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Ni growth on vicinal Pt(1 1 1): low temperature exchange and formation of ordered surface alloys

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Abstract

We present an STM study of submonolayer Ni growth on Pt(9 9 7). We show that Ni atoms exchange with Pt already at $T = 150$ K both at terrace and at step sites. A one-dimensional ordered alloy forms at the step edges. For $T < 300$ K Ni atoms on the terraces are randomly embedded in Pt. Deposition of 0.2 ML Ni at $T = 300$ K results in a 2×2 substitutional alloy corresponding to a $Ni_{20}Pt_{80}$ composition of the surface topmost layer.

Keywords: Nickel; Platinum; Vicinal single crystal surfaces; Epitaxy; Alloys; Scanning tunneling microscopy

1. Introduction

The atomic scale characterization of exchange and alloying processes in metal epitaxy provides a test for theories that model atomic interactions at surfaces. In addition, the ability to grow heterogenous films with controlled morphology and chemical composition can be used to investigate the influence of structural parameters on, e.g., the catalytic activity and the magnetism of an alloy. In both respects the Ni–Pt system constitutes an interesting candidate for investigations: Ni–Pt alloys have a high catalytic selectivity for certain reactions [1] and show a strong interplay between magnetic and spatial order [2,3]. Although many studies have dealt with the structure and composition of Ni–Pt alloy surfaces [4,5], very little is known about Ni epitaxy on Pt. Here we show that Ni deposition on surfaces vicinal to Pt(1 1 1) gives rise to the formation of metastable alloy phases whose order and dimensionality depend on the Ni coverage and on the substrate temperature. Despite previous results [6] showing that the first Ni monolayer grows pseudomorphically on Pt(1 1 1) at room temperature, we find that on Pt(9 9 7), in the whole temperature range addressed by this study (150–300 K), a large fraction of Ni atoms exchanges with Pt substrate atoms, thus forming a surface alloy. Exchange processes are shown to be favored at step sites.

2. Experimental results

The experiments were performed in a home-built low-temperature STM apparatus which is

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described elsewhere [7,8]. The Pt(9 9 7) surface was prepared in situ by repeated cycles of 800 eV Ar^+ sputtering and annealing to 850 K, followed by a brief exposure to 1×10^{-7} mbar oxygen and by a flash anneal to $T > 1000$ K. The base pressure in the STM chamber was 5×10^{-11} mbar. Ni was deposited by means of an e-beam evaporator. After evaporation, the sample was cooled to 77 K; all STM images have been recorded at this temperature. Undesired CO contamination effects that are well known to affect the diffusion properties along and across the Pt step edges [9,10] can be safely ruled out. In fact, at 77 K, CO molecules adsorbed at the Pt step edges are immobile and easily identified by STM [11].

Pt(9 9 7) is a vicinal surface constituted by (1 1 1) terraces that have an average width of 20.1 Å separated by {1 1 1} monatomic steps. In the absence of exchange, due to the small terrace width, deposition at temperatures above the onset of the adatom thermal mobility results in the growth of islands attached to the step edges [12]. In previous studies [12–14], we have shown that step decoration in the appropriate temperature range can be exploited to grow arrays of one-dimensional chains of metal and rare gas atoms. In the Ni case, however, we find a different behavior due to substantial Ni–Pt exchange. Fig. 1 shows three STM images taken after deposition of 0.2 ML of Ni at different temperatures. At $T = 150$ K, Fig. 1(a), we observe the nucleation of irregular monolayer islands that grow with one side attached to the ascending step edge. We also observe a large number of bright round spots that appear about 0.4 Å higher than the surrounding Pt. These features represent Ni atoms embedded in Pt, as shown by Schmid et al. in an STM study of the $Pt_{25}Ni_{75}$(1 1 1) surface [15]. Most of the embedded Ni atoms are found aligned at the step edges at a distance corresponding to two Pt lattice constants. Ni inclusions are also observed in the terraces, as indicated by the arrows. Deposition at $T = 200$ K, Figs. 1(b) and 2, results again in Ni–Pt exchange and in the formation of adislands attached to the steps. A close analysis reveals that the majority of the adislands are constituted by both Ni and Pt atoms. The arrows in Fig. 2 indicate a Ni atom incorporated in a Pt terrace (right) and in the outer

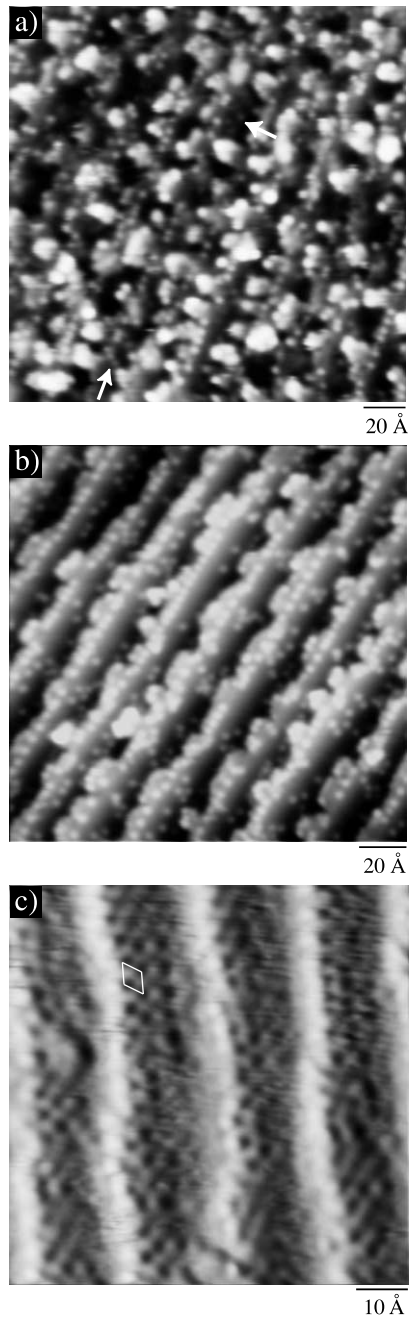

Fig. 1. STM images recorded after deposition of 0.2 ML Ni on Pt(9 9 7) at different temperatures. Step down direction is from right to left. (a) $T = 150$ K; tunneling current $I = 1.0$ nA, bias $V = 110$ mV. (b) $T = 200$ K; $I = 1.2$ nA, $V = 110$ mV. (c) $T = 300$ K; $I = 0.9$ nA, $V = 24$ mV. The latter image is displayed in $\partial z/\partial x$ mode to enhance the contrast on the terraces. The solid line represents a p(2 × 2) unit mesh.

edge of an adisland (left). While Ni atoms are found only at the perimeter, the inner part of the adislands appears to be pure Pt. The growth scenario can therefore be outlined as follows: Ni atoms evaporated on the surface readily exchange with Pt, expelling Pt atoms which nucleate at the step edges. Further Ni atoms than exchange at the Pt islands perimeter. The comparison of Fig. 1(a) and (b) shows that the adisland edges are more regular at higher temperature, probably due to faster edge diffusion processes [12].

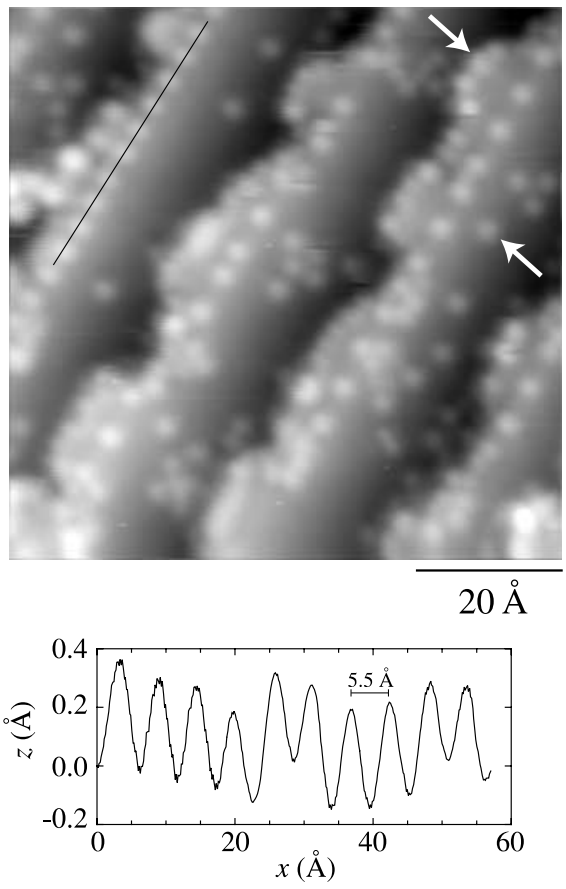

Fig. 2. STM image recorded after deposition of 0.2 ML Ni on Pt(9 9 7) at $T = 200$ K; $I = 2.0$ nA, $V = 12$ mV. The step down direction runs from the lower right to the upper left corner. The arrows indicate Ni atoms incorporated in a Pt terrace (right) and in an adisland edge (left). The plot is a line scan through the section indicated in the image. The distance between two adjacent Ni atoms is 5.5 Å, corresponding to an ordered 2×1 superstructure at the step edges.

In Figs. 1(a), (b) and 2 we notice that, whereas a clear 2×1 compositional ordering exist at the step edges, the Ni atoms that exchange at terrace sites are randomly distributed in the Pt terraces. This pattern changes drastically as the deposition temperature is raised to 300 K. Fig. 1(c) shows a detail of the surface after Ni deposition at 300 K. Although the quality of the STM images recorded in this case is not optimal, we observe that the adislands have disappeared and that a 2×2 superstructure has formed on the terraces. Between 200 and 300 K, therefore, the system goes through a transition from a disordered to an ordered surface alloy.

3. Discussion

Two issues merit further consideration and are discussed below: (1) the strong tendency of Ni atoms to diffuse into the Pt surface layer; (2) the ordering of the surface alloy.

3.1. Ni–Pt intermixing

Ni and Pt are known to form a continuous series of solid solutions in the bulk [16]. LDA and DFT calculations also show that Pt(1 1 1) has a lower surface energy than Ni(1 1 1) [17] and that Ni adatoms tend to diffuse into bulk Pt [18]. It is therefore expected that the two species will tend to mix in the thermodynamic equilibrium limit. Remarkably, we find that exchange processes are active already at $T = 150$ K and possibly below, meaning that the diffusion barriers which govern the concerted motion of Ni and Pt atoms are actually very low.

In principle, the formation of a mixed Ni–Pt surface layer could be triggered by a strain-relief mechanism that would lift the tensile stress of the Pt topmost layer. Due to the reduced coordination of the surface atoms, the Pt(1 1 1) surface bears a substantial tensile stress [19], and has thus an inherent tendency to reconstruct by transferring excess adatoms into the surface layer. Bott et al. [20] have shown that Pt atoms from a supersaturated Pt-vapor phase are incorporated into the Pt(1 1 1) surface between 400 and 650 K, whereby the

increased outmost layer density results in a network reconstruction. A similar mechanism holds for Co atoms evaporated on Pt(1 1 1) above 300 K [21]. On the basis of simple coordination arguments, one can expect the tensile stress of a densely stepped surface as Pt(9 9 7) to be higher than that of Pt(1 1 1), thus favoring the incorporation of adatoms. Unfortunately, we have no means here to draw a quantitative comparison of stress-induced effects on Ni–Pt exchange between Pt(9 9 7) and Pt(1 1 1), which we postpone to future investigations. Regarding exchange processes on terraces, however, in the Ni/Pt(9 9 7) system we observe no sign of reconstruction of the Pt terraces as we would expect if the Ni atoms were simply incorporated into the Pt layer. In this case the excess Ni atoms would induce some kind of dislocation pattern that would be easily detected by STM as a modulation of the corrugation amplitude on the Pt terraces [20,21]. The absence of stacking faults and the nucleation of Pt islands attached to the step edges (see Fig. 2) indicate, on the other hand, that Ni atoms expel Pt atoms from the surface layer. Since the lattice constant of bulk Ni–Pt alloys is smaller than that of pure Pt [16], it is unlikely that the substitution of Pt by Ni leads to a reduction of the tensile stress in the Pt layer.

Although relaxation effects may play a role in favoring Ni–Pt intermixing, we feel that the key to this process is related to the strong Ni–Pt atomic interactions. [1] This view is supported by the observation that Ni atoms in the Pt surface layer do not cluster. The analysis of the STM line scans reveals that each Ni is always surrounded by Pt nearest neighbors. This is in agreement with the calculations by Christensen et al. [18], which show that Ni atoms have a tendency to dissolve into a Pt host matrix. Interestingly, Pt atoms on Ni surfaces exchange at temperatures as low as 105 and 250 K on Ni(1 1 0) and Ni(1 0 0) surfaces, respectively [23].

Although we observe Ni atoms incorporated in the Pt terraces, it is clear that exchange is favored at step sites. In fact, the steps appear already saturated (2×1 superstructure) with Ni at 150 K. It obviously costs less energy to remove a Pt atom from an edge site, where it is 7-fold coordinated, than from a terrace site, where it is 9-fold coordinated. Also, the observation of preferential intermixing at the step edges, which implies migration of Ni adatoms to the steps, seems to exclude the occurrence of ballistic exchange processes [24].

3.2. 1D and 2D ordered surface alloys

We observe two distinct metastable phases for Ni/Pt(9 9 7): the first (Figs. 1(a), (b) and 2), at $T \leqslant 200$ K, consists of a 1D ordered alloy at the step edges and of Ni atoms randomly embedded in the Pt terraces; the second (Fig. 1(c)), at $T = 300$ K, consists of a 2D substitutional alloy with a 2×2 superstructure. The order of the 2×2 pattern does not seem to be perfect, but the latter phase interestingly corresponds to the truncated (1 1 1) surface of the bulk $NiPt_3$ alloy, which has a $L1_2$ structure. In fact, the stoichiometry of the surface layer corresponding to 0.2 ML Ni is close to that of the truncated $NiPt_3$(1 1 1) surface. [2]

The ordered 1D phase which forms at the step edges consists of alternated Ni and Pt atoms. Its structure can be considered the 1D analogue of the $NiPt_3$ alloyed phase in the bulk, since Ni atoms have only Pt neighbors. The stoichiometry, however, is not 1:3 but 1:7 taking into account all the Pt nearest neighbors. This phase appears already at $T = 150$ K. Generally, the transition from a disordered to an ordered phase is a thermally activated process. Here, on the other hand, we suggest that the structural order observed at the step edges is due to kinetic limitations. A thermally activated transition would imply that Ni atoms, which are randomly incorporated in the Pt step edges, collectively redistribute in order to form the

[1] Notice that Co and Cu, which are next to Ni in the periodic table, undergo a similar tensile stress (due to about 10% lattice mismatch) on Pt(1 1 1), and form bulk alloys with Pt in the whole composition range. However, Co atoms on Pt(9 9 7) and Pt(1 1 1) exchange only in moderate quantities between 250 and 400 K [13,21], while Cu grows pseudomorphically on Pt(1 1 1) at 340 K [22].

[2] Real $Ni_{1-x}Pt_x$(1 1 1) surfaces are always enriched in Pt with respect to the bulk average composition [4,5].

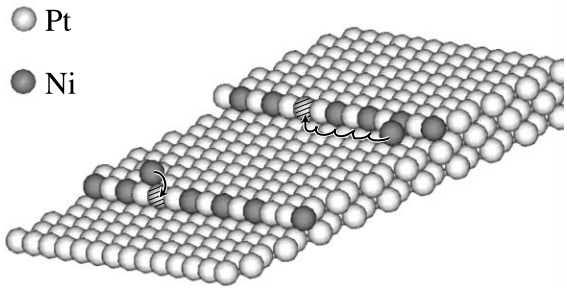

Fig. 3. Pictorial representation of the kinetically limited exchange process at the step edges. Ni adatoms exchange only with hatched Pt atoms which have no Ni nearest neighbors.

energetically favored 2×1 structure. This is rather difficult to imagine at $T \leqslant 150$ K. We propose instead that the Ni adatoms migrating on the Pt surface explore the step sites and exchange only where no other Ni nearest neighbors are found, as depicted in Fig. 3. This process naturally leads to Ni–Pt–Ni–Pt$\cdots$ or Ni–Pt–Pt–Ni–Pt$\cdots$ structures, which are both observed in Fig. 2 along the step edges. A similar mechanism comes into play in the 2×1 saturation of Pt steps by chemisorbed oxygen atoms [25].

4. Conclusions

In summary, we have shown that Ni deposition on Pt(9 9 7) in the 150–300 K temperature range results in significant incorporation of Ni atoms at step and terrace sites. At $T \leqslant 200$ K Ni atoms form a 1D substitutional alloy at the step edges with 2×1 order and isolated random inclusions in the Pt terraces. Exchange processes are favored at step sites. Deposition at $T = 300$ K leads to the formation of a 2×2 alloy on the Pt terraces.

The nature of chemical and magnetic interactions in Ni–Pt solid solutions can now be investigated with continuity with respect to 1D, 2D, and 3D ordered structures. It is known that the Curie temperature of bulk Ni–Pt compounds, for instance, has a strong dependence on the alloy composition and long-range spatial order [2,3]. The magnetic behavior of 1D atomic chains, in particular, is the object of intense research due to open questions relating to the stability of the magnetization in such structures. Recent experiments performed on Co monatomic chains grown by step decoration on Pt(9 9 7) [26,27] have shown that the Co chains display a superparamagnetic behavior and large magnetic moments per Co atom. In alloyed chains the magnetic behavior can be significantly different. We cannot predict neither the sign of the coupling, nor the magnitude of .the Ni magnetic moments in a Ni–Pt chain. Total energy calculations [28] relative to the Cu(1 0 0)c(2×2)Mn surface alloy have shown yet another perspective: it is the magnetic state which determines the stability of the alloy phase. The fabrication of low-dimensional alloy structures is but the first step towards a better understanding of the mutual relationship between chemical and magnetic order.

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References

[1] Y. Gauthier, R. Baudoing, Y. Joly, R. Rundgren, J.C. Bertolini, J. Massardier, Surf. Sci. 162 (1985) 342.
[2] C.E. Dahmani, M.C. Cadeville, J.M. Sanchez, J.L. Morán-López, Phys. Rev. Lett. 55 (1985) 1208.
[3] M.C. Cadeville, C.E. Dahmani, F. Kern, J. Mag. Mag. Mat. 54–57 (1986) 1055.
[4] Y. Gauthier, Surf. Rev. Lett. 3 (1996) 1663.
[5] P. Wiegand, P. Novacek, G. Vanhusen, T. Neidhart, P. Varga, Surf. Sci. 270 (1992) 1129.
[6] M. Sambi, E. Pin, G. Granozzi, Surf. Sci. 340 (1995) 215.
[7] O. Jeandupeux, L. Bürgi, A. Hirstein, H. Brune, K. Kern, Phys. Rev. B 59 (1999) 15926.
[8] A. Hirstein, Ph.D. Thesis, EPF Lausanne, 1999.
[9] P.J. Feibelman, Phys. Rev. Lett. 81 (1998) 168.
[10] M. Kalff, G. Comsa, T. Michely, Phys. Rev. Lett. 81 (1998) 1255.
[11] P. Gambardella, Ph.D. Thesis, EPF Lausanne, 2000.
[12] P. Gambardella, M. Blanc, H. Brune, K. Kuhnke, K. Kern, Phys. Rev. B 61 (2000) 2254.
[13] P. Gambardella, M. Blanc, L. Bürgi, K. Kuhnke, K. Kern, Surf. Sci. 449 (2000) 93.
[14] V.E. Marsico, M. Blanc, K. Kuhnke, K. Kern, Phys. Rev. Lett. 78 (1997) 94.
[15] M. Schmid, H. Stadler, P. Varga, Phys. Rev. Lett. 70 (1993) 1441.

[16] M. Hansen, Constitution of Binary Alloys, second ed., McGraw-Hill, New York, 1958.
[17] I.A. Abrikosov, A.V. Ruban, H.L. Skriver, B. Johansson, Phys. Rev. B 50 (1994) 2039.
[18] A. Christensen, A.V. Ruban, P. Stoltze, K.W. Jacobsen, H.L. Skriver, J.K. Nørskov, F. Besenbacher, Phys. Rev. B 56 (1997) 5822.
[19] R.J. Needs, M.J. Godfrey, M. Mansfield, Surf. Sci. 242 (1991) 215.
[20] M. Hohage, T. Michely, G. Comsa, Surf. Sci. 337 (1995) 249.
[21] E. Lundgren, B. Stanka, W. Koprolin, M. Schmid, P. Varga, Surf. Sci. 423 (1999) 357.
[22] B. Holst, M. Nohlen, K. Wandelt, W. Allison, Surf. Sci. 377–379 (1997) 891.
[23] G.L. Kellogg, Surf. Sci. 266 (1992) 18.
[24] G.L. Kellogg, Phys. Rev. Lett. 76 (1996) 98.
[25] P.J. Feibelman, S. Esch, T. Michely, Phys. Rev. Lett. 77 (1996) 2257.
[26] A. Dallmeyer, C. Carbone, W. Eberhardt, C. Pampuch, O. Rader, W. Gudat, P. Gambardella, K. Kern, Phys. Rev. B 61 (2000) R5133.
[27] P. Gambardella, A. Dallmeyer, K. Maiti, M.C. Malagoli, W. Eberhardt, K. Kern, C. Carbone, in press.
[28] M. Wuttig, Y. Gauthier, S. Blügel, Phys. Rev. Lett. 70 (1993) 3619.