Surface Science 603 (2009) 2879–2887

Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

Theoretical study of the Ni growth on Pt stepped surfaces

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ARTICLE INFO

Article history:
Received 9 April 2009
Accepted for publication 27 July 2009
Available online 7 August 2009

Keywords:
Computer simulations
Construction and use of effective interatomic interactions
Monte-Carlo simulations
Semi-empirical models and model calculations
Diffusion and migration
Growth
Surface energy

ABSTRACT

We have investigated the growth of Ni on Pt stepped surfaces with (1 1 1) terraces by means of potentials derived from the second moment approximation in a tight-binding model. The activation energies associated to these processes are determined. The Schwoebel barriers of Ni atoms descending steps of Pt stepped surfaces are calculated for different kinds of straight steps (A and B steps) differing by the orientation of the ledge. In addition, we study the diffusion of Ni adatoms at fcc or hcp sites in the presence of small adislands on the terraces, in the vicinity of the A and B steps. We show that a good estimate of the potential wells and diffusion barriers could be given by introducing a lateral effective pair interaction model, the interactions extending up to the next nearest neighbors. Finally, we have carried out Kinetic Monte-Carlo simulations to investigate the Ni wire formation at Pt step edges and the influence of the exchange processes in the alloy formation.

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1. Introduction

A growing number of surface science and nanoscience publications are devoted to the study of vicinal surfaces since they can provide an appropriate substrate for growing nanostructures. Vicinal surfaces, which exhibit a regular array of steps, introduce defined arrangements of surface defects, which have the ability to create specific functionalities of the surface. In particular, they can be used as template for the growth of low dimensional structures using selective step decoration [1,2]. The obvious processes taking place during and after deposition of metal atoms are essentially diffusion events. Surface diffusion on fcc(1 1 1) surfaces occurs by an hopping mechanism, i.e., an adatom jumps between adjacent minima of the potential energy surface [3]. For this reason, the knowledge of adatom–adatom and adatom–substrate interactions is of a great importance on a metal surface, in particular for the formation of multilayer structures [4]. Moreover, catalytic properties of bimetallic systems such as Ni/Pt have been found to differ strongly from either of pure metal components in some cases. For example, Goodman and coworkers [5] observed that Ni/Pt surfaces with a near monolayer coverage of Ni on Pt showed higher hydrogenolysis activity than pure Ni or Pt surfaces. It is also observed that recombinative D_2 desorption occurs at temperatures lower for bimetallic Ni/Pt(1 1 1) than for either Ni(1 1 1) or Pt(1 1 1) [6] and that hydrogenation of cyclohexene [7,8] is favored on a bimetallic system compared to a simple pure metal. Despite of all these studies, no information is available about the structure and the formation of bimetallic surfaces. At present, one of the major challenges to understand the properties of bimetallic surfaces is to control systematically the formation of these polycrystalline substrates in order to study more accurately their properties. Besides, the role of the defects has not been elucidated and the growth of the Ni monolayer can be dramatically changed upon external parameters of experiments.

In the present theoretical study, we want to elucidate particular growth aspects of Ni on a vicinal Pt(1 1 1) surface to understand the role of the kinetic parameters on the formation of the adsorbed Ni structures. We consider vicinal surfaces in order to introduce the effect of a step on a flat surface, the terraces being wide enough so that each step can be considered as isolated. Using potentials derived from the second moment approximation in a tight-binding model, we have calculated the potential energy surface of a Ni atom on stepped Pt(1 1 1) surfaces. This allows the determination of the preferred adsorption site on these surfaces both on perfect terraces and near steps and of the diffusion barriers, in particular the Schwoebel barriers encountered when descending steps. Then

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doi:10.1016/j.susc.2009.07.036

we have investigated the influence of neighboring adatoms on the binding energies and the diffusion barriers.

Our approach is first to calculate these quantities using the second moment tight-binding potential and second to try to fit them using a simple (effective) lateral pair interaction model in order to simplify further our Kinetic Monte-Carlo (KMC) calculations. We show that this fit needs to be extended to next nearest neighbors (i.e., a bond between two adatoms at the centers of equilateral triangles with a common apex, hereafter denoted as pseudo neighbor bond [9]) to reproduce successfully binding energy minima. Similarly, the introduction of an effective pair interaction corresponding to a next nearest neighbor bond at the bridge site, close to the saddle point, is necessary to model the diffusion barriers. Therefore, the diffusion barrier of any hopping process can be estimated from the number of first and second nearest neighbors at the initial and saddle points using a simple formula that will be used in KMC simulations. Then, improved KMC simulations will be performed to estimate qualitatively the role of the exchange process in the formation of the bimetallic alloy near the steps. The energy barrier responsible for the alloying is determined by comparing experimental and theoretical data.

This paper is organized as follows. After describing very briefly the step geometries (Section 2.1) the potential model and the KMC simulations are presented in Sections 2.2 and 2.3, respectively. Then the potential model is used in Section 3 to calculate the energy profile along a large number of diffusion paths for an adatom diffusing on the flat and stepped surfaces, from which the diffusion barrier are deduced. The model of the previous results using adatom–adatom effective pair interactions is discussed in Section 4. Finally in Section 5, we present the results of a simulation of Ni growth on Pt(1 1 1) surfaces using the KMC method. We introduce, as a parameter, the exchange process to determine its energy barrier.

2. Theoretical background

2.1. Geometry of the stepped surfaces

Fcc(1 1 1) surfaces exhibit two different kinds of straight steps with a close packed edge (see Fig. 1), the so called A and B steps, with (1 0 0) and ($\bar{1}$ 11) microfacets, respectively. The different geometries of the two steps is known to influence the activation energy barrier for an atom diffusing along or across the step [10,11]. Moreover, there are two types of three-fold adsorption sites on the terraces: the *f* site that continues the stacking order of (1 1 1) planes in the fcc structure, and the *h* site which initiates the hcp stacking order.

2.2. 2. Potential energy model

Many different approaches can be found in the literature to introduce N-body interactions which are required to describe the energetic properties of transition metals [12,13]. Note that Wang and coworkers [14] have used a modified embedded atom method (MEAM) and Monte-Carlo simulations to study Ni–Pt alloys to improve the segregation energy, which is a crucial variable when alloying appears. The calculations of the hopping processes presented in this paper are performed in the framework of the TB-SMA model, developed by several authors [15]. This potential has proved to be useful to interpret physical properties of metals driven by the effective width of the electronic density of states [12,16]. The exchange barriers are then determined by means of KMC method.

In this approach, the cohesive energy of a transition metal is written as the sum of a pairwise repulsive energy and a many – body attractive one:

$$E_{coh} = \sum_i \sum_{j,r_{ij}\langle r_c^{IJ}} A^{IJ} \exp\left[-p^{IJ}\left(\frac{r_{ij}}{r_0^{IJ}}-1\right)\right] \times f_c^{IJ}(r_{ij}) - \sum_i \left\{ \sum_{j,r_{ij}\langle r_c^{IJ}} (\xi^{IJ})^{\frac{1}{\alpha}} \exp\left[-2q^{IJ}\left(\frac{r_{ij}}{r_0^{IJ}}-1\right)\right] \times f_c^{IJ}(r_{ij}) \right\}^{\alpha} \quad (1)$$

where r_{ij} is the distance between two atoms at sites *i* and *j*, *I* and *J* indicate the chemical species (Ni, Pt) occupying site *i* or *j*, respectively. The parameter r_0^{II} is the first-neighbor distance between species I and $r_0^{IJ} = \left(\frac{r_0^{II}+r_0^{JJ}}{2}\right)$. The parameters (A^{IJ}, p^{IJ}) and (ξ^{IJ}, q^{IJ}) determine, respectively the repulsive and the attractive part of the interaction, ξ^{IJ} is an effective hopping integral and the exponent q^{IJ} characterizes its distance dependence. The term $f_c^{IJ}(r_{ij})$ is a cut-off function. In the bulk metals, the interactions are limited to first (r_0^{II}) and second ($\sqrt{2}r_0^{II}$) nearest neighbors, i.e., $f_c^{II}(r_o^{II}) = f_c^{II}(\sqrt{2}r_o^{II}) = 1$ and $f_c^{II}(r) = 0$ when $r\rangle\sqrt{2}r_0^{II}$. However, in the present work the interatomic distances are varied continuously. Therefore we must define the cut-off function in such a way that the total energy is continuous as well as its first two derivatives, so that the force and its first derivative do not present any discontinuities. To fulfill these conditions, we have chosen the function:

$$\begin{aligned} f_c^{IJ}(r_{ij}) &= 1 \quad \text{when } r_{ij}\langle r_{\min}^{IJ} \\ f_c^{IJ}(r_{ij}) &= \frac{1}{2} + \frac{1}{16}(-15x + 10x^3 - 3x^5) \quad \text{when } r_{\min}^{IJ}\langle r_{ij}\langle r_{\max}^{IJ} \\ f_c^{IJ}(r_{ij}) &= 0 \quad \text{when } r_{ij}\rangle r_{\max}^{IJ} \end{aligned} \quad (2)$$

with $x = \frac{r_{ij} - r_{moy}^{IJ}}{r_{dif}^{IJ}}$, $r_{\text{moy}}^{IJ} = \frac{r_{\min}^{IJ} + r_{\max}^{IJ}}{2}$, $r_{\text{dif}}^{IJ} = \frac{r_{\max}^{IJ} - r_{\min}^{IJ}}{2}$ and $r_{\min}^{IJ} = \sqrt{2}r_0^{IJ} + 0.1\text{Å}$, $r_{\max}^{IJ} = \sqrt{3}r_0^{IJ} - 0.1$ Å.

The value of α derived from the tight-binding theory in the second moment approximation is α =1/2.

The values of repulsive (A, p) and attractive (ξ, q) parameters for an homoatomic bond are determined by a least-mean-square fit of

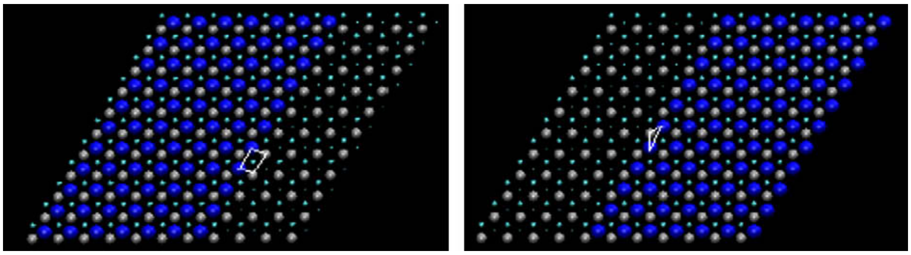

Fig. 1. The A step of a fcc(1 1 1) surface showing square microfacets on the step ledge (left hand side) and the B step showing triangular microfacets on the step ledge (right hand side).

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