Patterned nanostructure in AgCo/Pt/MgO(001) thin film

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The formation of patterned nanostructure in AgCo/Pt/MgO(001) thin film is simulated by a technique of combining molecular dynamics and phase-field theory. The dislocation (strain) network existing in Pt/MgO is used as a template whose pattern is transferred to AgCo phase in spinodal decomposition, resulting in regular arrays of Co islands that are attracted by the dislocations. The influence of various factors, such as component concentration and film thickness, is studied. It is found that the spinodal decomposition of AgCo in this system is mainly characterized by a competition between a surface-directed layer structure and the strain-induced patterned structure, where the patterned Ag-Co structure only dominates in a small range near the interface (less than 10 atomic layers). However, if the interlayer diffusion can be minimized by controlling film growth conditions, it is shown that the patterned structure can be formed throughout the entire film.

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I. INTRODUCTION

With the rapid development of the high-density information storage device, the control of grain size and grain size distribution in magnetic thin films will be required for the next generation of information storage technology, where the drive for decreased media noise and increased storage density is pushing the grain size below the 10 nm regime. Present technology involves the deposition of Co rich magnetic phases onto seed layers whose grain size determines the grain size of the magnetic layer through grain to grain epitaxy. For example, in IBM’s 10 Gbit/in.² demonstration, the magnetic film with an average grain size of 12 nm is obtained where a Co phase is deposited onto NiAl seed layers. Other methods to control grain size and grain size distribution were also explored in the labs. It was shown recently that monodispersed magnetic nanoparticles can be created by chemical means and deposited onto a substrate to form a highly regular array of particles.

There are several possibilities for introducing controllable length-scales into the film formation process, one of which is the self-organized growth on a substrate with preferred nano-pattern. For example, flat nanosized Co dots form in Au(111) substrate with surface reconstruction, and ordered arrays of vertical magnetic Co pillars can be further obtained by alternative deposition of Co and Au layers. When Co film is deposited on the Pt(111), fcc and hcp phases are arranged in regular patterns to reduce the strain energy. Recently, Kern et al showed that the strain-relief dislocation network in substrate can be transferred through heterogeneous nucleation to regular superlattice of almost mono-dispersed islands with great feasibility.

In a previous paper, the interaction between the spinodal decomposition of thin film and the dislocation network of substrate was briefly discussed with AgCo/Pt/MgO thin film as an example. It was revealed that Co phases are attracted by dislocations in the Pt/MgO interface, producing an interesting nanostructure. Such mechanism may provide a possibility to control the length scale for magnetic recording media layer. For example, after the patterned nanostructure of AgCo phases is established in spinodal decomposition as a seed layer, a Co-rich conventional medial alloy can grow on it. In this article, detailed simulations are conducted in AgCo/Pt/MgO(001) thin film to investigate the formation of nanostructure under various conditions.

FIG. 1: Schematic graphics of the AgCo/Pt/MgO(001) thin film. The symbols cross (+), triangle (Δ) and stars (*) represent atoms Mg, O, and Pt, respectively, while filled circle (●) for AgCo atoms. Pt atoms trend to sit atop the surface O atoms due to their favorable interaction energy. The arrows indicate the locations where dislocation will be generated. Axes are plotted in units of Å.
II. THEORETICAL MODEL AND SIMULATION METHOD

A. System model

The system considered here is the AgCo/Pt/MgO(001) thin film (see Fig. 1). MgO is preferred substrate material in many of the new information storage and processing devices made from thin metal films. MgO has a f.c.c. lattice structure with lattice parameter $a_{\text{MgO}} = 4.21\text{Å}$, which is slightly larger than that of Pt ($a_{\text{Pt}} = 3.924\text{Å}$). When Pt film is deposited on MgO substrate, due to the interactions between film and substrate, Pt phase will be subject to elastic mismatch strain. The mismatch strain energy is partly released by the formation of interfacial dislocation network. The dislocation network of Pt/MgO(001) with cube-on-cube orientation relationship appears as a square net with dislocation spacing 4.05 nm. Such dislocation network results in periodic variations of strain in Pt thin film (see Fig. 2). It has been pointed out by theoretical analysis and simulation that such periodic strain provides a nanopattern for the spinodal decomposition of AgCo phase. As most simulations on spinodal decomposition, the atoms of the initial AgCo phase are randomly arranged in regular (f.c.c.) crystal lattice. The model assumes that AgCo is deposited on Pt/MgO in a disordered state and we calculate the formation of nanostructure by a subsequent annealing process.

B. Simulation method

There are a number of approaches proposed to model the elastic effect on precipitate morphology in coherent systems, where the linear elasticity theory is employed to calculate the elastic energy. In this article, we adopt an alternative method of combining atomistic calculations and microscopic mean-field theory, which is applicable for noncoherent cases, to simulate the effect of dislocation, strain response and spinodal decomposition in AgCo/Pt/MgO(001) thin film. In this study, the morphology of the system is described by the position and occupation probability (atomic concentration) of all atoms, $\{r_i, n_i\}$. \{r_i\} are used to simulate local atomic motion such as strain response or dislocation, while \{n_i\} are used to simulate atomic diffusion of phase transformation. The atomic concentrations of MgO and Pt phases are fixed in simulation, while the AgCo phase undergoes a process of spinodal decomposition. After expressing the empirical potential and free energy as functions of \{r_i, n_i\} under mean-field approximation, i.e., $V(\{r_i, n_i\})$ and $F(\{r_i, n_i\})$, the evolution of atomic positions is given in molecular dynamics (MD) as

$$m_i \frac{d^2r_i}{dt^2} = -\nabla_i V(\{r_i, n_i\}),$$

while the diffusion process is described in microscopic mean-field theory as

$$\frac{dn_i}{dt} = \sum_j L_{ij} \frac{\partial F(\{r_i, n_i\})}{\partial n_j},$$

where $L_{ij}$ is the kinetic coefficient proportional to the inverse average time of elementary diffusional jumps from site $i$ to $j$. The timescale of diffusion is mainly determined by the magnitude of $L_{ij}$. In our calculation, $L_{ij}$ is assigned as a constant $L$ when $|r_i - r_j| < R_{\text{diff}}$ and 0 otherwise. Since diffusion is much slower than elastic response, the system is set in elastic equilibrium during the diffusion process. In numerical scheme, the simulation loop is as following:

1. run $n$ steps of MD by Eq. (1) with time step $\delta t$ to reach elastic equilibrium;
2. run one step of diffusion by Eq. (2) with time step $dt$;
3. goto (1).

It is a multiscale scheme overcoming the weakness of small time scale in MD since $n\delta t \ll dt$. Although the present work employed a microscopic diffusion equation for a binary system and assumed an atomic exchange mechanism for diffusion, it is rather straightforward to formulate the microscopic diffusion using a vacancy mechanism by introducing vacancy as the third component. With vacancy as the third component, the model can automatically model the surface morphology changes as a result of surface energy anisotropy and the balance of surface energies and the interphase boundary energy between the two phases in the film. However, as the first attempt, we assumed the simple exchange mechanism. The vacancy mechanism will be considered in a future publication.
C. Empirical potential

The empirical potential between Ag, Co and Pt atoms adopted in current simulation is the Tight-binding second-moment-approximation (TB-SMA) scheme,\(^{18}\) where the potential is comprised of a binding part and a repulsive part:

\[
V = \sum_i (E_R^i + E_B^i) .
\]

\[
E_R^i = \sum_j \left\{ n_i n_j A_{AA} \exp[-p_{AA}(r_{ij}/r_0^{AA} - 1)] + [n_i(1 - n_j) + (1 - n_i)n_j] A_{AB} \exp[-p_{AB}(r_{ij}/r_0^{AB} - 1)] + (1 - n_i)(1 - n_j) A_{BB}\exp[-p_{BB}(r_{ij}/r_0^{BB} - 1)] \right\} ,
\]

\[
E_B^i = - \sum_j \left\{ \frac{n_i n_j \xi_{AA} \exp[-q_{AA}(r_{ij}/r_0^{AA} - 1)]}{\left[ (1 - n_i)(1 - n_j) \xi_{BB} \exp[-q_{BB}(r_{ij}/r_0^{BB} - 1)] \right]^{1/2}} \right\}^{1/2} .
\]

where \( r_{ij} \) represents the distance between atoms \( i \) and \( j \) and \( r_0^{\alpha \beta} \) is the first-neighbors distance in the \( \alpha \beta \) lattice. \( A, p, \xi, q \) are some free parameters of the SMA scheme that are fitted to desired properties of the system. The parameters for the pure species are available in the literature.\(^{18}\) For the cross parameters of Ag-Co interaction, we fit \( A, \xi \) to the heat of formation (+26 kJ/g atom)\(^{19}\) and lattice parameter (3.81 \( \AA \) that is assumed to be the average value between pure Ag and Co) of the Ag\(_{0.5}\)Co\(_{0.5}\) disordered phase, while \( p \) and \( q \) are simply assigned to the average values of pure species. The result obtained is shown in Table I. Based on the potential scheme Eqns. (3-5) and the fitted parameters, the formation heat and the lattice constant at any atomic concentration can be calculated, which are depicted as Fig. 3. The curve of formation heat can be described by the parabolic law very well. The lattice constant approximately obeys the Vegard’s law. The elastic constants are also calculated (see Fig. 4). It appears that the elastic constants monotonously change with concentration. However, it should be noted that the curves do not satisfy the linear law that is assumed by many spinodal decomposition simulations.

The cross parameters of Ag-Pt and Co-Pt are also listed in Table I, which are fitted in a similar process. The heat of formation is assumed to be zero.

The importance of the Pt/MgO substrate in the current simulation lies in its dislocation network and the corresponding strain effect. We keep the MgO atoms fixed in simulation and describe the interactions between Pt and MgO as the Lenard-Jones potential:

\[
V_{LJ} = 4\varepsilon \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} .
\]

For AgCo phase, to include the influence of atomic concentration, the following formula is used under mean-field approximation for the potential (\( A \) and \( B \) denotes two atomic species, Ag and Co, respectively, and \( n_i, n_j \) are the concentrations of \( A \) atoms):

\[
\varepsilon = \sum_{\alpha \beta} \varepsilon_{\alpha \beta} = \sigma_{\alpha \beta} = \varepsilon_{\alpha \beta} = \sigma_{\alpha \beta} = \varepsilon_{\alpha \beta} = \sigma_{\alpha \beta} = \varepsilon_{\alpha \beta} = \sigma_{\alpha \beta} .
\]

The parameters are adopted as: \( \varepsilon_{\text{Mg-Pt}} = 0.336 \text{eV} \), \( \sigma_{\text{Mg-Pt}} = 2.3 \text{Å} \), \( \varepsilon_{\text{O-Pt}} = 1.34 \text{eV} \), \( \sigma_{\text{O-Pt}} = 1.783 \text{Å} \), with a distance cutoff 3.4 Å. With these parameters, isolated Pt atoms can be adsorbed by MgO substrate by sitting 1.99 Å atop the surface O atoms of MgO(001) with an adsorption energy of 2.35 eV as indicated by density-functional calculations.\(^{20}\) MD simulation shows that such potential can produce dislocation network as required and the corresponding periodic strain (see Fig. 2).

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**FIG. 3** Heat of formation and lattice constant of disordered AgCo phase as functions of Ag concentration. The curves are calculated by using the mean-field TB-SMA potential [Eqns. (3-5)] with parameters in Table I.
The diffusion cutoff in one diffusion step is $R_{\text{diff}}$ applied in 30 AgCo atoms and periodic boundary conditions are assumed.

Fig. 4: Elastic constants of disordered AgCo phase as functions of Ag concentration under the mean-field TB-SMA potential.

|                | $A$ (eV) | $\xi$ (eV) | $p$    | $q$    | $r_0$ (Å) |
|----------------|----------|------------|--------|--------|-----------|
| Ag-Co          | 0.0752   | 1.1944     | 11.261 | 2.7127 | 2.696     |
| Ag-Pt          | 0.1988   | 1.9399     | 10.770 | 3.5711 | 2.832     |
| Co-Pt          | 0.1449   | 1.9959     | 11.108 | 3.145  | 2.667     |

III. RESULTS AND DISCUSSIONS

A. Basic feature

A 3D system of AgCo/Pt/MgO(001) thin film with 1 monolayer (ML) of Pt and 10 ML of AgCo phase is simulated. Every monolayer in $xy$-plane contains 30 $\times$ 30 AgCo atoms and periodic boundary conditions are applied in $x$- and $y$-axes. Free boundary condition is used in $z$-axis. The average Ag concentration is $c_{\text{Ag}} = 0.5$. The diffusion cutoff in one diffusion step is $R_{\text{diff}} = 3.53$ Å, i.e., $L_{ij} = L$ for the nearest neighbors and $L_{ij} = 0$ in other cases. A reduced time is defined as $t^* = t/L$ to measure the simulation process. The time step of MD is kept as $\delta t = 0.15 \times 10^{-15}$ s, and the temperature is 600 K. The time step of diffusion simulation is dynamically adjusted to ensure the convergence of the result.

The simulation result corresponding to $t^* = 70$ is depicted in Fig. 5. 240000 MD steps are conducted in simulation. We can see that the surface of thin film is covered by Ag phase. The reason is that the surface energy of Ag (1.3 J/m²) is half that of Co (2.71 J/m²). Similar case occurs in CuCo system where Cu phase will diffuse onto the surface to form a metastable alloy in epitaxial growth. Due to the influence of surface, AgCo decomposed into layer structure near the surface. In fact, it is a kind of surface-directed spinodal decomposition. [23] Interesting phenomenon is observed near the AgCo/Pt interface: Co atoms are attracted to the strained regions near the dislocations because their atomic radius are smaller than Ag. As a result, AgCo decomposed phase produces interesting 2D nanostructure pattern [Fig. 5(b)]. So the basic feature of spinodal decomposition in AgCo/Pt/MgO(001) system can be described as a competition between the surface-directed layer structure and the substrate-dislocation-induced nanopattern. These features are consistent with previous results in 2D approximation. [8]

B. Effect of AgCo concentration

In this section, we investigate the effect of AgCo concentration on the spinodal decomposition. Two Ag concentrations, $c_{\text{Ag}} = 0.25$ and 0.75, are considered, and the results are compared with that of $c_{\text{Ag}} = 0.5$ in Section III.A.

A result of $c_{\text{Ag}} = 0.25$ is given in Fig. 6. The layer structure near the surface is similar to the case of $c_{\text{Ag}} = 0.5$. The difference occurs in the nanostructure near the interface: due to the reduction of Ag concentration, Ag-rich regions near the interface shrink in volume, and the nano-pattern changes from Co islands in Ag matrix [Fig. 5(b)] into Ag islands in Co matrix [Fig. 6(b)].
FIG. 6: Snap-shot of phase morphologies of the system with 1 ML of Pt and 10 ML of AgCo ($c_{Ag} = 0.25$). (a) The $x$-$z$ monolayer located at $y = 0$. (b) The second $x$-$y$ monolayer of AgCo phase.

FIG. 7: Atomic configuration of the system with 1 ML of Pt and 10 ML of AgCo ($c_{Ag} = 0.75$). (a) The $x$-$z$ monolayer located at $y = 0$. (b) The third $x$-$y$ monolayer of AgCo phase.

When the system is evolved in longer time, it is observed in simulation that the flat Ag islands get smaller and smaller. It means the surface Ag phase tends to absorb the Ag islands near the interface.

Now, we come to the case of $c_{Ag} = 0.75$ (Fig. 7). Compared with the result of $c_{Ag} = 0.5$, there is no layer structure of Co phase near the surface in present case.

FIG. 8: Atomic configuration of the system with 1 ML of Pt and 30 ML of AgCo ($c_{Ag} = 0.5$). (a) The $x$-$z$ monolayer located at $y = 0$. (b) The third $x$-$y$ monolayer of AgCo phase.

All Co atoms condense as cone-like islands on the dislocations of the substrate. They are covered by Ag-rich phase that spread to the surface. When $c_{Ag} = 0.5$, the Co phases near the interface also assume the shape of cone-like islands [Fig. 5(a)], but the cones stand upside down, merging with the layer structure near the surface.

It is noted that the Ag phase is important in forming the Co islands in the above process. If there is no Ag phase, Co thin film will grow in layer structure at small thickness. Ag phase acts as equivalent surfactant in assisting Co to decompose into islands. The present study suggests it may be possible to produce nanostructure by the following process. First, Co islands can be formed via spinodal decomposition of AgCo on periodic strained substrate. Subsequently, the Ag phase can be removed by chemical etching, leaving a regular array of Co islands. Experiments will be needed to test this conjecture.

C. Effect of AgCo phase thickness

To explore the effect of AgCo phase thickness, a system with 30 ML of AgCo with $c_{Ag} = 0.5$ is simulated with the result in Fig. 8. The basic characteristics is similar to the above results: a competition between the layer structure near the surface and the patterned structure.
FIG. 9: Pattern correlation function (solid line and circles) and layer Ag concentration (dashed line and triangles) of AgCo phase in the system with 1 ML of Pt and 30 ML of AgCo ($c_{Ag} = 0.5$). The pattern correlation function is normalized to make sure the self-correlation is equal to 1 ($R_{mm} = 1$ for $m = 3$ in this case).

near the interface. The patterned structure induced by the dislocations of the substrate decays within a distance of about ten monolayers while the layer structure presides in most regions. Surface energy is on the same order as the atomic cohesive energy while strain energy is higher order variation of the cohesive energy. So the surface effect dominates at the current film thickness.

In order to quantitatively analyze the competition between two kinds of structures, we define the pattern correlation function of two layers as:

$$R_{mn} = \frac{V_m \cdot V_n}{|V_m| \cdot |V_n|} - R_{mn}^0,$$  (7)

where $V_m$, $V_n$ are vectors composed of atomic concentrations within layers $m$ and $n$. $R_{mn}^0$ is the calculation result when there is no correlation between two patterns:

$$R_{mn}^0 = \frac{\sum_V V_{m\mu} \cdot \sum_V V_{n\nu}}{N_{layer}|V_m| \cdot |V_n|},$$  (8)

where $V_{m\mu}$ are components of $V_m$ and $N_{layer}$ is the number of components.

The third AgCo layer has a representative pattern induced by the dislocation of substrate. We calculate the correction function of all AgCo layers with respect to the third one and plot the result in Fig. 9, together with the layer concentration. It is clearly demonstrated that surface-directed spinodal decomposition (dashed line) penetrates throughout the thin film while the pattern structure (solid line) only exists in the range of ten monolayers near the interface. It suggests that the film thickness should be limited to small values if one is interested in producing nanostructure by spinodal decomposition on strained substrate. For example, when the thickness of AgCo phase decreases to 5 ML, a regular array of Co islands can be obtained in simulation (see Fig. 10).

D. Effect of Pt thickness

The strain induced by the dislocation declines in Pt phase. If the thickness of Pt phase is large, the strain acting on AgCo phase will be too weak to induce nanopattern.

Fig. 11 displays the simulation results on the system with 3 ML of Pt and 30 ML of AgCo ($c_{Ag} = 0.5$). The third $x$-$y$ monolayer of AgCo phase is depicted here.
FIG. 12: Atomic configuration of the thin film grown layer by layer where atomic diffusion is restricted within the same layers. The system has 1 ML of Pt and 10 ML of AgCo ($c_{Ag} = 0.75$). (a) The $x$-$z$ monolayer located at $y = 0$. (b) The third $x$-$y$ monolayer of AgCo phase.

is the critical thickness of Pt phase to produce patterned structure in the current case.

It has been illuminated in the previous sections that the influence of surface is competing with that of dislocation strain. With decreasing AgCo thickness, the structure near interface is more and more affected by the surface. We conduct simulation on the system with 3 ML of Pt and 10 ML of AgCo. Co islands appear only in the very early stage, and the final structure is a complete layer structure without any Co island.

Our analysis suggests there exists a critical value for the periodic strain of substrate to induce nanostructure in thin film. A previous study\(^{[1]}\) indicates that the imposed strain provides a pre-existing preference wavelength for the spinodal decomposition in initial stage, regardless of how small the strain is. The simulation results in this section shows that such preference wavelength may be lost in later stage and self-organized nanostructure may fail to realize if the strain is less than a critical value.

IV. CONCLUSIONS

Based on the above simulation results, it is concluded that patterned nanostructure can be obtained in AgCo/Pt/MgO thin film. The main feature of AgCo spinodal decomposition in this system is the competition between the surface-directed layer structure and the strain-induced patterned structure. Strain effect is weaker than the surface effect in the current cases. The patterned Ag-Co structure occurs only within a short range near the interface (no more than 10 monolayers), and the thickness of Pt phase should be small enough to effectively transfer the strain of dislocation in Pt/MgO interface to the AgCo phase to produce nanostructure. However, if spinodal decomposition of AgCo phase occurs within monolayers by careful film growth controlling, surface-directed layer structure will be prohibited and the patterned structure will form in a wide range.

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