Molecular Dynamics Simulations of Thin Solid Film Growth at Non-Equilibrium Process

Abstract

The annealing process of Co/Cu two-layer structure for the giant magnetoresistance (GMR) application is simulated by using MD simulation technique. The many-body, tight-binding potential is used to model the interatomic force acting between atoms and Langevin technique is adopted to incorporate into the motion equation to control the temperature maintaining at an equilibrium state. From the results of this study, it indicates that the Co atom is more difficult to activate to a flow state than the Cu atom. The Co/Cu interfacial roughness is not so sensitive to the elevation of the annealing temperature as the Cu surface roughness. Finally, the Co/Cu interfacial diffusion also found and the exchange of the Co and Cu becomes much severe as the annealing temperature increases.

Keywords: Molecular dynamics, Annealing process, Giant magnetoresistance, Tight-binding potential
simulate the atomic force between the aluminum film and the silicon substrate. They found that droplet formation depends strongly on the initial film-thickness distribution, the film temperature, and the bond energy between the film and the substrate. In their analysis, distribution of the sputtered aluminum was assumed to be completed before the start of the reflow process. However, this assumption, is at variance with actual practice. Similarly, our former study, Su et al. [14] was to investigate the reflow process for a damascene trench with uncompleted Cu filling. The initial reflow morphology was obtained by a more realistic deposition simulation to avoid the disadvantage of artificially applied in advance as the Saitos’ study. In addition, the many-body, tight-binding potential was used to model the interatomic force acting between atoms and the Langevin technique was adopted to model the heat flow through the thermal control layer.

In the present study, we followed the methodology of our previous study, but instead of the focus changing to the annealing simulation of the Co/Cu multilayer for the GMR application. The issues studied here include the surface roughness and Co/Cu interfacial roughness, annealing morphology, annealing microstructure, Co and Cu mean square displacement and the Co and Cu composition change arising from interdiffusion under the influence of the different annealing temperature. The detailed diffusion mechanisms as well as the annealing temperature effect are presented and discussed.

Simulation model
The initial annealing morphology is shown in Fig. 1(a), which is a two-layer Co/Cu structure composed by 6 Co lower layers and 5 Cu deposited upper layers. A separated deposition simulation obtains the Cu film morphology. The detailed deposition simulation can be seen elsewhere of our former researches [15-17]. The deposition conditions are summarized as follows. The substrate temperature is controlled to maintain at the constant room temperature of 300K. The incident energy of the Co atom is 0.1 eV and the deposition rate at 0.005 atom/ps. In the deposition simulation, an assumption is made that the Cu film is grown on a perfect flat Co substrate.

The whole time history of the temperature history, including the deposition and reflow processes, is assisted to state the critical time instants of the process, as shown in Fig.1 (b) for H1, H2, H3 and H4. The whole time history begins from the deposition process as zero reference and at the annealing process subsequently begins right after the end of deposition process. Three stages are included in the annealing process, a gradual heating from the substrate temperature to the annealing temperature at the beginning, then followed by a heating at the annealing temperature maintaining for a while and finally followed by a gradual cooling to the original substrate temperature. The temperature is controlled via the thermal control layers, which are located at the lower part of Co layers.

The temperature of these thermal layers varies according to a given annealing temperature condition, including heating rate, annealing temperature and cooling rate, within specified three time intervals. The thermal layer is govern by the rolled according to the Langevin equation, given as follows:

\[ m\dot{v}_i = F_i - mrv_i + R(i) \]  

where \( m \) is the atom mass, \( v_i \) is the atom velocity, \( \gamma_i \) is the damping constant, \( F_i \) is the atomic force acting between atoms deriving from the potential energy, which will be introduced in later, and \( R(i) \) is the random force which satisfies the following equation:

\[ \langle R_i(t)R_j(t+\tau) \rangle = 2mrtkT\delta(r)\delta_{ij} \]  

where \( T_r \) is the reference temperature of the substrate and \( \delta \) is the kronecker delta symbol.

In above Eq. (1), it can be clearly seen that the first term of the left side equation together with the first term of the right side equation is the classical Newton’s motion equation. The second term at the right side is damping term and the third term is the random forcing term. These two additional terms is to control the thermal layers to maintain the control layer staying at the equilibrium temperature in a random manner. A detailed description of this equation from theoretical aspect is not presented in this paper. However, interested readers are directed to the comprehensive computation of this thermal control algorithm presented in References [18-22].

Above the Co layer, all the Cu atoms are grown by the similar form of the motion equation, Eq. (1), however, the second and third terms at the left hand side of equation, corresponding to the damping and force terms, are neglected in the calculation.

The potential used in this simulation is the many-body, tight-binding potential as introduced by summing the band energy, which is characterized by the second moment of the d-band density of state, and a pairwise potential energy of the Born-Mayer type [23], i.e.,

\[ E_i = -\sum_j \exp \left[ -2d_0 \left( \frac{|r_{ij}-r_0|}{r_0} \right) \right] + \sum_{ij} A \exp \left[ -6\left( \frac{r_{ij}}{r_0} - 1 \right) \right] \]  

where \( d_0 \) is an effective hopping integral, \( r_0 \) is the distance between atom \( i \) and \( j \), and \( r_0 \) is the first-neighbor distance. The parameters \( A, p, q \) and \( d_0 \) which are used in the tight-binding potential model, are determined by the experimental data of cohesive energy, lattice parameter, bulk modulus, and two shear elastic constants (i.e. \( C_{44} \) and \( C' = (1/2)(C_{44} - C_{11}) \) ), respectively.

Finally, the interaction force on atom \( i \) can be expressed as:

\[ F_i = \sum_{\mu} \left( \frac{\partial E_{ij}}{\partial r_{ij}} \right) \tau \]  

The simulation uses the Gear’s predictor-corrector algorithm [24] to calculate the trajectories of atoms in the simulation.

Finally, the arrangements for the Co and Cu layers are according to their lattice structure; the Co layers are the hexagonal close-packed (hcp) structure and the Cu layers are face centered cubic (fcc). The total atoms used in the simulation have 9180 consisting 4680 atoms for Co layers and 4500 atoms for Cu layers. The lowest layer of the Co substrate is fixed to prevent the atoms from shifting. Periodic boundary conditions are applied in the x, y directions.

三、結果與討論

The initial reflooding morphology is calculated from a MD simulation at the end of the deposition process instead of an artificially applied film morphology, as shown in Fig. 1(a).

The heating to the four different annealing temperatures are conducted in the simulation to investigate the influence of different annealing levels on the film surface properties, including the film surface roughness, film morphology, film microstructure and diffusion ability. The time duration at constant heating stage maintaining at annealing temperature for all the four cases are equal to 100ps. The heating rate and cooling rate for the initial gradual heating stage and the final cooling stage are maintained at constant, respectively, namely, 5K/ps for heating rate and –0.5/ps for cooling rate. Due to the heating is to the different annealing temperatures at a constant
heating rate, the time to complete the heating stage, as well as the time to complete cooling stage, is different for these four cases. In order to clearly demonstrate the result, Table I is summarized critical time instants to distinguish the three stages of the reflow process. These are the starting point of heating stage, indicated by $H_1$ in Fig. 1(b), and the ending point of heating stage (also the starting point of constant heating stage), indicated by $H_2$, and the ending point of constant heating stage (also the starting point of cooling stage), indicated by $H_3$, and finally, the ending point of cooling stage, indicated by $H_4$.

A. Reflow morphology comparison

Figure 2(a), 2(b) and 2(c) show the reflow morphology at time instants of $H_2$, $H_3$ and $H_4$ for the annealing temperature at 800K. It can be seen that the Cu film atoms at the end of the gradual heating stage, $H_2$, as shown in Fig. 2(a), are first activated by the thermal energy at the vicinity of the V-shape cavity. The original deepest place in the V-shape cavity, shown in the darkest dots in Fig. 1(a), is filled up by the surrounding atoms. As maintaining at the annealing temperature of 800K for 100ps, thermal energy is allowed to diffuse more uniformly to the film surface. This makes the original bulge islands at two sides of the V-shape cavity becomes smoother due to the adatom migration as seen in Fig. 2(b) at the end of the constant heating stage, $H_3$. After a long time for the room temperature, all the adatoms reach their equilibrium positions undergo an equilibrium thermal motion. Figure 2(c) shows the final equilibrium morphology. It can be observed that the film thickness at four corners with a higher altitude than the place of the original V-shape cavity. It can be deduced that the atom migration activated by the thermal energy at this annealing temperature is not sufficient to further fill the concave film surface.

The morphology for annealing at temperature of 900 K at time instants of $H_2$ is similar to that of Fig. 2(a), except for more adatoms are accumulated above the V-shape cavity. Figure 3(a) shows the reflow morphology at the end of the constant heating stage, $H_1$. This implies that the elevation of the annealing temperature is helpful to the further film atom migration, which is beneficial to the yield of the smooth film surface property.

As the annealing temperature increasing to 1000K, the transition of the atom arrangement form order structure to disorder structure occurs in advance, as shown in Fig. 4(a) at an instant of $H_2$. The film atoms are activated to a violet motion state. Figure 4(b) shows the final reflow morphology.

Similar results are obtained as the annealing temperature increasing to 1100K, except the motion state are more violet and the atom arrangements are more disorder at the time instants of $H_2$ and $H_3$. Figure 5 shows the final reflow morphology at the constant heating point, $H_4$. As compared the final morphology of Fig. 6 to that of Fig. 4(b), it is hard to distinguish at a first glance, which is superior in surface roughness. This reveals another evidence for the former result shown in Fig. 2 that the discrepancy between two-interface width for two annealing temperatures of 1000K and 1100K is very small.

B. Reflow microstructure comparison

Figures 6 to 8 shows the radial distribution function (RDF) of the Cu film during the reflow process at different annealing temperature. This is to investigate the microstructure variation during the reflow process. Figure 6(a) to 6(d) shows the RDF of Cu film annealed at 800K for the four critical time instants, indicated by $H_1$, $H_2$, $H_3$ and $H_4$; the exact time instant of which can refer in the second row of the Table I.

The RDF of the Cu film at the starting point of heating stage, $H_1$, which is also the RDF at the end of the deposition process, shown at left upper part of the figure. There are five clear peaks appearing across the neighbor distance. This also means that the Co film structure is close to a solid state of a fcc structure. At the end of the gradual heating stage, $H_2$, shown in the left lower part of the figure, the decreasing in the second peak and that after reflect the change in its atom arrangement of a fcc structure due to the thermal excited motion. The upper part subfigure at the right hand side shows the RDF at the end of the constant heating stage, $H_3$. The comparison of RDF at time instants $H_3$ to that of $H_2$ shows that there is no further change in the Cu film structure for additional maintenance of the heat bath temperature at a constant annealing temperature. Finally, the RDF at the end of the cooling stage $H_4$, shown in the lower part at the right hand of the figure. It can clearly be seen that the peaks that decreases in the time instants of $H_2$ and $H_3$ have recovered to the similar structure before the reflow process, $H_1$ time instant.

Figures 7 to 8 show the RDF at the end of the gradual heating point, $H_2$ and the end of the constant heating point, $H_4$, for the other annealing temperatures of 900K, 1000K and 1100K. The omission of the illustration of the end of the cooling stage is for that the discrepancy of RDF after gradual cooled between them is very small.

Fig. 7 indicates the all the peaks appearing in the five specific neighbor distances obviously decreases as compared to those of Fig. 6. This also implies that the microstructure of the Cu film tends to a disorder structure as the annealing temperature is elevated. Similar results are also obtained in Figs. 8, however, the microstructure becomes more disorder toward to a liquidous structure as the annealing temperature is continuously elevated, as seen in Fig. 8 for H3. Comparison made between the Fig. 7, 8 for the instant of H2 also found that the disorder of the microstructure would occur advance in time when the annealing temperature is highly elevated. (liquidous state means the more better of the fluidity)

In this study, we have presented the annealing simulation of Co/Cu two-layer structure for the GMR application by using MD simulation technique. The many-body, tight-binding potential is used to model the interatomic force acting between atoms. In order to more accurately control the temperature, the Langevin technique is adopted to incorporate the two additional terms to the motion equation. From the results of this study, it indicates that the Co atom is more difficult to activate to a flow state than Cu atom. The Co atoms The Co/Cu interfacial roughness is not so sensitive to the elevation of the annealing temperature as the surface roughness. Finally, the Co/Cu interfacial diffusion also found and the exchange of the Co and Cu becomes much severe as the annealing temperature increases.

References


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Fig.1 (a) Initial annealing morphology and Co/Cu two-layers structure schematic diagram. (b) temperature history for deposition and annealing

Fig.2. Annealing morphology for an annealing temperature of 800K at an instant of: (a) H1 (b) H2 (c) H3

Fig.3. Annealing morphology for an annealing temperature of 900K at an instant of: (a) H1 (b) H2

Fig.4. Annealing morphology for an annealing temperature of 1100K at an instant of: H

Fig.5. Radial distribution function variation for an annealing temperature of 800K at instants of H1, H2, H3 and H4

Fig.6. Radial distribution function variation for an annealing temperature of 900K at instants of H2 and H3

Fig.7. Radial distribution function variation for an annealing temperature of 1000K at instants of H3 and H4

Fig.8. Radial distribution function variation for an annealing temperature of 1100K at instants of H3 and H4.