A comparing study on the evolution of Pd/Ni (10 0) and Pt/Ni(10 0) heteroepitaxial systems

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Abstract

Molecular dynamics simulations are performed to study the strain relief and the evolution of Pd/Ni(10 0) and Pt/Ni(10 0) heteroepitaxial systems by using embedded atom method. The atomistic mechanism for the formation of misfit dislocation in Pd/Ni(10 0) and Pt/Ni(10 0) epitaxial islands is analyzed by comparing the evolution behaviors of the two systems. The simulation results reveal that the strain of epitaxial islands due to lattice mismatch is released by the formation of misfit dislocations. However, the formation of misfit dislocations is different for the two systems. The formation of misfit dislocations in Pd islands is much easier than that in Pt islands. It is found that the positive solution heat of the alloy weakens the adhesion energy of heteroepitaxial system and facilitates the formation of misfit dislocations. The relative rigidity between the island and the substrate is also important for the formation of misfit dislocation, which can be related to the bulk modulus of the island.

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1. Introduction

Heteroepitaxial growth is a general phenomenon in metal-on-metal thin film growth. In a heteroepitaxial system, the lattice mismatch between film and substrate is a crucial factor that governs the growth of overlayers [1]. In the initial stage of growth, however, experimental results reveal that the growth behavior is more complicated than expected from the lattice mismatch. In contradiction to lattice mismatch consideration, Sander et al. [2] found that a tremendous compressive stress below 0.5 monolayer in Ni on W(110) surface. Similarly, tensile stress is expected from mismatch arguments while Fe film grows on W(110) surface; however, compressive stress was found in the experiment [3]. A giant compressive surface stress for the first few monolayers of silver on Pt(111) was reported, which is far beyond the stress induced by the misfit [4]. The phenomena have proved that heteroepitaxial growth cannot be completely explained by lattice mismatch and there must be other factors that affect the metal-on-metal growth behavior.

The atom systems chosen for this study are Ni substrates with Pd islands and with Pt islands. The reason for this choice is that Pd/Ni has a lattice mismatch similar to that of Pt/Ni [\(\Delta a_{\text{Pd}} = 0.389\) nm, \(\Delta a_{\text{Pt}} = 0.392\) nm] and therefore the effect of lattice mismatch on the two systems is almost the same. The Pd and Pt islands with the size ranging from 2 x 2 to 12 x 12 on the Ni(100) surfaces have been investigated using classical molecular dynamics (MD) simulation. In the present paper, more attention is paid to the misfit dislocations in islands as they are the main structural changes in the early stages of heteroepitaxial growth, and they directly reflect the stress in the epitaxial surface island. In addition, to give a comprehensive description of the initial heteroepitaxial growth, the dependence of adhesion energy, deformation energy, and average local pressure on the island size is also calculated.

2. Simulation method and model

In our MD calculations, the interactions among all atoms were calculated using the embedded atom method (EAM), which was found to be effective in describing the surface and bulk properties of noble metals and alloys [5,6]. EAM was first proposed by Daw and Baskes [7,8] and the general form for the total energy is given...
by

\[ E_{\text{total}} = \sum_{i} N_i \phi_i(r_i) + \frac{1}{2} \sum_{i,j} N_{i,j} \phi_{ij}(r_{ij}), \]

where \( i,j \) denote atoms; \( r_{ij} \) is the distance between atoms \( i \) and \( j \); \( \rho_i \) is the electron density at the \( i \)th nucleus resulting from the atomic electron densities of the neighboring atoms; \( \phi_i(r_i) \) is the embedding energy required to place atom \( i \) in electron density \( \rho_i \); and \( \phi_{ij}(r_{ij}) \) is the pair potential between atoms \( i \) and \( j \). In addition, \( \rho_i \) is determined by

\[ \rho_i = \sum_{j \neq i} \phi_j(r_{ij}). \]

where \( \phi_j(r_{ij}) \) is the contribution to the electron density at atom \( i \) due to atom \( j \) at distance \( r_{ij} \) from atom \( i \).

In the Pd/Ni(10 0) and Pt/Ni(10 0) systems, the Ni(10 0) surface was modeled by the top (10 0) layer of a 14-layer slab of atoms with the bottom four layers fixed and periodic boundary conditions in the [0 0 1] and [0 1 0] directions. Each layer included 1024 atoms. The initial temperature was set to 300 K, and then the systems were annealed to nearly 0 K in order to obtain the structures with the lowest energy.

3. Results and discussion

3.1. Evolution of morphology

The morphological evolution of initial islands provides the most direct view of the difference between Pd and Pt film growths on Ni(10 0) substrates. Comparing the two processes of evolution, we can find that when the island size is smaller than \( 7 \times 7 \), the Pd and Pt islands array themselves as Ni lattice and form the so-called pseudomorphic structure [9]. When the island size is up to \( 8 \times 8 \), a misfit dislocation first occurs in the center of the Pd island but the Pt island still keeps its pseudomorphic structure. Further increasing island size, more misfit dislocations form in the Pd islands but the Pt islands do not attain a misfit dislocation until the size increases to \( 12 \times 12 \). The detailed morphological evolution is shown in Fig. 1 (for Pd islands) and Fig. 2 (for Pt islands). Based on the evolution of surface islands, it can be found that Pd/Ni and Pt/Ni have similar lattice mismatch but the misfit dislocation forms more easily in the Pd islands than in the Pt islands. It proves again that the lattice mismatch is not the only factor in determining the evolution of surface islands.

In order to understand the behavior of the evolution, the dependence of the average bond length between the atoms in surface islands on the island size is plotted in Fig. 3. As indicated in Fig. 3, the average bond lengths of the Pd and the Pt islands both decrease at the beginning and approach the bond length of Ni substrate gradually. But, due to the continual formation of misfit dislocations, the average bond length of the Pd islands has some fluctuation after the size is larger than \( 8 \times 8 \). For the Pt islands, the average bond length keeps decreasing before the size reaches \( 12 \times 12 \). Additionally, the Pd islands have larger average bond length than that of the Pt islands, suggesting that the Pd islands tend to grow as its natural lattice constant and the Pt islands tend to grow as substrate lattice constant. The result of the average bond length shows again that Pd/Ni(10 0) has a different growth behavior from Pt/Ni(10 0), and the phenomenon cannot be explained completely by the lattice mismatch.

3.2. Analysis of local pressure

The distribution of stress in the surface island plays an important role in the structural changes. The analysis of local pressure gives a direct insight into the effect of stress on the formation of misfit dislocations. It can be defined as [10–12]

\[ P_l = -\frac{dE_l}{d\ln V}. \]
where $V$ is the atomic volume and $E_i$ is the potential energy of atom $i$. The sign of $P_i$ gives the pressure sign (it is positive for compression and negative for tension). The higher the absolute value means that the atom has larger local pressure and is more stable in its position.

Fig. 4 is the local pressure distribution of the $7 \times 7$ Pd and Pt islands. All the atoms in the two islands are under tensile pressure and the edge atoms have the higher tensile pressure than the centered atoms. The fact suggests that the edge atoms have an anchoring effect and block the island mobility and the formation of misfit dislocations. Comparing the $7 \times 7$ Pt island with the $7 \times 7$ Pd island, it seems that the atoms in the Pt island have larger local pressure than that in the Pd island, as shown in Fig. 4. In order to quantify the difference of local pressure between Pd and Pt islands, the average local pressure per atom as a function of the island size is plotted in Fig. 5. It is found that the Pt islands have the higher absolute value of average tensile pressure than that of the Pd islands. Larger pressure means a stronger anchoring effect in the Pt islands, which can prevent misfit dislocations from forming. This is consistent with the fact that the formation of misfit dislocations is more difficult in the Pt islands. In addition, the absolute value of the local pressure in islands decreases gradually with the increasing island size. When the absolute value drops to a certain value, the misfit dislocation occurs in island. At the same time, the tensile pressure becomes high after the formation of the misfit dislocations.

### 3.3. Analysis of adhesion energy and deformation energy

To find the other factor that affects the initial growth behavior, the adhesion energies of Pd and Pt islands as a function of island size are calculated, as shown in Fig. 6(a). The adhesion energy is used to describe the interaction between film and substrate and its expression is

$$E_{\text{Pd/Pr}}^\text{adh} = \frac{E_{\text{total}} - E_{\text{Pd/Pr}} - E_{\text{Pd/Pr}}^\text{island} - E_{\text{Pd/Pr}}^\text{sub}}{N_{\text{island}}}$$

where $E_{\text{total}}$ is the total energy of the system after the relaxation; $E_{\text{Pd/Pr}}^\text{island}$ is the binding energy of Pd or Pt islands; $E_{\text{Pd/Pr}}^\text{sub}$ is the binding energy of Ni substrate, and $N_{\text{island}}$ is the number of atoms in the surface island.

As seen in Fig. 6(a), with the increasing island size, $E_{\text{Pd/Pr}}^\text{adh}$ increases similarly with $E_{\text{Pd/Pr}}^\text{sub}$, indicating that the small islands are more stable than the large islands. It is also found that the formation of misfit dislocations has no obvious effect on the adhesion energy. The quantitative analysis shows that $E_{\text{Pd/Pr}}^\text{adh}$ is 1.2-fold higher than $E_{\text{Pd/Pr}}^\text{sub}$. The result means that Pd islands have less lattice constraint from Ni (100) substrate. Therefore, compared with Pt islands, Pd islands are easier to grow as an atomic
arrangement of (111) face, the lowest energy face in fcc. The misfit dislocation is the transition from pseudomorphic structure to the structure of (111) face, as the local pseudohexagonal structure induced by the formation of misfit dislocations has similar structural characters with fcc(111). So, when the island size becomes large, the low adhesion energy between the Pd islands and the Ni substrate results in the misfit dislocation to form easily in the Pd islands. Based on the above analysis, it can also be concluded that high adhesion energy facilitates the formation of misfit dislocations.

The difference of adhesion energies in Pd/Ni(100) and Pt/Ni(100) can be attributed to the difference of the solution heats. In the present systems, the values of solution heats of Pd and Pt atoms in the host Ni are 0.18 and 0.30 eV, respectively [7]. The positive/negative sign indicates an endothermic/exothermic process. For the Pd–Ni, it is an endothermic process, which means a weak binding ability and high adhesion energy between film and substrate. On the contrary, for the Pt–Ni, it is an exothermic process, which means a strong binding ability and low adhesion energy. So it can be concluded that the positive alloy solution heat promotes the formation of misfit dislocations.

Fig. 4. Local pressure maps on the atomic sites of 7 × 7 Pd (a) and Pt (b) islands. The gray scale is chosen as follows: the black gray (respectively, white gray) sites are the most tensile (respectively, least tensile) ones with the following value: $P_{\text{max}} = -1.60 \text{ eV/atom}$ and $P_{\text{min}} = -0.80 \text{ eV/atom}$.

Fig. 5. The average local pressure of Pd and Pt islands as a function of the island size.

Fig. 6. The adhesion energy (a) and the deformation energy (b) as a function of the island size.
To exhibit the effect of surface islands on the deformation of the substrate, the average deformation energy of substrate, \( E_{\text{def}} \), is also discussed in this work, as presented in Fig. 6(b). \( E_{\text{def}} \) is defined by

\[
E_{\text{def}} = \frac{E_{\text{sub}} - E_{\text{sub}0}}{N},
\]

where \( E_{\text{sub}} \) and \( E_{\text{sub}0} \) are the energies of the substrate before and after deformation, respectively. For Pd/Ni(100), the island size does not affect \( E_{\text{def}} \) in Ni substrate and \( E_{\text{def}} \) has a value of about 19 meV. For Pt/Ni(100), the value of \( E_{\text{def}} \) is about 21 meV, and also does not change greatly with the island size. Obviously, in Fig. 6(b), the Pt islands cause a larger deformation in Ni substrate than the Pd islands do. Based on the view of the mechanics of elasticity, \( E_{\text{def}} \) relates to the relative rigidity between island and substrate. A great \( E_{\text{def}} \) means a large relative rigidity. This is in agreement with the fact that the bulk modulus of Pt is higher than that of Pd (\( B_{\text{Pd}} = 195.50 \text{ GPa}; B_{\text{Pt}} = 288.40 \text{ GPa}; B_{\text{Ni}} = 187.60 \text{ GPa} \) [13]). Compared with Pd/Ni, Pt/Ni has a larger difference between \( B_{\text{Pt}} \) and \( B_{\text{Ni}} \), which induces more deformation in the Ni substrate and less deformation in the Pt islands. That is to say, the formation of misfit dislocations is difficult in Pt islands. Thus, the relative rigidity between the island and the substrate is a factor in determining the formation of misfit dislocations and the deformation in substrate.

4. Conclusions

We have investigated the evolution of Pd and Pt islands on Ni(100) surface by using embedded atom method. It is found that Pd/Ni and Pt/Ni have similar lattice mismatches but the growth behaviors are different. Compared with the Pt islands, the atoms in the Pd islands have a lower tensile local pressure and the misfit dislocation forms more easily in the Pd islands. The analysis of adhesion energy and deformation energy shows that two main factors affect the formation of misfit dislocations. One is the alloy solution heat. The positive alloy solution heat facilitates the formation of misfit dislocations. The other is the relative rigidity between island and substrate. When islands have a larger bulk modulus than that of the substrates, the formation of misfit dislocations in the islands is more difficult.

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