Surface Alloying of Au Atoms on a Ni (110) Surface: a Theoretical Study

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Abstract: We investigated the surface alloying of Au atoms on a Ni (110) surface using a molecular dynamics (MD) method. It is found that the concentration of deposited Au atoms and the depositing temperature determine the topological surface structures, which can be ascribed to the variation in Gibbs free energy of the system. Dimer formation on the over layer is used to explain the surface alloying of the miscible system and in good agreement with the experimental results.

1. Introduction
When one metal is deposited on another one, the deposited metal may either form islands on the substrate or alloy into the first or deeper layer of the substrate [1]. Alloying may take place at the surface whether the two metals form an alloy or not. Experiments showed [2] that interface mixing could have quite a strong influence on the electronic and magnetic properties of different systems, which promote the investigation of atomic structures of the substrate surface. The experiment of Au growth on a Cu (100) surface [3] have demonstrated that a c (2×2) Cu-Au layer is developed on the Cu (100) surface. When Au is deposited on a Ag (110) surface [4], the gold atoms can intermix with the first two Ag layers. The intermixing of Cu-Au and Au-Ag systems are characterized by the fact that these two metals are miscible. If two metals can’t form stable alloys, one would expect the deposited metal to grow only on top of the substrate. However, two-dimensional surface alloys have already been found in such immiscible systems, such as Co on Cu (001) [5], Ag on Cu (001) [6] and Fe on Cr (100) [7]. It means that surface alloying might be responsible for the initial structure of metal-on-metal growth.

Nielsen et al. [8] investigated the nucleation and growth of Au on Ni (110) by in situ scanning tunneling microscopy (STM) and Rutherford backscattering spectroscopy at room temperature. The results shows that deposited Au atoms can replace surface Ni atoms forming an Au-Ni surface alloy and the surplus Ni atoms nucleate into [1 ̅1 0] elongated islands. Jacobsen et al. [9] calculated the energetics of Au deposited on Ni surfaces using the effective medium theory and have found that the surface alloy is considerably more stable than the Au overlayer on Ni (100) or (110) surfaces. This phenomenon was modeled by Bozzolo et al. [10] using the Bozzolo-Ferrante-Smith (BFS) method.

In this work, in the viewpoint of kinetics and thermodynamics, we investigated the dynamical process of depositing Au atoms on a Ni (110) surface and elucidated the dependence of surface morphological structures on the Au coverage and the system temperature by using molecular dynamics (MD) simulations.
2. Calculation Method

Atomic scale simulations are performed using Molecular Dynamics (MD) method based on tight binding theory [11]. According to N-body potential scheme, the site energy of the atom \( i \) is written as the sum of two terms, an attractive band energy \( E_i^b \) and a repulsive pair interaction \( E_i^r \) [12].

\[
E_i = E_i^b + E_i^r
\]  

In the framework of the second moment approximation of tight binding theory (TB-SMA), the real density of states is replaced by a schematic rectangular one having the same full width at half maximum, then

\[
E_i^b = -\left( \sum_j \xi_{\alpha\beta}^2 \exp\left[ -2q_{\alpha\beta}\left( \frac{r_{ij}}{r_{0\alpha\beta}} - 1 \right) \right] \right)^{1/2}
\]  

\( \alpha \) and \( \beta \) indicate the chemical species. \( \xi_{\alpha\beta} \) is an effective hopping integral and the exponent \( q_{\alpha\beta} \) characterizes its distance dependence. \( r_{0\alpha\beta} \) is the equilibrium distance between the atoms \( i \) and \( j \). The summation runs over all the neighbors \( j \) of the atom \( i \).

The repulsive term \( E_i^r \) is described by a sum of Born-Mayer ion-ion repulsions

\[
E_i^r = \sum_j A_{\alpha\beta} \exp\left[ -p_{\alpha\beta}\left( \frac{r_{ij}}{r_{0\alpha\beta}} - 1 \right) \right]
\]  

Where \( p_{\alpha\beta} \) is related to the bulk modulus of the metal. The estimation of the TB-SMA parameters has been made by fitting bulk (cohesive energy, the lattice parameters, the bulk modulus, the elastic constants, and mixing enthalpy) and surface properties (surface energy and surface misfit) [13,14]. The technical details and parameters of interatomic potentials can be found in the previous work [14].

3. Results and Discussion

![Figure 1](image)

*Figure 1* Top view of the surface layer of depositing submonolayer Au atoms on a Ni (110) surface: (a) 0.09ML Au (black circles) at 300K. Dimer formation of Au atoms substituting into the Ni (110) surface layer; (b) 0.26ML Au at 300K. Appearance of dimers in the first surface layer; (c) 0.43ML Au at 300K. Appearance of trimers in the surface layer; (d) 0.26ML Au at 600K.

MD simulations are performed at a given temperature by using the Nose-Hoover method [15] to control the system temperature. The initial velocities of the atoms are assumed to be in the Boltzmann distribution at the desired temperature. We choose a cutoff distance to be two times as long as the lattice parameter of a gold crystal at 273 K, for all these simulations. In this method, the trajectory of each atom in the MD cell is followed through time and Newton’s classical equations of motion with a
time step of $5.0 \times 10^{-16}$ s are integrated in a step-wise manner over finite time steps in terms of a fifth-order predictor-corrector method [16].

The initial MD cell consists of a 20-layer Ni (110) slab with 70 atoms in each layer. The downmost three Ni layers are fixed to keep the volume property. Varying numbers of Au atoms are deposited on the Ni (110) surface as an overlayer within the force range of its nearest surface atoms. Periodic boundary conditions are applied only in the directions parallel to the Ni (110) surface. The MD simulations are performed for different Au coverage at 300K and the results are shown in Figs. 1(a), 1(b) and 1(c).

In a low Au coverage, Au atoms would tend to form an overlayer because of its smaller surface energy than Ni. Due to the large lattice mismatch between Au (4.08 Å) and Ni (3.52 Å), the resulting overlayer is highly strained and will be a certain kind of structure in which the strain can be relieved. Similar to the experimental results [17], it can be seen from Figure 1(a) that a monomer and a dimer along the close-packed (110) direction appear in the alloying surface layer at the coverage of 0.09ML. As the Au coverage increased to 0.26ML, more Ni atoms are substituted and more dimers form as shown in Figure 1(b). At the coverage of 0.34ML, a trimer can even form by connecting a dimer together with a monomer, as shown in Figure 1(c).

Positive interface energy, in combination with the size mismatch, may lead to the formation of the alloying surface layer. Strain is partially relieved by the presence of the surface. In fact, as discussed by Tersoff [18] for systems dominated by a large size mismatch, strain effects can also be favor of the alloying at the surface even though they suppress the intermixing in the bulk. Large atoms will prefer to stay in the surface layers instead of penetrating into the bulk to decrease the system energy.

The above results demonstrate clearly that the possibility of forming dimers along the close-packed (110) direction on the Ni (110) surface at 300K is much higher than that forming a monomer. The concept of effective coordination number is used to interpret this phenomenon. Au atoms substituting into the first surface layer increase the coordination of Ni atoms and thus lower the system energy. However, the substituted Ni atoms forming Ni islands decrease its effective coordination number and thus increase the system energy. The competition of these two processes determines the morphology of Au atoms deposited on the Ni (110) surface.

![Figure 2](image)

**Figure 2** Dynamical evolution process of Au deposition on a Ni (110) surface at the Au coverage of 0.57ML: (a) 50 time steps. (b) 150 time steps. (c) 350 time steps. (d) 2000 time steps.

To explain how the alloying takes place, we monitor the whole process of Au alloying into the first Ni (110) surface layer at the Au coverage of 0.57ML. As the simulation proceeds, an interesting phenomenon can be observed (shown as Figure 2(a)-(d)). Single Au atoms begin to substitute into the Ni (110) surface and form either monomer by substituting Ni atoms separately or dimer by substituting the adjacent Ni atoms. Sequentially, trimer, even Au cluster, can be seen in the alloying surface layer.

With the increase of the system temperature, the number of Au atoms entering the Ni (110) surface layer increases. Similar to the Ag-Cu system [19], the results shown in Figure 1 (b) and (d) for 0.26
ML at different system temperatures imply that the surface topological structures also depend on the system temperature. It is a competing result of energetically favorable intermixing and energetically unfavorable clustering.

To understand the driving force of surface alloying at finite temperature, one should assess Gibbs free energy (GFE) of the system. The GFE of an alloy system can be written as

$$ G = H - TS $$

(4)

Where $H$ is the enthalpy of the system, and $S$ is the configuration entropy of the system. It is assumed that there are $n$ A atoms and $(N-n)$ B atoms in a binary alloy consisting of N atoms, and that these atoms will diffuse spontaneously. The total number of probable arrangements is

$$ \Omega = \frac{N!}{n!(N-n)!} $$

(5)

Then

$$ S = -K \ln \Omega $$

(6)

When the system reaches equilibrium in a MD relaxation, we can count the number of the arrangement states, and then obtain the entropy of the equilibrium system. In fact, the atoms far away from surface layers (usually several atomic layers) in the matrix are hardly affected by the coverage of deposited solute atom and the system temperature. Here we only count the nearest-neighbor configuration number of the two topmost layers.

![Figure 3](image)

**Figure 3.** The Gibbs free energy of the Au-Ni system: (a) as a function of the concentration of deposited Au atoms on the Ni (110) surface at 300K; (b) as a function of its temperature at fixed Au coverage of 0.26ML.

The GFE of the Au-Ni system, as a function of the concentration of deposited Au atoms, is shown in Figure 3(a). One can find that the GFE decreases with the increase of Au coverage at lower coverage of less than 0.45ML, resulting in surface alloying. The tendency of surface alloying, however, decreases with the increase of the Au coverage. The GFE of the Au-Ni system as a function of the system temperature at 0.26ML is shown in Figure 3(b). The GFE decreases almost linearly with the increase of the system temperature. It is seen that the GFE decreases and the driving force of surface alloying can be enhanced by increasing the system temperature. Comparing Figure 3(a) with Figure 3(b), it can be concluded that the effect of temperature on surface alloying is much stronger than that of the coverage of the deposited atoms.
4. Summary
In summary, we simulated the kinetic behavior of depositing Au atoms on a Ni (110) surface using the MD method. It is found that surface alloying of Au atoms substituting into the Ni (110) surface depends on the concentration of deposited Au atoms and the system temperature. For the low Au coverage, Au atoms substitute into the Ni (110) surface and mostly appear in the form of dimer, in good agreement with the experimental results. With the increase of the deposition temperature, driving force for surface alloying is enhanced, leading to the formation of different surface topological structures, even the energetically unfavorable Au clusters. It can be attributed to the decrease in GFE of the Au-Ni system.

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6. References
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