XSW-XAFS characterization of ion-irradiated Pt/Ni/C multilayer

Nitya Ramanan1, Debdutta Lahiri1,* Sumalay Roy2,†, Surinder M Sharma1 and B N Dev2
1 High Pressure and Synchrotron Radiation Physics Division, Bhabha Atomic Research Centre, Mumbai 400085, India
2 Department of Materials Science, Indian Association for the Cultivation of Science, Jadavpur, Kolkata-700032, India
*E-mail: debduttalahiri@yahoo.com

Abstract. We employ XSW assisted XAFS at Ni K edge to characterize ion-irradiated Pt/Ni/C multilayer, particularly the nanoclusters formed within C layer, revealed by X-TEM and angle-resolved fluorescence studies. Retrieving the structural model from XAFS coordination results involved intriguing steps such as accounting for the intensity variation across the layers, determination of extra pre-diffused Ni into C layer (beyond the reflectivity determined roughness) and decoupling interfacial, layer and cluster coordination. The clusters are determined to be Ni centered Ni-Pt bimetallic nanoclusters (Ni:Pt = 60:40), formed due to irradiation induced diffusion of Pt atoms from the disrupted Pt/C interface towards pre-diffused Ni atoms present in C layer. They are highly disordered beyond nearest neighbor and resemble glassy structure which could find wide-scale applications in magnetic devices.

1. Introduction
In this work, we employ XAFS in conjunction with X-ray Standing Wave (XSW)[1-2] to characterize structural changes in Pt/Ni/C multilayer (ML), following irradiation with 2MeV Au2+ of fluence 2×1015 ions/cm²[3]. The purpose of ion irradiation was simulation of possible high energy x-ray induced defects. XTEM[3] and angle resolved fluorescence studies at 14 keV (Figure 1(c-d)) on the ion-irradiated ML revealed completely mixed Ni-Pt layers and nano-cluster (of diameter ~ 1.7 nm) formation C layer. Such nanoclusters on C matrix could find application as patterned ultra-high density recording media [4] if their composition is ferromagnetic, conductive ink for fabrication of electronic circuit elements [5], if bimetallic etc. Ion irradiation method, being dry, is particularly useful in fabricating clusters for electronic devices where wetting is an issue.

XAFS study is objected at addressing questions pertaining to nature, composition and degree of order of these nanoclusters. Our results would establish whether Ni and Pt would form isolated clusters or core-shell particles or alloy in C matrix. These implications cannot be drawn simply from bulk Ni-Pt phase diagrams. Factors such as surface energetics [6], Ni/C and Pt/C interactions would play an important role.

XAFS was employed with XSW–the latter results from the superposition of incident and Bragg diffracted x-rays from the ML. The antinode of XSW is centered successfully in each layer of the ML by scanning across the Bragg angle [2]. Hence, XSW selectively filters out information from different

† Present Address: Max Planck Institut fuer Microstructurephysik, Weinberg 2, 06120 Halle, Germany.
locations of the ML. The grazing angle of incidence is set such that antinodes and nodes of XSW are respectively located at the centre of the C layer and Ni/Pt interface (Figure 1(e)) and rising edge of the antinodes coincides with Ni/C interfaces. Therefore, fluorescence mode Ni K edge XAFS yields structural information of Ni/C interface and around Ni diffused deeper into C layer. In irradiated ML, antinodes and nodes of XSW are respectively located at centre of C layer and centre of Ni+Pt mixed layer (Figure 1(f)). Therefore, fluorescence mode Ni K edge XAFS yileds structural information of Ni/C interface, C layer and Ni+Pt mixed layer.

2. Experimental Details

Fluorescence mode XAFS at Ni K edge (8.333 keV), in conjunction with XSW, was recorded on (i) Pristine Pt/Ni/C ML (dPt+Ni+C = 70Å × 15 layers) on float glass substrate (deposited by ion beam sputtering), and (ii) irradiated Pt/Ni/C ML (with 2MeV Au 2+ ions at a fluence of 2×10^{15} ions/cm², at ROEMO (E2) beamline (HASYLAB, Germany). XSW was used to selectively filter out information from Ni/C interface, as is also evident from Figure 1(b). To maintain the antinodal-nodal positions during energy scan of XAFS experiments, the angle of incidence was appropriately adjusted continuously. The fluorescence photons were collected using a Si (Li) detector.

XAFS data were processed using ATHENA and the structural parameters (coordination number (N), Debye Waller Factor (DWF) and bond length (R)) were retrieved using FEFF6 and FEFFIT.

Figure 1. Positions of antinodes and nodes of the XSW (a) before and (b) after irradiation; Fluorescence results (c) before and (d) after irradiation; Structural model for C layer and its interfaces (e) before and (f) after irradiation.

3. Results and discussion

EXAFS data for the first coordination shell (R = 1.2-3.4Å in Figure 2. (b)) around Ni were analyzed. \(k^1-k^2\) weighted Fourier Transforms for each individual dataset (transformed over \(k = 2.2-8Å^{-1}\)) were simultaneously fit to increase the degrees of freedom and reduce uncertainties in N, DWF and R. Various structural models and several fitting strategies were considered to derive unique conclusion. We considered several strategies for fitting, viz. including (or excluding) third cumulant in disorder, correcting for background contribution, constraining the structure around Ni to be fcc, or the coordination number for pristine and irradiated MLs to be same. Figure 2. (c) shows an example of fit quality (R-factor = 0.001-0.014).

Figure 2. (a) XAFS data at Ni K edge; (b) Fourier transform of XAFS data; (c) Example of fit quality.

3.1. Pristine ML: XAFS data for this ML was fit with Ni and C nearest neighbors. Attempts to include Pt nearest neighbors resulted in bad fit. This is consistent with the pristine ML structure from
reflectivity. Part of the Ni layer, Ni/C interface and sporadically diffused Ni atoms in C layer contribute to the XAFS data (Figure 1(e)). The fit results obtained were: (i) $N_{Ni/Ni} = 5.46(12), N_{Ni-C} = 0.88(18)$; (ii) DWF ($Ni-Ni$) =0.0180(4) Å$^2$, DWF ($Ni-C$) = 0.0166(6) Å; $R_{Ni-Ni} = 2.445(3)$ Å, $R_{Ni-C} = 1.964(7)$ Å. Extracting the structural model from these fit results involved rigorous considerations and simulations:

a. From reflectivity measurements, Ni/C interfacial roughness $\sigma_{Ni/C} = 1.7$Å [7] and thickness of Ni layer = 22Å. We preliminarily consider the roughness to represent the interface thickness and the distribution of Ni atoms within the Ni layer to be uniform. From these assumptions, we derive the fraction of Ni atoms at Ni/C interface = 7%.

b. Not all of these Ni atoms are x-ray excited. The number of x-ray excited Ni atoms ($(N_{Ni})_{ex}$) that contribute to XAFS signal, at different locations of the ML, follow the normalized intensity variation plot. The location-specific fractions of $(N_{Ni})_{ex}$ are thus extracted.

c. The structure of Ni -layer is fcc and the Ni/C interfacial plane consist of {111}:{110}:{100} = 1:1:1. The weight-averaged surface coordination for Ni atom at this interface would be 3.67.

d. We calculate the weighted average $N_{Ni/Ni}$ and maximum $N_{Ni-C}$ as:

$$N_{Ni-Ni} = \frac{[(12 \times (N_{Ni})_{ex} \text{ in Ni layer}) + (8.33 \times (N_{Ni})_{ex} \text{ at Ni/C})]}{Total \ (N_{Ni})_{ex}} - (0) \ (N_{Ni-C})_{max} = \frac{3.67 \times (N_{Ni})_{ex} \text{ at Ni/C}}{Total \ (N_{Ni})_{ex}} - (2) \cdot$$

A sharp interface, would have yielded $N_{Ni/Ni}=11.63 \ [((N_{Ni})_{ex})_{XAFS}=5.46]$ and a maximum average interfacial $N_{Ni-C} = 0.37 \ [(N_{Ni-C})_{XAFS} = 0.879]$. These being different from our XAFS results suggest diffusion of Ni atoms into C layer. $N_{Ni-C}$ now has contributions from Ni/C interface and Ni-C bonds within C layer. To estimate the % of the latter, we included Ni/C contribution from C layer in eqn. (2) and further decoupled the interfacial and layer contributions to $N_{Ni-C'}$. $N_{Ni-C'}$ = $N_{Ni-C}$ + $N_{Ni-C'}$ = $N_{Ni-C}$. $N_{Ni-C}$ = 0.51. C layer being amorphous C, the coordination within the layer = 2. Therefore, the % of Ni atoms diffused deeper into the C layer = 0.51/2 = 26% (beyond reflectivity determined roughness [7]). The final model for pristine ML includes a significant proportion of sporadically diffused Ni in the C layers (Figure 1(e)).

3.2. Irradiated ML: At the very outset, it may be clarified that Au$^{2+}$ beam undergoes elastic collisions with atoms in the ML and gets deposited onto the substrate [3]. XAFS data for this ML has contributions from Ni+Pt mixed layer, Ni/C interface and C layer. Besides, X-TEM images the irradiated ML revealed the presence of nanoclusters within C layers. Hence, the data was fit by considering Ni,C and Pt atoms as nearest neighbors. The fit results obtained were : (i) $N_{Ni-Ni} = 6.24(17), N_{Ni-C} = 0.33(18), N_{Ni-Pt} = 4.14(14)$; (ii) DWF ($Ni-Ni$) =0.0210(5) Å$^2$, DWF ($Ni-C$) = 0.0166(6) Å$^2$, DWF ($Ni-Pt$) = 0.0242(2) Å$^2$; $R_{Ni-Ni} = 2.612(1)$ Å, $R_{Ni-C} = 1.964(7)$ Å, $R_{Ni-Pt} = 2.727(7)$Å.

Disruption of Pt/C interface and subsequent diffusion of Pt atoms into C layer[8-10] (consistent with corresponding 400% increase in $\sigma_{Pt/C}$ [3]) leads to the emergence of $N_{Ni-Pt}$. To extract the structural model from XAFS results, the following were involved:

a. Steps a-d from Section 3.1 were repeated for irradiated ML (Note that Ni layer is now replaced by Ni+Pt mixed layer). Clearly from eqn (2), contribution to $N_{Ni-C}$ is from Ni/C interface alone, hence Ni atoms in C layer have no Ni nearest neighbors.

b. Deduction of the structure of nanoclusters within C layer involved decoupling the contributions to $N_{Ni/Ni}$ from Ni/C interface, mixed Ni-Pt layer and C layer. The % of Ni atoms in C layer, Ni+Pt mixed layer and Ni/C interface are respectively 26% (from (i)), 64% and 10%. Considering coordination around Ni in Ni-Pt mixed layer, C layer and Ni/C interface to be 6 (since the layers are completely mixed), n and 8.33 respectively, n was calculated using:

$$N_{Ni-Ni} = \frac{n \times (N_{Ni})_{ex} \text{ in C layer} + 6 \times (N_{Ni})_{ex} \text{ in Ni + Pt layer} + 8.33 \times (N_{Ni})_{ex} \text{ at Ni/C}}{Total \ (N_{Ni})_{ex}}.$$
Similarly the Ni-Pt coordination in C layer was deduced (note that this does not have any contribution from Ni/C interface). The calculated values of $N_{Ni-Ni}$ and $N_{Ni-Pt}$ are listed in Table 1. Various models for nanoclusters considered are listed in Table 1, and most of them are ruled out.

The final model for Ni-Pt clusters in C layer is Ni centered Ni-Pt bimetallic clusters, highly disordered beyond first neighbor, and having Ni:Pt = 60:40 (Figure 1(f)). This composition is reported to be ferromagnetic [11] (using FEFFIT, we simulated XAFS data (Fourier transform) for different values of $N_{Ni-Ni}$ and $N_{Ni-Pt}$ and observed that for both $N_{Ni-Ni}$ and $N_{Ni-Pt}$, there is a resolution limit of $\Delta N=2$). These clusters resemble the short range order of multi component glasses, with the C matrix (probably) helping in the amorphous structure[12]. The first shell radius of these clusters is estimated to be 0.25nm (corresponding to XAFS derived $R_{Ni-Pt}$).

### Table 1. Various models for Nanoclusters.

| XAFS result | Isolated Ni fcc clusters | Isolated Pt fcc clusters | Ni fcc core Pt shell | Pt fcc core Ni shell | Ni centered icosahedral bimetallic | Pt centered icosahedral bimetallic | Ni centered Ni-Pt bimetallic |
|-------------|--------------------------|--------------------------|---------------------|---------------------|-----------------------------------|-----------------------------------|-----------------------------|
| $N_{Ni}$    | 6.35                     | 12                       | 0                   | 9 (minimum)         | $N_{Ni-Ni}+N_{Ni-Pt}=7$             | $N_{Ni-Ni}+N_{Ni-Pt}=7+N_{Pt-Pt}=7$ | $9 \leq N_{Ni-Ni}+N_{Ni-Pt}$ |
| $N_{Pt}$    | 3.64                     | 0                        | 0                   | 3 (maximum)         | 0.3                               | Ruled out                         | Final model                 |

**4. Conclusion**

We have characterized ion-irradiated Pt/Ni/C ML using a combination of XSW and Ni K edge XAFS. The XTEM-XRF identified nanoclusters in C layer have been determined to be Ni centered Ni-Pt bimetallic (Ni:Pt = 60:40). They are formed due to diffusion of Pt atoms from the disrupted Pt/C interface towards pre-diffused Ni atoms in C layer, following irradiation. These clusters have ferromagnetic composition, highly disordered beyond first neighbor and resemble short range ordered metallic glasses. They show good promise as magnetic devices.

**5. References**

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