Surface energy anisotropy of FePt nanoparticles

Suklyun Hong

Department of Physics and Institute of Fundamental Physics, Sejong University, Seoul 143-747, Republic of Korea

M. H. Yoo

Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejon 305-701, Republic of Korea

(Received 10 December 2004; accepted 6 January 2005; published online 8 April 2005)

To investigate the surface energy anisotropy of FePt nanoparticles, we have performed self-consistent pseudopotential density-functional calculations. Wulff plots are constructed based on the calculated surface energy anisotropy, and these are used to analyze the structural feature in the reported high-resolution transmission electron microscopy images of FePt nanoparticles.

I. INTRODUCTION

Stoichiometric FePt alloy of the $L_1_0$ structure has been known as a hard magnetic material owing to its high magnetocrystalline anisotropy energy along the crystallographic c axis ($K_c = 7 \times 10^6$ J/m$^3$). Because of this anisotropy and the high-saturation magnetization ($M_s = 1130$ emu/cc), FePt alloys are considered as an important class of materials for ultrahigh-density magnetic storage applications. Accordingly, dispersoids of FePt nanoparticles are of great research interest today, because the size of ferromagnetic particles less than 10 nm in diameter translates into an areal density of 1 Tbit/in$^2$ in recording media.

Many synthesis and fabrication processes have been developed recently in order to obtain a regular monodisperse array of stable $L_1_0$ FePt nanoparticles. These include vapor deposition or sputtering techniques, a solution-phase chemical (wet chemistry) procedure, and a gas-phase-based method. To realize the full potential of nanoparticle arrays as a recording medium, however, it is necessary to have a detailed physical understanding of the constituent nanoparticles and the nanoparticle arrays. For example, in using self-assembly techniques, the coherence length of self-assembly is affected by the size distribution of the particles, the surface properties of the particles, the interfacial properties of particle/particle and particle/substrate interfaces, and so forth.

In this paper, we present a set of surface free energies for low-index planes of $L_1_0$ FePt at thermodynamic equilibrium, and analyze the equilibrium shape of an FePt crystal based on the surface energy anisotropy. By comparing the experimentally observed shapes of $L_1_0$ FePt nanoparticles with the calculated equilibrium shape, we form the physical basis on which kinetic factors associated with the various processing techniques for the formation of regular arrays of $L_1_0$ FePt nanoparticles can be addressed.

II. IDEAL WORK OF ADHESION AND CALCULATION METHOD

Consider a crystalline slab as schematically illustrated in Fig. 1(a), where the big arrows indicate the direction of uniaxial tensile stress $\sigma$ as a function of the separation distance $\nu$ as shown in Fig. 1(b). The change in the total energy of a slab, $\Delta E$, as it is separated into two halves is to increase with increasing $\nu$ until $\Delta E(\nu)$ reaches, asymptotically, a constant value $G_c$ at a large value of $\nu$. Thus, the ideal work of adhesion, or the ideal cleavage energy, is given by

$$G_c = \int_0^\infty \sigma(\nu)d\nu = \gamma_1 + \gamma_2,$$

where $\gamma_1$ and $\gamma_2$ are the specific energies per unit area of the two surfaces created, as indicated in Fig. 1(b). For a chosen cleavage habit plane $(hkl)$ in an AB compound of the $L_1_0$ structure, the two resulting surface energies are not equal, in general, owing to the difference in their chemical compositions.

A quantitative determination of the ideal work of adhesion can be made by electronic structure calculations within the framework of the density-functional theory. The results of such calculations made on transition-metal aluminides and silicides have been summarized earlier. In this work, to determine $G_c$ values of low-index surfaces in FePt, we have performed ab initio calculations within a generalized gradient approximation using a spin-polarized version of the VIB.
The anisotropy of the surface energy $\delta$ can determine the equilibrium crystal shape of the crystals. The procedure to find the crystal shape is given in Ref. 10.

### III. RESULTS

When an FePt crystal is cleaved on any one of the (100), (011), and (111) planes, two exposed surfaces consist of both Fe and Pt atoms in the same composition. The cleavage energies $G_c$ for those planes, taking into account relaxation, are 4.23, 3.95, and 3.49 J/m$^2$, respectively. Correspondingly, the specific surface energies, $\gamma = \frac{G_c}{2}$, are 2.12, 1.98, and 1.74 J/m$^2$, respectively. These values are listed in Table I. On the other hand, in the cases of both (001) and (110) cleavages, one surface consists entirely of Fe atoms while the other matching plane consists entirely of Pt atoms. After relaxation, the cleavage energies of the (001) and (110) planes are 4.37 and 4.08 J/m$^2$, respectively. It is worth mentioning that our value gives the sum of the two types of surface energy for the (001) or (110) plane, but no information is obtained on the difference between the two.

The anisotropy of the surface energy $\gamma$ can determine the equilibrium crystal shape of the crystals. The procedure to find the crystal shape is given in Ref. 10. To construct the crystal shape with respect to the [011] viewing direction, we mark the energy points corresponding to the (100), (111), and (011) facets along the respective normal directions. We then assume that the Wulff plot makes concave contact with those points in order to obtain the crystal shapes related to these points of the surface energy function. The crystal shape viewed from the [011] direction is shown in Fig. 2. From the plot, the surface areas corresponding to the {111} facets are found to be the largest since the (111) surface energy is the lowest.

In the case of the (001) plane we have information only on the sum of Fe(002) and Pt(002) surface energies. If the two specific surface energies are assumed to be equal ($\gamma_1 = \gamma_2$), and/or if both surfaces are assumed to contain ledges of one atomic height in equal surface areas, then the above equation can be applied also for the (001) and (110) planes. Using either one of the assumptions, we find that $\gamma_1 = \frac{G_c}{2} = 2.18$ and 2.04 J/m$^2$, respectively, for the (001) and (110) planes, as shown in column (a) of Table II. The result of a two-dimensional equilibrium shape of FePt crystal with respect to the [110] viewing direction is shown in Fig. 3(a), which is very similar to Fig. 2 on account of a rather small difference in the $G_c$ values between the (100) and (001) planes, i.e., only 0.14 J/m$^2$ between 4.23 and 4.37 J/m$^2$, and also a small difference ($\sim 3\%$) in $G_c$ between the (001) and (110) planes.

Another possible assumption in the case of the (001) and (110) planes is that the specific energies of two exposed surfaces are different, for example, by $\gamma_2 - \gamma_1 = G_c/6$. Column (b) of Table II lists the two different surface energies and Fig. 3(b) shows the equilibrium shape viewed along the [110] direction when the lower $\gamma_1$ values of the (001) and (110) surfaces are taken into account.

### IV. DISCUSSION

Using the wet-chemical processing method$^5$ and an amorphous carbon surface, Dai et al. reported a picture series of Fe$_{52}$Pt$_{48}$ nanocrystals (about 6 nm in size) by high-intensive electron microscope calculations.

### TABLE I. Cleavage energy $G_c$ (J/m$^2$) and surface energy $\gamma = G_c/2$ (J/m$^2$) of FePt.

<table>
<thead>
<tr>
<th>(hkl)</th>
<th>$G_c$</th>
<th>$G_c$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>4.32</td>
<td>4.23</td>
<td>2.12</td>
</tr>
<tr>
<td>001</td>
<td>4.42</td>
<td>4.37</td>
<td>...</td>
</tr>
<tr>
<td>011</td>
<td>4.22</td>
<td>3.95</td>
<td>1.98</td>
</tr>
<tr>
<td>111</td>
<td>3.54</td>
<td>4.08</td>
<td>...</td>
</tr>
</tbody>
</table>

### TABLE II. Two possible cases of (001) and (110) surface energies in FePt (in units of J/m$^2$).

<table>
<thead>
<tr>
<th>(hkl)</th>
<th>$G_c$</th>
<th>$\gamma_1$</th>
<th>$\gamma_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>001</td>
<td>4.37</td>
<td>2.18</td>
<td>1.82</td>
</tr>
<tr>
<td>110</td>
<td>4.08</td>
<td>2.04</td>
<td>1.70</td>
</tr>
</tbody>
</table>
resolution transmission electron microscopy (HRTEM). These represent the as-synthesized form of the hexagonally packed nanocrystal (disordered fcc) assemblies, an individual chemically-ordered \(L1_0\)-crystal after annealing, coalescent nanocrystalline grains containing \{111\} twin interfaces, and a relatively large coalescent grain with many twin boundaries. Facets of these particles identified on the HRTEM images, which are nearly parallel to the beam direction and perpendicular to the broad dimension of the particles, consist only of \{111\} and \{001\} surfaces [see Figs. 2(a) and 3(a), and 4(b) of Ref. 11].

The faceted boundary shown on one of the intact \(Fe_{52}Pt_{48}\) nanoparticles shown in the HRTEM image, Fig. 3(a) of Ref. 11, is reasonably consistent with the equilibrium shape of Fig. 3, even though the \{110\} facets are not sharply in contrast. Also, in a coalescent \(Fe_{52}Pt_{48}\) particle, Fig. 3(a) of Ref. 11, the top grain of three individual nanocrystals conforms very closely to the equilibrium shape. These analyses of geometrical and morphological comparison suggest that annealing of as-synthesized \(Fe_{52}Pt_{48}\) nanoparticles at 530 °C for 1 h and further annealing of the particles at 600 °C for 1 h produce \(Fe_{52}Pt_{48}\) nanoparticles, growing on an amorphous carbon substrate, to be near to the state of thermodynamic equilibrium, and also that the coherent \{111\} twin boundary energy in \(L1_0\) FePt must be rather low in magnitude.

It has been known for decades that transition metals of fcc (A1) structure form multiply twinned particles (MTPs) such as icosahedra or decahedra in the nanoparticle size regime. At such small particle sizes, the contribution of the surface free energy \(\gamma_s\) to the total energy becomes important and may even help shifting the thermodynamic equilibrium, e.g., from fcc (bulk) to icosahedral structures. Thus, the stability of icosahedra, which are solely terminated by \{111\} facets, is mainly due to a lower surface free energy of the \{111\} facets as compared to that of the \{100\} facets \(^3\) (see Table I). In the as-synthesized fcc FePt samples (prior to annealing), Dai et al. \(^14\) presented direct evidence by HRTEM imaging of disordered MTPs as well as truncated octahedral nanocrystals of which shape is enclosed by \{100\}, stepped \{111\}, and zigzag \{110\} facets.

Fivefold MTPs of chemically-ordered \(L1_0\) FePt nanocrystals were identified by HRTEM in \(Fe_{53}Pt_{49}\) after codeposition of Fe and Pt, followed by \textit{in situ} TEM isothermal annealing, \(^3\) and also in \(Fe_{62}Pt_{38}\) after inert-gas condensation and subsequent sintering in the gas phase. \(^15\) In this case of MTPs, facets along the nanocrystal edges are not as sharply defined as in the HRTEM images reported by Dai et al. \(^11\) Nevertheless, Kovacs et al. \(^3\) commented the following as a typical structural feature: “the surface of the \(L1_0\) FePt grains (MTPs) consists of both \{001\} and \{111\} facets.”

Following their earlier work, \(^11\) Dai et al. \(^14\) have made detailed analysis of atomic arrangements at the surface structures in \(L1_0\) FePt nanocrystals. The atomic arrangements on the \{100\} and \{111\} surfaces are not flat due to the presence of atomic steps. The \{110\} surface is rough on atomic scale and displays zigzag consisting of \{111\} facets. During the annealing treatment for \(A1-L1_0\) transformation, \{110\} surfaces tend to disappear, and \{100\} and \{111\} surfaces evolve. Image simulations of the HRTEM images indicate that the \{001\} surface terminates with one type of atoms, plausibly with Fe atoms, which may imply that in Table II and Fig. 3 assumption (b) is more valid than assumption (a).

V. SUMMARY

We calculated surface free energies of \(L1_0\) FePt for the \{100\}, \{001\}, \{110\}, \{011\}, and \{111\} planes. Two equilibrium shapes of an FePt crystal, in a two-dimensional plot perpendicular to the \{011\} or \{110\} viewing direction, were constructed based on the surface energy anisotropy. The latter case (Fig. 3) requires simplifying assumptions on Fe(002) and Pt(002) surface energies, and also on Fe(220) and Pt(220) surface energies. The structural feature of facets on the edges of \(L1_0\) FePt nanocrystals observed by HRTEM (Refs. 3, 11, and 13–15) is, in the main, consistent with the calculated equilibrium shape. However, \(L1_0\) FePt nanocrystals in the form of fivefold MTPs, which are reported to form in the early stage of annealing, do not show obvious surface faceting, indicating that their structural feature is dictated more by kinetic factors than by free surface energies.

ACKNOWLEDGMENT

This work was supported by grants from the KOSEF through the Center for Nanotubes and Nanostructured Composites and from the MOST through KAIST TOP10 Project.


\(^3\) A. Kovacs, K. Sato, G. Safran, P. B. Barna, and Y. Hirotsu, Philos. Mag.
84, 2075 (2004).
7M. H. Yoo and K. Yosimi, Intermetallics 8, 1215 (2000).