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Bonding Analysis of [Au (3.16 nm)/Co (1.5 nm)]$_{x35}$/Si (100) Multilayer Thin Film

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The bond lengths and other local structure parameters of [Au (3.16 nm)/Co (1.5 nm)]$_{x35}$/Si (100) having ultra-thin individual layers were investigated using X-ray Absorption Spectroscopy (XAS). The multilayer structure was synthesized by electron beam evaporation method under ultra-high vacuum environment. To make a composition of 20 weight percent (wt. %) of Co atoms in Au matrix, the thickness and number of layers were specifically chosen. For the XAS measurements, L_{III}-absorption edge (11919 eV) of Au and K-absorption edge (7709 eV) of Co atom were used. A theoretical model was generated by using crystallographic information file (CIF) of both (Au and Co) atoms and then a computer software package IFEFFIT was used for fitting and data analysis. In this study, the short-range order structural geometry of individual layers such as oxidation state, surrounding atomic information, edge shift, bond distance and Debye-Waller factor were analyzed.

Keywords: Electron beam evaporation, XANES, EXAFS, Thin film, Multilayer.

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1. INTRODUCTION

In this present era of nanotechnology, demand of high speed and low dimensional with large data storage capacity devices is increasing day by day. Some materials possessing these properties include nanowires, thin films, multilayers and granular materials. Such nanostructures are of great interest in research owing to their fundamental research as well as application aspects. Some novel properties like perpendicular magnetic anisotropy (PMA) [1], giant magneto resistance (GMR) [2, 3], spin reorientation transition [4], spin torque transfer effect (STT) [5] etc. are found to be useful in wide range of device applications designed for low power consumption such as in magnetic recording media like read and write heads [2], magnetic ratchet memories [6, 7], sensors [8, 9] and magneto-plasmonic properties in biomedical field [10-12].

Among all the available combinations of materials for this particular interest, magnetic materials in non-magnetic matrix have particular technological importance [13, 14]. In this research work, we have chosen the combination of ultra-thin layer of magnetic material Co sandwiched between adjacent non-magnetic Au layers with comparatively higher thickness and this combination is repeated several times to make the multilayer. In the past, several researchers have investigated this particular system [15-20] and exhibited an enhancement in the multilayer quality depending on the periodicity of bilayers, resulting in the modification PMA, which is due to the fact that there is ~ 14 % lattice mismatch between Au and Co unit cells. This system also exhibits immiscibility among constituent elements [21], even when annealed even up to very high temperatures (~ 800 °C or more) [22]. However, this promotes agglomeration of magnetic material (Co) in the matrix of non-magnetic material (Au) without any chemical bonding between them. For this kind of studies, Au is found to be a suitable non-magnetic matrix as it has chemically stable properties with high oxidation resistance even at very high temperature range and the Co-Au alloy formation energy is also very high (~ + 11 kJ·mol^{-1}) [21], which prevents any alloying, however intermixing can take place between the adjacent layers.

To prepare these nanomaterials, several techniques are available such as chemical synthesis, sputtering (ion beam sputtering or magnetron sputtering), molecular beam epitaxy or evaporation etc. For present study, electron beam evaporation (EBE) technique under ultra-high vacuum environment is used to deposit multilayer thin film. In our previous study of this multilayer, we found magnetic phase transition and modification in structural and morphological properties as a function of annealing temperature [23]. On the basis of those results, in the present work, we have investigated the local structural information of the constituent elemental layers by X-ray absorption fine structure spectroscopy.

2. EXPERIMENTAL DETAILS

2.1 Multilayer Deposition

The multilayer sample (MLS) was prepared by electron beam evaporation method under ultra-high vacuum conditions with a base pressure of ~ 5·10^{-10} mbar. This multilayer film consisted of 35 bilayers with the layer structure of [Au (3.16 nm)/Co (1.5 nm)] on Si (100) substrate, which was covered by a native oxide layer. The reason behind the selection of these particular individual layer thicknesses is that for obtaining optimized magnetic properties, it is required to maintain ~ 20 wt. % of Co concentration inside Au matrix, which can be achieved with this thickness combination. To maintain the periodicity of the film, the thickness of Au and Co layers in all bilayers was kept same, i.e. the bilayers were periodically deposited [23].

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2.2 Characterization Technique

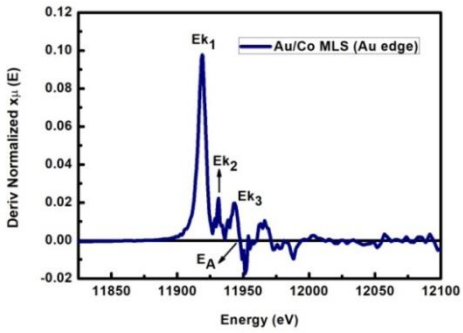
The X-ray absorption spectroscopy (XAS) measurements at Au L_{III}-absorption edge (11919 eV) and Co K-absorption edge (7709 eV) of MLS were carried out at energy scanning XAS beam line (BL-9) of Bhabha Atomic Research Centre installed at Indus-2, 2.5 GeV synchrotron radiation source (SRS) of Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India [24]. The recorded data was processed and then analyzed by a computer software program *IFEFFIT*. For this purpose, a theoretical model has been generated and fitted on the data using suitable standard .cif files [1100138] and [9008492] for Au and Co atoms, respectively.

3. RESULTS AND DISCUSSION

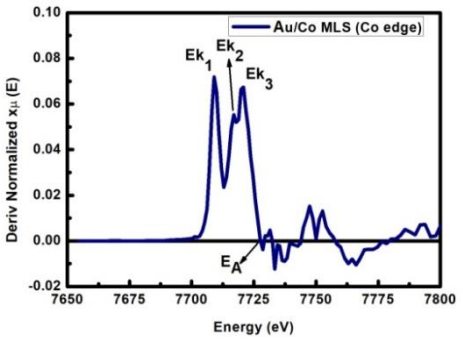
3.1 XANES Region

XANES region (between 40 eV below absorption edge and 80 eV above it) was investigated to extract the oxidation state and coordination geometry of central the absorbing atom (Co and Au in their corresponding layers). In Fig. 1, the first derivative of XANES spectra around Au edge (Fig. 1a) and Co edge (Fig. 1b) of MLS are shown. In both figures, the spectra exhibit three main peaks which indicate the three variation points, i.e. E_{k1}, E_{k2} and E_{k3} along with the position of principal absorption maxima (E_A). The values obtained from the data analysis are given in Table 1.

From these positions, it is clear that both type of atoms (Au and Co) in the sample are present in their + 3 oxidation state.



a



b

Fig. 1 – Derivative of XAFS spectrum of (a) Au and (b) Co edge in multilayer system

To calculate the edge shift in multilayer film with respect to the metal foil, the following equation is obtained:

$$\Delta E_k = E_{k1}\text{ (sample)} - E_{k1}\text{ (metal)}. \quad (1)$$

There is no significant modification in the edge shift compared to pure metal foil, which is in agreement to the argument of due to the non-bonding or no alloy formation between the constituent atoms (Co and Au) present in multilayer film. Au atoms shows very low (0.37 eV) shift in higher energy side but Co atom shows shifting towards the negative energy side with the value of 5.65 eV with respect to corresponding metals.

Table 1 – XANES study of multilayer sample and metal foil

Metal/ Sample	Au edge (MLS)	Au metal	Co edge (MLS)	Co metal
E_{k1} (eV)	11919	11919	7709.08	7709
E_{k2} (eV)	11931.25	11930.14	7716.88	7716.30
E_{k3} (eV)	11943.54	11943.91	7720.77	7722.25
E_A (eV)	11947.26	11946.89	7727.61	7733.26
ΔE_k	0	–	0.08	–
Shift in principal absorption maxima	0.37	–	–	– 5.65
E_w (eV)	28.26	27.89	18.53	24.26

From Table 1, it is clear that there is no significant change (~ 0.37 eV) in edge width for Au atom of MLS with respect to the pure metal, may be due to its chemical stability. While for Co atom that there is significant change (~ 5.65 eV) compared to corresponding pure metal, which may be attributed to its island type growth in between the interface of multilayer thin film [23].

3.2 EXAFS Region

Fig. 2 and Fig. 3 show the fitted Fourier transform results in R space of multilayer film in Au and Co absorption edge regions respectively. The .cif data files were used to generate the theoretical model which was then fitted to the experimental data. The obtained information from the fitting and analysis is reported in Table 2.

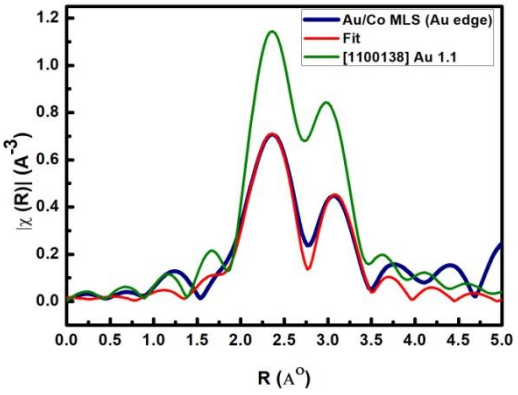


Fig. 2 – Magnitude of Fourier transform of the $X(R)$ curve for Au absorption edge

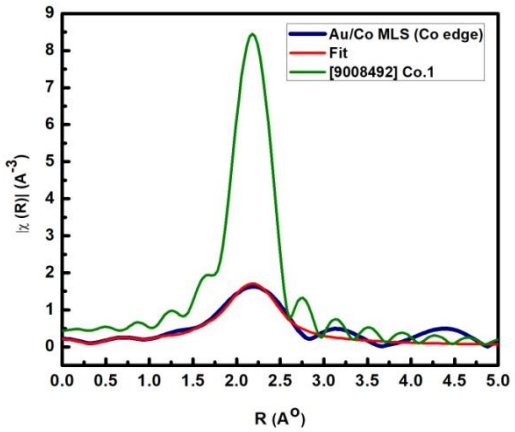


Fig. 3– Magnitude of Fourier transform of the $X(R)$ curve for Co absorption edge

Table 2 – Information obtained from fitted Fourier transform curve

Path	S_0^2	ΔE_0	σ^2	R	ΔR
[100138] Au1.1	0.759	8.598	0.01014	2.83518	– 0.04272
[9008492] Co.1	0.708	8.212	0.01236	2.49358	– 0.00832

Here S_0^2 is the electron reduction factor, ΔE_0 is the energy shift, σ^2 is the Debye-Waller factor, R is the nearest neighbor distance or bond length from first coordinating shell to central absorbing atom and ΔR is the difference in between bond length of scattering path and central absorbing atom of the sample.

To fit and analyze the obtained data, maximum frequency of the background, i.e. R_{bkg} was set to 1.0 Å and data were fitted in the R-space with the value of k-weight taken as 2 for both (Au and Co) absorption edges. For Au edge fitting, Fourier transform was performed over the k-range from 3 to 9.5 Å, while for Co edge, it was done in the range from 3 to 11 Å. Only single scattering paths were used as [100138] Au1.1 and [9008492] Co.1 for Au and Co edges, respectively, followed by FEFF calculation.

All the fitted parameters were found to be well within the acceptable range. From Table 2, we can see that the bond distance (R) for Au edge (considering Au atom as central atom) was found to be ~ 2.83 Å and for Co edge (considering Co atom as the central atom) was found to be ~ 2.5 Å. Both the edges have the same value of Debye-Waller factor as 0.01.

4. CONCLUSIONS

The XAFS spectra of [Au (3.16 nm)/Co (1.5 nm)]$_{x35}$/Si (100) multilayer film have been investigated and the short-range order structural information was analyzed. The XANES features around both Co and Au absorption edges revealed + 3 oxidation states of atoms present in the film with no significant changes in corresponding edge shift. Also the EXAFS spectra suggested the bond length from nearest neighbor atom to first coordinating shell as ~ 2.83 Å and ~ 2.5 Å for Au and Co central atoms, respectively, with the same value (0.01) of Debye-Waller factor. The overall results provide local structural information which is very useful in some technological importance as per application point of view. These results also support initial work performed on the sample as reported in our previous study [23].

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REFERENCES

1. A. Walczak, T. Slusarski, A. Lehmann-Szweykowska, G. Kamieniarz, *Acta Physica Polonica A* **121**, 653 (2012).
2. C. Khe, A. Aziz, Z. Lockman, *Nanosci. Nanotechnol. Lett.* **4**, 1 (2012).
3. M. Sakamaki, H. Abe, R. Sumii, K. Amemiya, T. Konishi, T. Fujikawa, L.T. Baczewski, A. Wawro, A. Petroutchik, Z. Kurant, A. Maziewski, *Acta Physica Polonica A* **115**, 309 (2009).
4. M. Sakamaki, T. Konishi, T. Fujikawa, A. Persson, C. Andersson, O. Karis, D. Arvanitis, H. Rossner, E. Holub-Krappe, *J. Phys.* **190**, 012113 (2009).
5. M. Mann, G.S.D. Beach, *APL Mater.* **5**, 106104 (2017).
6. N. Marsot, R. Belkhou, H. Magnan, P. Le Fevre, C. Guillot, D. Chandesris, *Phys. Rev. B* **59**, 3135 (1999).
7. P. Kluth, B. Hoy, B. Johannessen, S.G. Dunn, G.J. Foran, M.C. Ridgway, *Appl. Phys. Lett.* **89**, 153118 (2006).
8. M. Katagiri, J.L.C. Huaman, T. Matsumoto, K. Suzuki, H. Miyamura, J. Balachandran, *ACS Appl. Nano Mater.* **3**(1), 418 (2020).
9. C. Rizal, S. Pisana, I. Hrvoic, *Photonics* **5**(3), 15 (2018).
10. M. Afsharnia, S.M. Hamidi, *IEEE Trans Magn.* **54**(1), 4000207 (2018).
11. S.M. Hamidi, O. Ghaebi, *J Magn. Magn. Mater.* **414**, 122 (2016).
12. C. Rizal, Pisana, I. Hrvoic and E.E. Fullerton, *J. Phys. Commun.* **2**, 055010 (2018).
13. Z. Kurant, M. Tekielak, I. Sveklo, A. Wawro, A. Maziewski, *J Magn. Magn. Mater.* **475**, 683 (2019).
14. A.S. Trevizo, A.M. Hodge, *Nanotechnology* **31**, 292002 (2020).
15. C. Rizal, E.E. Fullerton, *J. Phys. D.: Appl. Phys.* **50**(35), 355002 (2017).
16. A.V. Kornilov, V.M. Pudalov, Y. Kitaoka, K. Ishida, G.-Q. Zheng, T. Mito, J.S. Qualls, *Phys. Rev. B* **69**, 220404 (2004).
17. G. Gubbiotti, G. Carlotti, F. Albertini et al., *Thin Solid Films* **428**, 102 (2003).
18. C.H. Lee, H. He, F.J. Lamelas, W. Vavra, C. Uher, R. Clarke, *Phys. Rev. B* **42**, 1066 (1990).
19. H.Y. Zhang, Y.J. Wang, G.G. Aheng, *IEEE Trans Magn.* **29**, 3376 (1993).
20. G. Gubbiotti, G. Carlotti, *J. Appl. Phys.* **93**, 7241 (2003).
21. S. Pizzini, F. Baudelet, E. Dartyge, M. Fontaine, Ch. Giorgetti, J.F. Bobo, M. Piecuch, C. Marlire, *J. Magn. Magn. Mater.*

121, 208 (1993).
22. J.B. Gonzalez-Diaz, A. Garcia-Martin, J.M. Garcia-Martin, A. Cebollada, G. Armelles, B. Sepulveda, Y. Alaverdyan, M. Kall, *Small* **4**, 202 (2008).
23. J. Tripathi, A. Sharma, D. Kumar, J. Singh, R. Bisen, S. Tripathi, *Surf. Interface Anal.* 1 (2020).
24. https://www.rrcat.gov.in/technology/accel/srul/beamline/exafsscan.html.

Аналіз зв'язків в багатошаровій тонкій плівці [Au (3,16 нм)/Co (1,5 нм)]$_{x35}$/Si (100)

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Довжини зв'язку та інші локальні структурні параметри плівки [Au (3,16 нм)/Co (1,5 нм)]$_{x35}$/Si (100) із надтонкими окремими шарами досліджували за допомогою абсорбційної рентгенівської спектроскопії (XAS). Багатошарова структура була синтезована методом електронно-променевого випаровування в умовах надвисокого вакууму. Щоб отримати склад з 20 ваг. % атомів Co в матриці Au, були спеціально обрані товщина та кількість шарів. Для вимірювань XAS використовували край поглинання L_{III} (11919 eB) атома Au і край поглинання K (7709 eB) атома Co. Теоретична модель була створена за допомогою файлу кристалографічної інформації (CIF) обох (Au і Co) атомів, а потім для підгонки та аналізу даних був використаний пакет комп'ютерних програм IFEFFIT. У цьому дослідженні була проаналізована структурна геометрія ближнього порядку окремих шарів, а саме стадія окиснення, інформація про атоми оточення, зсув краю, довжина зв'язку та коефіцієнт Дебая-Уоллера.

Ключові слова: Електронно-променеве випаровування, XANES, EXAFS, Тонка плівка, Багатошаровість.