

Intermixing-driven scenario for the growth of nanowires on (110) metal surfaces

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The growth scenario of monatomic wires on fcc (110) metal surfaces via intermixing of deposited and substrate atoms is reported. We present theoretical investigation of self-assembly of one-dimensional nanostructures during thermal deposition of Fe and Co atoms on Pd(110) in the submonolayer regime. Calculations performed by means of density-functional theory demonstrate that deposited atoms incorporate into the top-most substrate layer. Kinetic Monte Carlo simulations based on *ab initio* calculated diffusion barriers of relevant atomic processes indicate that surface diffusion of expelled atoms is responsible for growth of atomic wires consisting mainly of Pd atoms.

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Epitaxial growth of thin films opens an opportunity to create atomic structures with novel physical properties.¹ In most cases epitaxy involves a lattice mismatch between deposit and substrate that substantially affects the details of growth. Generally, the interface intermixing can be expected in systems dominated by atomic mismatch.² Mismatch renders the elements immiscible in the bulk, and could confine the deposited atoms in substrate layer.² The interface intermixing in the submonolayer deposition regime has been observed in a numerous number of systems: Au/Ni(110),³ Au/Ni(111),⁴ Rh/Ag(100),⁵ Ag/Cu(100),⁶ Ag/Cu(110),⁷ Co/Cu(110),^{8,9} and Ge/Pt(100).¹⁰ Under such conditions, the deposited atoms are accommodated in the surface layer, while the expelled substrate atoms participate in the formation of the adlayer structure.

Room-temperature kinetically controlled homoepitaxy and heteroepitaxy allows one to create two-dimensional (2D) nanoscale islands on the unreconstructed (100) and (111) close-packed surfaces.^{11,12} On the contrary, a (110) substrate is an ideal template for self-organization of one-dimensional (1D) atomic structures.¹³ An unreconstructed fcc (110) surface consists of closed-packed atomic rows oriented along the [1–10] direction and separated by deep channels.¹⁴ Since the preferential diffusion of deposited atoms takes place along these channels, one could expect formation of linear chains within the channels. Indeed, growth of monatomic wires during deposition of Cu on Pd(110) (Refs. 13 and 15) and Co on Pd(110) (Ref. 16) has been observed. A detailed understanding of different growth regimes on a fcc (110) surface during homoepitaxy has been achieved in the studies of Ferrando *et al.*^{17,18} Several investigations indicate that in the heteroepitaxial case intermixing could substantially affect atomic self-assembly. Scanning tunneling microscopy (STM) experiments and theoretical calculations for Au/Ni(110) have given a clear evidence that embedding of deposited Au atoms drives the growth process, and surprisingly, the thin film consists mainly of expelled Ni atoms.³ Recent studies at the Co/Cu(110) interface have demonstrated the existence of the similar phenomenon.⁸ Theoretical investigations have shown that adatoms can replace surface atoms on a (110) surface via

an exchange process during heteroepitaxy with reasonably low activation barriers.^{9,19}

In this paper we demonstrate that the growth scenario via intermixing of deposited and substrate atoms could lead to the formation of monatomic wires on fcc (110) metal surfaces. We report on theoretical investigation of self-assembly of 1D nanostructures during thermal deposition (TD) of Fe and Co atoms on Pd(110) in the submonolayer regime. Our density-functional theory (DFT) studies reveal that the incorporation of Fe and Co adatoms into the substrate layer is energetically and kinetically feasible at room temperature. Kinetic Monte Carlo (kMC) simulations based on *ab initio* calculated diffusion barriers give a clear evidence that surface diffusion of Pd atoms is responsible for the growth of atomic wires consisting mainly of Pd atoms.

The DFT results are obtained using Vienna *ab initio* simulation package (VASP) code²⁰ using the Perdew-Wang 1991 version of generalized gradient approximation (GGA).²¹ Ultrasoft pseudopotentials have been exploited in our calculations.²² The Fermi-level smearing approach of Methfessel and Paxton²³ (with a Gaussian width of 0.2 eV) is employed for electronic states near the Fermi level. The optimized atomic geometries are achieved when the forces are smaller than 0.01 eV/Å. The bulk lattice constant of Pd is found to be 3.965 Å. The nudged elastic band method is involved to obtain diffusion barriers of relevant atomic events. The slab in our calculations is constructed of seven layers and 140 Pd atoms in the periodic supercell. Four bottom layers are kept fixed at their bulk positions. The vacuum region of 10 Å separates the slabs. We perform calculations using a $2 \times 2 \times 1$ mesh in the Brillouin zone.²⁴ Local density approximation (LDA) for exchange-correlation functional has been also probed. However, we have not found any crucial difference in the results obtained within GGA and LDA.

First we study the behavior of an individual Fe adatom landed on a Pd(110) surface. We find that a Fe adatom diffuses along the [1–10] direction [Fig. 1(a)] with a barrier $E_1=0.30$ eV. At room temperature the adatom easily overcomes this barrier. However, a Fe adatom has to overcome the barrier of 1.57 eV [Fig. 1(b)] to diffuse along the [001] direction. This barrier is too high; hence such motion is

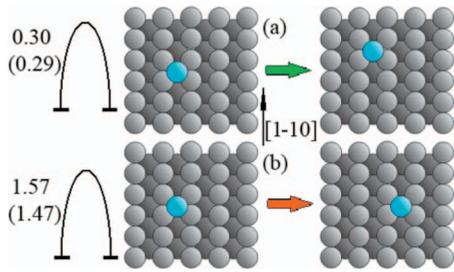


FIG. 1. (Color) Diffusion barriers (in eV) of Fe (in parenthesis: of Co) adatoms on Pd(110). (a) Diffusion of a Fe (Co) adatom on Pd(110) along the $[1-10]$ direction. (b) The same along the $[001]$ direction. Gray circles represent Pd atoms, blue circles correspond to Fe (Co) atoms.

suppressed.²⁵ Incorporation of a Fe adatom into the topmost substrate layer [Figs. 2(a) and 2(b)] decreases the total energy of the system by 0.34 eV and takes place with the barrier $E_2=0.32$ eV. Due to the fact that (i) the values of barriers E_1 and E_2 are close and (ii) embedding of Fe is energetically favorable, we conclude that deposited Fe atoms incorporate into the substrate shortly after landing. We have also carried out calculations for Co adatoms on Pd(110). DFT studies demonstrate that diffusion barriers for surface diffusion (Fig. 1) and incorporation (Fig. 2) of Co atoms on Pd(110) are very close to those for Fe on Pd(110). Thus a replacement of a substituted Pd atom by a Co atom is energetically and kinetically feasible at room temperature.

Now we concentrate on the behavior of expelled Pd atoms. The diffusion barrier of a Pd adatom on Pd(110) along the $[1-10]$ direction is found to be 0.45 eV. The barrier for the direct hop along the $[001]$ direction is 1.26 eV. However in contrast to Fe and Co atoms, a Pd atom migrates along the $[001]$ direction via exchange with one of Pd atoms of the topmost layer (the barrier is 0.54 eV, Fig. 3). Not all hollow sites are energetically equal for a diffusing Pd, and there are

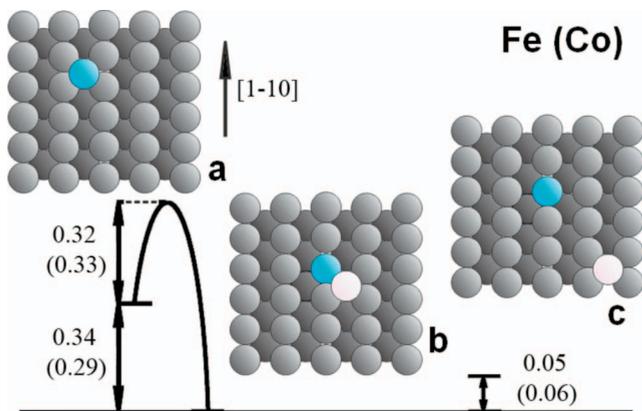


FIG. 2. (Color) Top view of the surface model, showing the first phase of Pd wires formation. Gray (light gray) circles represent Pd atoms of the surface (of the first adlayer). Blue circles correspond to Fe (Co) atoms. The relative energies between atomic configurations (in eV) and activation barriers (in eV) are presented. (a) A Fe (Co) adatom is on Pd(110). (b) An embedded Fe (Co) atom and an expelled Pd adatom nearby. (c) An expelled Pd adatom is located far from the buried Fe (Co) atom.

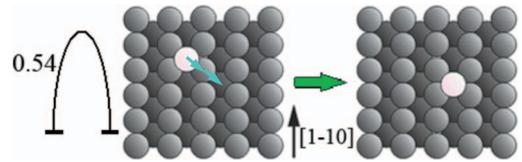


FIG. 3. (Color) Diffusion of a Pd adatom on Pd(110) along the $[001]$ direction via exchange mechanism. The colors of the circles are the same as in Fig. 2.

preferable positions: hollow sites in a vicinity of an embedded Fe atom [Fig. 2(b)]. When a Pd adatom is located near an embedded Fe, the energy gain is 0.05 eV [Figs. 2(b) and 2(c)]. Nevertheless, this energy is too small to bind together an expelled Pd and embedded Fe atoms at room temperature. As a result, a Pd atom follows 2D random diffusion along the surface.

The following question arises, whether or not embedded Fe atoms could form compact structures within the surface Pd layer. In order to clarify this point we have calculated the magnitude of binding energy of an embedded Fe (Co) dimer oriented along the $[1-10]$ direction (Fig. 4). We have found that this energy is repulsive and equals to 0.20 eV (for an embedded Co dimer it is also repulsive and equals to 0.08 eV). Combining all above mentioned results we conclude that first of all, incorporation of Fe (Co) takes place. The embedded Fe (Co) atoms repel each other and thus form a disperse array within the surface layer. These Fe (Co) atoms are further excluded from the process of formation of adlayer structure. Expelled Pd atoms exhibit 2D surface diffusion and coalescence into short chains elongated along the $[1-10]$ direction.

Previous studies have revealed that the main factor affecting the morphology of a (110) surface is the interplay between the barriers for attachment and detachment to a chain (or a cluster).^{17,18} Increasing temperature T at fixed flux F one can find the following growth regimes: (i) small agglomerates at low T ; (ii) atomic chains along the in-channel direction at intermediate T (when T is not enough to break in-channel Pd-Pd bonds); (iii) 2D anisotropic islands elongated along the $[1-10]$ direction at high T (when T is high enough to break in-channel Pd-Pd bonds). Figure 5 presents basic diffusion events happening on a Pd(110) surface in the vicinity of a growing Pd atomic wire. The barrier for diffusion of a Pd adatom along the chain along the $[1-10]$ direction is 0.52 eV. The Pd adatom migrating along the $[1-10]$ direction detaches the wire with a barrier of 0.49 eV (the barrier for an opposite hop is 0.46 eV). The barrier for the breaking of in-channel Pd-Pd bond is 0.73 eV. All these atomic events, except the last one, are operative at room temperature.²⁵ Thus according to Refs. 17 and 18, we expect

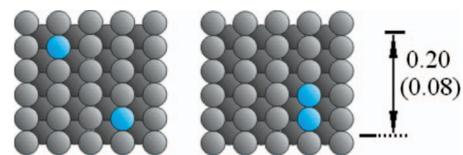


FIG. 4. (Color) Binding energy of an embedded Fe (Co) dimer. The colors of the circles are the same as in Figs. 1 and 2.

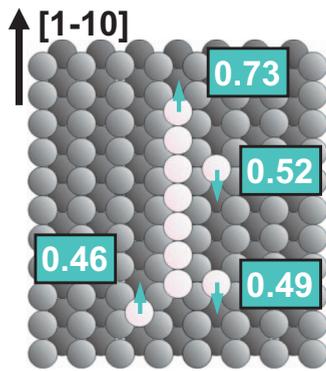


FIG. 5. (Color) Basic atomic events responsible for the growth of Pd atomic wires elongated along the $[1-10]$ direction. The colors of the circles are the same as in Figs. 1 and 2. The activation barriers are given in eV.

the growth of elongated along the $[1-10]$ direction Pd wires.

Next we employ large-scale atomic simulations by means of kMC method,²⁶ taking into account activation barriers of different relevant atomic events (Figs. 1–5). We concentrate on Fe on Pd(110); however similar results have been obtained for Co/Pd(110). Our kMC model describes epitaxial growth in terms of rates of elementary stochastic processes (deposition, surface diffusion, and detachment/attachment to/

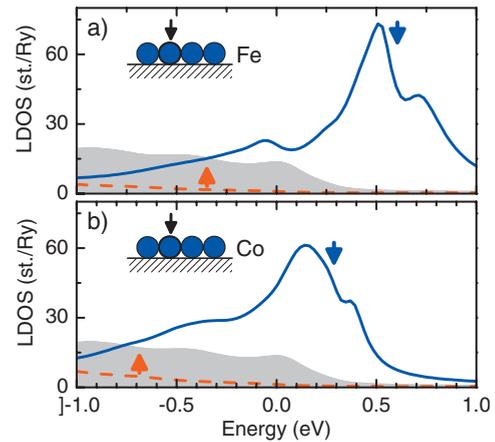


FIG. 7. (Color) Partial minority (solid blue curves) and majority (dashed red curves) d -LDOS calculated at central atoms of a (a) Fe and a (b) Co chain of four atoms. Shaded gray areas represent d -LDOS at central atom of a Pd chain of four atoms. The calculations have been performed by means of the Korringa-Kohn-Rostocker Green's function method (Ref. 27).

from a chain or cluster).^{9,17,18} The rate of an atomic event is calculated using the Arrhenius expression $\nu = \nu_0 \exp[-E_D/(k_B T)]$, where $\nu_0 = 1 \times 10^{12}$ Hz is the prefactor, T is the temperature, and E_D is the activation barrier. The kMC simu-

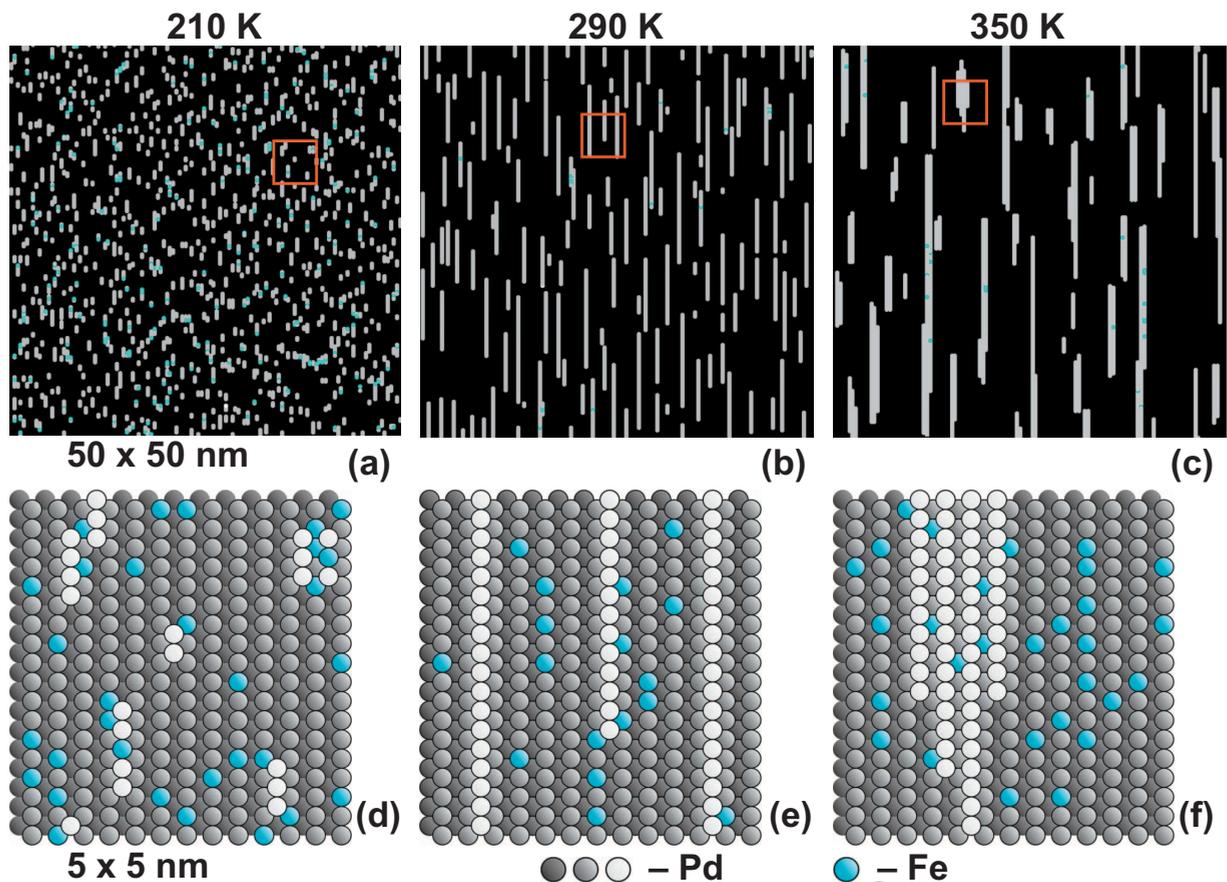


FIG. 6. (Color) [(a)–(c)] Top view of a Pd(110) surface exposed by 0.12 ML of Fe atoms at (a) 210 K, (b) 290 K, and (c) 350 K: the kMC simulations. Light gray (blue) color demonstrates Pd (Fe) in the adlayer structure. [(d)–(f)] An atomic-scale view of the areas, marked in (a)–(c) with red rectangles. The colors are the same as in Figs. 1 and 2.

lations are carried out on a close-packed (110) lattice consisting of 142×200 atoms (56×56 nm²). Periodic boundary conditions are applied in a surface plane. We set flux $F = 0.005$ ML/sec. The central result of the kMC simulations is presented in Fig. 6(b), which demonstrates the morphology of a Pd(110) surface exposed by 0.12 ML of Fe atoms at $T = 290$ K. Formation of randomly distributed monatomic chains elongated along the $[1-10]$ direction is observed. In Fig. 6(e) we show the atomic-scale resolution of the area marked with the red rectangle in Fig. 6(b). A strong intermixing between deposited and substrate atoms is seen, and growing monatomic wires consist mainly of Pd atoms.

Our systematic kMC studies demonstrate that there is a temperature interval suitable for fabrication of wires. At $T \sim 200$ K an insufficient mobility of adatoms leads to the growth of small aggregates. Figure 6(a) shows the morphology of a Pd(110) surface exposed by 0.12 ML of Fe at $T = 210$ K. Self-assembly of densely located short atomic chains is seen. Figure 6(d) demonstrates an enlarged view of the area, marked with the red rectangle in Fig. 6(a), and indicates accommodation of Fe adatoms into the substrate. The adlayer chains are 3–5 atoms long and consist mainly of expelled Pd atoms. Already at 350 K we observe growth of compact 2D islands (elongated along the $[1-10]$ direction), rather than formation of atomic chains [see Fig. 6(c)]. This agrees with the results of Ferrando *et al.*:¹⁷ when the Pd-Pd in-channel bond breaks (the barrier is 0.73 eV, Fig. 5), transition from 1D wires to 2D clusters takes place.

Our systematic studies demonstrate that qualitatively there is no difference between growth of Fe/Pd(110), Co/Pd(110), and Pd/Pd(110) in the submonolayer regime (< 0.2 ML) since the mechanisms for the formation of an adlayer structure in these three systems are the same.

Our results give a deeper insight in the recent experiments on TD of Co on Pd(110).¹⁶ We reveal that at low coverage (~ 0.1 ML of Co) the wires consist of expelled Pd atoms, while it has been believed that formation of Co atomic chains is observed.¹⁶ However, when the coverage increases, the embedding of Co atoms is getting suppressed since the barrier for exchange of a Co adatom next to already embedded Co

atoms is quite high and equals to 0.60 eV (0.79 eV in LDA). Hence, above the coverage of ≥ 0.5 ML, Co atoms contribute remarkably to the formation of adlayer structure. This is why the magneto-optic Kerr effect (MOKE) signal measured for 0.5 ML of Co on Pd(110) (Ref. 16) relates to the Co nanostripes on Pd(110) and reflects their magnetic anisotropy.

Now we turn to a possible experimental confirmation of our results. We suggest that scanning tunneling spectroscopy (STS) technique could allow distinguishing between Fe (Co) and Pd atomic chains on Pd(110). In Fig. 7 we plot d -partial local density of states (LDOS) calculated at central atoms of Fe, Co, and Pd chains of four atoms. It is easy to see that there is a substantial difference in the d states near Fermi level E_F for Fe and Pd chains [Fig. 7(a)]. For the Fe chain the peak at $E = 0.5$ eV above the Fermi energy E_F is observed, while for the Pd chain it is at Fermi level E_F . The difference is also seen if one compares a Co and a Pd chain; however it is not so pronounced: the Co chain exhibits peak at $E = 0.1$ eV above E_F [Fig. 7(b)].

In summary, we have revealed that growth atomic wires on a fcc(110) surface could be promoted by the incorporation of deposited atoms into the substrate. We have performed theoretical studies of growth of nanostructures during submonolayer deposition of $3d$ adatoms (Fe, Co) on a Pd(110) surface at different temperatures. At room temperature all these systems have been found to follow the general rules: (i) incorporation of deposited atoms into the topmost substrate layer, (ii) formation of a disperse array of Fe (Co) atoms within the topmost Pd layer, and (iii) growth of atomic chains consisting mainly of the expelled Pd atoms. The universal nature of the underlying physics suggests that the discovered mechanism of atomic self-assembly may be of general importance for the growth of 1D nanostructures on different metal substrates.

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