

Direct Observation of the Self-Diffusion Mechanism on the Ag(100) Surface

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Perturbed angular correlation experiments using soft-landed ¹¹¹Ag probe atoms on a Ag(100) surface allow monitoring of the self-diffusion of Ag on the surface. In total, three different sites are observed as a function of substrate temperature: the adatomic terrace site in the temperature interval between 80 and 150 K, the adatomic step site between 130 and 180 K, and the substitutional terrace site starting from 150 K, where adatoms are still present on the surface. These data could be explained only by assuming that the hopping diffusion mechanism is active at low temperatures, while the exchange diffusion mechanism is responsible for the observed substitutional terrace site at 150 K. [S0031-9007(98)07711-4]

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In the conventional picture, adatoms diffuse on surfaces by hopping between adjacent binding sites on the surface, across a potential barrier. During a growth experiment adatoms migrate towards island edges, where they get trapped. This mechanism has been directly observed by field ion microscopy for a variety of bcc and fcc adatom-substrate combinations [1]. However, another adatom diffusion mechanism has been experimentally observed in the case of self-diffusion of Ir on Ir(100) [2] and of Pt on Pt(100) [1]. In this case, the diffusing adatom replaces a substrate atom, which becomes in this way an adatom and continues the diffusion process in the same manner. This exchange diffusion process has also been theoretically predicted for self-diffusion of Al on Al(100) [3]. Recent density functional theory calculations [4,5] performed for Ag on Ag(100) predict that Ag diffuses by hopping on flat terraces, while it exchanges across step-down edges, replacing an in-step atom. Eventually, the latter atom will diffuse along the step until it will get trapped at a kink.

In this paper we address the specific case of self-diffusion of Ag on Ag(100), by performing a perturbed angular correlation (PAC) study on ¹¹¹Ag probe atoms, deposited on the surface by the soft-landing technique [6]. The PAC method is highly suited to study this system because it gives information about the *local* environments of the ¹¹¹Ag probe atoms which are *different* for the two proposed diffusion mechanisms and because the PAC probe atom is *not* an impurity atom. Figure 1 illustrates initial and final situations for the two different diffusion mechanisms and for the step-correlated exchange process proposed by Yu *et al.* [4,5], where an adatom residing on the terrace edge can replace a step atom which will occupy an adatomic step site after the exchange process.

Figure 2 shows the decay schemes of the ¹¹¹Ag and ¹¹¹In isotopes, which both feed the 245 keV intermedi-

ate state of ¹¹¹Cd used in the PAC technique. The 171–245 keV cascade in the ¹¹¹In decay is much more efficiently populated than the 97–245 keV cascade in the ¹¹¹Ag decay. Therefore, we can study the characteristics of the observable surface sites of the probe atoms by using the ¹¹¹In probe, which allows for better statistics.

A vicinally cut Ag(100) crystal was prepared by a number of sputter and anneal cycles. Low-energy electron diffraction patterns indicated the formation of monoatomically high terraces having a width of 8.5 interatomic distances. No contamination was detected with Auger electron spectroscopy. A second sample was made by growing a 20 nm Fe buffer layer on a MgO(100) substrate, at a substrate temperature of 523 K, annealing it at 615 K and then depositing a 1 μ m thick Ag layer at 423 K. Reflection high-energy electron diffraction patterns recorded during growth revealed an intense reflection spot, sharp rods, and even a Kikuchi pattern. These are clear indications that the Ag layer grew in a layer-by-layer mode. An x-ray diffraction measurement of the region around the MgO (2,2,4) diffraction peak indicated that the Ag layer was crystalline and epitaxial. The measured Ag lattice parameters, perpendicular and parallel to the surface, were found to be within 0.2% equal to that of bulk Ag. This indicates that the Ag layer was almost fully relaxed. The mosaicity of the grown layer was 0.23°, which is 40% higher than the mosaicity of the substrate. Despite the crystalline quality of the layer, an atomic-force microscopy study revealed a complicated surface morphology with “valleys and hills,” containing terraces having widths varying between 2 and 30 nm. Even though this is an unexpected result, a relative high density of steps could increase the probability of observing the predicted exchange process across the steps [4,5]. Auger electron spectroscopy, performed before and after the PAC measurements, could not detect any surface contamination, including Fe.

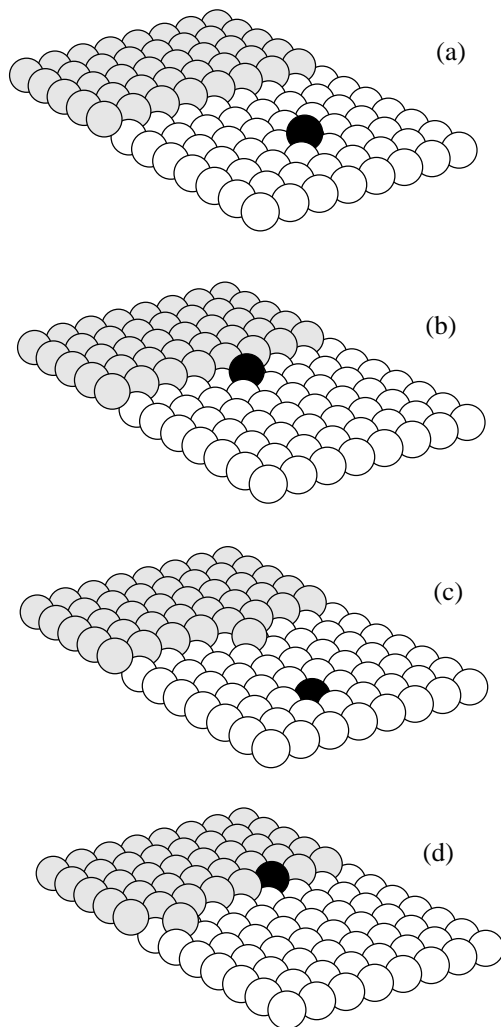


FIG. 1. The initial situation after deposition (a), final sites of radioactive ^{111}Ag atoms (black spheres) on a $\text{Ag}(100)$ surface in case the adatom diffusion proceeds via the hopping mechanism (b) or the exchange mechanism (c). The exchange mechanism across the steps would give the sites observable in (d).

This second sample has the advantage that the MgO substrate is more transparent to the low-energy γ rays of ^{111}Ag and all of the available detector combinations can be used for the PAC analysis. The $\gamma\gamma$ -coincidence count rates were measured using a standard four detector slow-fast setup. All of the PAC measurements were performed at 80 K. In the case of ^{111}Ag , typical measurement times varied between 24 and 36 hours.

About 0.01% ML (monolayer) of ^{111}In was soft-landed on the vicinal surface at 80 K, where thermally activated diffusion is inhibited. Directly after the deposition, 20% of the total visible ^{111}In probe atoms resides at steps (f_{as}), while 60% resides on terraces, as adatoms (f_{at}). The PAC spectrum recorded after the deposition and its Fourier transform are shown in Fig. 3. Upon annealing, more ^{111}In atoms reach the steps starting from 100 K; they are incorporated into steps between 160 and 200 K and, finally, in terraces. This behavior is similar to earlier

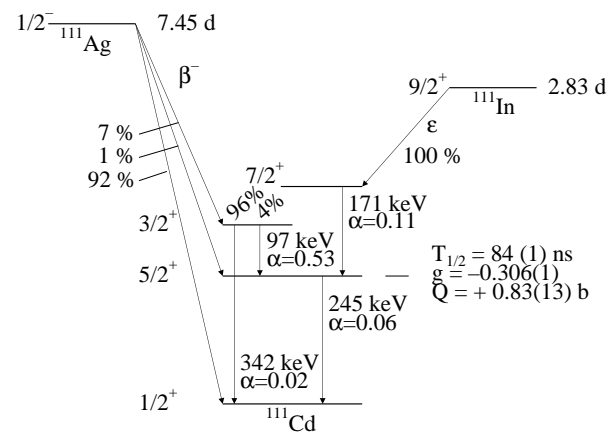


FIG. 2. The (partial) decay scheme of ^{111}In and ^{111}Ag PAC probes to the ground state of ^{111}Cd .

experiments where evaporated ^{111}In probe atoms were used [7]. The quadrupole coupling constants ν_Q of the observed surface sites are also in good agreement with those reported by Fink *et al.* [7] and by Wesche *et al.* [8].

A series of 5 eV depositions of ^{111}Ag probe atoms on the $\text{Ag}(100)$ surface was performed at substrate temperatures varying from 80 to 240 K, in concentrations of approximately 1% ML. The deposition times varied between 45 and 90 min.

Typical PAC spectra together with their Fourier transforms are illustrated in Fig. 4. Three different sites are observable: the adatomic terrace site (f_{at}) at temperatures up to 150 K, the adatomic step site (f_{as}) between 120 and 180 K, and the substitutional terrace site (f_{st}) which appears at temperatures as low as 150 K. The substitutional step site (f_{ss}) has not been observed with certainty. There is an indication that this site might be populated at 180 K, but the corresponding fraction is barely significant, i.e., 8%, which is close to the detection limit in these experiments.

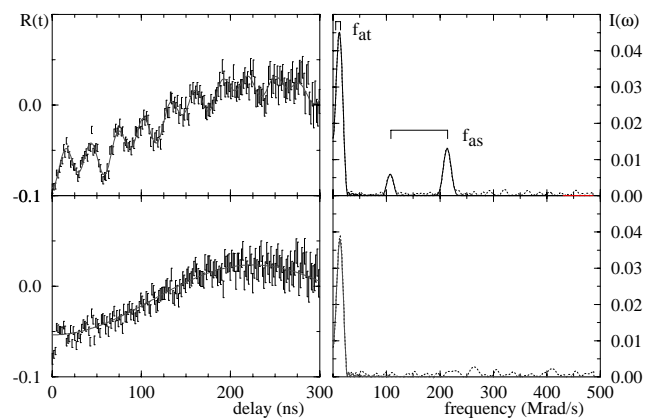


FIG. 3. PAC spectra and their Fourier transforms after deposition of ^{111}In on vicinal $\text{Ag}(100)$ (top) and on $\text{Ag}(100)$ with an energy of 5 eV, at a substrate temperature of 80 K. Solid lines represent the fit. Because of the chosen geometry, the third interaction frequency ($\omega_1 + \omega_2 = \omega_3$) is not observable.

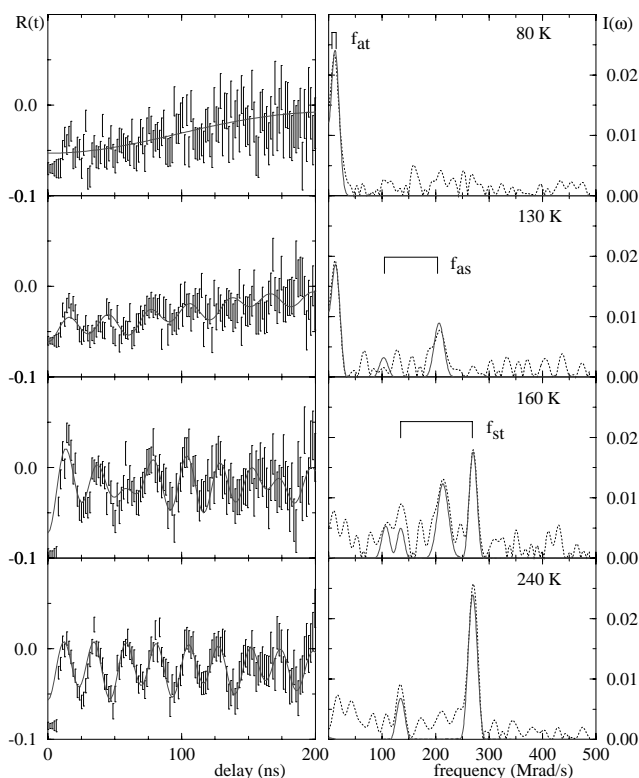


FIG. 4. PAC spectra and their Fourier transforms after deposition of ^{111}Ag on $\text{Ag}(100)$ with an energy of 5 eV. The substrate temperatures are mentioned at the right-hand side. Solid lines represent the fit. Because of the chosen geometry, the third interaction frequency ($\omega_1 + \omega_2 = \omega_3$) is not observable.

In Fig. 5, the measured atomic site fractions of the ^{111}Ag atoms as a function of the deposition temperature are plotted. At temperatures lower than 120 K the ^{111}Ag adatoms are immobile and they occupy adatomic terrace sites (f_{at} in Fig. 4). At slightly higher temperatures (130 K) the adatomic step sites (f_{as}) are also populated.

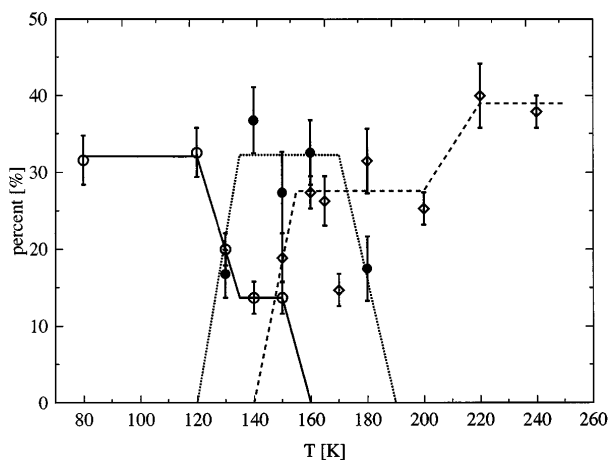


FIG. 5. Atomic site fractions of ^{111}Ag probe atoms [f_{at} (\circ); f_{as} (\bullet); f_{st} (\diamond)] as measured after deposition at different substrate temperatures. The lines in the figure are meant only to guide the eye.

This fraction increases in the temperature interval between 130 and 140 K, while the adatomic terrace site fraction decreases gradually. This is exactly what is expected if the Ag diffusion proceeds by hopping. The fact that the transition is not sharp is, at least partially, caused by the large terrace length distribution in our sample.

The fraction of probe atoms residing at steps remains approximately constant up to 160 K and it vanishes at 190 K, without a corresponding increase of the fraction of another site. In the temperature region between 165 and 200 K the total visible fraction is relatively low. Probably incorporation of ^{111}Ag probe atoms residing at steps starts at this temperature, resulting in the creation of several different sites. As a consequence, the total visible fraction decreases because of the distribution of local electric field gradients. This behavior is also observed for the step-mediated diffusion of ^{111}In into terraces on vicinal $\text{Ag}(100)$ and $\text{Cu}(100)$ [9]. Above 200 K the atoms that diffused into the terrace via the steps occupy already well-defined substitutional terrace sites and contribute to the increase of this fraction. However, this scenario is not able to explain the surprising observation that a significant fraction of the ^{111}Ag probe atoms occupies substitutional terrace sites (f_{st}) at temperatures as low as 150 K, where adatoms are still present on the surface. This fraction becomes even higher at 160 K at the expense of the adatomic terrace fraction, and it remains constant up to 170 K.

In the following, we discuss a number of scenarios which could explain the presence of ^{111}Ag atoms in terraces at low temperatures.

(1) We assume that hopping adatoms recombine with already existing surface vacancies. At 160 K, approximately 25% of the deposited ^{111}Ag atoms occupies substitutional terrace sites (see Fig. 5). In order to accommodate 25% of the deposited atoms in the surface vacancies, we need a vacancy concentration of about 2.5×10^{-3} ML, corresponding to roughly one vacancy per five atoms in each direction. This vacancy concentration is unrealistically high. Still, let us assume that this vacancy concentration is present at the surface. When the adatoms become mobile, they recombine with vacancies while a small fraction may be able to reach the steps. So, adatomic step sites and substitutional terrace sites have to coexist in the PAC spectrum at the temperature where adatoms become mobile, i.e., in the temperature interval 130–140 K. However, this is in contradiction with the experimental results plotted in Fig. 5.

(2) If the deposition energy is slightly higher than the threshold for surface-vacancy creation, the deposited atom will occupy these vacancies athermally [6]. In this case substitutional terrace sites will be occupied already at 80 K. However, this is not observed.

(3) The decay scheme of ^{111}Ag given in Fig. 2 shows that the 342 keV excited level of ^{111}Cd is populated after a β^- decay. The end point energy of the corresponding β spectrum is 698 keV, implying that the maximum recoil energy of the ^{111}Ag nucleus is 6 eV. The average

recoil energy is much lower, approximately 1.5 eV. We conclude that there is a low probability that the recoiling Ag nucleus creates a surface vacancy during the β decay preceding the intermediate state in ^{111}Cd . Nevertheless, the recoiling atom has a very high probability to recombine with the vacancy athermally. This implies that the substitutional terrace site has to be observed in each measurement, independent of the substrate temperature. Figure 5 shows that this is not the case.

(4) Island formation during the deposition process may also lead to the observation of substitutional terrace sites at low temperatures. In order to observe this site, an island size of at least 3×3 probe atoms is needed. Dynamical Monte Carlo simulations of the deposition process [10], using 1% ML Ag deposited at 140 K with a deposition rate of 4×10^{-6} ML/s, indicate that most of the atoms are isolated and approximately 20% form dimers. Deposition of the same dose at 160 K results mainly in the formation of trimers, tetramers, and pentamers, which cannot host substitutional terrace sites. Larger islands give rise to 3% of occupied substitutional terrace sites, which is 1 order of magnitude lower than the measured occupation. Therefore, we conclude that formation of large islands cannot explain that the substitutional terrace and the adatomic step site fractions are about equal at 160 K.

(5) Let us consider the formation of islands at kinks or steps. At least two parallel rows consisting of three atoms are needed in order to create one substitutional terrace site. This effect would be enhanced if the exchange mechanism proposed by Yu *et al.* [4,5] is active since the atoms which diffuse downwards across the step will be incorporated in the steps, and only one row has to be formed along the incorporated probe atom to give rise to a substitutional terrace site. However, also in this case the majority of the atoms would occupy step-correlated sites, in particular, substitutional step sites, which is in disagreement with the measured fractions plotted in Fig. 5.

(6) Until now, we have assumed that diffusion proceeds only by hopping and found that the various scenarios did not offer a satisfactory explanation of the experimental data. Let us now assume that the site-exchange mechanism is responsible for the population of the substitutional terrace site at 150 K. If diffusion takes place by exchange with a terrace atom, the radioactive ^{111}Ag atom (black spheres in Fig. 1) will occupy a substitutional terrace site directly after exchange, while a stable Ag atom (grey spheres in Fig. 1), which is not "seen" by PAC, will finally reach a step edge. The probability that a probe atom returns to an adatomic terrace site is given by the local concentration of adatoms which is about 1% ML. Thermally activated adatom generation is negligible at such low temperatures because the difference in binding energies between adatoms and terrace atoms is approximately 1 eV.

From Fig. 5, one concludes that diffusion by hopping sets in between 120 and 130 K, while site exchange oc-

curs at temperatures about 150 K. The corresponding activation energies can be calculated by assuming a simple Arrhenius behavior. Taking into account the terrace length distribution, we estimate that about 100 hops are necessary in order to reach a step. Taking the prefactor $10^{12 \pm 1} \text{ s}^{-1}$, an activation energy of 0.35(3) eV is obtained. This compares well with the value of 0.40(5) eV found by Langelaar *et al.* [11] from low-energy ion scattering data, especially because that experiment gives precise indications about the moment when all of the adatoms have reached the steps rather than about the onset of the migration.

In the case of the exchange mechanism, one movement is enough to occupy a substitutional terrace site. This gives an activation energy of 0.46(3) eV, i.e., about 0.1 eV higher than the activation energy for hopping. This difference is appreciably lower than theoretically predicted by Yu *et al.* [4,5].

In conclusion, PAC experiments performed on soft-landed ^{111}Ag on a Ag(100) surface allow precise monitoring of the sites occupied by probe atoms after deposition at different substrate temperatures. The observation of the substitutional terrace site at temperatures lower than expected in the case when the probe atoms would be incorporated into terraces via steps could be explained only by assuming that the site-exchange mechanism is active in this temperature region.

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