

Pd Atomic Chain Formation as a Result of Submonolayer Deposition of 3d Metals on Pd(110)

D. H. Wei, C. L. Gao,* and Kh. Zakeri

Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, 06120 Halle, Germany

M. Przybylski

*Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, 06120 Halle, Germany
and Faculty of Physics and Applied Computer Science, AGH University of Science and Technology,
Mickiewicza 30, 30-059 Kraków, Poland*

(Received 5 August 2009; published 25 November 2009)

Submonolayer deposition of 3d transition metals such as Cr, Mn, Fe, Co, and Ni on Pd(110) at room temperature causes the formation of monoatomic chains of Pd as identified with scanning tunneling microscopy and spectroscopy. In agreement with recent theoretical predictions [Phys. Rev. B **79**, 155410 (2009)], the substitution of Pd substrate atoms with the deposited atoms of 3d metals is found to be responsible for the formation of Pd atomic chains. This finding clarifies the long-debated issue about the chemical composition of the atomic chains grown on Pd(110) and points out the intriguing processes in the formation of self-assembled and self-organized nanostructures.

DOI: 10.1103/PhysRevLett.103.225504

PACS numbers: 61.46.-w, 81.16.Dn

The innovative applications of nanoscience rely mostly on the ability to design and fabricate nanoscale structures [1]. Complementary to the current lithographic techniques used for miniaturization which reach their limit at a few tens of nanometers [2], self-assembly (SA) or self-organization (SO) has gained interest as one of the most promising methods to further diminish the size of nanoscale objects [3].

The SA or SO, which occurs at the deposition of one or more materials onto substrates, involves various surface processes including diffusion [4–6], aggregation [6–8], and intermixing (atomic substitution) [9,10]. Among these surface processes, though intermixing is generally recognized, its importance in determining the formation of nanodots, nanowires, and nanoislands is seldom studied due to the difficulty in identifying the chemical composition of single nanostructures on the atomic level. When the surface intermixing dominates at the initial stage of growth, instead of depositing the material, the formation of nanostructures made of the substrate's material may occur.

In the literature, the atomic chains formed on Pd(110) were generally considered as composed by deposits, such as Cu/Pd(110) [6,11] and Co/Pd(110) [12]. This assumption, however, was not exclusively validated.

In this Letter we demonstrate a formation of Pd monoatomic chains after depositing a submonolayer of 3d transition metals like Cr, Mn, Fe, Co, and Ni on Pd(110). Using scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS), we measured the atomically resolved electronic structure of nanostructures formed on the Pd(110) substrate. We confirm the formation of atomic chains made of Pd instead of a 3d transition metal. The results are in perfect agreement with the recent theoretical prediction [13].

These experiments were carried out under ultrahigh vacuum conditions. The Pd(110) single crystal was cleaned *in situ* by cycles of Ar⁺ sputtering and subsequent annealing at 900 K. The 3d transition metals (Cr, Mn, Fe, Co, and Ni) were deposited on the Pd(110) substrate with a deposition rate of 0.2 ML/min. During STM/STS measurements, the sample was kept at 4.7 K. The differential conductivity dI/dU was measured in tunneling spectroscopy mode using a lock-in technique with modulation of 5 mV at 17 kHz. Note that all the spectra were taken with carefully prepared clean W tips and crosschecked by taking spectra on clean Pd(110) surface to rule out any polluting feature from tips.

Figures 1(a) and 1(b) show the topographic images after depositing 0.08 monolayer (ML) of Fe and 0.12 ML of Co on Pd(110) at room temperature (RT). Single atomic chains along the $[1\bar{1}0]$ direction are formed which are up to 30 nm long. The density of the atomic chains increases with increasing coverage, i.e., with an increasing number of adatoms. A few double atomic chains can also be found at the surface. Similar chains (which are not shown here) can also be formed by the deposition of Cr, Mn, or Ni on Pd(110). The dI/dU spectra of the atomic chains and of the Pd(110) substrate are shown in Fig. 1(c). Surprisingly, the spectra taken from the atomic chains look exactly the same regardless of the material that was deposited (i.e., Co and Fe). The spectra are nearly the same as the spectrum taken from the Pd substrate with a characteristic peak at the Fermi level (E_F). Furthermore, the spectra for chains formed on Pd(110) after deposition of Cr, Mn, and Ni are identical with the spectra of the chains after deposition of Co and Fe.

There are only two possibilities that can explain this phenomenon. First, the atomic chains are formed by 3d transition metals, but these chains have exactly the same

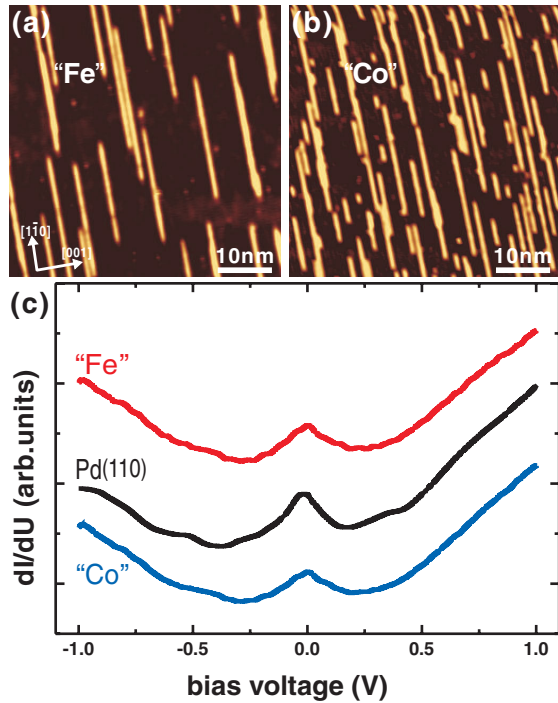


FIG. 1 (color). Topography (a), (b), and dI/dU spectra (c) of atomic wires formed by Fe and Co deposition on Pd(110) at RT. STM image conditions: $50 \text{ nm} \times 50 \text{ nm}$; $V = 0.4 \text{ V}$, $I = 20 \text{ nA}$. The spectrum of Pd substrate is plotted for comparison.

density of states as the Pd substrate within the investigated energy range (from -1 V to 1 V of the bias voltage with respect to E_F). From the universal resemblance of the spectra taken from the atomic chains of Cr, Mn, Fe, Co, and Ni with the one from the Pd(110) substrate, it is very unlikely that all these materials have identical density of states. The second possibility is that these atomic chains are made of Pd instead of the $3d$ transition metal while Pd chains very likely show electronic structures similar to that of the Pd substrate. Careful comparison shows that there is a small bump around -0.5 V in the spectrum of Pd substrate besides the common pronounced peak at the Fermi level in Fig. 1(c). This is most probably due to the slightly different electronic structure of Pd in the atomic chain and Pd in the substrate surface. The formation of Pd chains may happen if the intermixing process between the deposited and substrate atoms is energetically more preferable than the surface diffusion.

Exclusive clarification of these two possibilities comes both from theoretical calculations [13] and from experimental observations. The calculated local density of states (LDOS) [13] shows a substantial difference in the density of d states near E_F for Fe and Pd chains on Pd(110). There is a peak at $E = 0.5 \text{ eV}$ above E_F for Fe chains and at E_F for Pd chains. Comparing the spectra of Fig. 1(c), it is very likely that the atomic chains shown in Figs. 1(a) and 1(b) are made of Pd. Furthermore, since the spectra of Fe chains

are expected to be quite different from those of Pd, Fe was chosen to be grown on Pd(110) at a low temperature (6 K). In this case, the deposited atoms are expected to be frozen when they arrive at the surface (i.e., the atomic intermixing process is expected to be suppressed). Figure 2(a) shows the topography after the deposition of less than 0.01 ML of Fe on Pd(110). Both the Pd atoms of the substrate and the Fe atoms occupying the hollow sites are clearly atomically resolved. As shown, most of the deposited atoms form monomers and dimers along the $[1\bar{1}0]$ and $[001]$ directions; trimers are formed along the $[1\bar{1}0]$ direction. The dI/dU spectra taken at the deposition temperature (i.e., without warming up the sample) of monomers, dimers, and trimers [marked by stars in Fig. 2(a)] are shown in Fig. 2(b). The spectrum of the Pd substrate is also plotted for comparison. The spectra of the Fe adatoms are very different from the spectrum of the Pd substrate. As shown in Fig. 2(b), in the spectrum of the monomer a shoulder is observed at 0.53 V above E_F . The spectrum of the dimers oriented along the $[001]$ direction is similar to the monomer spectrum. However, the shoulder is shifted slightly towards lower energies. The spectrum of dimers oriented along the $[1\bar{1}0]$ direction reveals a shoulder at 0.36 V with a small peak at 0.52 V . For trimers oriented along the $[1\bar{1}0]$ direc-

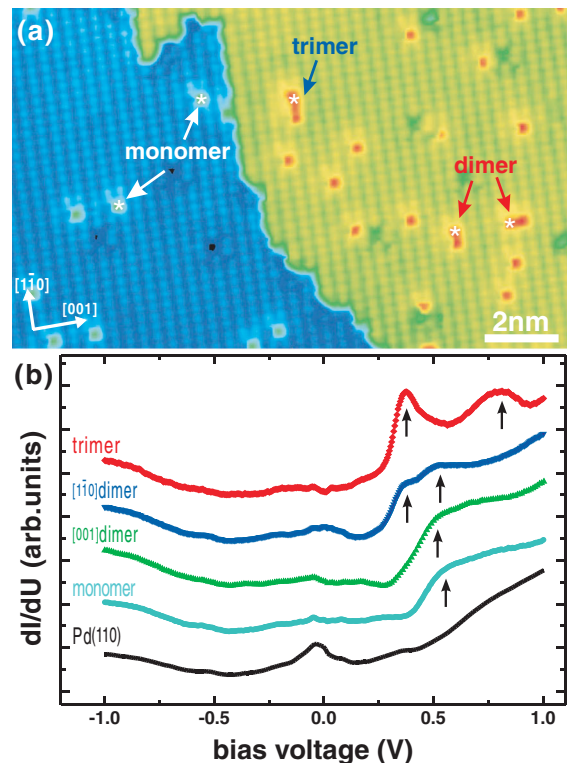


FIG. 2 (color). Topography image of Fe adatoms deposited at 6 K . Imaging conditions: $15 \times 9.1 \text{ nm}$; $V = 24.9 \text{ mV}$, $I = 20 \text{ nA}$. (b) dI/dU spectra for Fe monomers, dimers, and trimers [marked by stars in (a)] on Pd(110) taken at the deposition temperature (6 K). The spectra of Fe adatoms show shoulders or peaklike features at around $0.3\text{--}0.5 \text{ V}$.

tion, two peaks are observed: one at 0.37 V and another at 0.80 V. The Fe atoms can be easily distinguished from the Pd substrate that shows only a peak just at E_F .

A similarity between the spectra of the Fe monomers and the dimers oriented along [001], which differ from the spectrum of the dimers oriented along $[1\bar{1}0]$, is clearly visible. This suggests that the atomic interaction within the dimers oriented along $[1\bar{1}0]$ is stronger than the interaction within the dimers oriented along [001]. This is consistent with the different atomic distances for these two types of dimers (0.275 and 0.389 nm, respectively). This phenomenon indicates that the formation of atomic wires is favored along the $[1\bar{1}0]$ direction. Comparing the spectrum of the trimers (oriented along the $[1\bar{1}0]$ direction) with the calculated d -LDOS of the Fe atomic chains [13], one can see that two peaks above E_F characterize them both. This means that the spectrum of the Fe trimers is representative of the Fe atomic chains formed on Pd(110). With this, we can conclude that a presence of peaks at approximately 0.5 V above E_F is clearly a fingerprint of the Fe atoms, which does not change excessively with the increasing length of the chains. Comparing the spectra of Fe deposited at 6 K with the spectrum taken for the atomic chains formed by an Fe deposition at RT, a conclusion can be immediately drawn: the atomic chains shown in Fig. 1(a) are made of Pd, not Fe. Since all the spectra taken from the atomic chains after deposition of Cr, Mn, Fe, Co, and Ni at RT are identical, in all cases the atomic chains are formed from Pd regardless of the material which was deposited on Pd(110).

Based on our results, it is immediately clear that the growth process of $3d$ metals on Pd(110) and the mechanism of self-organization of the Pd atomic chains is associated with the atomic intermixing between the deposited atoms and the substrate. As usual for epitaxy, the formation of Pd monoatomic chains on Pd(110) by depositing a submonolayer of $3d$ metals involves intermixing, diffusion, and aggregation. The interface intermixing is believed to originate from the large lattice mismatch between the deposited material and the substrate [taking Ni on Pd(110) as an example; the lattice mismatch is larger than 5% in this case [13]]. The deposited atoms are confined to the topmost substrate layer, while the expelled substrate atoms form the adlayer structures [14,15]. Conversely, a (110) substrate is an ideal template for self-organization of one-dimensional atomic structures if compared to (111) and/or (100) surfaces. The deep channels along $[1\bar{1}0]$ favor the diffusion along this direction. Large atomic distances along [001] suggests that the surface structures aggregated along $[1\bar{1}0]$ are more stable than the aggregates formed along the [001] direction. In summary, the atomic intermixing, anisotropic surface diffusion, and aggregation of the $3d$ atoms deposited on Pd(110) at RT result in the formation of Pd monoatomic chains oriented along the $[1\bar{1}0]$ direction.

The growth mechanism has been confirmed by a recent theoretical calculation [13]. When a deposited atom lands at the Pd surface, at first it incorporates into the topmost substrate layer leaving a Pd atom at the surface. Then the Pd atom diffuses along the $[1\bar{1}0]$ direction until it meets other Pd atoms forming a dimer, a trimer, or a chain. These surface processes and their priorities are governed by the different energies involved. For the surface diffusion, the adatoms jump from one atomic site to the next with the total energy of the system remaining unchanged. Incorporation of an adatom into the topmost substrate layer decreases the total energy of the system by 0.34 eV. This occurs with the barrier for intermixing of $E_2 = 0.32$ eV, which is comparable to the barrier for diffusion along the $[1\bar{1}0]$ direction of $E_1 = 0.30$ eV. From this calculation, one can conclude that a replacement of a substituted Pd atom by a deposited atom is energetically and kinetically feasible at RT. Thus, it favors the formation of atomic chains made of Pd instead of the chains made of the deposits.

The diffusion rate of the adatoms on the surface strongly depends on the temperature of the substrate that would

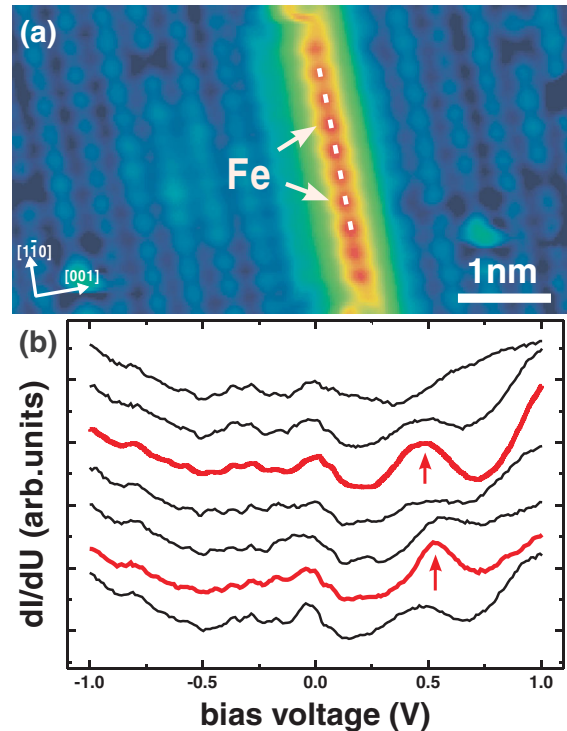


FIG. 3 (color). (a) Topography image for 0.12 ML Fe deposited on Pd(110) at $T = 40$ K and then slightly warmed up to RT. Imaging conditions: 6×3.3 nm; $V = 17.6$ mV, $I = 17.7$ nA. (b) The dI/dU spectra of an atomic chain taken at the positions marked by white spots in (a). Most of the spectra (drawn in black) are identical to the spectra of Pd. Only the spectra drawn in red, recorded at two positions [marked by white arrows in (a)], show a peak (indicated by red arrows) at around 0.47 and 0.52 V, which confirm the presence of Fe atoms at these positions.

eventually alter the final topography of the surface. The energy barrier for diffusion, $E_1 = 0.30$ eV, corresponds to a diffusion temperature (i.e., the temperature below which the thermal energy of the atoms is too small to overcome the diffusion barrier) of about 120 K [16]. At temperatures well below the diffusion temperature, the atoms landing at the surface are frozen [as shown in Fig. 2(a)] and thus mostly monomers are formed. Only by chance, two or three adatoms landing at the surface close to each other can form dimers or trimers. For RT growth, the thermal energy is well above the barrier E_1 for diffusion along the $[1\bar{1}0]$ direction and above the intermixing barrier E_2 . Thus, the atomic incorporation into the surface layer happens shortly after landing. At RT, all the adatoms exchange their positions with the substrate Pd atoms before they would meet other adatoms or substituted Pd atoms and form stable atomic chains. This is why all the atomic chains shown in Fig. 1 are made of Pd and show identical spectra.

By depositing 3d metals at low temperature and then gently warming them up to RT, one may enhance the probability that the deposited Fe atoms and expelled Pd atoms will meet each other and form mixed Fe-Pd atomic chains. Results of the corresponding experiment, mainly the dI/dU spectra taken from each atom of the chain formed after growing at 40 K, are shown in Fig. 3. It is clearly visible that there are two spectra (drawn in red) which show a pronounced peak (indicated by the red arrows) at around 0.47–0.52 V. This peak is strongly reduced for adjacent atoms such that all the other spectra are similar to the spectrum of the Pd chains. According to the discussion above, we identify the peak as characteristic for Fe atom. This means that the chain, made mostly of Pd, contains two Fe atoms. A slight difference in the peak shape and the peak position in comparison to the single atoms of Fe is not surprising. This is because the Fe atoms embedded in the Pd chain are not expected to have electronic structure identical to those of the single Fe atoms. The stabilization of mixed Fe-Pd chains at RT reflects the high stability of the Fe-Pd bonding within the atomic chains.

With the ability to identify single Fe atoms embedded in the Pd surroundings, it should be possible to identify the Fe atoms incorporated into the topmost substrate layer. No indication of Fe, however, was found with the spectra taken from each atom of the substrate surface layer within the investigated sample area. Most likely, after substituting the Pd atoms, the adatoms do not stabilize at the topmost layer, but instead continue diffusion into the crystal volume. This observation needs to be confirmed by theoretical calculation.

In summary, by applying the STM/STS technique we have experimentally confirmed the formation of Pd monoatomic chains on Pd(110) after depositing submonolayer of 3d transition metals like Cr, Mn, Fe, Co, and Ni.

The growth mechanism is explained by intermixing, anisotropic diffusion, and aggregation in agreement with recent theoretical calculations [13]. The results clarify the long-debated issue of the chemical composition of the atomic chains formed on Pd(110). Our finding indicates the complexity of the surface processes. In particular, we emphasize atomic intermixing, which must be considered seriously when fabricating self-assembled and self-organized nanostructures.

*clgao@sjtu.edu.cn

- [1] See, e.g., R.J. Warburton, C. Schaflein, D. Haft, F. Bickel, A. Lorke, K. Karrai, J.M. Garcia, W. Schoenfeld, and P.M. Petroff, *Nature (London)* **405**, 926 (2000); Yi Cui and C.M. Lieber, *Science* **291**, 851 (2001); S.S. Parkin, M. Hayashi, and L. Thomas, *Science* **320**, 190 (2008).
- [2] Y. Chen and A. Pepin, *Electrophoresis* **22**, 187 (2001).
- [3] J. Tersoff, C. Teichert, and M.G. Lagally, *Phys. Rev. Lett.* **76**, 1675 (1996); H. Brune, M. Giovannini, K. Bromann, and K. Kern, *Nature (London)* **394**, 451 (1998); Z. Gai, B. Wu, J.P. Pierce, G.A. Farnan, D. Shu, M. Wang, Z. Zhang, and J. Shen, *Phys. Rev. Lett.* **89**, 235502 (2002); Th. Schmidt, J.I. Flege, S. Gangopadhyay, T. Clausen, A. Locatelli, S. Heun, and J. Falta, *Phys. Rev. Lett.* **98**, 066104 (2007).
- [4] De Wolf and J. Villain, *Europhys. Lett.* **13**, 389 (1990).
- [5] L.E. Jensen, M.T. Bjork, S. Jeppesen, A.I. Persson, B.J. Ohlsson, and L. Samuelson, *Nano Lett.* **4**, 1961 (2004).
- [6] H. Röder, E. Hahn, H. Brune, J.-P. Bucher, and K. Kern, *Nature (London)* **366**, 141 (1993).
- [7] H. Brune, *Surf. Sci. Rep.* **31**, 121 (1998).
- [8] Z. Zhang and M.G. Lagally, *Science* **276**, 377 (1997).
- [9] F. Nouvertne, U. May, M. Bamming, A. Rampe, U. Korte, G. Guntherodt, R. Pentcheva, and M. Scheffler, *Phys. Rev. B* **60**, 14382 (1999).
- [10] J. Lindner, P. Pouloupoulos, F. Wilhelm, M. Farle, and K. Baberschke, *Phys. Rev. B* **62**, 10431 (2000).
- [11] J.P. Bucher, E. Hahn, P. Fernandez, C. Massobrio, and K. Kern, *Europhys. Lett.* **27**, 473 (1994).
- [12] L. Yan, M. Przybylski, Y. Lu, W.H. Wang, J. Barthel, and J. Kirschner, *Appl. Phys. Lett.* **86**, 102503 (2005).
- [13] O.V. Stepanyuk, N.N. Negulyaev, P.A. Ignatiev, M. Przybylski, W. Hergert, A.M. Saletsky, and J. Kirschner, *Phys. Rev. B* **79**, 155410 (2009).
- [14] S. Rousset, S. Chiang, D.E. Fowler, and D.D. Chambliss, *Phys. Rev. Lett.* **69**, 3200 (1992).
- [15] J. Tersoff, *Phys. Rev. Lett.* **74**, 434 (1995).
- [16] Considering the coverage of 0.01 ML and deposition rate of 0.2 ML/min, the deposition time is 3 sec. For diffusion from one site to the next, its probability is $\nu_0 \exp(-E_{1\bar{1}0}^b/k_B T)$, where $\nu_0 = 1 \times 10^{12} \text{ s}^{-1}$ and k_B is the Boltzmann constant. The diffusion happens when the diffusion probability summed for the deposition time is larger than 1. The $E_{1\bar{1}0} = 0.30$ eV and the deposition time of 3 sec give the critical diffusion temperature $T = 120$ K.