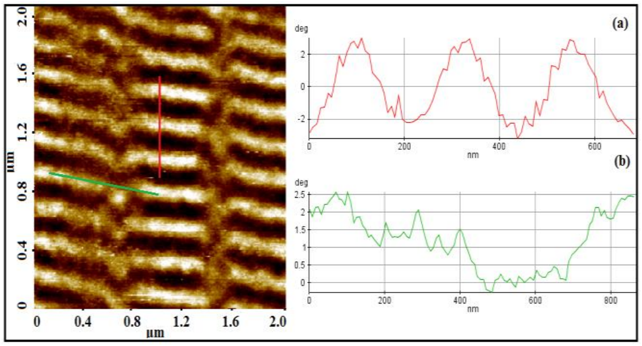

Fig. 5. MFM phase image of hard disk drive.

Fig. 4(**b**) represents the phase profile of Ni-filled MWCNT captured in lift mode. Remarkable, phase shifts have observed as confirmed by line profiling in filled parts as shown in **Fig. 4**(**g**) and (**i**). Along the tube axis bright contrasts appeared to be uniform. In line profile if we moves from darker to brighter portion the phase is shifted from 0 to 12.5° and again it goes down to 0º in darker region. The same phenomenon occurs in other filled part where phase shift goes to 20° degree and vice-versa. Importantly, there is no significant phase shift observed in unfilled part of MWCNT (**Fig. 4h**). The contrast in phase image has been reported to depend on nature of interaction which present between tip and sample, either attractive or repulsive **[29]**. Bright contrast is presumed due to repulsive magnetic interaction, and results in positive phase shift. Therefore, in the studied sample strong repulsive magnetic interaction was found to be acting between probe and filled parts of MWCNT. Similarly, line profiles were taken along the radial direction of the tube as shown in **Fig. 4**(**k**, **l** and **m**). Nearly exact phase shifts in positive direction have been observed. Uniformity of contrast as well phase shift confirmed the existence of single domain in both radial or along the axis of Ni nanorod. Consequently, in studied sample nickel nanorod having single domain structure is confirmed. In order to study the phase shift behaviour more extensively, we have compared the MFM phase image of standard hard disk drive (**Fig. 5**). In **Fig. 5**(**a**) the profile shows that from darkest to brightest region the phase shifted from -2.5° to 2.5° while in darkest contrast it again fell down to -2.5°. Therefore, for each cycle (darkest to brighter contrast), phase shifted from -2.5° to 2.5°. The negative shift occurs due to attractive magnetic force while positive is due to repulsion. This confirmed that in hard disk poles were formed perpendicular to bit length. However, line profile along the length of bit area (**Fig. 5b**) the phase shift was not negative anywhere but was positive in brighter contrast area with the same value as in **Fig. 5b**. In the scanned image along length of bit area has the darker contrast with almost negligible phase shift (**Fig. 5b**) is not as dark as appeared in perpendicular to the bits length because the less darker portion does not show any pole in that direction. Therefore, it has been confirmed that transition in the direction of magnetization is only observed along the width of the bits.

In Ni-filled MWCNT, the direction of magnetization was found to be perpendicular to the tube axis. This is evident by the result, i.e. no negative phase shift either along or perpendicular to tube axis. The line profile of MFM phase is somewhat similar to the line profile along length of bit area (in **Fig. 5**) of the phase image of the hard disk where only one type of interaction is observed (in bright contrast) and rest part does not seem to have magnetic responses. If direction of magnetization is along the tube axis then magnetic contrast should be bright at one end and negative at the other end because poles would be formed along the tube axis. Lutz *et. al.* have reported the direction of magnetization in case of Fe and Fe_3C nanowire inside MWCNTs **[29]**. In their report they have mentioned the MFM images of both types of nanowires and explained the direction of magnetization taking contrast into account. However, they have reported that in case of Fe poles form along the tubes axis but in our case filling of Ni inside MWCNT causes pole formation perpendicular to the tube. The studied Ni-filled MWCNT are grown randomly and mostly found to be lying in substrate plane. So we assume that radial direction is perpendicular to substrate plane. As reported in Ref **[30]**, a magnetic field gradient in radial direction was applied in order to maintain the temperature during growth. Instead of shape or magnetocrystalline anisotropy this gradient may be controlling the direction of magnetization in Ni nanorod.

Conclusion

We have demonstrated the growth of Ni filled MWCNTs on metallic and non-metallic both kinds of substrates. The filling of metal inside MWCNT takes place in fragmented manner which is confirmed by probing the filled MWCNTs with MFM. Positive variation in the phase in both directions along as well as perpendicular to the tube axis confirmed that in Ni nanorod poles are formed in radial direction. In magnetization shape anisotropy is not playing a decisive role. The strong magnetic interaction proposes that filled MWCNT can be used for storage devices capable of storing data for long term.

Reference

1. Coleman, J.N.; Khan, U.; Gun′ko, Y.K.; *Adva. Mater.*, **2006**, *18*, 689.
   DOI: 10.1002/adma.200501851
2. Mathur, A.; Wadhwa, S.; Tweedie, M.; Hazra, K.S.; Dickinson, C.; Roy, S.S.; Mitra, S.K.; Misra, D.S.; McLaughlin, J. A.; *Physica E*, **2011**, *44*, 29.
   DOI: 10.1016/j.physe.2011.06.035
3. Shpak, A.P.; Kolesnik, S.P.; Mogilny, G.S.; Petrov, Yu. N.; Sokhatsky, V.P.; Trophimova, L. N.; Shanina, B. D.; Gavriljuk, V. G.; *Acta Mat*., **2007**, *55*, 1769.
   DOI: 10.1016/j.actamat.2006.10.039
4. Jian-hua, L.; Ruo-yu, H.; Gua-hua, L.; Dong-guang, W.; *Ne. Carb. Mater*., **2010**, *25*, 192.
   DOI: 10.1016/S1872-5805(09)60026-3
5. Wolny. F.; Mühl, T.; Weissker, U.; Lipert, K.; Schumann, J.; Leonhardt A.; Büchner B.; *Nanotech.*, **2010**, *21*, 435501.
   DOI: 10.1088/0957-4484/21/43/435501
6. Weissker, U.; Hampel, S.; Leonhardt, A.; Büchner, B.*; Mater.*, **2010**, *3*, 4387.
   DOI: 10.3390/ma3084387
7. Bao J.; Zhou, Q.; Hong, J.; Xu, Z.; *Appl. Phys. Lett*., **2002**, *81*, 4592;
   DOI: 10.1063/1.1526461
8. Che, G.; Lakshmi, B. B.; Martin, C. R.; Fisher, E. R.; *Langmuir*, **1999**, *15*, 750.
   DOI: 10.1021/la980663i
9. Kawano, T.; Christensen, D.; Chen, S.; Cho, C.Y.; Lin, L.; *Appl. Phys. Lett.*, **2006**, *89*, 163510.
   DOI: 10.1063/1.2364151
10. Winarski, T. Y.; U. S. Patent 7976966 B2, **2011**.
11. Freemantle, M.; *Chem. Eng. News*, **1996**, *74*, 62.
12. Tyagi, P.K.; Singh, M. K.; Misra, D. S.; *Encyl. of Nanos. Tech.*, **2003**, *3*, 416.
13. Loiseau, A.; Pascard, H.; *Chemical Physics Lett.*, **1996**; *256*, 246.
    DOI: 10.1016/0009-2614(96)00459-9
14. Thess, A.; Lee, R.; Nikolaev, P.; Dai, H.; Petit, P.; Robert, J.; Xu, C.; Kim, S. G.; Rinzler, A.G.; Colbert, D.T.; Scuseria, G. E.; Tománek, D.; Fisher, J. E.; Smalley, R. E.; *Science*, **1996**, *273*, 483
    DOI: 10.1126/science.273.5274.483
15. Hayashi, Y.; Tokunaga, T.; Kaneko, K.; Henley, S. J.; Stolojan, V.; Carey, J.D.; Silva, S.R.P.; *IEEE Trans. Nanotech.*, **2006**, *5*, 485.
    DOI: 10.1109/TNANO.2006.880456
16. Huczko, A.; *App. Phys. A: Mater. Sci. Process*, **2002**; *74*, 617.
    DOI: 10.1007/s003390100929
17. Rao, C.N.R.; Govindraj, A.; Sen, R.; Satishkumar, B.S.; *Mat. Res. Innov.*, **1998**, *2*, 128.
    DOI: 10.1007/s100190050075
18. Leonhardt, A.; Ritschel, M.; Kozhuharova, R.; Graff, A.; Mühl, T.; Huhle, R.; Mönch I.; Elefant D.; Schneider C. M.; *Diam. Rela. mater.*, **2003**; 12: 790.
    DOI: 10.1016/S0925-9635(02)00325-4
19. Leonhardt, A.; Hampel, S.; Müller, C.; Mönch, I.; Koseva, R.; Ritschel, M.; Elefant, D.; Biedermann, K.; Büchner, B.; *Chem. Vap. Deposition*, **2006**,*12*, 380.
    DOI: 10.1002/cvde.200506441.
20. Karmakar, S; Sharma, S.M.; Mukadam, M.D.; Yusuf, S.M.; Sood A. K.; *J. Appl. Phys.*, **2005**, *97*, 054306-01-054306-05.
    DOI: 10.1063/1.1858878.
21. Poswal, H. K.; Karmakar, S.; Tyagi, P. K.; Misra, D. S.; Busetto, E.; Sharma, S. M.; Sood, A. K.; *Phys. Stat. Solid. (b)*, **2007**, *244*, 3612.
    DOI: 10.1002/pssb.200642608
22. Tyagi, P.K.; Misra, A.; Singh, M. K.; Misra, D. S.; Ghatak, J.; Satyam, P.V.; Normand, F.L.; *Appl. Phys. Lett.*, **2005**, *86*, 253110.
    DOI: 10.1063/1.1953881
23. Geng, F.; Cong, H.; *Phys. B*, **2006**, *382*, 300.
    DOI: 10.1016/j.physb.2006.03.003
24. Iskhakov, R. S.; Komogortsev, S.V.; Balaev, A.D.; Okotrub, A.V.; Kudashov, A.G.; *JETP Lett.*, **2003**, *78*, 236.
    DOI: 10.1134/1.1622038
25. Weissker, U.; Löffle, M.; Woln, F.; Lutz, M.U.; Scheerbaum, N. *J., Appl. Phys.*, **2009**, *106*, 054909-5.
    DOI: 10.1063/1.3204495
26. Singh, M.K.; Titus, E.; Tyagi, P.K.; Palnitkar, U.A.; Misra, D.S.; Roy, M.; Dua, A. K.; Cojocaru, C. S. ; Normand, F.L., *J. Nanosci. Nanotech.*, **2003**, *3*, 165.
    DOI: 10.1166/jnn.2003.200
27. Tyagi, P.K.; Janowska, I.; Cretu, O.; Pham-Huu, C,.; Banhart, F.; *J. Nanosci. Nanotechnology*, **2011**, *11*, 1.
    DOI: 10.1166/jnn.2011.3740
28. Bramowicz, M.; Kulesza, S.; Czaja, P.; Maziarz, W.; *Arch. Metall. mater.*, **2014**, *59*, 451.
    DOI: 10.2478/amm-2014-0075
29. Lutz, M.U.; Weissker, U.; Wolny, F.; Müller, C.; Löffler, M.; Mühl, T.; Leonhardt, A.; Büchner, B.; Klingeler, R., *J. Phys. Conference Series*, **2010**, *200*, 072062.
    DOI: 10.1088/1742-6596/200/7/072062.
30. Kumari, R.; Krishnia, L.; Kumar, V.; Singh, S.; Singh, H. K.; Kotnala, R.K.; Juluri, R. R.; Bhatta, U. M.; Satyam, P. V.; Yadav, B. S.; Tyagi, P.K., Article in preparation.
    DOI: 10.1039/c0cs00136h