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# Surface diffusion of Ag on Pd(100) measured with specular helium scattering

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## Abstract

We present a new method to determine surface diffusion constants using specular reflected thermal helium scattering. The specular reflected helium intensity is recorded in real time as a function of surface coverage of the adsorbate and surface temperature. The experiment is compared to a model calculation based on rate equations for the generation and destruction of adatoms and clusters. We find  $E_{d1} = 0.35 \pm 0.03$  eV and  $\nu_{01} = 3 \times 10^9$  s<sup>-1</sup> as surface diffusion barrier and pre-exponential factor for the system Ag/Pd(100).

**Keywords:** Adatoms; Atom–solid scattering and diffraction – elastic; Clusters; Diffusion and migration; Low index single crystal surfaces; Molecular beam epitaxy; Palladium; Silver

## 1. Introduction

The growth mechanisms of thin films on solid surfaces are strongly dependent on the mobility of the adatoms or small clusters of the deposited material. Reliable measurements of surface diffusion coefficients, however, are difficult to obtain, particularly for very low coverages, where adparticle–adparticle interactions can be neglected. Most of the experimental data available so far are based on direct visualization techniques like the field ion microscope (FIM) [1] or the scanning tunneling microscope (STM) [2]. While the first method visualizes simple atomic hops, the second requires a relation of the diffusion constants with the island density. Macroscopic techniques based on the coverage change of an initially well-defined distribution of adatoms [3,4]

are restricted to gases with no or repulsive interaction. A variety of other particular methods have been developed which are extensively reviewed in the literature [5,6].

In the present paper we present a study of surface dynamics in the very early stages of growth for metal–metal systems based on the measurement of the specular reflected helium intensity ( $I/I_0$ ) as a function of coverage ( $\theta$ ) and surface temperature ( $T_s$ ). Using thermal energy atom scattering (TEAS) to study surface dynamics is not new (see for example Refs. [7–11]). The method proposed here is based on the change of the scattering cross section of the adparticles depending on their distance due to geometrical overlap. The principle of the measurement is the following: silver atoms are condensed on the surface at various temperatures between 80 and 1200 K while the specular reflected helium intensity is recorded during and after the deposition process.

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The evolution of the helium signal is then compared to a simulation based on a rate equation approach for adatom and cluster densities, where the scattering cross section of each particle is computed by geometrical overlap of atomic cross sections. From the best fit between experiment and model the hopping frequency of adatoms and possibly larger clusters is extracted. The diffusion barrier and the pre-exponential factor are deduced from an Arrhenius plot.

## 2. Experimental

The measurements are performed in a UHV – molecular beam apparatus which has been described in detail elsewhere [12]. The He beam is produced by a rotatable nozzle beam source and detected in a separately pumped chamber either by a mass spectrometer or by an ionization gauge. Due to the different acceptance angles of the two detection methods different transfer widths of the helium scattering system are obtained. Parallel recording of the two signals allows one to distinguish between the coherent and non-coherent part of the signal. The

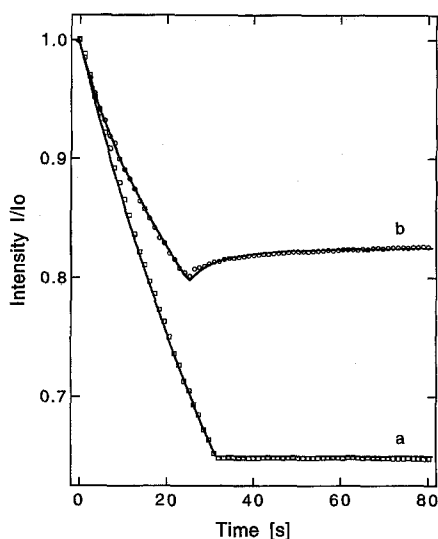


Fig. 1. He specular intensity as a function of time for two different surface temperatures (a)  $T_s = 80$  K; (b)  $T_s = 215$  K. The Ag flux is started at time 0 and stopped after approximately 30 s. While  $I/I_0$  stays constant at low temperatures, a clear increase of the  $I/I_0$  is seen in (b) when the Ag flux is stopped. The solid curves correspond to model calculations; for details see text.

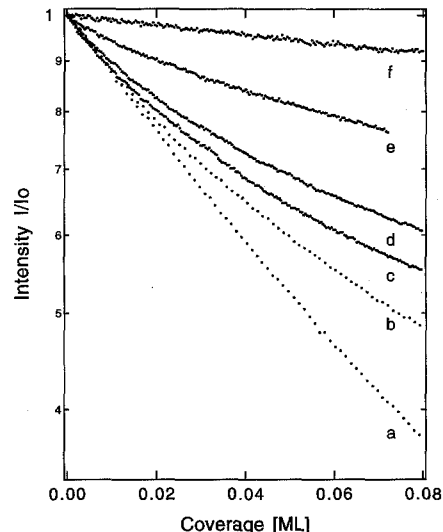


Fig. 2. He specular intensity as a function of Ag coverage for different surface temperatures: (a) 80 K; (b) 190 K; (c) 200 K; (d) 210 K; (e) 250 K; (f) 750 K.

base pressure in the analysis chamber is in the low  $10^{-11}$  mbar range. The Pd(100) crystal is mounted on a sample holder allowing for  $xyz$ , polar angle and tilt displacement. The sample temperature, measured by a thermocouple spot-welded to the crystal, can be controlled between 80 and 1300 K employing liquid nitrogen cooling and electron bombardment heating. A temperature stabilized Knudsen cell directed almost normal to the surface is used to evaporate silver, with fluxes ranging from  $10^{-4}$  to  $10^{-2}$  monolayer/s. The geometry allows for simultaneous measurement of the reflected He beam.

Repeated sputtering ( $\text{Kr}^+$ , 1 keV,  $1 \mu\text{A cm}^{-2}$ ) and oxidation cycles have been employed to initially clean the crystal surface. Everyday cleaning of the surface is performed by short (15 min) sputtering periods at room temperature, followed by an annealing of 3 min at 1000 K and 15 s at 1300 K. The fluxes are calibrated by evaporating silver at 400 K while measuring the reflected He beam. Since at this temperature Ag grows epitaxially on Pd(100) [13], the He intensity recovers upon completion of a monolayer, permitting to evaluate the total flux on the surface.

### 3. Results and discussion

In the following part of the paper we will concentrate on the very beginning of the deposition and discuss the behavior of  $I/I_0$ ,  $I_0$  being the intensity reflected from the bare surface, as a function of surface temperature and silver flux. Fig. 1 shows two deposition curves as a function of time. Curve (a) is recorded at a surface temperature of  $T_s = 80$  K. At time  $t = 0$  the shutter of the Knudsen cell is opened and we observe a strong decrease in the  $I/I_0$  signal until after 30 s (which corresponds to a surface coverage of 2%) the silver flux is stopped. The specularly reflected helium intensity remains constant from this time on. This is different in curve (b) which has been recorded at a higher surface temperature ( $T_s = 215$  K). After stopping the silver flux, the helium signal does not remain constant but increases with time and stabilizes after a while. Further on, the

initial slope is smaller than for the low temperature deposition. This becomes even more evident in Fig. 2, where six deposition curves at different surface temperatures  $T_s$  but constant flux  $R$  are displayed. The initial slope of the  $I/I_0$  versus coverage curve decreases as  $T_s$  increases. The slope change with temperature is attributed to the mobility of adatoms (and larger aggregates). The temperature range in which the dynamical behavior is measurable ranges from 160 K to about 200 K. In this temperature range we find surface morphology changes which happen on a timescale comparable to the experiment ( $\tau_{\text{typ}} = 1$  s). For higher surface temperatures  $T_s$  the dynamics is so fast, that the measurement sees almost an equilibrium. It should be noted here that the temperature intervals given in the foregoing discussion depend on the silver flux. Since the hopping frequency of the mobile adparticles changes exponentially with the surface temperature this effect is

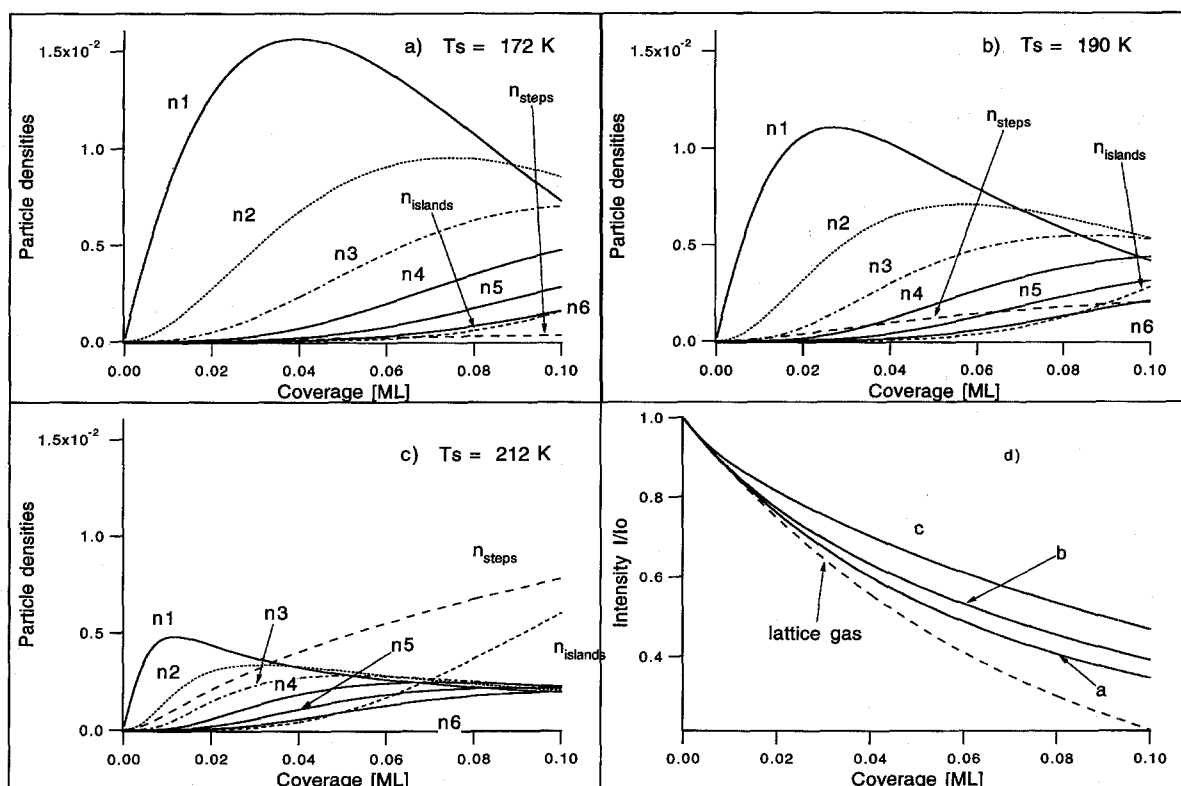


Fig. 3. Calculated cluster and island densities in units of Pd(100) surface sites density ( $1.3 \times 10^{15} \text{ cm}^{-2}$ ) as a function of coverage, for different dynamical parameters and the corresponding  $I/I_0$  curves (d). (a)  $\nu_1 = 0.1$ ; (b)  $\nu_1 = 1$ ; (c)  $\nu_1 = 10$ ;  $\nu_2 = \nu_3 = 0$  in all cases. The corresponding surface temperatures for Ag/Pd(100) are marked on the graphs.

clearly dominant and flux changes of one order of magnitude will shift the temperature ranges discussed above only slightly.

In order to extract quantitative information about the surface diffusion parameters we calculate  $I/I_0$  using the expression [14,15]

$$\frac{I}{I_0}(\theta) = \left(1 - \sum_i \sigma_i n_i(\theta) - \sigma_{\text{step}} n_{\text{step}}(\theta)\right)^2, \quad (1)$$

relating the attenuation of the intensity  $I$  with respect to the intensity from the clean surface  $I_0$  to the perturbed area per particle:  $n_i$  is the number of clusters containing  $i$  atoms,  $n_{\text{step}}$  is the number of atoms which condense on steps. The corresponding cross sections  $\sigma_i$  and  $\sigma_{\text{step}}$  are obtained in a unique way from the cross section of isolated adatoms by geometrical overlap, assuming that the atoms of a cluster occupy fcc adlayer sites of the Pd(100) surface. The atomic cross section  $\sigma_1$  is defined by the measurements at low temperatures, where mobility is not present, and at coverages below 2% of a monolayer where statistical aggregation of the adatoms during the deposition process can be neglected. The key step to evaluate  $I/I_0$  as a function of  $\theta$  and  $T_s$  is the calculation of the cluster size distribution  $n_i(\theta)$ . This is done by solving numerically a system of rate equations for  $n_i$ . The variation of  $n_i$ ,  $dn_i/dt$ , is due to the statistical formation from the gas phase and to the capture of diffusing adatoms. The mobility of adatoms and clusters enter into these equations by allowing them to perform a random walk trajectory on the surface with a hopping frequency  $\nu_i$  of the adparticle of size  $i$

$$\nu_i = \nu_{0i} \exp(-E_{di}/kT), \quad (2)$$

where  $\nu_{0i}$  is the pre-exponential factor for diffusion and  $E_{di}$  the diffusion barrier, for particle of size  $i$ .

The rate equations are limited to size  $i = 6$ , everything larger than this is considered in a single rate equation. This is justified by the fact that the coverages under consideration are small, and the intensity decrease is mostly determined by the aggregation of adatoms in small islands. Note that only the hopping frequencies  $\nu_i$  are varied to fit the intensity curves with formula (2).

A more detailed description of the model goes beyond the scope of this article and will be published elsewhere [16]. We briefly illustrate the outcome of

the calculation referring to Fig. 3. The particle size distributions calculated for three different hopping frequencies  $\nu_1$  (0.1 (a), 1 (b), 10 (c),  $\nu_2 = \nu_3 = 0$ ) are shown as a function of coverage, for an incoming flux of  $10^{-3}$  ML s $^{-1}$ . The corresponding helium reflectivity  $I/I_0$  is shown in Fig. 3d).

Several characteristics appear in these curves:

- The lifetime of the adatom depends on coverage and hopping frequency  $\nu_1$ . However one observes a similar decrease of  $I/I_0(\theta)$  at very low coverage (up to about 1%) in the temperature range of low dynamics since the adatoms are far apart from each other. The same value of the atomic cross section can therefore be deduced from the beginning slope of the  $I/I_0(\theta)$  curve.

- As the coverage increases, the lifetime of the adatom is strongly reduced, and larger aggregates and islands are formed. This leads to a bending towards decreasing slope of the relative helium intensity as a function of coverage due to the reduction of cross sections by overlap. This effect is strongly temperature dependent and well reproduced in the measurements (Figs. 2b–2d).

- The role of the steps in the dynamics depends also strongly on the temperature. When  $\nu_1 \gg 1$  a significant part of the deposited atoms condenses on the steps.

The condensation on steps sets a limit to our model since no coherence effects in the scattering of the helium atoms have been taken into account in the calculation of the intensity reflected by the surface of the sample. We find indeed considerable deviations in the experimental data measured with the ionization gauge (small transfer width) and the mass spectrometer (large transfer width) for high surface temperatures while the data are almost identical in the low dynamic range.

The agreement between experiment and model is excellent in the very low and low dynamic range. This can be seen in Fig. 2, where the calculated curves are superposed to the experimental data. Poor agreement is obtained in the high dynamic range as illustrated in the above discussion.

The surface diffusion barrier  $E_{di}$  and the pre-exponential factor  $\nu_{01}$  can be determined from the hopping frequencies of the adatom as a function of  $T_s$  which shows an Arrhenius-type behavior. This is shown in Fig. 4. The experimental values obtained

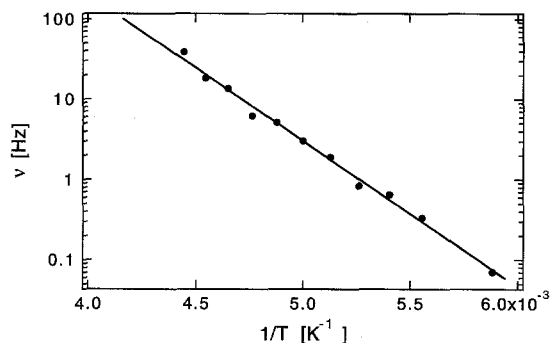


Fig. 4. Arrhenius plot of  $\nu_1$  for Ag/Pd(100). The corresponding surface diffusion barrier is  $E_{d1} = 0.35 \pm 0.03$  eV and the pre-exponential factor  $\nu_{01} = 2.7 \times 10^9$  s<sup>-1</sup>.

for Ag/Pd(100) are:  $E_{d1} = 0.35 \pm 0.03$  eV and  $\nu_{01} = 2.7 \times 10^9$  s<sup>-1</sup>. We have also tried to extract the diffusion barriers of higher aggregates but this has failed so far.

There are no published experimental data for the system Ag/Pd(100) available to our knowledge. Evans et al. [17] determined the surface self-diffusion barrier of Pd(100) via LEED experiments. They find  $E_{d1} = 0.56$  eV but had to assume a pre-exponential factor of  $5 \times 10^{12}$ . This high barrier is in contrast to STM measurements of Hahn [18] for the system Cu/Pd(100) where a diffusion barrier as low as 0.28 eV was found.

Molecular dynamics calculations reported by Sanders and DePristo [19] for a variety of fcc(001) surfaces yield  $E_{d1} = 0.42$  eV for Ag/Pd(100), which is fairly close to our experimental value, but find a pre-exponential factor of  $\nu_{01} = 8 \times 10^{12}$  s<sup>-1</sup>, three orders of magnitude larger than in our experiment.

#### 4. Conclusions

We have presented a new method to determine surface diffusion constants from the specular re-

flected helium intensity recorded in real time during the deposition of Ag on Pd(100). This method is based on the cross section overlap when the adatoms form larger aggregates. We feel that this method is a good alternative compared to other techniques in particular since measurements are performed in real time, at low surface coverages and low surface temperatures.

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