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Indium adsorption sites at Pd(100) surfaces studied by PAC spectroscopy

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Abstract. Perturbed $\gamma\gamma$ -angular correlation (PAC) experiments have been performed to study the occupation of different surface sites by ^{111}In probe atoms at vicinal Pd surfaces with (100) terrace orientation. Within an isochronal annealing sequence In probes are observed to dwell in adatomic and substitutional step and terrace sites, in agreement with earlier experiments on Cu, Ag and Ni surfaces. The temperature dependence of the electric field gradient for ^{111}In atoms occupying substitutional terrace sites deviates from the behaviour detected on Cu(100), Ag(100) and Ni(100) surfaces. The observed deviation in the low-temperature regime is attributed to the adsorption of hydrogen.

1. Introduction

The number of experimental techniques which can be used for studying surface properties with atomic resolution is limited. Techniques like scanning tunnelling microscopy (STM), field ion microscopy (FIM) and scanning transmission electron microscopy (STEM) produce direct images of the surface structure. Although these techniques have restrictions with respect to the substrates, they have proven to be very powerful. Hyperfine techniques like nuclear magnetic resonance (NMR), Mössbauer spectroscopy and perturbed $\gamma\gamma$ -angular correlation (PAC) spectroscopy can be used to study surfaces as well as interfaces with atomic resolution. The quantity measured in the case of non-magnetic materials is the electric-field-gradient tensor at the nuclear site of suitable probe atoms and can be used as a 'fingerprint' for the occupied site. The quantity is commonly described in its principal-axis system by the largest component V_{zz} ($|V_{zz}| > |V_{yy}| > |V_{xx}|$) and the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$, which reflects the structural symmetry about the principal z -axis [1]. The quadrupole coupling constant $\nu_Q = eQV_{zz}/h$ may be equivalently used to describe the strength of the quadrupole interaction. Since the electric-field-gradient tensor is mainly influenced by the nearest-neighbour atoms, surface properties can be probed on a scale of atomic distances.

Among the hyperfine methods PAC spectroscopy has turned out to be preferable for studying surface diffusion processes. So far PAC experiments using ^{111}In as nuclear probes have been carried out at several low-index surfaces of Cu [2,3], Ag [4], and Ni [5], respectively. First PAC results for probe diffusion on Pd(111) surfaces have been reported by Hunger and Haas [6]. In these experiments four different adsorption sites were identified, each being characterized by a well defined electric field gradient. In particular, adatomic positions on the low-index terraces, adatomic as well as substitutional step sites and substitutional In positions within the topmost monolayer could be distinguished. The

development of the site population was then monitored after low-temperature deposition in the course of isochronal annealing sequences yielding estimates for the activation energies of the respective microscopic diffusion paths. In this paper, first results for ^{111}In diffusion on the Pd(100) surface are reported and compared to earlier results on the (100) surfaces of other FCC metals.

2. Results and discussion

For the present PAC experiments we utilized the isomeric nuclear state ($I = 5/2$, $T_{1/2} = 84$ ns) intermediate between the 172–247 keV $\gamma\gamma$ -cascade in ^{111}Cd , which is populated through electron capture from ^{111}In . The nuclear quadrupole moment of this state ($Q = 0.83(13)$ b) senses the electric field gradient at the probe nuclear site, resulting in an energy splitting of the isomeric nuclear level, characterized by three transition frequencies ω_i . From the measurement of these transition frequencies by the coincident detection of the two γ -quanta the hyperfine interaction parameters can be deduced. For a detailed description of the method we refer to the review article by Klas *et al* [7].

Pd surfaces with (100) terrace orientation and average terrace width in the range between 30–80 Å were prepared by about 20 cycles of Ar^+ sputtering and subsequent annealing to 800 K. Heating the crystals to 1400 K by electron bombardment from the reverse side resulted in high-quality LEED patterns; within a detection limit of about 0.01 ML no impurities were detected by Auger electron spectroscopy. Carbon impurities could only be estimated with an accuracy of about 0.1 ML since the 272 eV carbon peak is superimposed on the Pd MNN line at 274 eV. ^{111}In probe atoms were deposited to an amount of about 10^{-4} ML at a sample temperature of 78 K. With the In deposition, Cl impurities in the range up to 0.02 ML were introduced.

Figure 1 shows PAC time spectra and corresponding Fourier transforms directly after probe deposition and after annealing. Directly after the deposition a weak electric field gradient of $|V_{zz,ad}| = 2.8(5) \times 10^{17}$ V cm $^{-2}$ and an asymmetry parameter of $\eta_{ad} = 0.05(5)$ ($\nu_{Q,ad} = 57(2)$ MHz) were measured (figure 1(a), fraction f_{ad}). The principal z-axis points along the (100) terrace normal. For reasons to be discussed later this electric field gradient is attributed to In probes occupying adatomic sites on the Pd terraces. Annealing to 250 K (figure 1(b)) leads to a new frequency pattern in the Fourier transform, denoted by fraction f_{S1} . The corresponding electric field gradient is characterized by $|V_{zz,S1}| = 6.8(11) \times 10^{17}$ V cm $^{-2}$ and $\eta_{S1} = 0.33(4)$ ($\nu_{Q,S1} = 137(2)$ MHz). After annealing above 300 K two new field gradients were measured: a non-axially symmetric electric-field-gradient tensor with $|V_{zz,S2}| = 7.9(12) \times 10^{17}$ V cm $^{-2}$ and $\eta_{S2} = 0.87(5)$ ($\nu_{Q,S2} = 158(2)$ MHz, fraction f_{S2}) and an almost axially symmetric electric field gradient with $|V_{zz,0}| = 8.1(12) \times 10^{17}$ V cm $^{-2}$ and $\eta_0 = 0.16(3)$ ($\nu_{Q,0} = 163(2)$ MHz, fraction f_0). The principal z-axis of fraction f_0 points along the terrace normal and, in addition, the principal y-axis is found to point along the [110] axis. This fraction is identified with ^{111}In probes on substitutional sites within the (100) terraces, which has turned out to be the most stable site on the Pd(100) surface. It was detected up to annealing temperatures as high as 800 K.

Unfortunately the frequency patterns for the fractions f_{S1} and f_{S2} partly overlap making it impossible to clearly determine the orientation of the corresponding principal-axis systems. However, there is a clear correspondence with results obtained from diffusion experiments on vicinal Cu and Ag surfaces with (100) terraces and steps along [110] directions [3, 4]. In these studies electric-field-gradient tensors of comparable strength and symmetry were detected, which show a clear correlation of the principal-axis system with step orientations. The principal z-axis is tilted with respect to the terrace normal by about 20°; in addition,

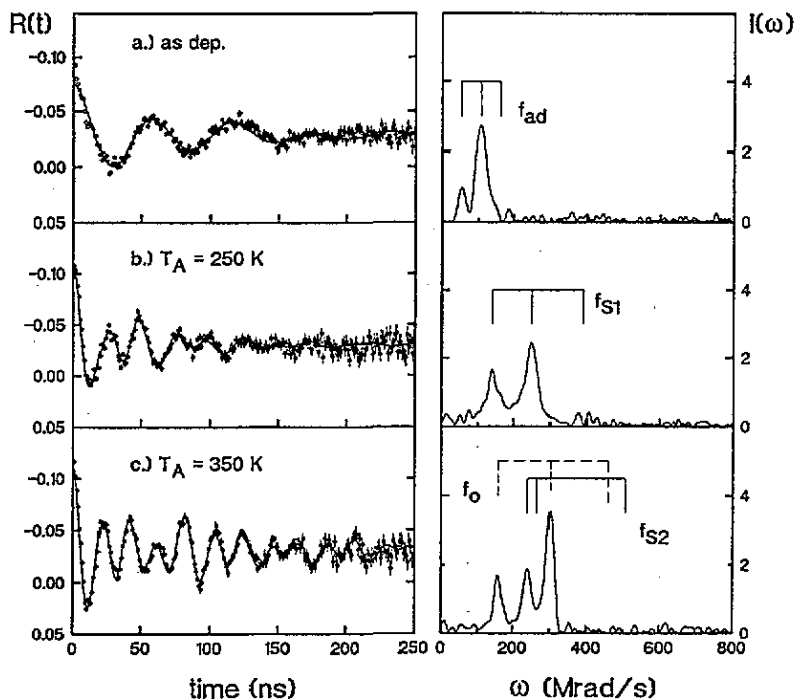


Figure 1. $R(t)$ spectra and corresponding Fourier transforms for ^{111}In on Pd(100) after deposition at 78 K and for two different annealing temperatures (annealing time 10 min). Corresponding transition frequencies are indicated, the identified fractions f_i are discussed in the text. Due to the orientation of the different field-gradient principal-axis systems, some transition frequencies are not visible in the Fourier transforms.

either the principal y or x -axis points along the prepared step directions. Although an unambiguous determination of the principal-axis-system orientation is impossible for the experiments presented here, for both f_{S1} and f_{S2} the z -axis orientation is found to deviate clearly from the [001]-terrace normal. From this analogy with earlier experiments an attribution of the fraction f_{S1} to In probes on adatomic step sites and f_{S2} to In atoms incorporated into the steps seems plausible.

The annealing behaviour for the various fractions is summarized in figure 2. We have plotted the sum of the two fractions ($f_{S1} + f_{S2}$) because of the above mentioned frequency overlap for the two step-correlated sites. Owing to these difficulties, the numbers stated for ($f_{S1} + f_{S2}$) are based on electric-field-gradient orientations obtained in diffusion experiments on Cu(100) surfaces [3]. The observed behaviour fits the microscopic model for surface diffusion we proposed in an earlier publication [2]. It is similar to the terrace-ledge-kink (TLK) model and justifies the attribution of the observed electric field gradients to different In probe sites on the Pd(100) surface: after deposition at 78 K, the probes occupy adatomic sites on the low-index terrace (f_{ad}), while thermal activation leads to the occupation of surface sites of increasing coordination. Residing at step-correlated sites (f_{S1} , f_{S2}) for moderate annealing temperatures, the In atoms finally populate substitutional terrace sites within the topmost layer (f_0).

However, in comparison with experiments on Ag(100), Cu(100) and Ni(100) we find clear differences for the conversion temperatures between the different sites. In particular the adatomic terrace site (fraction f_{ad}) is observed up to annealing temperatures of 180 K

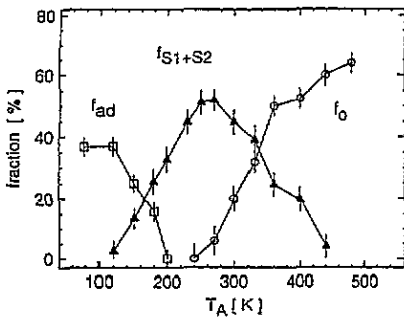


Figure 2. Fraction of ^{111}In probes occupying different probe sites on the Pd(100) surface during an isochronal annealing experiment (annealing time 10 min).

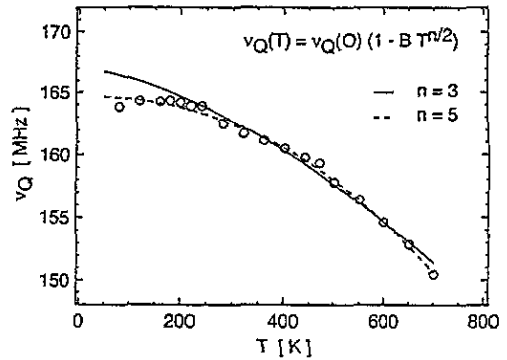


Figure 3. Temperature dependence of the quadrupole coupling constant ν_Q for ^{111}In occupying substitutional terrace sites. The dashed line corresponds to a $T^{5/2}$ -dependence ($\nu_Q(0) = 164.3(1)$ MHz, $B = 6.62(15) \times 10^{-9} \text{ K}^{-5/2}$). The solid line represents a $T^{3/2}$ -dependence, which has been fitted to data points above 200 K.

on Pd(100) whereas on Ag(100) and Cu(100) surfaces this site is depopulated for annealing temperatures as low as 120 K. Hunger and Haas [6] find indications for the occupation of adatomic terrace sites on Pd(111) surfaces at 78 K; such a site has not yet been observed on Cu(111) and Ag(111) surfaces for ^{111}In depositions at 78 K [2]. Obviously the mobility of indium atoms is lower for Pd surfaces. Indeed, calculations by Miedema *et al* show a significantly increased binding energy for In on Pd as compared to Ag and Cu surfaces [8]. The lower In mobility on the (100) surfaces due to the higher corrugation of the surface potential as compared to the densely packed (111) structures is in agreement with the Pd(111) results, where atoms are more mobile and occupation of adatomic terrace sites can only be observed at liquid nitrogen temperatures [6].

The incorporation of ^{111}In into substitutional terrace sites is also shifted to higher temperatures as compared to Ag and Cu surfaces. Since the formation of step vacancies as well as self-diffusion is correlated with the substrate melting temperature, the higher melting point of Pd metal influences the diffusion behaviour of In atoms, which in our opinion is governed by vacancy migration within steps and terraces, respectively. On the assumption of an Arrhenius-type diffusion, activation energies for the different diffusion steps can be estimated. Assuming 10^{12} Hz as exponential prefactor we estimate an activation energy of 0.45(4) eV for adatom diffusion and 1.04(6) eV for the incorporation into the terraces. Although the prefactor for the adatomic terrace site might be significantly lower, the general tendency for increased activation energies at the Pd(100) surface as compared to Ag(100) and Cu(100) surfaces is clearly seen from the direct comparison of annealing behaviours. For migration into the Pd crystal a lower limit of 2.2 eV can be given. Isothermal annealing experiments are in preparation in order to measure directly the respective diffusion constants.

The PAC studies on Pd(100) surfaces do not, however, agree in all respects with the results on metal surfaces investigated so far. Whereas in all previous studies on Cu, Ag and Ni surfaces with (100) orientation, axially symmetric field gradients for ^{111}In probes on substitutional terrace sites were measured, on Pd(100) a slight deviation from axial symmetry is found. Since the asymmetry parameter η reflects the structural symmetry around the PAC probe, one expects axial symmetry for (111) as well as (100) surface orientations and non-axial symmetry for (110) surfaces, which has been confirmed in case of Cu and Ag surfaces [1]. For the Pd(100) surface we find $\eta = 0.16(3)$ over the whole temperature range covered in our experiments on various samples.

So far no conclusive statement can be made to explain the deviation from axial symmetry. Indium probes are impurities on the surface and will therefore cause changes in the local structure. But since we are dealing with a highly symmetric surface, non-symmetric relaxations around the probe cannot be expected. Such relaxations could originate from other surface impurities like a single carbon or chlorine atom close to the In probe. However, chlorine impurities could be reduced by annealing the sample to 800 K without any influence on the detected quantities. Moreover, annealing leads to a much narrower linewidth ($\Delta V_{zz}/V_{zz} = 0.015(1)$) as compared to those shown in figure 1 and therefore allows a more accurate determination of the asymmetry parameter η .

We can also take into account the very pronounced interaction of palladium metal with hydrogen. For Pd(110) and Pd(111) surfaces experimental evidence has been found that hydrogen occupies sites beneath the topmost layer [9, 10]. On Pd(100) hydrogen forms a $c(2 \times 2)$ superstructure in case of low hydrogen coverage (≈ 0.5 ML) and a $p(1 \times 1)$ superstructure for hydrogen coverage of about 1 ML [11]. Here, however, the above condition holds: neither 'subsurface hydrogen' nor the reported hydrogen superstructures can cause a non-axially symmetric electric field gradient as is easily concluded from geometrical considerations. Moreover, the hydrogen superstructure is stable only up to 350 K [11] and does therefore not explain an η -value of 0.16(3) for the temperature range between 78 K up to 650 K.

However, when measuring the temperature dependence of the quadrupole coupling constant ν_Q , we observe a behaviour which we can attribute to the adsorption or chemisorption of hydrogen. The temperature behaviour is commonly regarded to be influenced by the mean square displacement of the probe atoms and consequently many non-cubic structures exhibit a behaviour described by $\nu_Q = \nu_Q(T = 0)(1 - BT^{3/2})$. However, there is no theory to date that can completely explain the observed temperature behaviours for electric field gradients.

At low-index metal surfaces we find the temperature dependence to be well represented by $\nu_Q = \nu_Q(T = 0)(1 - BT^n)$ with an exponent n between 1 and $3/2$ [1, 4, 7]. For the Pd(100) surface we find a deviation from either a linear or $T^{3/2}$ -dependence for sample temperatures below 200 K. In figure 3 we have plotted the results for least-square fits of a $T^{5/2}$ -dependence (dashed line) and $T^{3/2}$ -dependence (solid line), respectively. For the latter we used all data points above 200 K. The least-square fitting procedure taking into account all data points yields an exponent of $n = 2.4$. A deviation from $T^{3/2}$ -behaviour has up to now only been observed for In probes occupying substitutional terrace sites at Cu(115) and Cu(117) surfaces [12] which undergo a roughening transition at 380 K and 315 K, respectively. For these two surfaces, we believe the $T^{5/2}$ -dependence is due to strongly anisotropic mean square displacements in the rough phase. However, since substitutional terrace sites have strong nearest-neighbour correlation, a vibrational behaviour similar to In probes on roughened surfaces cannot be expected. We therefore attribute the observed temperature behaviour to hydrogen adsorbed at the Pd(100) surface leading to a slight decrease of the electric field gradient by changing the electronic structure around the ^{111}In probes. A preliminary experiment at a hydrogen partial pressure of 2×10^{-6} Pa resulted, within the experimental error of 0.5%, in the same quadrupole coupling constants ν_Q as given in figure 3 in the low-temperature region. This result supports our interpretation that hydrogen adsorption at low temperatures slightly reduces the strength of the electric field gradient.

The high sensitivity of electric field gradients to other surface impurities could also be demonstrated in our experiments on Pd(100). For chlorine impurities in a concentration of 0.08 ML introduced when depositing the ^{111}In probes at 78 K, the quadrupole coupling

constant ν_Q for In probes on terrace adatom positions is reduced to 49(1) MHz. In addition, there is a slight asymmetry resulting in an η -value of 0.27(3) ($|V_{zz}| = 2.8(5) \times 10^{17} \text{ V cm}^{-2}$), leading to the conclusion that we are dealing with an 'unsymmetric' arrangement of chlorine atoms close to the ^{111}In probes.

Finally we would like to comment on speculations of a ferromagnetic surface layer of Pd(100). Although Rau [13] suggested the existence of a magnetization at the Pd(100) surface from the results obtained by electron capture spectroscopy (ECS), we do not find any indications of a magnetic hyperfine interaction at the surface. Since the interaction of the magnetic hyperfine field with the nuclear dipole moment of ^{111}In is easy to observe in our measurements, from the broadening of the transition frequencies we can estimate an upper limit for the magnetic hyperfine field B_{hf} of about 0.015 T at 78 K, which is only 0.4% of the value measured at Ni(100) surfaces [5]. However, the line broadening could also be due to structural imperfections. For thin epitaxially grown Pd films with larger lattice distances as in bulk, there are theoretical predictions [14] that Pd atoms carry a magnetic moment. The application of PAC spectroscopy to ultra-thin Pd films epitaxially grown on, for example, a Ag(100) substrate will therefore be of great importance.

3. Summary

We have measured the diffusion behaviour of ^{111}In probe atoms on Pd(100) surfaces, which we find is similar to In diffusion on Ag and Cu surfaces. The differences for the activation energies for the various diffusion steps are explained by the increased binding energy for In on Pd as compared to copper and silver surfaces. Further investigations should give more insight into the influence of hydrogen on surface electric field gradients and might finally explain the observed deviation from axial symmetry for ^{111}In dwelling in substitutional terrace sites.

Acknowledgments

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