NUCLEATION OF TWO DIMENSIONAL CLUSTERS OF Ag ON Mo(110)

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The initial stage of Ag thin film growth on Mo(110) substrate has been simulated by molecular dynamics aided kinetic Monte Carlo method. Island structure, especially the azimuthal orientation at the coverage of 0.1 monolayers (ML) is discussed. A dense part of the largest island at 0.1 ML has a distorted hexagonal lattice with the angle of 118° between the two dimensional unit vectors, a_1 and a_2. The magnitudes of a_1 and a_2 are 2.83 and 2.76 Å which are the values between the bulk nearest neighbor distances of Mo and Ag (2.73 and 2.88 Å, respectively). The top substrate layer beneath the regular part is distorted from the perfect bcc(110) alignment to a denser structure and the Ag atoms sit top of the Mo atoms in the region. This part of the Ag island has an orientation between the Kurdjumov-Sachs and Nishiyama-Wasserman orientations with the perfect bcc(110) as the reference, though the Kurdjumov-Sachs orientation is known from experiments for thicker films.
Key words: Kurdjumov-Sachs orientation, Nishiyama-Wasserman orientation, MD-Aided-KMC

1. INTRODUCTION

Epitaxial growth of fcc(111) films on bcc(110) substrates is a fundamental issue in the field of thin film growth. Two fundamental orientation relations are known, namely Kurdjumov-Sachs (K-S) orientation: fcc<1-10> // bcc<1-11> and Nishiyama-Wasserman (N-W) orientation: fcc<1-10> // bcc<001>. If the interaction between the film and the substrate is strong, pseudomorphic growth occurs where the film keeps the symmetry of the substrate lattice. Growth modes and equilibrium structures of a monolayer of fcc metals on bcc(110) substrates have been intensively studied both theoretically and experimentally [1]. The structure of a small island can be different from that of a monolayer and it can be evolved during the film growth. There, however, exist few studies of the structure of small islands and their evolution in a submonolayer regime, especially in the nucleation stage of the film growth. The difficulty of the experimental research of the structural evolution of small islands comes from the limitation of diffraction techniques. Diffraction from small islands is very broad and is buried in the diffuse background.

The purpose of the present study is to simulate the growth of a fcc metal on a bcc(110) substrate in a submonolayer regime and to obtain knowledge about the island structure in the nucleation stage.

We choose Ag as a film and Mo(110) as a substrate among the well-studied fcc(111)/bcc(110) systems. Ag grows on Mo(110) in the Stranski-Krastanov (SK) growth mode. Bauer et al. have reported that the first two monolayers (ML) grow in the layered fashion and agglomeration starts during the third layer growth [2]. Another report by Gotoh et al. says that the island growth starts already in the second layer [3]. Ag(111) film and Mo(110) substrate take the K-S orientation above 1 ML [3]. Low energy electron diffraction (LEED) has shown that a distorted triangle lattice of Ag above 0.5 ML transforms into a perfect triangle lattice as the film thickness increases [2].

Kinetic Monte Carlo (KMC) is a powerful method to simulate thin film growth. It has been successfully reproduced island nucleation density, island shape, ripening of islands, etc. [4-7]. KMC simulations are usually performed with the solid-on-solid model where adatoms can occupy only lattice points and structural relaxation is prohibited. Since our purpose is to simulate structural evolution of a growing island, ordinary KMC is not adequate for the present study. We use the molecular dynamics aided kinetic Monte Carlo (MD-aided-KMC) method which is proposed by the author previously [8]. In order to realize growth simulations in the real time scale with structural relaxation thermally activated adatom migration is dealt with by KMC and MD is performed when an adatom meets another one or is incorporated into an island.

2. SIMULATION METHOD

The Mo(110) substrate consists of 4 atomic layers and a layer has the sizes of 16x32 measured by the [1-10] and [001] vectors or 1024 atoms. The periodic boundary condition is applied in the in-plane directions. The deepest substrate layer is kept fixed and the other 3 layers are moveable during the MD procedures. The interatomic potentials are modeled by the modified embedded atom method (MEAM) [9] with the elliptic screening function [10]. The energy barriers for various migration events of Ag on the Mo substrate and on the (100), (110), and (111) planes of Ag are calculated by making potential maps around the event sites. The energy barriers for basic migration events calculated by MEAM are in good agreement with experimental results as well as with other theoretical calculations. The barrier for a free Ag adatom diffusion on Ag(100) is 0.37 eV by MEAM, while the experimental value is 0.40±0.05 eV [11], another many-body potential proposed by Rosato, Guillope, and Legrand (RGL) [12] gives 0.42 eV [5], and *ab initio* calculation gives 0.45 eV [13]. For the diffusion on Ag(110) the barriers by MEAM are 0.29 eV for the [1-10] direction and 0.37 eV for the [001] direction, while the RGL potential gives 0.28 and 0.38 eV [5] and corrected effective-medium calculations give 0.26 and 0.34 eV [14]. On Ag(111) the

Table I. Energy barriers (eV) for diffusion events on the substrate surface that are used in the simulations. Ni and Nf are the numbers of in-plane nearest neighbors at the initial and destination sites, respectively. (01), (11), and (10) represent the diffusion directions or atomic alignment in steps or dimers of <001>, <1-11>, and <100> directions of the substrate, respectively. Calculated energy barriers are written only when they are larger than the values used in the simulations.

event	Ni	Nf	used barrier (eV)	calc. barrier (eV)
diff. on terrace	0	0	0.15	
diff. on terrace to make dimer	0	> 1	0.15	0.17
dissociation from dimer	1	0	0.24	
diff. (01) in dimer	1	1	0.15	
diff. (11) in dimer	1	1	0.25	
make trimer with dimer (10)	1	2	0.30	
corner to step (01)	1	2	0.19	
corner to step (11)	1	2	0.26	
corner to kink (01)	1	> 3	0.19	0.21
corner to kink (11)	1	> 3	0.26	
step (01) to terrace	2	0	0.27	
step (11) to terrace	2	0	0.40	
dissociation from trimer to make dimer (10)	2	1	0.13	
step (01) to corner	2	1	0.20	
step (11) to corner	2	1	0.31	
diff. along film step (01)	2	2	0.19	
diff. along film step (11)	2	2	0.37	
diff. along film step to kink (01)	2	> 3	0.19	0.22
diff. along film step to kink (11)	2	> 3	0.37	0.38
kink (01) to corner	3	1	0.27	
kink (11) to corner	3	1	0.32	
kink to step (01)	3	2	0.30	
kink to step (11)	3	2	0.43	
kink to kink (01)	3	> 3	0.30	
kink to kink (11)	3	> 3	0.43	

barriers for diffusion on the terrace, along A step (with a {100} microfacet), and along B step (with a {111} microfacet) by MEAM are 0.13, 0.26, and 0.19 eV, respectively. These values seem to be reasonable because those for Pt calculated by the effective-medium theory are 0.16, 0.23-0.25, and 0.18-0.20 eV [4]. The variations of the energy barriers along the steps depend on the number of nearest neighbors at the destination sites. The adsorption energy of a Ag atom on Mo(110) surface is calculated as 2.62 eV by MEAM. Thermal desorption spectroscopy measurement gives 2.30 eV [15]. Table I shows the energy barriers for the surface migration events of Ag on Mo(110) substrate that are used in the simulations. The energy barriers on the substrate have more influences on the simulation results at the small coverage than those on the Ag film. The calculated values of the energy barriers for the movements by which the number of nearest neighbors of the moved atom increases (e.g. terrace to a dimer site, step site to kink site, etc.) are about 0.01-0.03 eV larger than the those for the movements which keeps the number of nearest neighbors (e.g. simple diffusion on a terrace, simple diffusion along a step, etc.). The same energy barriers are used in the simulations regardless of the number of nearest neighbors at the destination site because the usage of the original calculated barriers makes adatom aggregation less favorable. Which migration event for an adatom on the substrate takes place is judged by the number of in-plane nearest neighbor atoms at the initial and destination sites.

Other key conditions in the MD-aided–KMC simulations performed in the present study are as follows.

The deposition rate is assumed to be 1 ML/s. The substrate temperature is set to be 120 K. Hops in the four <1-11> directions of the substrate are allowed for an adatom on the substrate. Moreover, hops in the [001] and [00-1] directions are also allowed when an adatom moves along a step or in a dimer. The movements such as dissociation of a dimer, detaching from a step to the terrace, detaching from a kink to the step are included. The adatoms with more than or equal to four in-plane nearest neighbor atoms are assumed to be immobile in the KMC procedures. MD is performed for the atoms within $4 \times R_{Ag}$ from the moved atom, where R_{Ag} is the bulk nearest neighbor distance of Ag (2.88 Å), with the atoms farther than $3 \times R_{Ag}$ or from the deepest substrate layer fixed when a new deposition atom has arrived or the number of nearest neighbors of the moved atom has increased by the KMC. The MD is terminated when all the MD atoms are judged to be moving around their local equilibrium positions or the MD steps reaches 1000. The velocity of a deposition atom is set so as to correspond to the melting temperature of Ag. The velocity of the deposition atom is not scaled during the MD, while those of the other atoms are scaled so as that the average kinetic energy corresponds to the set substrate temperature. The velocity of the moved atom is scaled if the MD is performed after a surface migration.

3. RESULTS AND DISCUSSIONS

Fig. 1 shows the whole simulation area at the coverage of 0.1 ML. Only the top layer is depicted for the substrate. Five islands or clusters are seen. The number of islands (a
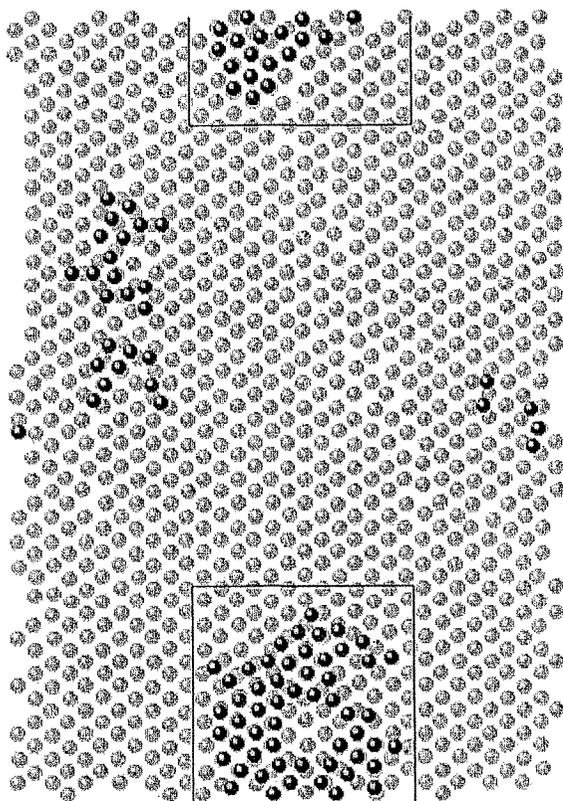
Fig. 1. The snapshot of the whole simulation area at the coverage of 0.1ML. The substrate atoms of Mo are in gray and Ag atoms are in black. Only the top layer is depicted for the substrate.

Fig. 2. The magnified picture of the region in the rectangular in Fig. 1. Mo atoms are in black and Ag atoms are in gray. Three regions, A, B, and C of regular atomic arrangements are indicated. (a_1,a_2), (b_1,b_2), and (c_1,c_2) are the sets of unit vectors of the regions A, B, and C, respectively. α, β, and γ are the angles between the unit vectors of A, B, and C, respectively.

dimer is defined as the smallest island) is always 4 or 5 by checking every 0.0125ML up to 0.1ML in spite of dissolution, nucleation, and migration of the islands. The island density is calculated as 5.6-7.0×10^{12} (cm^{-2}).

The region in the rectangular in Fig. 1 is magnified and depicted in Fig. 2 to show the structure of the island. Three regions, A, B, and C of regular atomic arrangements are indicated. Unit vectors of each region have been calculated by averaging the distance vectors between in-plane nearest neighbors in the region.

Ag forms a distorted close-packed lattice in the region A. The unit vectors in this region are a_1=(2.46, 1.41) Å and a_2=(-2.34, 1.47) Å. The magnitudes of a_1 and a_2 are 2.83 and 2.76 Å, respectively. Those are the values between the bulk nearest neighbor distances of Mo (2.73 Å) and Ag (2.88 Å). The angle α between a_1 and a_2 is 118.1° which is already close to the angle of 120° for the perfect hexagonal lattice. The region A has the orientation between K-S and N-W with the substrate lattice of the perfect bcc(110) alignment as the reference. It should be noticed that the top substrate layer beneath the region A is distorted from the perfect bcc(110) alignment. The Ag atoms in the region sit on top of the Mo atoms though single Ag adatoms and Ag atoms in clusters of a few atoms prefer to locate at the triangle sites where a film atom is supported by three substrate atoms. A similar close-packed structure like the region A is also found at the lower-left corner of the island. Distorted film structures of Ag with the unit vectors of

different magnitudes and with the angle between the unit vectors of less than 120° observed by LEED in ref. 2 could be similar to the structure described above.

The unit vectors in the region B are b_1=(2.38, 1.43) Å and b_2=(-1.14, 2.48) Å. $|b_1|$ and $|b_2|$ are 2.78 and 2.73 Å, respectively. β =83.8°. Those values for the region C are as follows. c_1=(-2.24, 1.44) Å, c_2=(1.29, 2.40) Å, $|c_1|$=2.66 Å, $|c_2|$=2.72 Å, and γ =85.7°. The regions B and C are equivalent with each other. b_1 and c_2 align almost in the <1-11> directions of the substrate. Ag atoms in the atomic pair in these directions sit on the top sites or on the bridge sites where a pair of substrate atoms in the <1-11> directions supports a film atom. Each of the Ag atomic rows in the substrate <1-11> directions with the two different atomic locations appears every other row. More regular alignment of such a structure has been recognized at the coverage of 0.0875ML (not shown here).

4. CONCLUSIONS

Thin film growth of Ag on the Mo(110) substrate has been simulated up to 0.1ML by the MD-aided-KMC method. In the limit of the present simulations

the following conclusions can be noted. The dense part of the Ag island has a distorted close-packed structure with the orientation between K-S and N-W that are different from the experimentally observed orientation for the film of more than 1ML, namely, K-S orientation. Another regular alignment with smaller packing density is also recognized.

Ag/Mo(110) is the system that takes the SK growth mode. It is an interesting problem to challenge whether the MD-aided-KMC simulations can reproduce such a growth mode, as well as to reveal the film orientation evolution as the coverage increases.

5. ACKNOLEDGEMENT

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