Adsorption-Site Location by Transmission Channeling: Deuterium on Ni(100)

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It is demonstrated that transmission channeling may be applied to determine positions of atoms adsorbed on clean crystal surfaces under UHV conditions. For the case of deuterium on Ni(100), we conclude that the D atoms are adsorbed in fourfold hollow sites at 0.5 ±0.1 Å above the first Ni layer and obtain a value of the rms displacement parallel to the surface in qualitative agreement with a delocalization model.

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The equilibrium position of atoms adsorbed on crystal surfaces is of fundamental interest in all types of adsorption studies. A number of experimental methods have been developed to yield information about adsorption sites. However, only a few of these methods (LEED, EELS, and He diffraction) may be used in the case of hydrogen adsorption, and even then the position information is obtained in a very indirect way.

In this Letter, we report the first successful application of transmission channeling to locate atoms adsorbed on a clean surface under UHV conditions. The versatility of the method is demonstrated by the choice of adsorbate, hydrogen (deuterium), but other measurements in our laboratory, using tellurium as an adatom, confirm that the method works equally well for heavy adsorbates. It is shown that qualitative structural information may be deduced from transmission-channeling data without any calculations. Quantitative information about position as well as vibrational properties of the adsorbate results from a more detailed analysis.

Transmission channeling through thin crystals has previously been used to study the structure of interfaces[1,2] and the registry of multilayer adsorbates,[3] but has never before been applied to determine adsorption sites under controlled, UHV conditions.

The basic idea is the following: If an ion beam is made incident along a low-index axial direction, the incident ions will undergo correlated collisions with the atoms of the rows, thereby experiencing a steering effect. As a consequence, these channeled ions will obtain a flux distribution in the transverse plane which is very small close to the atomic rows, and which may exceed unity in the center region of the channels. If the crystal is sufficiently thin, this flux distribution is, to a very good approximation, conserved at the exit side of the crystal, thus constituting a probe with atomic-scale resolution for interactions with atoms adsorbed on that side of the crystal.

As will be illustrated, detailed information about adatom positions can be deduced from complete angular scans (i.e., interaction yield versus tilt angle) around the main axes of the crystal.

In the present experiment, Ni(100) crystals of ~3000-Å initial thickness were grown epitaxially on (100) planes of rocksalt and then floated onto freshly etched, high-purity Ni rings with an aperture of ~3 mm diam.[4] After being mounted in a goniometer, the crystals were cleaned *in situ* in the UHV-experiment chamber by a few cycles of argon sputtering and annealing above 700 K. This treatment resulted in impurity-free surfaces (as shown by Auger and subsequent Rutherford-backscattering measurements) and in excellent crystalline quality, evidenced by the appearance of sharp (1×1) LEED patterns and by the channeling properties of the crystals.

In the experiment phase, the crystal surface to be studied was cleaned and then exposed to deuterium from a capillary-tube inlet system after cooldown to ~170 K. The pressure rise during exposure was $\sim 1\times10^{-10}$ Torr. This procedure ensures that negligible amounts of deuterium adsorb at the other side of the crystal. The deuterium coverage was not measured and is not needed for the interpretation of the data, a further advantage of the method.

All measurements took place in a UHV system interfaced to a 2-MV Van de Graaff accelerator via differential pumping. The pressure during measurements was $\lesssim 1\times10^{-10}$ Torr. Detection of deuterium was carried out by means of the nuclear reaction $D(^3He,p)^4He$. The energy of the incident ^3He ions from the accelerator was chosen to be 800 keV to get particle energies at the exit side of the crystal in the broad region of maximum reaction cross section[5] after energy loss through the thin crystal. A movable, bakable solid-state detector covered with a 32-μm Al foil with several pinholes allowed simultaneous detection of nuclear-reaction protons and ^3He particles elastically scattered from the nickel atoms. No ion-beam–induced desorption of deuterium during measurements was detected.

Typical experimental angular scans for the [100], [110], and [111] directions measured with the crystal at ~120 K are shown in Fig. 1. While the substrate yields in all three cases follow the usual channeling-dip shape, the proton yield from the adsorbate is drastically different in the three directions. The large reduc-

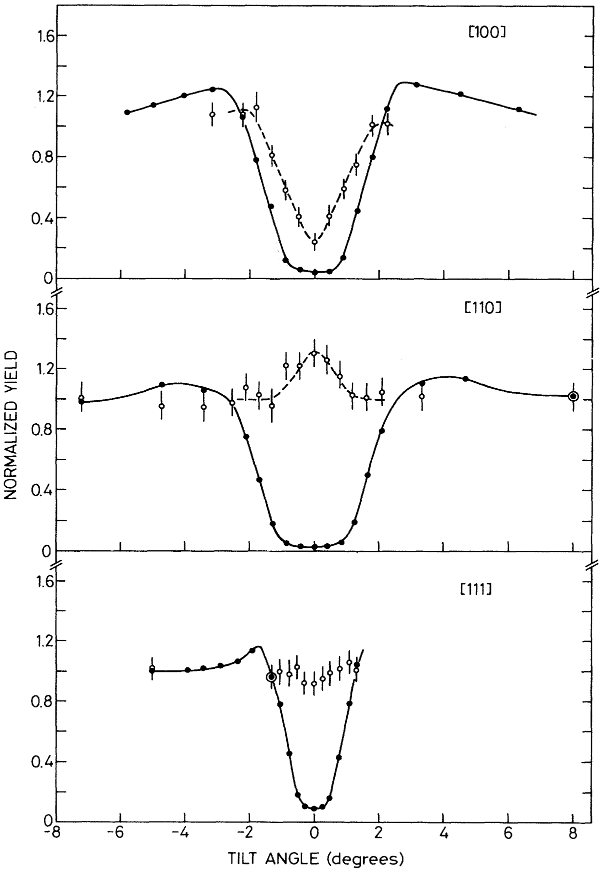

FIG. 1. Deuterium on Ni(100): Experimental angular scans showing normalized yields from D (open circles) and from bulk Ni (filled circles) vs angle of beam incidence, with the [100], [110], and [111] axes. The yields were normalized to unity for random incidence. The ^{3}He beam energy was 800 keV.

tion in proton yield observed for [100] alignment, in connection with the symmetry properties of the surface, indicates that the D atoms are located along the [100] atomic rows. This immediately rules out the bridge position. The flux peak observed for [110] incidence indicates that the deuterium height above the surface is not close to a lattice site. This observation is further supported by the [111] data. Finally, the observed narrowing of the proton dip relative to the Ni yield for [100] incidence indicates a significant enhancement of the deuterium vibration amplitude. Clearly, important qualitative information can be deduced from the data without any calculations. Before a more detailed data analysis is made, we briefly recapitulate the existing structural information about hydrogen on Ni(100).

The available theoretical and experimental information about hydrogen adsorption on Ni(100) supports a model with hydrogen atoms adsorbed in the fourfold coordinated hollows. The prependicular vibrational frequency observed with EELS[6] is in good agreement with the theoretical value for only this position, which also corresponds to the lowest energy.[7,8] The height of the hydrogen atoms above the first Ni layer has been found to be 0.3 Å (first-principles Hartree-Fock calculations on Ni cluster[7]), 0.3 Å (linear augmented plane-wave method used on Ni slab[9]), and 0.8 Å (effective-medium theory[8]). The only experimental value reported is 0.9–1.0 Å, based on He diffraction.[10] The theoretical values of the adsorption height are valid also for deuterium adsorption.

The fourfold site is clearly consistent with the [100] channeling data, and in the following detailed analysis of angular scans, it therefore remains only to determine the height of the D atoms above the surface.

The experimental data have been analyzed by comparison with results from a multirow continuum-model[11] calculation. In this type of calculation, the ion-flux density inside the channels is calculated, under two fundamental assumptions: (1) Conservation of transverse energy $E_\perp = U(\mathbf{r}_{\text{in}}) + E\psi_{\text{in}}^2$ of the channeled ions. Here, $U(\mathbf{r}_{\text{in}})$ is the transverse potential at the entrance position $\mathbf{r}_{\text{in}}$ of the channel, E is the energy of the incident ion, and ψ_{in} is the angle of incidence with the channel axis. (2) Statistical equilibrium, i.e., the assumption that the position probability in the transverse plane of a channeled particle is uniform within the area $A(E_\perp)$ allowed by the transverse energy $E_\perp$ of the particle.

The potential U was calculated as a sum of thermally averaged potentials from several (~ 14) neighboring atomic rows, with use of the analytical Doyle-Turner approximation to the atomic potential.[12]

With the flux distributions calculated in the continuum model, it is straightforward to generate theoretical angular scans for different position-probability distributions of the adsorbed atoms. This has been done for [100] incidence for a series of different values of the deuterium rms vibration amplitude parallel to the surface. The result is that the observed narrowing of the adsorbate dip relative to the bulk dip (cf. Fig. 1) corresponds to an rms displacement amplitude parallel to the surface of ~ 0.21 Å for the deuterium atoms.

In a recent Letter, Puska *et al.*[13] calculated the wave functions and energy levels for hydrogen on the Ni(100) surface. The resulting potential was found to be very anharmonic and associated with a considerable delocalization of the hydrogen atoms. Using the same procedure, Puska[14] has calculated the probability density parallel and perpendicular to the surface for deuterium adsorbed on Ni(100). The resulting distributions can, for computational purposes, be approximated with normal distributions with rms displacement distances of ~ 0.24 Å parallel to the surface (two dimensions) and ~ 0.12 Å perpendicular to the sur-

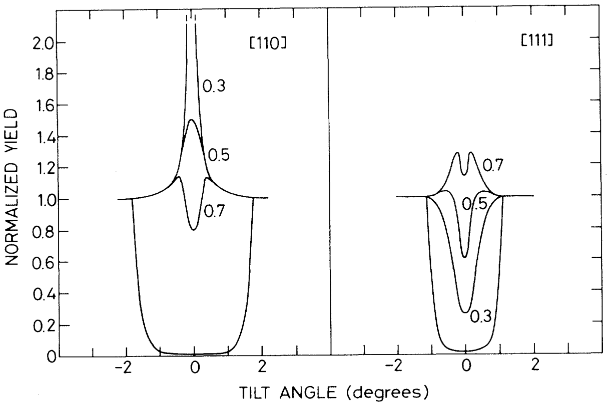

FIG. 2. Deuterium on Ni(100): Calculated transmission-channeling angular scans showing normalized substrate yield (lower curve) and yields from D atoms assumed to reside in the fourfold hollow position at 0.3, 0.5, and 0.7 Å above the first Ni layer (upper curves). The yields are shown for a ^{3}He beam energy of 800 keV for the [110] and [111] axes.

face (one dimension). Although the continuum model used to obtain the experimental value does not include multiple scattering (see below), and the theoretical model neglects possible adsorbate-adsorbate interactions, the qualitative agreement between measured and calculated rms displacement values supports the delocalization picture.

The calculated angular scans for the [110] and [111] directions for deuterium in fourfold sites, but at different heights above the surface, are shown in Fig. 2. For these scans, the sensitivity to the rms displacements of the D atoms is rather small, and a two-dimensional value of 0.21 Å was used throughout.

As shown in Fig. 2, the variation in shape of the adsorbate angular scans with deuterium-adsorption height is quite dramatic. In comparing the measured and calculated scans, one should bear in mind that the computational model does not include effects such as electron and nuclear multiple scattering. While such effects are difficult to treat on an exact basis,[15] their qualitative influence is known. Inclusion of multiple scattering would result in a smearing of the features of the scans, giving rise to less steep sides of the channeling dips, broader (and lower) flux peaks, etc. Still, it appears safe to conclude from the two sets of data that the deuterium atoms are located 0.5 ±0.1 Å above the bulklike position of the first nickel layer.

In transmission channeling, the adsorbate location is made relative to the bulk lattice, with neglect of a possible surface relaxation. In the present case, with the error bars quoted, the distinction is not very relevant. The relaxation of clean Ni(100) is small,[16] and the same is to be epxected for the deuterium-covered surface.

The measured adsorption height of the D atoms falls within the range of theoretical values but differs considerably from the He-diffraction result of 0.9–1.0 Å.[10] However, this value was obtained in a more indirect way than is the value from the present experiment.

In conclusion, we have demonstrated that transmission channeling may be used to determine positions of atoms adsorbed on clean crystal surfaces. For deuterium on Ni(100), we find that the D atoms are located in fourfold hollow sites 0.5 ±0.1 Å above the surface and obtain a value of the deuterium rms displacement amplitude parallel to the surface.

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