



Structures and stability of Ag clusters on Ag(111) and Ni(111) surfaces

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ABSTRACT

The structures of the lowest total energy for small Ag_N clusters with $N=2-20$, which are grown on Ag(111) and Ni(111) surfaces, have been determined using a combination of the embedded-atom method and the basin-hopping algorithm. It is found that the particularly stable Ag clusters with $N < 18$ have similar geometries on both surfaces when comparing clusters of the same size. On the other hand, the geometries of the less stable Ag clusters in the same size range differ for the two surfaces. From $N \geq 18$, the sizes of the particularly stable structures are different for the two different substrates. Due to the large size mismatch of the two types of atoms it is energetically unfavorable for Ag to form a pseudomorphic monolayer structures on Ni(111) and there is considerable strain produced at the interface. The effect of this strain and the increased adatom–substrate interactions lead to irregular and elongated structures of the adsorbed Ag clusters.

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1. Introduction

The preparation of individual nanostructures or thin films on solid surfaces has become increasingly important during the last years because of their technological importance in the field of catalysis and microelectronics, where it is exploited that novel magnetic and electronic effects result from low-dimensional structures. Moreover, the creation of bimetallic surfaces by heteroepitaxial metal growth offers the potential to grow artificially structured materials with novel physical and chemical properties. Beside the importance for nanotechnological applications, the geometrical structures of clusters adsorbed on single-crystal surfaces are dictated by the adatom–adatom and adatom–substrate interactions and studying them can accordingly provide insight into the initial stages of crystal growth modes and nucleation processes. Thus, systematic studies of the changes of the structural properties of clusters on surfaces as a function of cluster size can give a detailed understanding of such processes.

In this respect, one fundamental question that has to be answered is, what is the structure of the initial stage of thin film formation and crystal growth of the investigated metals: do the clusters develop chains on the substrate or do they form islands, and, in the latter case, what is the dominant geometry of these islands.

More studies have addressed these issues. Thus, Zhuang et al. [1–3] performed global optimization on a series of adatom–

surfaces systems, including Ag/Ag(111), Ni/Ni(111), Cu/Cu(111), and Au/Au(111) with selected sizes of the clusters up to $N = 52$ atoms using a genetic algorithm combined with the embedded-atom method. They found closed-packed islands of hexagonal shape with maximum number of nearest-neighbor bonds, which was in good accordance with observations in scanning tunneling microscopy (STM) experiments [4]. Also for Ir/Ir(111) and Ni/Au(111) compact islands were found to be preferred, as observed in STM and field ion microscopy (FIM) experiments [5,6]. Linear chains have been predicted for, e.g., Pt_N clusters ($N = 3$ and 5) on the Pt(001) surface by semiempirical calculations [7], as well as for small Pt_N ($N = 1-7$) and Pd_N ($N = 1-17$) clusters on the Ag(110) surface through photoemission experiments [8], and for Pt and Ir clusters on W(110) using FIM experiment [9].

Instead of forming a layer on top of a surface, a deposited cluster may alloy into the first or even more layers. For example, Ni adatoms can replace Ag atoms in the first surface layer of a Ag(111) surface under the formation of a surface alloy [10,11], although Ag and Ni show no tendency for alloying in the bulk. The reason is the strong tendency of Ag atoms towards surface segregation. In contrast to Ni/Ag(111), recent STM experiments have shown that Ag atoms, deposited on a Ni(111) surface, aggregate in complex islands of two monolayer thickness and do not show any diffusion processes at the Ag/Ni interface [12]. However, as often is the case, experiments, unfortunately, can not provide detailed information on the exact structure of the Ag islands whereas additional theoretical investigations can provide this information.

To our knowledge there is no theoretical study which determines the geometry and energetics of Ag clusters interacting with a Ni surface. However, such investigations could provide important

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information on the initial stages of Ag thin film formation on Ni surfaces. Furthermore, the Ag–Ni system possesses a large lattice mismatch (the lattice constant of Ag is 16% larger than that of Ni) and a large difference in the cohesive energies (2.96 eV for Ag and 4.44 eV for Ni [13,14]). By comparing the properties of Ag clusters deposited on Ag and deposited on Ni, one can obtain information about how the system releases the strain induced by a size mismatch and about the influence of a large difference in the cohesive energies. Most clearly this can be identified in the evolution of the most stable equilibrium structures of the adsorbed Ag clusters.

Therefore, the aim of the present study is to determine and analyze the ground-state structures of Ag_N clusters grown on a Ni(111) surface with $N = 2–20$, using an unbiased approach for the structure determination and to compare these with the structures of Ag_N clusters on a Ag(111) surface. In addition, we shall explore whether those values of N that for the Ag clusters on the Ni(111) surface correspond to particularly stable structures also do so for Ag clusters on the Ag(111) surface. We shall determine the lowest-energy structures of Ag_N clusters with $N = 2–20$ adsorbed on a Ag(111) or a Ni(111) surface using a basin-hopping algorithm combined with the embedded-atom method.

The paper is organized as follows. In Section 2 we briefly outline the embedded-atom method and the basin-hopping algorithm. The main results are presented in Section 3, and a brief summary is offered in Section 4.

2. Computational methods

Our theoretical approach combines the embedded-atom method, that is used in calculating the total energy for a given structure, with the basin-hopping method, that is used in determining the structure of the global total-energy minimum. We shall now briefly outline the main ideas behind the two methods.

2.1. The embedded-atom method (EAM)

In order to describe the homoatomic and heteroatomic interactions Ag–Ag, Ni–Ni, and Ag–Ni between the atoms in the Ag/Ag(111) and Ag/Ni(111) systems we use the EAM in the version of Daw, Baskes and Foiles (DBF) [15–17]. The main idea of the EAM is to split the total energy of the system into a sum of atomic energies,

$$E_{\text{tot}} = \sum_i^N E_i \quad (1)$$

with E_i consisting of two parts, i.e., an embedding energy (which is obtained by considering the i th atom as an impurity embedded into the host provided by the rest of the atoms) and a pair-potential interaction with all other atoms. Accordingly,

$$E_i = F_i(\rho_i^h) + \frac{1}{2} \sum_{j \neq i} \phi_{ij}(r_{ij}), \quad (2)$$

where ρ_i^h is the local electron density at site i , F_i is the embedding energy, and ϕ_{ij} is a short-ranged repulsive potential between atoms i and j separated by distance r_{ij} . The local density at site i is assumed being a superposition of atomic electron densities,

$$\rho_i^h = \sum_{j(\neq i)} \rho_j^a(r_{ij}), \quad (3)$$

where $\rho_j^a(r_{ij})$ is the spherically averaged atomic electron density provided by atom j at the distance r_{ij} .

For homoatomic systems, the values of the parameters entering the model are determined by fitting to experimental information on the extended systems (crystals, surfaces, etc.).

As in Ref. [17] the A–B/B–A heterointeractions can be approximated in the EAM by the geometric mean of the pair interaction for the individual species, $\phi_{AB}(r) = \sqrt{\phi_{AA}(r) \cdot \phi_{BB}(r)}$. Daw, Baskes and Foiles determined the embedding functions for the Ag–Ni system empirically by fitting to experimental data for the bulk sublimation energy, the elastic constant, and the heat of solution of binary alloys [17]. Finally, ρ_i^a , F_i and ϕ_{ij} are available in numerical form for Ni, Cu and Ag [18]. The validity of the embedding functions for the Ag–Ni system has been tested by computing a wide range of properties including the segregation energy of substitutional impurities to the (100) surface [17].

The EAM has been successfully applied to many bulk and low-symmetric problems in transition metals such as defects, surface structures, and segregation [19]. Furthermore, in our previous studies [20–23] we have found that this approach provides accurate information on pure nickel and silver clusters, which is our main reason for choosing this potential for studying the structures of Ag clusters on Ag(111) and Ni(111) surfaces.

2.2. The basin-hopping algorithm (BH)

In order to find the lowest-total-energy structures of the Ag/Ag(111) and Ag/Ni(111) systems we use the BH method [24–27]. The basic idea of this method is to transform the complex energy landscape as a function of $\vec{X} \equiv (\vec{R}_1, \vec{R}_2, \dots, \vec{R}_N)$ (with \vec{R}_i being the position of the i th atom) to a new reduced energy landscape, which consists of plateaus of energy minima only

$$\tilde{E}(\vec{X}) = \min \{E(\vec{X})\}, \quad (4)$$

where $\min\{\dots\}$ represents a local-energy minimization process with \vec{X} as initial structure. Subsequently, a Monte Carlo procedure is applied to this modified energy surface. Also perturbations are introduced, which correspond to changing slightly the latest set of coordinates and carrying out a gradient-based optimization from the resulting geometry. In the Monte Carlo procedure, moves are accepted or rejected depending on the energy difference between the new and old local minima. Thus, compared to a standard Monte Carlo algorithm, the BH algorithm is based on a local total-energy minimization before the Metropolis acceptance rule is applied. The BH approach can also be viewed as a generalization of the ‘Monte Carlo plus energy minimization’ procedure of Li and Scheraga [28]. The Monte Carlo part of the BH algorithm is introduced in order to allow the system to hop from one plateau to another at a thermal energy $k_B T^*$. The hopping probability depends highly on the choice of the ‘temperature’ T^* and on the reduced-energy difference between the plateaus of two consecutive steps. In our study the Monte Carlo simulation was performed at a constant reduced ‘temperature’ of $k_B T^* = 0.8$.

In our approach we took as the initial structure a randomly generated cluster structure which is placed at a distance of $a_1/2$ above the relaxed Ag(111) and $a_2/2$ above the relaxed Ni(111) surface, where $a_1 = 4.09 \text{ \AA}$ is the bulk lattice constant of Ag and $a_2 = 3.52 \text{ \AA}$ is the one of Ni. Subsequently, we disturb randomly the coordinates of the cluster and perform a gradient-based optimization on the total cluster + surface system. Afterwards the Metropolis acceptance rule is applied using the old and new local minima of the cluster + surface system. In the next step the cluster atoms that belong to the latest set cluster + surface coordinates are disturbed randomly again. This procedure is repeated until the lowest total energy of the cluster + surface system is found. Thus, in contrast to the optimization procedure of Ref. [1] in which relaxation is carried out only for the cluster, we relax the complete system including the surface after each structural change.

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