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A Molecular Dynamics Study of the Deposition and the Diffusion Behaviors of Al on a Cu Surface

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The deposition and the diffusion behaviors of Al atoms on Cu surfaces of various orientations were investigated by using classical molecular dynamics simulations and molecular static calculations. Al atoms with a kinetic energy of 0.1 eV were deposited at room temperature. On the Cu(001) surface, the deposited Al atoms tend to agglomerate only with adjacent atoms. In the case of the Cu(111) surface, surface diffusion of Al atoms is significant even as a time scale between two consecutive depositions (5 ps). Most deposited atoms are, thus, agglomerated near the surface step. In contrast, Al atoms deposited on Cu(011) hardly diffuse on the surfaces but intermix with the Cu atoms, resulting in an atomistically rough interface. These behaviors are consistent with changes in the activation barrier for a possible kinetic process that depends on the orientation of the substrate.

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I. INTRODUCTION

As the scale of devices is decreased to an atomic level, controlling and understanding the phenomena at the surface or the interface become very important. Furthermore, nanoscale manipulation considerably enhances the performance of electro-magnetic devices. Fukuzawa *et al.* proposed a new current perpendicular to plane (CPP) mode for a giant magneto-resistance (GMR) spin valve having a current confined path structure made of a nano-oxide-layer (NOL) with many small metallic contacts [1]. They reported that the MR ratio increased while the resistance of the area contact (RA) was kept small, presumably due to confining the spin movement by forming a current confined path (CCP) in a nonmangnetic oxide layer between two magnetic layers [1]. Hence, controlling the size and the distribution of nano metallic channels inside the NOL is essential to optimize CPP-GMR devices [2–5]. An Al-Cu thin film is widely used for the channel layer of a CCP-GMR device because the chemical affinity to oxygen is very different between Al and Cu. Exposed to an oxidation environment, Al will be easily oxidized to form NOL whereas Cu will form nano metallic channels inside the NOL. Kawasaki *et al.* reported that the surface morphology of an Al-Cu thin film was strongly influenced by the position of Al on the Cu surface while the microstructural change during oxidation was negligible [6]. Therefore, understanding on the atomic scale of the surface structure and of the kinetic behavior of Al atoms on the Cu surface are crucial for controlling the nano metallic channels inside the NOL.

A quantitative investigation of the atomic structure and composition of the thin films is still a challenging is-

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Table 1. Properties of Al, Cu and their intermetallic compounds predicted by using the EAM potentials employed in this study in comparison with experimental data from the literature.

Property	Al		Al_3Cu		$AlCu_3$		Cu	
	Expt. or DFT	Calc.	Expt. or DFT	Calc	Expt. or DFT	Calc	Expt. or DFT	Calc
Structure	FCC (A1)		$L1_2$		$L1_2$		FCC (A1)	
a_0 [Å]	4.05^a	4.05	3.94^d	3.9	3.72^d	3.654	3.615^a	3.615
E_{coh} [eV]	3.36^a	3.32	-	3.48	-	3.65	3.52^a	3.52
B [GPa]	76^b	75.74	-	88.51	-	117.37	140^b	139.64
C' [GPa]	26^b	9.742	-	10.76	-	15.56	48^b	20.6
γ_{111} [mJ/m^2]	935^c	529	-	738	-	1143	1952^c	1166
γ_{100} [mJ/m^2]	1081^c	584	-	812	-	1228	2166^c	1248
γ_{110} [mJ/m^2]	1090^c	643	-	874	-	1316	2237^c	1354

[a] Ref. 23.
[b] Ref. 24.
[c] Ref. 25.
[d] The values are from the prediction of Vegard's law.

sue due to the limits of experimental analyses. However, a molecular dynamics (MD) simulation using valid interatomic potentials provides quantitative information on the deposition, diffusion, thermal and mechanical properties on an atomic scale. Thin film growth behaviors in many metallic systems, such as Cu/Cu, Ag/Ag [7–12], Au/Cu [13, 14], Co/Cu [15, 16], Pb/Cu [17] and Al/Co [18] were successfully investigated by using MD simulations. The simulation results contributed to an understanding on the surface phenomena and suggest a kinetic model to explain the experimental results [19]. In the present work, we elucidated the deposition and the surface diffusion behaviors of Al on a Cu surface by using a molecular dynamics simulation with embedded atom method (EAM) potentials for Al and Cu. The morphology of the Al thin film on Cu strongly depends on the orientation of the Cu substrate. The kinetic energy barriers calculated for the various surface processes by using a molecular statics (MS) method with the same interatomic potentials are consistent with the observed thin film morphologies.

II. COMPUTATIONAL PROCEDURE

Semi-empirical embedded-atom method (EAM) potentials were used for simulating the deposition behavior in the Al-Cu system [20]. The potentials used in this study were rigorously benchmarked by using the calculated or experimentally observed physical properties of Al, Cu and AlCu intermetallic compounds [21]. Table 1 summarizes the benchmark test of the potentials used in this study. Single crystal Cu with orientations of (001), (011) and (111) was used for the substrate for the present simulation. To investigate the effect of the surface step, we introduced as atomic plateau of 1 ML in thickness on the atomically smooth surface. The size of the substrate was approximately 90 Å × 90 Å × 25 Å in the x, y and z directions. The total numbers of substrate atoms on the (100), (011) and (111) surfaces were 12,897, 13,221 and 12,409, respectively. Periodic boundary conditions were utilized in the x and the y directions. The position of the bottom-most 3 layers was fixed so that the layers acted as a thermal bath during deposition. All the other layers of the substrate were unconstrained while the initial temperature was set at 300 K using the atom-velocity-rescale method. After the substrate atoms with the plateau had been fully relaxed, the Al atoms were randomly placed on the xy plane at a distance sufficiently far from the surface. The kinetic energy of the deposited Al atoms was set to 0.1 eV, which is typical in evaporation or molecular beam epitaxial growth. A 0.5 monolayer (ML) of Al was deposited. The MD time step was set to 1.0 femtosecond (fs) to obtain accurate atomic trajectories. The time interval between two consecutive depositions on the substrate was fixed at 5 pico-seconds (ps). Various kinetic paths of the deposited Al on Cu surface were determined by using the present MD simulation results. A molecular static calculation was then employed to calculate the diffusion energy barriers. We found the most stable position of Al atom at 20 points along the diffusion path between two stable positions to calculate the energy barrier from the energy-path curve.

III. RESULTS AND DISCUSSION

Figure 1 shows the atomic configurations after 0.25 and 0.5 ML of Al had been deposited on the three kinds of Cu surfaces with artificial plateaus. In spite of the random deposition with a low incident energy of 0.1 eV, the deposited Al atoms formed an atomic layers not an island. This is consistent with the conventional model of thin film growth [22] because the surface energy of Al

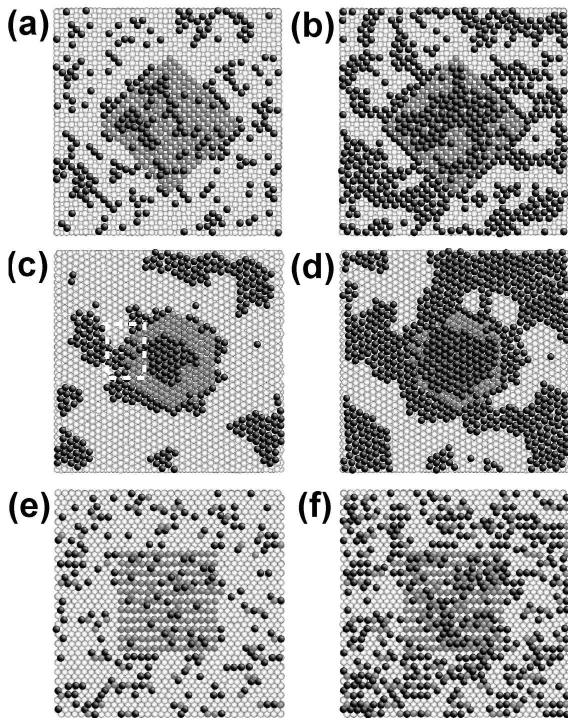

Fig. 1. Atomic configurations for (a) 0.25 ML and (b) 0.5 ML Al on Cu(001), (c) 0.25 ML and (d) 0.5 ML Al on Cu(111) and (e) 0.25 ML and (f) 0.5 ML Al on Cu(011) with a plateau. White, gray and black colored atoms correspond to Cu substrate atoms, Cu plateau atom and shifted substrate Cu atoms and deposited Al atoms, respectively.

is much lower than that of Cu, as shown in Table 1; Al films forms on the Cu surface in a layer-by-layer growth mode. However, the thin film morphologies strongly depended on the surface orientation. As shown in Figures 1(a) and (b), the Al atoms deposited on the Cu(001) surface did not actively diffuse and agglomerated only when Al was deposited near the Al islands. Al atoms deposited on the Cu plateau showed a similar behavior without diffusion down to the surface because of the Ehrlich-Schwoebel (ES) barrier at the edge. Hence, the surface morphology reflects the randomness of the position of Al deposition. In the case of the Cu(111) surface (Figures 1(c) and (d)), deposited Al atoms diffused very actively to form a large agglomerate of Al atoms even at room temperature. Because of the high mobility on the (111) surface, the atomic sites of the surface step were covered preferentially by Al atoms. Interestingly, when Al atoms were deposited on the plateau, an Al cluster was grown from the center of the plateau. It was also observed that some Al atoms on the plateau pushed the Cu atoms of the plateau edge to descend to the Cu surface (see dotted square of Figure 1(c)). This is a typical downward diffusion [9]. A significantly different morphology of deposited Al atoms was observed on the Cu(011) surface. As shown in Figures 1(e) and (f), deposited Al atoms hardly diffuse on the (011) surface so that agglomerates of deposited Al atoms were not observed. However, some Al atoms were aligned 1-dimensionally along the open direction of the (011) surface. Moreover, some of the deposited Al atoms were exchanged with the surface Cu atoms to form a surface intermixing. Both deposition and intermixing occurred simultaneously on the Cu(011) surface.

Table 2. Surface diffusion energy barrier (in eV).

	Cu(001)	Cu(011)	Cu(111)
Surface diffusion	0.33	$0.816^{\perp}/0.303''$	0.055
Toward the step	0.269	0.256	-*
Along the step	0.262	$0.797^{\perp}/0.306''$	0.308

* Spontaneous reaction.

To investigate the diffusion behavior of Al atoms on the Cu surface quantitatively, we calculated the energy barrier for surface diffusion of Al adatoms. Various diffusion paths were classified into seven types and each path is shown schematically in Figure 2. These diffusion behaviors were commonly observed in this study on the surface of any orientation. Table 2 summarizes the calculated results of the energy barriers for the surface processes. The energy barrier for surface diffusion on the (111) surface was very low, 0.055 eV. One should further note that diffusion toward the step occurs even without an energy barrier. Therefore, a very fast arrangement of the deposited Al atoms occurs on the Cu(111) surface. In the case of the (011) surface, the energy barrier strongly depends on the direction, which would be a natural consequence of the asymmetry of the surface atomic structure. Hence, the diffusion of Al is very constrained along the open channel of the Cu(011) surface, resulting in aligned Al atoms. The strong dependence of the diffusion barrier on the surface orientation can be understood if one considers the atomic configuration of the surface. On the (111) surface, substrate atoms are closely packed so that the energy barrier from a hollow site to a nearby hollow site is very small. On the other hand, the (001) surface has deeper hollow sites than the (111) surface, resulting in a higher diffusion barrier. The atomic configuration of the (110) surface is highly anisotropic: an open channel is formed along <110> direction with the deepest hollow sites. Hence, the deposited atoms are bound by the substrate atoms, which significantly suppresses the surface diffusion especially across the open channel. The energy barrier for the diffusion along the step was the lowest on the (001) surface, 0.262 eV, which is even lower than that on the (111) surface. It is, thus, expected that the Al atoms attached to the step on the (001) surface will diffuse along the step more easily than on the other surfaces.

The diffusion behavior on the plateau is essentially the same as that on the bottom surface (see Table 3). However, the energy barrier for diffusion on the edge of the (111) plateau was calculated to be even lower than that

Table 3. Diffusion energy barrier on the plateau (in eV).

	Cu(001)	Cu(011)	Cu(111)
Away from the step on the plateau	0.316	$0.814^{\perp}/0.302''$	0.018
Along the step on the plateau	0.33		
ES barrier	0.571	0.495	0.331
Downward	0.424	0.434	0.106

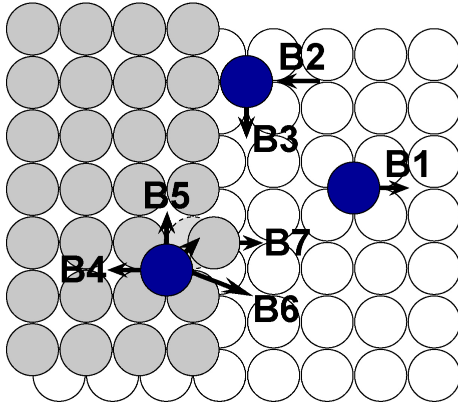

Fig. 2. Schematic description for the possible diffusion behavior of an Al adatom on the plateau and at the step (B1: surface diffusion, B2: toward the step, B3: along the step, B4: away from the step on a plateau, B5: along the step on a plateau, B6: Ehrlich-Schwoebel barrier, B7: downward diffusion).

for the surface diffusion on the Cu(111) surface. This result would support the observation that the Al atom that landed on the plateau tends to diffuse inside the plateau as shown in Figure 1(c). The Ehrlich-Schwoebel (ES) barriers of Al on the Cu(001), (011) and (111) plateaus were 0.571, 0.495 and 0.331 eV, respectively. All the values were higher than those of surface diffusion, which implies that the Al atoms deposited on the Cu plateau prefer to stay on the plateau until the plateau is completely covered. It must be noted in Table 3 that the energy barrier for the downward diffusion by pushing the edge Cu atom of the plateau is much smaller than ES barrier, especially on the (111) surface. It is, thus, more favorable for the Al atoms on the plateau to diffuse downward by pushing the edge Cu atoms away. This phenomenon is frequently observed on Cu(111) surfaces as shown in Figure 2(c).

IV. CONCLUSION

Using molecular dynamics simulation and molecular static calculations, we investigated the deposition and the diffusion behaviors of Al atoms on Cu surfaces in an atomic scale. It was observed that the deposited Al atoms move on the Cu(111) surface very rapidly, forming large Al agglomerates on the surface. Furthermore, an atomic step on the (111) surface is favorably covered by deposited Al atoms. Downward diffusion of the Al atoms deposited on the plateau of the Cu(111) surface was more favorable than overcoming the ES barrier. On the Cu(001) surface, deposited Al atoms tend to agglomerate only with adjacent atoms. However, diffusion along the step seems to occur on the (001) surface. In the case of the (011) surface, the deposited atoms hardly diffuse on the surface while intermixing with the substrate Cu atoms is frequently observed.

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