Ion-beam induced transformations in nanoscale multilayers: Evolution of clusters with preferred length scales

S. Bera, B. Satpati, D. K. Goswami, K. Bhattacharjee, P. V. Satyam, and B. N. Dev

Institute of Physics, Sachivalaya Marg, Bhubaneswar 751005, India

(Received 6 January 2005; accepted 14 February 2006; published online 4 April 2006)

Ion-irradiation-induced modifications of a periodic Pt/C multilayer system containing a small amount of Fe have been analyzed by transmission electron microscopy and grazing incidence x-ray diffraction (GIXRD) studies. The multilayer stack with 16 Pt/C layer pairs (period of 4.23 nm) was fabricated on a glass substrate. A 2 MeV Au\textsuperscript{2+} ion beam was rastered on the sample to obtain uniformly irradiated strips with fluences from $1 \times 10^{14}$ to $1 \times 10^{15}$ ions/cm\textsuperscript{2}. Ion irradiation has been found to cause preferential migration of Fe towards Pt layers [Bera et al., Nucl. Instrum. Methods Phys. Res. B \textbf{212}, 530 (2003)]. Cross-sectional transmission electron microscopy (XTEM) shows considerable atomic redistribution for irradiation at the highest ion fluence ($1 \times 10^{15}$ ions/cm\textsuperscript{2}). This structure is composed of small clusters. Phase separation and cluster formation processes are discussed. Periodic multilayers have periodicity only in the direction normal to the multilayer surface. However, Fourier transform (FT) of the XTEM images of the sample irradiated at the highest fluence shows extra off-normal Fourier components of superlattice periodicities arising due to ion irradiation. These extra spots in the FT are due to preferential length scales in intercluster separation in three dimensions. With a proper understanding of this phenomenon it may be possible to fabricate useful three-dimensional self-assembled structures of nanoclusters. Our high resolution transmission electron microscopy and GIXRD results reveal the formation of an FePt alloy. As FePt is a magnetic alloy, our observation raises the possibility of fabrication of ion-beam induced magnetic nanocluster lattices. © 2006 American Institute of Physics. [DOI: 10.1063/1.2184429]

I. INTRODUCTION

Multilayer structures, nanostructured in one dimension, have structural, magnetic, and electronic properties with a wide range of applications. Artificial multilayers are metastable due to their high content of interfaces as well as their metastable microstructure arising from specific conditions of layer deposition. Therefore the stability and modification of multilayers under thermal and ion irradiation treatment have important consequences for their appropriate applications. Ion-beam irradiation of magnetic multilayers has been found to show a spin-orientation transition, indicating the suitability of such systems for patterned ultrahigh density recording media.\textsuperscript{4} Structural analysis has shown that in periodic multilayers ion-beam irradiation causes mixing, interface broadening, and period dilation.\textsuperscript{5} All these changes may be responsible for the spin-orientation transition in magnetic multilayers. However, a proper correlation of properties with these parameters is still lacking. In a magnetic multilayer, a small concentration of magnetic impurity in the nonmagnetic layer can drastically change magnetic coupling and magnetoresistance.\textsuperscript{5} As ion beam can introduce such magnetic impurities into the nonmagnetic layers by ion-induced displacements of atoms from the magnetic layers into the nonmagnetic layer,\textsuperscript{5} ion irradiation could possibly be used to tune magnetic coupling and modify magnetoresistance. In Pt/C multilayers with Fe impurities [hereafter denoted as Pt(Fe)/C(Fe)], ion irradiation has been found to cause preferential migration of Fe towards Pt layers.\textsuperscript{5} Although each layer (Pt or C) in the multilayer is about 2 nm thick, migration of Fe from C to Pt layers could be easily detected. This preferential migration of Fe was detected by generating standing waves of x rays in the multilayer and measuring the change of Fe Kα fluorescence yield caused by the standing wave field. The details about this technique may be found in Ref. 8. Considering that Fe–Pt forms magnetic alloys, this phenomenon raises the possibility of fabrication of magnetic clusters with the nonmagnetic layers of the multilayer providing the nonmagnetic matrix to isolate the magnetic particles. We have investigated the aspect of ion-beam induced cluster formation in Pt(Fe)/C(Fe) multilayers.

We have carried out transmission electron diffraction (TED) and transmission electron microscopy (TEM) studies on virgin and ion-irradiated Pt(Fe)/C(Fe) multilayer systems to investigate the morphological modification due to ion bombardment. One-dimensional (1D) periodicity of the multilayer has been found to evolve into a three-dimensional (3D) structure with preferential length scales close to 3D periodicity upon ion irradiation. These aspects of ion-beam modification are presented here.

\textsuperscript{a}Electronic mail: sbera@iopb.res.in
\textsuperscript{b}Present address: Paul Drude Institute for Solid State Electronics, Hausvogteiplatz 5-7, 10117 Berlin, Germany.
\textsuperscript{c}Present address: Materials Science Department, North Western University, Cook Hall, 2220 Campus Drive, Evanston, IL 60208.
\textsuperscript{d}Electronic mail: blupen@iopb.res.in
standing wave and reflectivity experiments were carried out at DESY and Hamburg Synchrotron Radiation Laboratory. The virgin and the irradiated strips were analyzed with x-ray reflectivity scans showing the first- to the fourth-order Bragg peaks (Fig. 1) from the virgin and the irradiated (fluence of $1 \times 10^{15}$ ions/cm$^2$) Pt(Fe)/C(Fe) samples indicate that the periodic structure in the surface-normal direction of the multilayer is preserved in the irradiated sample. The first-order Bragg peaks are shown in the linear scale in the inset of Fig. 1. For the irradiated sample the intensity of the Bragg peak is reduced and the position of the Bragg peak indicates that there is a contraction of the multilayer period compared to the virgin sample. In fact, the Bragg peaks of all orders are systematically shifted to higher angles.

A cross-sectional TEM (XTEM) image of the virgin sample (Fig. 2) shows the periodic multilayer structure with the top and the bottom Pt layer thicker than other Pt layers. Fourier transform (FT) of the marked square region of the XTEM image in Fig. 2, presented in the inset (a), shows this periodicity in one dimension in the direction normal to the multilayer surface. The diffraction pattern from the multilayer displaying the 1D periodicity is shown in the inset (b). This 1D periodic pattern is expected from the structure seen in Fig. 2 and its FT. In order to probe the crystallinity of the constituent layers, a selected area diffraction pattern from the multilayer (virgin sample) is shown in Fig. 3. From the diffraction pattern it appears that the Pt layers are polycrystalline, while the C layers are amorphous. The indexed spots are from polycrystalline Pt. No diffraction features from C are observed. The amorphous nature of C is also evident from the higher resolution XTEM image in Fig. 4, where lattice images of Pt crystallites are seen.

A XTEM image of the irradiated multilayer shows atomic redistribution and cluster formation (Fig. 5). The FT taken from the marked square region in Fig. 5 is shown in the inset (a). In addition to the spots in the surface-normal direction, evolution of extra spots in the FT shows the development of extra periodicities within the irradiated multilayer.
expression given by Cheng\textsuperscript{12} incorporating atomic move-
ment of thermal spikes due to energetic penetrating ions. Another
the absolute temperature,
olute value of the average cohesive energy of the system,
is the ratio of the diffusion coefficients describing the chemi-
sification. The sign of diffusion coefficient is determined by
between components and negative coefficient leads to phase
positive or negative. Positive coefficient leads to mixing be-
cluding many clusters seem to be connected).

Let us try to understand why clusters are formed due to
ion irradiation. It was shown that in a heterogeneous system
all kinds of mixing processes associated with ion bombard-
ment, including ballistic and chemically guided atomic
movements, can be incorporated in a diffusion equation.\textsuperscript{10–12}
The sign of the effective diffusion coefficient can be either
positive or negative. Positive coefficient leads to mixing be-

giving the sign of the diffusion coefficient is determined by
\begin{equation}
F = 1 - \frac{2\Delta H^1_{m}}{k_B T} \frac{p}{p + 1}.
\end{equation}

In Eqs. (1) and (2) $\Delta H^1_{m}$ is the heat of mixing of the alloy
containing 50 at. \% of each component, $|\Delta H_{coh}|$ is the abso-
lute value of the average cohesive energy of the system, $T$ is
the absolute temperature, $k_B$ is Boltzmann’s constant, and $p$
is the ratio of the diffusion coefficients describing the chemi-
cally guided and the random atomic relocation. The value of
$p$ is found to increase rapidly as temperature is raised. Its
value at room temperature, at which our experiments were
carried out, is around $p = 0.1$ and does not vary much with
materials of the pair to be irradiated.\textsuperscript{10}

On the basis of the “macroscopic atom model” of
Miedema \textit{et al.},\textsuperscript{13} we have calculated the change of enthalpy
$\Delta H_m$ of Pt–C mixing. The enthalpy change can be expressed as
\begin{equation}
\Delta H_m = \frac{2Pf(c^i)(c_{Pt}V_{Pt}^{2/3} + c_C V_{C}^{2/3})}{(n_{WS})^{-1/3} + (n_C)^{-1/3}}
\times \left[ - (\Delta \phi)^2 + \frac{Q}{P} (\Delta n_{WS}^{1/3})^2 - \frac{R}{P} \right]
+ c_C [\Delta H(C_{element} \rightarrow C_{metal})],
\end{equation}

where
\begin{align*}
f(c^i) &= c_{Pt}^i c_C^i, \\
c_{Pt}^i &= c_{Pt} V_{Pt}^{2/3} (c_{Pt} V_{Pt}^{2/3} + c_C V_{C}^{2/3}), \\
c_C^i &= c_C V_{C}^{2/3} (c_{Pt} V_{Pt}^{2/3} + c_C V_{C}^{2/3}), \\
P &= 12.3, \quad \frac{Q}{P} = 9.4 V^2 (d.u.)^{-2/3}, \quad \frac{R}{P} = 2.1 V^2.
\end{align*}

Here $c_{Pt}$ and $c_C$ are atomic concentrations of Pt and C, re-
spectively. $V_{Pt}$ and $V_{C}$ are the molar volumes of Pt and C, re-
respectively. $c^i$ is the surface concentration. $\phi^i$ is a modified
work function and $n_{WS}$ is the electron density at the first
Wigner-Seitz boundary. $P$, $Q$, and $R$ are constants. $\Delta H_m$ is
expressed in kJ/mole, $\phi^i$ in volts, $n_{WS}$ in density units (d.u.),
and $V^{2/3}$ in cm$^2$. In Eq. (3), the first term represents the
charge transfer between Pt and C. The second term repre-
sents the discontinuity in electron density at the Wigner-Seitz
boundary of Pt and C atoms. The third term represents a
hybridization contribution. Both the first and the third terms,
which are negative, favor a tendency for compound forma-
tion, while the second term favors a tendency for phase sepa-
ration. The last term is a transformation energy that accounts
for the enthalpy difference between elementary and metallic
carbon. According to the theory of Miedema,\textsuperscript{13} alloys of
transition metals with C can be treated as the other alloys of
transition metals with polyvalent nontransition metals. The
only difference is to introduce an additional positive contri-
bution to account for the enthalpy difference between carbon
in diamond structure and a more conventional metallic struc-
ture. For carbon, the corresponding transformation energy
equals 180 kJ/mol.\textsuperscript{15}

The cohesive energy of a Pt–C alloy $|\Delta H_{coh}|$ can be ap-
proximated using regular solution theory\textsuperscript{16} by
\begin{equation}
|\Delta H_{coh}| \approx (c_{Pt} H_{Pt}^0 + c_C H_{C}^0) + \Delta H_m,
\end{equation}

where $H^0$ is the cohesive energy of individual element. $\Delta H_m$
is the regular solution heat of mixing. The values of $\phi^i$, $n_{WS}^{1/3}$,
$V^{2/3}$, and $H^0$ for C, Pt, and Fe are listed in Table I.

Using Eqs. (1)–(4), we have calculated $\Delta H_{m}^{1}$, $|\Delta H_{coh}^{1}|$, and $F$ for Pt–C, Pt–Fe, and Fe–C systems. Calculated values

![FIG. 4. A HRTEM image from the virgin Pt(Fe)/C(Fe) multilayer.](image)

![FIG. 5. A cross-sectional TEM image of the irradiated Pt(Fe)/C(Fe) multilayer. Fourier transform of the marked square region of the TEM image is shown in the inset (a). Inverse Fourier transform of inset (a) is shown in the inset (b).](image)
incorporated into Pt by ion beam, would diffuse out of Pt by a chemically driven process. This C can accumulate in the grain boundary region between Pt nanocrystalline grains within the Pt layers, leading to the formation of isolated Pt nanoparticles. In our previous study ion fluence was lower. At this fluence the Pt/C layers preserve their identity as continuous layers. Compared to this the ion fluence in the present work is an order of magnitude higher. This does not necessarily produce a stronger ion-beam induced atomic displacement and mixing at the end of the irradiation process. Besides ballistic mixing, the role of the chemically guided diffusion has to be taken into account. This process is well documented in diffusional relaxation of ion-bombarded systems. Inclusion of this factor [Eqs. (1) and (2)] leads to phase separation for the Pt/C system, leading to Pt nanoparticles surrounded by C.

It was previously observed that Fe impurity atoms in the Pt/C multilayers, upon ion irradiation, migrate preferentially from C layers to Pt layers. This was explained by comparing Fe–Pt (Ref. 24) and Fe–C (Ref. 25) phase diagrams. In conjunction with this behavior, the structure in Fig. 5 indicates that the Pt nanoparticles contain Fe and the formation of FePt nanoparticles should be investigated. FePt is an interesting and useful material because in the face centered trigonal $L_{10}$ chemically ordered phase they exhibit a very high magnetic anisotropy and giant magneto-optical effects. In order to search for FePt formation, we carried out TEM studies at higher resolution on various parts of sample represented in Fig. 5. One XTEM image from these studies is shown in Fig. 6, where we find two sets of lattice images, one corresponding to $d=0.218\pm0.005$ nm and another corresponding to $d=0.251\pm0.007$ nm. $d=0.218$ nm is closer to the (111) planar spacing of bulk Pt ($d=0.227$ nm). The lattice spacing of $d=0.251$ nm does not match with any available $d$ spacing of either Pt or Fe structures. However, it is close to the (110) planar spacing of bulk FePt ($d=0.272$ nm). This points to FePt nanoparticle formation. GIXRD results appear to corroborate this. GIXRD results from the irradiated sample are shown in Fig. 7. Neither Pt nor Fe diffraction pattern agrees with the observed peak positions. The peak positions are in good agreement with the diffraction pattern of FePt. As the peaks are very broad (because of small particle size), it is difficult to identify the appropriate phase of FePt, considering the small difference in the diffraction patterns of disordered fcc FePt structure and the ordered fct FePt ($L_{10}$) structure. With the formation of FePt one would expect magnetism in the sample. Indeed

![HRTEM image from the irradiated sample](image)

**FIG. 6.** A HRTEM image from the irradiated sample. The region with the planar spacing of 0.251 nm is likely to be an FePt region.
we have observed evolution of soft ferromagnetism in ion-irradiated Pt(Fe)/C(Fe) samples by magnetic force microscopy (MFM) and magneto-optical Kerr effect (MOKE) measurements. In the MOKE hysteresis loop the coercive field was found to increase with increasing ion fluence. These aspects are beyond the scope of the present paper. Results of these studies will be published elsewhere.\(^{26}\)

With the method presented here, one may visualize the possibility of fabrication of a 3D structure of FePt magnetic nanoparticles with an appropriate Fe concentration. Although the observed structure is not an ordered 3D structure, it has preferred length scales. An ordered array of such nanoparticles is expected to show unusual properties due to interparticle coupling.

**IV. CONCLUSIONS**

We have carried out irradiation of Pt/C multilayers, containing a small amount of Fe, with 2 MeV Au\(^{2+}\) ions at different ion fluences. Cross-sectional transmission electron microscopy (XTEM) of ion-irradiated (fluence of \(1 \times 10^{15}\) ions/cm\(^2\)) Pt(Fe)/C(Fe) multilayers shows the formation of clusters within the layers. Fourier transform of the XTEM micrographs shows extra Fourier components representing extra superlattice periodicities arising due to ion irradiation. A 1D-periodic multilayer appears to undergo a transformation to a structure with preferential length scales in 3D upon ion irradiation. With a proper understanding of this phenomenon it may be possible to fabricate three-dimensional periodic structures of nanoclusters by ion irradiation. Considering the preferential Fe migration to Pt layers and the possible magnetic phases of Fe–Pt alloys, our observation raises the possibility of fabrication of ion-beam induced magnetic nanocluster lattices.

**ACKNOWLEDGMENTS**

We thank Professor K. Yamashita for providing the virgin Pt(Fe)/C(Fe) samples and Dr. G. Kuri and Dr. F. Eichhorn for the help in x-ray measurements.


\(^{9}\)In our earlier irradiation experiment at a lower fluence we observed a period dilation (Ref. 5). Here also we have observed (not presented here) period dilation for an ion fluence of \(3 \times 10^{14}\) ions/cm\(^2\).


