Surface diffusion and incorporation of adatom in Co/Al (0 0 1) system

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Abstract

The surface diffusion and the incorporation of an adatom on early stage of Co/Al (001) interface formation was investigated using the density functional theory (DFT). The energy barrier for the surface diffusion (migration of Co adatom to an adjacent hollow site passing the bridge site) was calculated as 1.01 eV. Large displacement of neighboring Al atoms was accompanied by the surface diffusion of Co adatom. For incorporation process, the energy barrier was 0.39 eV, only 38.6% of the barrier for surface diffusion and the energy gain of the system was 0.43 eV. After the incorporation process was completed, the Co adatom and Al atoms formed seven Co–Al bonds of highly coordinated B2-like configuration.
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1. Introduction

The magnetic properties of ultra thin film multilayer system generally applied to spintronic devices are largely affected by atomistic behaviors and the characteristics of the interface during the early stage of the magnetic tunneling junction (MTJ) fabrication [1–4]. Especially, the diffusion behavior of the adatom which determines the factors such as the alloy formation and the layer growth mode at the interface has been actively studied because of their own physical properties and applicability to related devices. Many different systems such as Co/Al [2], Al/Co [5], Co/Mo [6], Co/Au [7–9] bilayer systems and Co/Al$_2$O$_3$/Co [10], CoFe/AlO$_x$/Co [11] trilayer systems have been extensively investigated in the view point of improving the ordering of growth on substrates. In a study performed with the molecular dynamics method, it was reported that 90%, 56% and 82% of deposited Co adatoms were intermixed with the Al atoms of (0 0 1), (0 1 1) and (1 1 1) surface. For the

case of deposition on (0 0 1) surface, B2 intermetallic compound was formed very uniformly because of its thermodynamical stability [12]. It was also found that the driving force of the intermixing was the local acceleration of the Co adatom in the vicinity of the surface. The locally accelerated Co adatom could overcome the energy barrier for penetrating the substrate [13]. Similar tendencies of the atomistic behavior were found in the experimental studies using the X-ray photoelectron spectroscopy (XPS) intensity analysis. When the Co adatom was deposited on the Al (0 0 1) substrate, the Co adatom could penetrate the Al substrate actively and consequently, a ratio of 1:1 for the Co–Al phase was observed down to the three monolayers from the surface [2].

In quantitatively analyzing the tendencies of atomistic behavior, the first-principle investigation was performed to obtain the important parameters which determine the morphology of the interface. The energy barrier, the energy gain, and the displacement of the substrate atoms for the surface diffusion and incorporation that occurs on the initial stage of the thin-film junction fabrication were calculated.

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2. Calculation methods

The density functional theory (DFT) calculation was performed using the Vienna ab initio simulation package [14–16]. The exchange-correlation energy of the system was calculated by using the ultrasoft pseudopotential (USPP) [17] with local density approximation (LDA) [18,19]. For an accurate calculation the plane-wave basis was expanded to 280 eV (20.58 Ry) to describe a single electron wave function [20]. Theoretical equilibrium lattice constant of *fcc* Al, 3.98 Å obtained by solving the equation of state, was applied to substrate construction. It was 1.8% smaller than experimentally measured value 4.05 Å [21]. The difference is due to the general tendency of applied LDA which is known to underestimate some physical properties such as cohesive energy, band gap and lattice constant [22]. For the *k*-point sampling in the Brillouin zone, the $4 \times 4 \times 1$ grids of Monkhorst–Pack points were employed [23]. The supercell model with five-layer-Al (0 0 1) slab of the (2×2) surface unit and 23.79 Å vacuum region was prepared to simulate the adsorption and incorporation of Co adatom. Cobalt adatom and all Al atoms except for the centered layer of substrate were fully relaxed until the Hellmann–Feynman forces were in the range of ± 0.01 eV/Å. The relaxation scheme was based on the residual minimization method direct inversion in the iterative subspace (RMM-DIIS) [24]. Adsorption sites were defined as follows: The hollow site is the center position of four fold Al of the surface and the on top site indicates the position above of one Al atom. The bridge site is the midpoint of two adjacent Al atoms (see Fig. 1(a)). The energy barrier for the incorporation into the substitutional site (Fig. 1(b)) was calculated with the drag method [25] often used to find the minimum energy path (MEP) for the diffusion of atoms or molecules. The magnitude of displacement of substrate atoms was measured by comparing the position of the Al atoms, before and after of the Co adsorption. The positive and negative sign was assigned depending on the direction of the displacement, such as positive for the case of receding from and negative for the case of approaching to the Co adatom, respectively.

3. Results and discussion

To obtain the energy barrier for the diffusion of Co adatom on the Al (0 0 1) surface, the adsorption energies, E_{ad}, for the hollow, on top, and bridge site were calculated by

$$E_{ad} = -E_{Co/Al(2 \times 2)} + E_{Al(2 \times 2)} + E_{Co}, \qquad (1)$$

where $E_{Co/Al(2 \times 2)}$ is the total energy of the Co adatom with the fully relaxed clean Al (0 0 1)—(2×2) substrate, $E_{Al(2 \times 2)}$ is the total energy of the unrelaxed Al (0 0 1)—
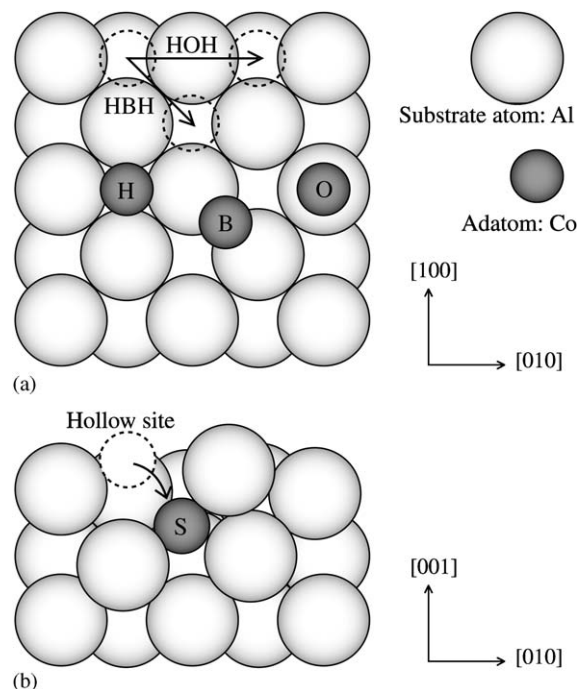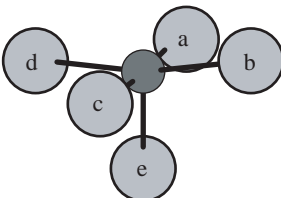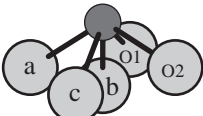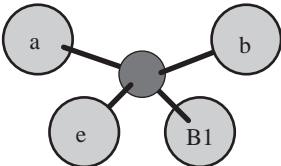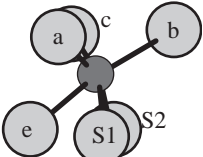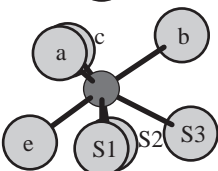

Fig. 1. Schematics of Al (0 0 1) substrate and adsorption sites. (a) (Top view) H, O and B indicate the hollow, on top and bridge site, respectively. Abbreviation HBH and HOH correspond to Hollow → Bridge → Hollow and Hollow → On top → Hollow, respectively. (b) (Side view) The arrow shows the path of Co adatom incorporation into the substitutional site (S) of Al substrate. Co adatom substituted into the substrate by pushing the existing Al atoms to the surface.

(2×2) substrate, and E_{Co} is the total energy of a free Co atom in super cell of same size.

As Co adatom was placed at each adsorption site, there was charge depletion near the Co adatom (< -0.60 bohr^{-3}) and charge accumulation near the Al atoms (> 0.048 bohr^{-3}) between Co adatom and every surrounding Al atoms. Therefore strong covalent Co–Al bonds were formed in addition with its original Al–Al bonds by partial displacement of Al atoms. The interatomic distance between the Co and the Al was close to the theoretical bond length, 2.54 Å which was calculated with the covalent radii [26,27] and the difference of electronegativity of each atom irrespective of adsorption sites (Table 1, fourth column). For on top site adsorption, an Al atom placed under the Co adatom was downwardly displaced by 0.82 Å after the relaxation and the interatomic distance became 2.16 Å. Four other neighboring Al atoms were moved toward the Co and thus shortening the interatomic distance from 3.11 to 2.47 Å. By the displacements, the C_{4V} symmetry configuration was observed near the Co adatom and surrounding Al atoms and the E_{ad} was calculated to be 5.62 eV/(2×2). When Co was adsorbed on the bridge site, Co placed at the center of two Al atoms and these atoms contacted with Co moved apart to 1.01 Å after relaxation. The Co adatom and four surrounding Al

Table 1
Bonding configuration of Co adatom with Al substrate

Position of Co	Structure	Al atoms	l^a (Å)	Displacement (Å)	N^b
Hollow site		a, b, c, d	2.25	+0.36	5
		e	2.19	+0.18	
On top site		a, c, O1, O2	2.47	−0.68	5
		b	2.16	+0.82	
Bridge site		a, b	2.22	+1.01	4
		e, B1	2.33	+0.08	
Barrier site of incorporation		a, c	2.32	−0.35	6
		b	2.27	+1.31	
		e	2.17	+0.40	
		S1, S2	2.41	−0.24	
Substitutional site		a, c	2.43	−0.50	7
		b	2.27	+1.53	
		e	2.27	+0.20	
		S1, S2	2.31	+0.13	
		S3	2.41	+0.03	

[a]l: Bond length.
[b]N: Number of total bonds.

atoms including these two and other two under the Co configured the C_{2V} symmetry and the E_{ad} was 7.30 eV/(2 × 2). The most stable adsorption site on the surface of Al (0 0 1) was, naturally, the hollow site where the E_{ad} is 8.30 eV/(2 × 2). It was understood that the highest E_{ad} was derived from the structural benefits such as negligible small displacement of the Al atoms and short average length of five Co–Al bonds for the adsorption. The Co atom at the hollow site formed the C_{4V} symmetry configuration with the four Al atoms in plane and one below. The bonding configuration and accompanied displacement for the hollow, on top, and bridge site adsorption were summarized in Table 1 with illustrations.

Based on the adsorption energy calculations, we elaborately analyzed the energetics and structural characteristics occurred in surface diffusion. By assuming that the surface diffusion begins from the hollow site that is the most stable adsorption site, we considered two case of diffusion path such as hollow → on top → hollow site (HOH, Fig. 1(a)) and hollow → bridge → hollow site (HBH, Fig. 1(a)). While the Co adatom moved through each path, the original stable configuration of the hollow site adsorbed system was disappeared. During the HOH diffusion, Co–d and Co–e bonds were broken apart and formed two new bonds with O1 and O2 (See Table 1). Vertical displacement of Al atom a, c, O1 and O2 is 0.39 Å outwardly and the b atom moved by 0.82 Å inwardly. The value of 0.82 Å corresponds to the 0.41 monolayer of the substrate slab. The energy barrier for the diffusion through the HOH path was calculated to be 2.68 eV and there was no energy gain of the system (Table 2). During the diffusion through the bridge site (the saddle point of the potential energy surface (PES)), two of five original bonds of the hollow site adsorbed system were broken (c–Co and d–Co) and a new bond was formed (B1–Co). The large displacement of the atom a and b allowed the system to maintain the existing Co–e bond and to form a new bond with B1. The energy barrier required for this

processing was 1.01 eV and the energy gain of the system was zero, same as the HOH diffusion (Table 2).

In order to find out the effects of the relaxation of substrate Al atoms on the energetics of the system, similar investigations with the frozen substrate were performed. All of Al atoms in the substrate were fixed at the position of the clean substrate. The Co adatom was allowed to move along only in vertical direction for finding the position which minimizes the energy of the system. Under this condition, we obtained the adsorption energy 7.43 eV/(2 × 2), 4.05 eV/(2 × 2) and 5.47 eV/(2 × 2) for the hollow, on top and bridge site adsorption, respectively. The values were 10.5–27.9% lower than those for the adsorption on the relaxed substrate. While considering the diffusion process on the frozen substrate, three Co–Al bonds out of four were broken when the Co diffused through the HOH path. Required energy barrier was 3.38 eV. If the Co adatom diffuse through the HBH path, two Co–Al bonds were lost and the required energy barrier was 1.97 eV. These calculated energy barriers for both diffusion types were larger than the ones for the relaxed substrate (Table 2). It is interesting to note that the ratio of the broken bonds to the number of the initial bonds was very high during the diffusion due to no displacement. This observation could possibly explain the higher energy barrier although the adsorption energy for each site were relatively low. Also, absence of newly formed bonds at the barrier site of HOH and HBH diffusion was another factor of the higher energy barrier for the diffusion on the frozen substrate.

The incorporation process of one Co adatom using the drag method was investigated in order to quantitatively analyze the intermixing property of the adatom and the Al substrate. Co adatom which was adsorbed on the hollow site was incorporated into the substitutional site (Fig. 1(b) and fifth row in Table 1) through minimum energy path (MEP) by breaking and forming the bonds with Al atoms. The configuration change

during the incorporation was shown as follows: The Co adatom at the center of the atom a, b, c and d began to move to the position between atom b and e by breaking the bond with d (The indexes of the adtoms are illustrated in the figure of the hollow site adsorbed system in Table 1). When the adatom places at the barrier site (Table 1, fourth row) where the system is most unstable, Co adatom bonded with atoms S1 and S2 additionally. After the incorporation process was completed, the Co adatom at the substitutional site additionally bonded with the atom S3. The atom b was displaced by 1.53 Å to the surface of the substrate due to the substitution by Co adatom. Except for the atom b, atoms a (and c), e, S1 (and S2) and S3 were displaced slightly. The required the energy barrier for this incorporation was 0.39 eV and there was the energy gain of 0.43 eV in the system (See Table 2). The energy gain was defined as the decrease of total energy relative to the hollow site adsorbed system. The total number of Co–Al bonds was seven and its length was turned out to be very similar to the theoretical bond length of the CoAl B2 structure, 2.42 Å. (This value was obtained by solving the equation of state using the ultrasoft pseudopotential with LDA for the bulk of unit cell containing the Co at (0, 0, 0) and Al at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.) If another Al atom approached to the Co adatom, B2-like structure could be formed where the Co adatom is placed at the body centered site of the simple cubic-like structure with eight Al atoms at the corner. The cohesive energy of the B2 CoAl bulk, 6.85 eV/atom was larger than that of the fcc Co bulk, 5.53 eV/atom, and the fcc Al bulk, 3.14 eV/atom. It can be inferred that the intermixing by the incorporation process is favorable behavior in the surface and interface in terms of energetics. This result highly support the observation of Kim et al. [12] which reported that 90% of Co atoms deposited on Al (0 0 1) surface with very low incident energy, 0.1 eV, could penetrate into the substrate through active intermixing, and formed the thermodynamically stable B2 intermetallic compound.

4. Summary and conclusion

The energetics and the atomistic behaviors of the Co adatom and Al substrate atoms during the early stage of the thin Co film growth on the Al (0 0 1) surface were investigated. The energy barrier for the surface diffusion through the bridge site which occurs after the hollow site adsorption was calculated as 1.01 eV. For the incorporation process, the energy barrier was 0.39 eV, smaller than the one for the surface diffusion. Contrary to the surface diffusion, there was an energy gain of 0.43 eV during incorporation and accompanied significantly smaller displacement of Al atoms. Also, thermodynamically stable B2-like structure was formed by the

Table 2
Energy barrier (E_b) and difference of the total energy of the system (ΔE_t) for the surface diffusion and incorporation of Co adatom on the Al (0 0 1) substrate

Diffusion path	E_b (eV)		ΔE_t[a] (eV)
	Relaxed substrate	Frozen substrate	
HOH[b]	2.68	3.38	0.00
HBH[c]	1.01	1.97	0.00
HS[d]	0.39	—	−0.43

[a] ΔE_t: Difference of adsorption energy for substitutional and hollow site.
[b] HBH: Hollow site → Bridge site → Hollow site.
[c] HOH: Hollow site → On top site → Hollow site.
[d] HS: Hollow site → Substitutional site.

substituted Co adatom and the seven neighboring Al atoms. The previously observed active intermixing and formation of the intermetallic compound at the interface of the Co/Al multilayer were successfully explained by the surface diffusion on the substrate and the incorporation of Co adatom into the Al substrate.

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