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Formation of one-dimensional ordered alloy at step edges: An atomistic study of the (2×1) Ni/Pt alloy on the Pt(997) surface

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1. Introduction

Transition metals and their associated alloys are considered to be promising candidates as constituents of synthetic magnetic structures due to their favorable properties [1-4]. Intensive theoretical and experimental studies are devoted to investigate the physical properties of such structures [5]. Moreover, the study of the chemical properties of bimetallic surfaces has also drawn considerable attention, particularly with the development of bimetallic catalysts which present properties strongly different from pure metals [6–10]. These properties are to a large extent determined by the morphology and the composition of the catalyst surface that can differ significantly from the corresponding bulk [11].

For example, Ni–Pt alloys have a high catalytic selectivity for various reactions [12] and show a strong interplay between magnetic and spatial order [13,14]. In the bulk, Ni and Pt are known to form a continuous series of solid solutions [15]. Many studies have also dealt with the structure and composition of Ni–Pt surface alloy [16,17]. The modifications of the alloy properties are especially important when the admetal coverage is in the submonolayer to monolayer regime. Two critical factors can contribute to the modi-

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ABSTRACT

Kinetic Monte Carlo simulations based on a semi-empirical description of the metal-metal interactions are developed to interpret the formation of a one-dimensional Ni/Pt alloy observed at the step feet of the vicinal Pt(997) surface. Deposition of 0.15 monolayer of Ni atoms at T<300 K leads to the formation of a (2×1) well-ordered nanowire in agreement with scanning tunneling microscopy observations. Exchange process between Ni and Pt atoms at the upper step edge and neighboring influence appear to be the key point to explain such a well-ordered 1D alloy. In addition, a subtle decoration of the step adsorption sites is also necessary.

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fications of the electronic and chemical properties of a metal in a bimetallic surface. First, the hetero-atomic bond formation changes the local environment of the metal surface, giving rise to the evolution of the electronic structure through the ligand effect [18]. Second, the geometry of the alloy is typically different from that of the parent metals. It often involves important strain effects which can modify appreciably the electronic structure of the metal through changes in orbital overlaps [19,20]. For all these reasons, the knowledge of the alloy structure is of fundamental importance in order to further infer the electronic properties of the bimetallic structure.

Surprisingly, very little is known about Ni epitaxy on Pt surface. Three main features, namely diffusion, deposition and exchange processes usually govern the growth. Diffusion of adatoms on metal surfaces plays a crucial role since it determines the growth mode (2 or 3-dimensional), influences the nucleation regime and controls the island formation (density, shapes and size distributions) in the growth regime but also when coalescence takes place [21]. Diffusion also tunes the decoration of the defects which often occur on surfaces. This latter feature is particularly important in the case of the Pt(997) vicinal surface investigated here since steps, which are present periodically on that surface, act as a template for adsorbates [22,23]. In general, diffusion competes with adsorbate deposition and a subtle equilibrium appears, depending on the substrate temperature (which activates the diffusion) and the deposition flux (which governs the arrival of the adsorbates during the growth), leading to

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W. Essolaani et al. / Surface Science 605 (2011) 917-922

particular arrangements on the surface. In addition, Ni adatoms are known to diffuse into the bulk Pt since Pt has a lower surface energy than Ni, especially for the dense (111) face. This Niinterlayer mass transport is done according to an exchange process activated with temperature. This migration mechanism is drastically different from conventional hopping between adjacent sites since it consists of substituting a Pt substrate atom by an adatom located in the terrace or in the step by pushing it farther. This exchange phenomenon was used to explain the peculiar Ni growth on Pt(997) observed by Gambardella et al. [24]. Experimentally, two distinct metastable phases were observed. At T<200 K, a 1D ordered alloy with a (2×1) structure was observed at the step edges while at T = 300 K a 2D substitutional alloy with a (2×2) geometry appears.

The goal of the present paper is two-fold. First, we want to determine the precise role of diffusion, deposition and exchange processes in the submonolayer growth of Ni on Pt surface. Second, we would like to clarify the mechanism by which an organized incorporation in the Pt step of this vicinal surface can occur and lead to the formation of the (2×1) 1D alloy.

Atomistic simulations are very helpful to gain deeper insights in the mechanisms and driving forces that drive the growth of Ni on Pt surface. Kinetic Monte Carlo (KMC) simulations together with realistic semi-empirical potentials have proved during the last decade that they could be an excellent tool to interpret submonolayer growth experiments [25–27]. In the standard growth model, atoms are impinging on the substrate with a flux F and diffuse on it with a temperature dependent diffusion rate D. In previous papers [27], we have already shown how one can monitor the Ag, Co and Ni wire formation at the step edge of Pt(997) surface by taking into account all the diffusion processes and their associated energy barriers calculated using a semi empirical potential approach [28–31].

The goal of the present paper is to study the occurrence of the (2×1) superstructure using the same method as [27] but varying the exchange probability of Ni atoms as a function of their neighboring atoms in order to understand the precise role of this exchange phenomenon and to determine under which conditions such an organized bimetallic alloying appears. The paper is organized as followed: Section 2 is devoted to the presentation of the growth model including its approximations and its limits. In Section 3, the KMC results are presented to precise the ideal conditions for the (2×1) superstructure formation.

2. Theoretical background

2.1. The system

Ni deposition is done onto regularly stepped platinum surfaces. These surfaces are modeled by close-packed (111) terraces of width w separated by steps. Periodic conditions are applied along the directions parallel to the steps. We assume here that the substrate is rigid and that no reconstruction occurs (see Fig. 1).

2.2. Kinetic Monte Carlo model

The understanding of the microscopic processes involved in heteroepitaxial growth requires defining a model which accounts for most of the experimental observations, in well-defined physical conditions, and with basic information given by the interaction potential. The KMC model used here takes into account the four fundamental ingredients responsible for the growth, namely the deposition, the diffusion, the aggregation and the exchange between the adsorbate and the substrate atoms. To be consistent with experimental conditions under which the molecular beam heteroepitaxy proceeds, we generate atoms at random points on the vicinal face of Pt(997) with a flux F per site and time units. F is chosen to be



Fig. 1. Schematic representation of the model surface exhibiting regular steps separated by terraces of width *w*. Ni adatoms are deposited on these vicinal surfaces with a flux F and can either diffuse, aggregate and exchange with Pt atoms belonging to steps.

equal to 10^{-3} ML/s to be consistent with the experimental growth conditions [24]. Atoms diffuse on the substrate with a temperature dependent diffusion coefficient D that follows an Arrhénius law $(D = D_0 \exp[-\Delta E / (k_{BT})]$. The value of D₀ is constant and equal to 9.7×10^{-7} m²/s while the energetical barriers ΔE have been calculated before, for each direction of diffusion and each neighborhood of the diffusing adsorbate. For Ni adsorption, the interactions have been modeled according to a semi-empirical approach based on a second moment approximation. For clarity reason, we do not present the whole set of activation energies derived from this model which are reported in Ref. [27]. For example, the coefficient diffusion at T = 300 K for a free atom on a perfect surface is equal to D = $D_0 \exp\left(-\frac{229}{300k_B}\right) = 1.4 \times 10^{-10} \text{ m}^2/\text{s}$. We limit this study to coverage lower than the monolayer and we disregard the formation of 3D islands on the surface. Hence, we neglect the atom deposition above already preformed islands even if it could appear for coverage $\theta \leq 0.3$ ML. The exchange barrier will be varied continuously to order the alloy formation in the Pt steps. When Ni (or Pt) neighbors are present during this exchange, the phenomenological law depicted in Ref. [27] will be used to simplify the calculations and reproduce at best the reality. This law can be written for the diffusion barriers as:

$$E_{f \to h} = E_{f \to h}^{0} + N_{d_{1}^{*}} E_{1}^{*} + N_{d_{2}^{*}} E_{2}^{*} - N_{d_{1}}^{f} E_{1} - N_{d_{2}}^{f} E_{2}$$

where N_{d1} , N_{d2} , N_{d1^*} , and N_{d2^*} are the nearest and next nearest neighbors in respectively the starting diffusion site and its associated bridge site [27]. The value of E_1 , E_2 , E_1^* and E_2^* are summarized in the table of Ref. [27].

It should be also emphasized that exchange processes are authorized only at the step sites and not on the terraces in our

Table 1

Parameters (A, p, ξ, q) of the potential (see Eq. 1) for the pure Ni, Pt metals and for the heteroatomic Ni—Pt bonds.

	Ni–Ni	Pt-Pt	Ni-Pt
A(eV)	0.097	0.204	0.150
Р	11.165	11.854	11.509
ξ (eV)	1.562	2.371	1.966
q	2.268	3.473	2.870
p/q	4.92	3.41	

simulations. This is fully licit since it was shown experimentally that until 300 K, mixing of Ni atoms appears preferentially near steps and not on the terraces.

2.2.1. Calculation of the energy barriers for diffusion: potential model

The potential used for the determination of the energy barriers is derived from the tight-binding model in the second moment approximation. Since it has been described in details in Ref. [27] we just recall here its main features. It is expressed as a sum of a repulsive pairwise contribution and a many-body, non additive, attractive one. The total energy of the system is thus:

$$E_{coh} = \sum_{i} \sum_{j} A^{IJ} \exp\left[-p^{IJ}\left(\frac{r_{ij}}{r_{0}^{IJ}}-1\right)\right] \times f_{c}^{IJ}\left(r_{ij}\right) - \sum_{i} \left\{\sum_{j} \left(\xi^{IJ}\right)^{2} \exp\left[-2q^{IJ}\left(\frac{r_{ij}}{r_{0}^{IJ}}-1\right)\right] \times f_{c}^{IJ}\left(r_{ij}\right)\right\}^{1/2}$$
(1)

where r_{ij} is the distance between atom *i* and atom *j*, *I* and *J* specify the chemical species (Ni or Pt), r_0^{II} is the first-neighbor distance between species *I*, i.e. 2.77 Å for Pt and 2.489 Å for Ni, $r_0^{IJ} = (r_0^{II} + r_0^{IJ})/2$. The values of the repulsive (A^{II}, p^{II}) and attractive (ξ^{II}, q^{II}) parameters are determined by a least mean square fit of the bulk cohesion energy, the bulk modulus, the elastic constants and the main surface energies of the bulk metal. In addition the bulk equilibrium condition must be satisfied. For the interaction between heteroatoms (Ni–Pt), the values of the parameters are given by the arithmetic average of the corresponding values of the two bulk metals. Their adequacy was tested by directly comparing with available experimental data or *ab initio* calculations of the dissolution energy and alloy formation energies. Finally $f_c^{II}(r_{IJ}) = 1$ when $r_{IJ} < \sqrt{2}r_0^{II} + 0.1$ Å and $f_c^{IJ} = 0$ when $r_{IJ} > \sqrt{3}r_0^{IJ} - 0.1$ Å. We report the values of these parameters for Ni–Ni, Pt–Pt and Ni–Pt interactions in Table 1.

This semi-empirical potential is used to determine all the potential barriers responsible for any Ni displacement onto the stepped Pt surface. It is also at the origin of a model based on lateral effective pair interactions [27,32] which helps us to simplify the KMC code. The effect of the neighboring atoms will be thus completely described at the step sites. The key processes that guide the growth and the alloy ordering are listed in Table 2. Note that the exchange processes like diffusion ones depend strongly on the Ni atom environment.

Table 2

Main	barriers	responsible	for the	allov	formation.
IVIGIII	Durrers	responsible	ioi uic	anoy	iormation.

3. Results

In a previous paper [27], we have determined 967 potential barriers that characterize all diffusion paths which could potentially occur on the surface. We showed that this comprehensive analysis and, in particular, the inclusion of pseudo-neighbors was necessary to describe correctly the growth of Ni on Pt surfaces in a large set of temperatures 50 < T < 700 K and deposition flux $10^{-4} < F < 1$ ML/s. 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. We carried out Kinetic Monte-Carlo simulations to investigate the Ni wire formation at Pt step edges. Still, we estimated, by means of KMC simulations and energetical optimization, that the exchange process could alter the growth of perfect monatomic Ni wire at step edges. We found that a barrier less than 200 meV was sufficient to prevent the formation of perfect Ni monatomic wires at the Pt step edges. This latter process was introduced as a tunable parameter without taking into account the true possible exchange mechanisms and no influence of neighbors on exchange process was introduced. Here, we address this more precisely since, as already explained above, the conditions by which the (2×1) superstructure is obtained certainly depends on specific exchange barriers and more precisely on the atomic surrounding of Ni adatom undergoing exchange with Pt atoms at step edges (see Table 2).

Fig. 2a shows the image obtained when 0.15 ML of Ni is deposited on the Pt(997) with an exchange barrier equal to 230 meV and T = 300 K. In these conditions, Ni can incorporate easily the Pt step and pushes out the Pt atoms to form an alloy near the step. More interesting is the formation of the (2×1) superstructures which appear clearly on particular steps and for a quite long distance. In fact, regarding the whole surface and not only the step row, there are two adjacent rows near the step which present the 2×1 structure. This involves the apparition of a single 2×2 stripe on step which could nicely be compared to the so-called 2×2 observed in experiments at this temperature. This result obtained with KMC simulations is in very good agreement with the STM images obtained at T = 200 K (despite a small understandable shift [26] in the temperature range), where the organized 2×1 alloy is observed in the step (Fig. 2b).

It should be also noted that small clusters of alloy of same size and shape can be observed both in numerical simulations and experiments. This again confirms the good agreement between the two approaches. Note that Pt atoms expelled from the steps easily bind to other Ni atoms, so that the (2×1) phase can never be pure. Also, long (1×1) chains of Ni are found in our simulations in addition to the



920



Fig. 2. Pictorial representation of the kinetically limited exchange process at the step edge. Ni adatoms exchange only with hatched Pt atoms which have no Ni nearest neighbors: (a) theoretical results at T = 300 K and θ = 0.15 ML, (b) STM experimental results at T = 200 K and θ = 0.2 ML, c) and d) Zoom of the theoretical and experimental images showing the (2×1) superstructure.

 (2×1) phase. This can be explained by mechanical constraints which are not taken into account in the present Kinetic Monte Carlo approach and could eventually prevent two Ni atoms to be nearest neighbors after exchange. Note that exchange on terraces could also play a role here.

Apart from this, these results clearly show that the key to obtain ordered 1D alloy at step edges is related to the specific values of the Ni–Pt interactions. In order to fully understand the growth mechanism and the formation of the (2×1) superstructure, the role of the exchange barrier value needs to be intensively studied. Fig. 3 shows the density of the (2×1) alloy as a function of the exchange barrier value (0.5 is the density maximum Ni in a perfect 1D (2×1) alloy). The maximum of density is obtained when the exchange barrier has a value belonging to the range [200–250] meV. It drastically drops for lowest or highest values. This can be easily understood in terms of probability. Indeed, a small barrier would increase the Ni incorporation inside the step and cannot lead to the formation of the (2×1) structure due to a large number of Ni atoms trapped inside the step. On the other hand, when the barrier becomes large, the probability of exchange is low and this structure does not arise as confirmed by the snapshots shown in Fig. 3.

Fig. 4 clarifies the role played by the temperature. As expected, the temperature range where the (2×1) structure could occur, appears extremely narrow since below 150 K and above 330 K, the density of



Fig. 3. Density of (2×1) structure in the first row along the step edge as a function of the exchange barrier values *E* with T = 300 K. A perfect (2×1) alloy is obtained for a density of 0.5.

W. Essolaani et al. / Surface Science 605 (2011) 917-922



Fig. 4. Density of the (2×1) structure in the first row along the step edge as a function of the temperature for the same exchange barrier E (230 meV) and with coverage $\theta = 0.15$ ML. A perfect (2×1) alloy is obtained for a density of 0.5.

the (2×1) alloy decreases drastically below 0.3. Note that this curve can explain why, at T = 200 K, the experimental (2×1) superstructure is not observed in every Pt step. The thermal agitation should be activated to observe the ordered alloying (T>150 K). Note also that, at high temperatures, the Ni exchange on the terraces should normally appear, as suggested by experiments [21]. This has not been taken into account in our simulations. This adatom loss could prevent the complete (1×1) incorporation of Ni inside the step at high temperatures.

The occurrence of the (2×1) alloy is thus very difficult to observe. A fine analysis shows that it results from a complex balance between the diffusing atoms on the lower terraces and the exchanging atoms at the upper step edges. Indeed, when an exchange process occurs, the temperature must be sufficiently high to activate also the diffusion processes on the terraces. This allows the atom reaching the upper step sites to exchange but also other atoms to diffuse in the step wells. Moreover, to be effective, the exchange process should appear when no Ni atoms are already present in the step. Table 2 witnesses this feature since Ni neighbors lead to an increase of the exchange barrier up to 340 meV and thus induces less incorporation in the step. However, when Ni atoms are present in a next nearest neighbor site (filled step well), this increases the exchange probability with a Pt atom only slightly since the energy barrier is now 293 meV. When the nucleation of the structure is performed, this involves naturally a continuous progression of the (2×1) ordered alloy due to favorable energy barriers that increase the probability of an alternative filling of the step well combined with alternative incorporation of Ni in the step due to the influence of the second nearest neighbors. However, the superstructure can be stopped if another Ni wire nucleation center (inside the step or in the step well) has been built far from it. This determines the local length of the (2×1) alloy (about 30 Å).

4. Conclusion

Using a realistic and semi-empirical model and KMC simulations to describe all the kinetic processes appearing on the surface including exchange phenomenon, we found that the ordered (2×1) Ni/Pt alloy can only appear in a small range of temperature when the diffusion and the exchange processes are activated in a complementary way. We have shown that exchange can only appear at the upper step site

and should be coupled to an alternative filling of the step in order to increase the exchange probability. An exchange barrier in the range [200-230] meV is ideal at T = 300 K to observe such an alloy in the Ni/Pt system. Finally, these KMC simulations supported by STM experiments could serve as an indirect probe to determine exchange barriers.

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W. Essolaani et al. / Surface Science 605 (2011) 917-922

- 922

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