

## Diffusion Kinetics in the Pd/Cu(001) Surface Alloy

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We use atom-tracking scanning tunneling microscopy to study the diffusion of Pd in the Pd/Cu(001) surface alloy. By following the motion of individual Pd atoms incorporated in the surface, we show that Pd diffuses by a vacancy-exchange mechanism. We measure an effective activation energy for the diffusion of incorporated Pd atoms of 0.88 eV, which is consistent with an *ab initio* calculated barrier of 0.94 eV.

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Whereas the stability of many alloy structures is understood quantitatively, the kinetics of alloy formation and ordering are largely unknown. Characterizing these processes is difficult because the local chemical and structural environment is usually inhomogeneous. In addition, determining the motion of individual atoms is challenging experimentally. However, by choosing simple alloy geometries it is possible to characterize particular kinetic processes in detail. In this letter, we investigate the ordering kinetics of Pd/Cu alloys by following the motion of individual Pd atoms incorporated in the Cu(001) surface. By measuring the time between diffusion events and the distribution of jump lengths, and comparing the results to Monte Carlo simulations and first-principles total-energy calculations, we show that incorporated Pd atoms diffuse via lateral exchange with surface vacancies.

Pd atoms are immediately incorporated into the Cu(001) surface when deposited at room temperature. For coverages greater than 0.4 monolayers (ML), an ordered  $c(2 \times 2)$  alloy structure is observed [1]. The Pd atoms are confined to the top layer of the substrate in a checkerboard pattern characterized by Cu-Pd nearest-neighbor. First-principles electronic structure calculations show that the tendency to form this ordered surface alloy is particularly strong [2]. Annealing the alloy structure above 425 K results in Pd diffusion into the bulk [3]. The mechanism by which randomly incorporated Pd atoms form the ordered  $c(2 \times 2)$  alloy phase remains unknown. Two possible ordering mechanisms have been considered in the literature [4–6]. One possibility is that an incorporated Pd atom exchanges with a Cu adatom. The Pd atom, now on the surface, diffuses rapidly and eventually incorporates at a new location. Schmid *et al.* found that this mechanism is operative for a Cu/Co monolayer on Ru(001) [5]. An alternative mechanism, originally proposed by Flores *et al.* in a study of Mn/Cu(001), is vacancy-mediated diffusion [4]. In this scenario, an incorporated Pd atom diffuses via lateral exchange with a vacancy at the surface. In contrast to

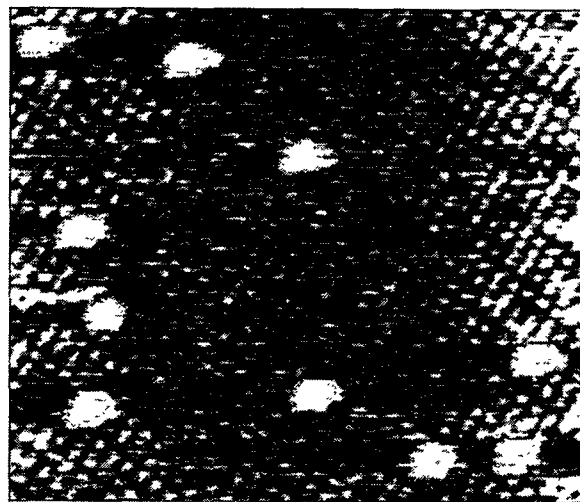


FIG. 1: STM Image ( $95 \times 85 \text{ \AA}^2$ ) of the Cu(001) surface after deposition of 0.01 ML of Pd at room temperature. The large protrusions are incorporated Pd atoms.

adatom-mediated diffusion, the Pd atom remains incorporated as it diffuses. Recent measurements show that Pd atoms incorporated in Cu(001) diffuse via this mechanism [6].

We use atom-tracking scanning tunneling microscopy (STM) [7] to follow the motion of incorporated Pd atoms with a time resolution of 1 ms. In atom tracking STM a lateral feedback mechanism is used to lock the tip above an incorporated Pd atom as it moves. By recording the position of the atom as a function of time, we determine the mechanism of diffusion. Specifically, by comparing the measured distributions of residence times and jump lengths to Monte Carlo simulations, we show that incorporated Pd atoms diffuse via vacancy exchange. From measurements of the average hop rate as a function of substrate temperature, we extract an activation energy

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for Pd diffusion of  $0.88 \pm 0.03$  eV. Formally, this activation energy is the sum of the vacancy formation energy and the vacancy-Pd exchange barrier.

To compute configuration energies, we use the VASP (Vienna *ab initio* simulation package)[8] total-energy code, its ultrasoft pseudopotentials[9], and the Perdew-Wang '91 version of the Generalized Gradient Approximation[10]. The computational unit cells are  $2\sqrt{2} \times 2\sqrt{2} \times 6$  layers and the total energy is determined from 8-10 k-points. We find that the large number of k-points is critical to determine a properly converged energy. To compute the transition barrier energies, we use Jónsson, Mills, and Jacobsen's nudged elastic band method[11] within the VASP total-energy code.

The experiments are performed in ultra-high vacuum (base pressure  $1 \times 10^{-10}$  torr) using a variable-temperature STM. A clean Cu(001) surface is obtained by repeated cycles of sputtering for 15 minutes with 1kV  $\text{Ne}^+$  ions, followed by annealing at 800 °C for 5 min. Low coverages of Pd ( $< 0.01$  ML) are deposited by heating a tungsten filament wrapped with Pd wire. The STM images and tracking data were recorded in constant current mode with a tip-sample bias of -20 mV. Use of tunneling biases in the range -3 V to +3 V produced no measurable effect on the measured kinetics or images.

Upon deposition at room temperature, Pd atoms immediately place exchange with Cu atoms in the surface layer, forming an ultra-thin alloy. An image of the surface following deposition is shown in Fig. 1. The Pd atoms are imaged as large protrusions and are located on lattice sites. A lateral feedback mechanism that continuously moves the tip 'uphill' is used to lock the tip above a Pd atom. The diffusion path of the Pd atom is determined by recording the position of the tip as a function of time. Typically the tip position is recorded at a rate of 1 kHz. A two-dimensional map of the sites visited by a Pd atom at 62 °C is shown in Fig. 2. In this particular data set, the diffusing Pd hopped 71 times in 431 seconds (some sites are visited more than once).

By analyzing the Pd coordinates as a function of time we determine the residence time – the time between hops. The distribution of residence times for a Pd atom diffusing at 62 °C is shown in Fig. 3. In this data set, the atom hopped 853 times in a time interval of 5557 s. If the time between Pd hops is uncorrelated, the distribution of residence times should decay exponentially. The solid line in Fig. 3 is an exponential decay with decay constant equal to the average residence time. The agreement between the solid line and the data points indicates Pd diffusion is an activated process, and there is no correlation between Pd diffusion events.

An analysis of the temperature dependence of Pd diffusion shows that from 31 °C to 69 °C, the average residence time decreases from 145.3 s to 5.0 s. Because Pd diffusion is an activated process, the hopping rates measured for this temperature range follow an Arrhenius form with an activation energy of  $0.88 \pm 0.03$  eV (Fig.

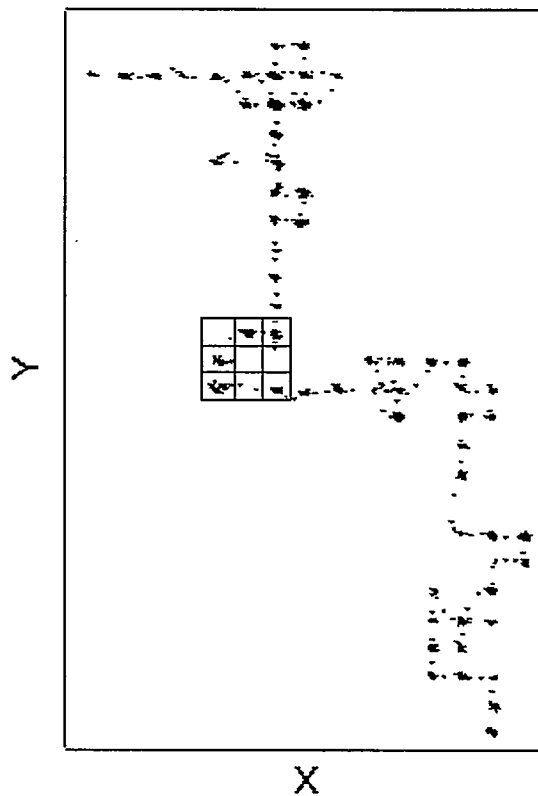


FIG. 2: Site visitation map of a Pd atom at 62 °C, with the Cu(001) unit mesh superimposed.

4).

From the experimental data taken at 62 °C, we compile the distribution of jump lengths, as seen in Fig. 3 (dark bars). The distribution shows that many of the jumps are longer than the Cu(001) nearest-neighbor distance ( $a = 2.55$  Å). There is a 75.2% chance that the Pd atom appears to take a single hop, 17.0% for a diagonal ( $\sqrt{2}a$ ) hop, and 4.2% probability of a longer jump ( $2a$ ). Within the statistical error, the distribution of jump lengths is independent of temperature over the range 31 °C to 69 °C. Jumps greater than unit length are actually comprised of a 'burst' of single hops in rapid succession. Because the motion of the Pd atom during the burst is too fast for the atom tracker to resolve, we cannot measure the details of the path during the long jump. Rather, we measure the time between the short bursts of jumps.

In the context of the two potential diffusion mechanisms, a burst has distinct meanings. For the adatom-exchange mechanism, the burst corresponds to the Pd adatom diffusion on the surface before re-incorporation back into the surface. We would measure only the initial and final incorporated states. In this picture, the rate at which bursts occur is governed by the rate at which an incorporated Pd atom exchanges with the Cu adatoms. For vacancy-mediated diffusion, a burst corresponds to

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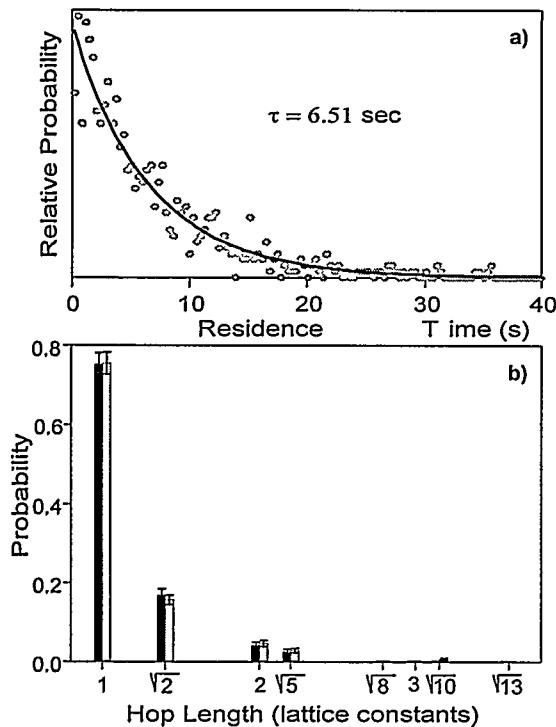


FIG. 3: (a) Residence time distribution (time between measured Pd hops) at 62 °C. The solid line is the expected exponential decay if the time between hops is uncorrelated. (b) Distribution of jump lengths at 62 °C. Dark bars represent experiment whereas the shaded bars are simulation.

the repeated visitation of the Pd atom by a (rapidly) diffusing surface vacancy. The rate of Pd diffusion is determined by the visitation rate of surface vacancies. These two rates are governed by very different energetics. First-principles calculations indicate the activation energy for Pd-Cu adatom exchange is 1.16 eV, while the activation energy for vacancy diffusion is only 0.466 eV.

The distributions of jump lengths for the two mechanisms are also quite different. To see this, we consider the fraction of jumps of length  $\sqrt{2}a$ . Since Pd atoms incorporate randomly at room temperature, rather than at steps, the probability of incorporation must be comparable to that of surface diffusion. In this limit, a Pd atom that exchanges with a Cu adatom will not diffuse far before re-exchanging. The jump length distribution can be computed trivially if we assume the Pd atoms immediately re-exchange into the surface. The number of  $\sqrt{2}a$  hops will be half that of single hops. For vacancy-mediated diffusion, the fraction of  $\sqrt{2}a$  hops is much lower. The reason for this is that the vacancy must execute a minimum of *four* coordinated hops in order to move the Pd atom diagonally. In our experiments, we measure a ratio of  $\sqrt{2}a$  to single hops of about 0.23, significantly lower than the estimate for the adatom-exchange mechanism

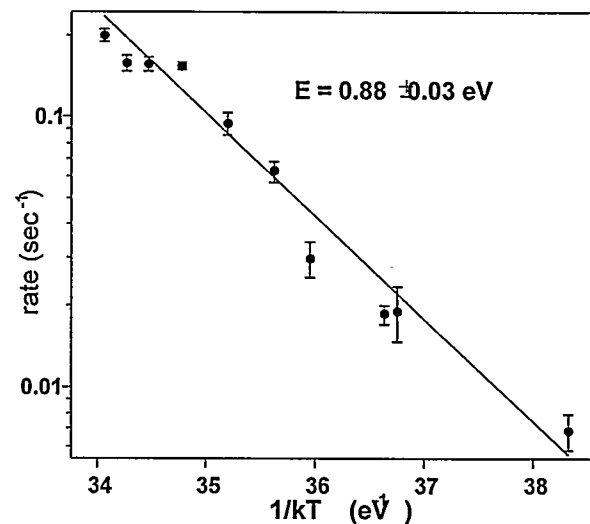


FIG. 4: Temperature dependence of the average hop rate of an incorporated Pd atom. The data follow an Arrhenius form with an activation energy of 0.88 eV and measured prefactor of  $10^{12.4 \pm 0.4}$  Hz.

(0.5).

These simple arguments can be made precise by simulating the two diffusion processes using Monte Carlo techniques. In the simulation for exchange diffusion there is one free parameter: the average number of hops completed on the surface before re-incorporation. This parameter is governed by the ratio of the surface hop rate to the incorporation rate. The best agreement with experiment is achieved when the incorporation rate is comparable to the hop rate. However, even in this limit the computed jump length distribution does not describe experiment: there are far too few single hops, too many diagonal hops (greater than 30%), and a long tail of hops greater than  $2a$ . Consequently, the measured distribution of jump lengths can never be attained for the exchange diffusion model, due to the consistently-high percentage of predicted diagonal hops.

On the other hand, Monte Carlo simulations for vacancy-mediated diffusion accurately describe the data. In the simulation a vacancy executes a random walk on a grid with periodic boundary conditions. We initially assume no interaction between the vacancy and Pd. Since there is infinite time resolution in the simulation, only single hops of the Pd are observed. We account for the finite sampling time of the atom tracker ( $\Delta t = 1$  ms) by 'binning' the simulation data. The free parameter in this model is the ratio of the vacancy hop rate to the sampling rate. Once binned, the simulation data exhibits the anticipated trend of a low probability of diagonal jumps.

However, a small but significant discrepancy between the simulation and measurement remains. Experimentally 75% of the hops are of unit length, whereas the vacancy simulation predicts 62%. This discrepancy arises

from our initial assumption of negligible interaction between the Pd atom and vacancy. A repulsion between the vacancy and Pd reduces the number of long jumps. Intuitively, we expect a repulsion. Pd exchanges with a Cu atom in the first place due to its higher affinity for Cu neighbors. Therefore, removing one of those neighbors through the presence of a vacancy results in a higher energy configuration. Including a small nearest-neighbor ( $< 50$  meV) repulsion between the vacancy and Pd atom in the simulation leads to quantitative agreement between the measured and calculated jump length distributions. This is seen in the shaded bars of Fig. 3, where a 40 meV repulsion between the vacancy and Pd atom[12] results in a high percentage of single hops, with the appropriate number of diagonal hops. Consequently, we conclude that the diffusion of the Pd in the surface alloy proceeds via a vacancy mediated mechanism.

Since the hop rate is not correlated, the rate should be proportional to both the vacancy concentration and vacancy hop rate. Therefore, the activation energy for Pd diffusion is equal to the sum of the vacancy formation energy and the energy barrier associated with lateral Pd-vacancy exchange. The computed energies using VASP are 0.474 and 0.466 eV, respectively. The sum (0.94 eV) is consistent with the measured activation energy of 0.88 eV. In the adatom-exchange model, the activation energy corresponds to the sum of the Cu adatom formation energy and the Pd-Cu exchange barrier. Within VASP the sum of these barriers is 1.73 eV and is clearly inconsistent with the measured activation energy. These results further support our conclusion that the diffusion of incorporated Pd atoms occurs via vacancy diffusion.

In summary, by measuring the motion of incorporated Pd atoms as a function of temperature, and comparing the results to Monte Carlo simulations and first-principles total-energy calculations, we conclude that Pd atoms diffuse via a vacancy-mediated mechanism. Comparison of the measured distribution of jump lengths agrees well with Monte Carlo simulations of vacancy-exchange if a small repulsion between the Pd and vacancy is assumed. The measured activation energy for Pd diffusion (0.88 eV) is consistent with the first-principles calculations of the sum of the vacancy formation energy and vacancy diffusion barrier. The experiments were performed at Sandia National Laboratories, a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the US DOE under contract No.

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## REFERENCES

- [1] S. H. Lu, Z. Q. Wang, S. C. Wu, C. K. C. Lok, J. Quinn, Y. S. Li, D. Tian, F. Jona, and P. M. Marcus, *Phys. Rev. B* **37**, 4296 (1988); P. W. Murray, I. Stensgaard, E. Laegsgaard, and F. Besenbacher, *Phys. Rev. B* **52**, R14 404 (1996); P. W. Murray, I. Stensgaard, E. Laegsgaard, and F. Besenbacher, *Surf. Sci.* **365**, 591 (1996).
- [2] J. Kudrnovsky, S. K. Bose, and V. Drchal, *Phys. Rev. Lett.* **69**, 308 (1992).
- [3] A. R. Koymen, K. H. Lee, G. Yang, K. O. Jensen, and A. H. Weiss, *Phys. Rev. B* **48**, 2020 (1993).
- [4] T. Flores, S. Junghans, M. Wuttig, *Surf. Sci.* **371**, 14 (1997).
- [5] A. K. Schmid, J. C. Hamilton, N. C. Bartelt, and R. Q. Hwang, *Phys. Rev. Lett.* **77**, 2977 (1996).
- [6] R. van Gastel, E. Somfai, W. van Saarloos, and J. W. M. Frenken, (unpublished).
- [7] B. S. Swartzentruber, *Phys. Rev. Lett.* **76**, 459 (1996).
- [8] G. Kresse and J. Hafner, *Phys. Rev. B* **47**, 558 (1993); *Phys. Rev. B* **49**, 14251 (1994); G. Kresse and J. Furthmüller, *Comput. Mat. Sci.* **6**, 15 (1996); *Phys. Rev. B* **54**, 11169 (1996).
- [9] D. Vanderbilt, *Phys. Rev. B* **41**, 7892(1990); A. Pasquarello, K. Laasonen, R. Car, C. Lee and D. Vanderbilt, *Phys. Rev. Lett.* **69**, 1982(1992); K. Laasonen, A. Pasquarello, R. Car, C. Lee and D. Vanderbilt, *Phys. Rev. B* **47**, 10142(1993); G. Kresse and J. Hafner, *J. Phys.: Cond. Mat.* **6**, 8245(1994).
- [10] J. P. Perdew, in *Electronic Structure of Solids '91*, edited by P. Ziesche and H. Eschrig (Akademie Verlag, Berlin, 1991); J. P. Perdew and Y. Wang, unpublished.
- [11] H. Jónsson, G. Mills, and K. W. Jacobsen, in *Classical and Quantum Dynamics in Condensed Phase Simulations*, edited by B. J. Berne, G. Ciccotti, and D. F. Coker (World Scientific, Singapore, 1998).
- [12] The VASP total-energy calculations yield a vacancy-Pd repulsion of 45 meV.