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LEED Analysis of a Nickel Cylindrical Single Crystal

Abstract

We have studied the surface structure of a hollow cylindrical nickel single crystal with its axis along the [110] direction, that was polished on its outer surface. Using a low energy electron diffraction analysis, we show that our cleaning procedure yields monoatomic steps for the low step density regimes. At moderately high step densities, some streaking is observed. It is attributed to increased disorder and may result from partial reconstruction of the surface. For the (211) vicinal surfaces, it is shown that the streaking is related to the presence of an adsorbate, most likely oxygen, on the steps. The adsorbate creates patches with doubled steps. In the highest step density regions, around (311) and (331), the surface exhibits only monoatomic height steps again.

5.1 Introduction

Many gas-surface reactions show a profound structural dependence [1–3], requiring catalysts to be structurally optimized. Knowledge of structural dependencies in reactivity is therefore a vital step in the enabling of rational catalyst design. Ultrahigh vacuum studies on single crystals allow for a very much controlled system, in which the reactivity of terraces, steps and kinks can be determined [4]. Usually, experiments are performed on flat crystals, which have the same surface structure over the entire working area. Cylindrical single crystals may provide a promising alternative, as the surface structure varies along the circumference, allowing for the study of a
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whole range of surface structures using only one crystal [5]. Here, we discuss our LEED analysis of the surface structure of a nickel cylindrical single crystal with its longitudinal axis along the [110] direction. We will show that the steps on the crystal are predominantly monoatomic and that no reconstructions occur in the low and high step density regions.

Among the few publications on cylindrical single crystals which mostly stem from the 1980’s [5–17], structural studies are scarce. To the best of our knowledge, Bauer’s group is the only one to publish LEED images of a clean surface [8]. It was shown that a tungsten cylindrical single crystal with its axis along the [110] direction possessed a smoothly varying average terrace length. No faceting or step bunching was observed. In a study on a platinum cylindrical single crystal with its axis along the [100] direction [17], Veser et al. showed that faceting does occur in the region between (100) and (210). A nickel cylindrical single crystal was used by Woodruff’s group to study initial oxidation kinetics in the [110] zone [11]. No surface structure determination was performed however.

Using flat and polished single crystals, the stability of several high Miller index nickel surfaces has been shown to be strongly dependent on contamination concentration, in particular oxygen [18–27]. For the Ni(977) surface at moderate temperatures (390-470 K), Niu et al. showed that oxygen concentrations as low as 0.0024 ML can cause step doubling of a surface initially prepared with single atom height steps [18]. When more oxygen is added or the temperature is further elevated, resingling of the steps occurs [19].

Although the oxygen impurity level in a new single crystal will most likely not have a profound effect on the surface structure, oxygen treatments as part of the cleaning procedure to remove impurities [25,27] might do so. As oxygen readily dissolves into nickel at temperatures higher than 500 K [23], annealing alone after an oxygen treatment may not suffice to completely remove it [23,26]. This could explain the findings of some authors, who observed doubled steps at low temperatures for the (771) [27], (755) [27] and (111)5°[110] [25] surfaces. Other authors, using sputtering and annealing alone for cleaning, have found single steps at low temperatures for the (911) [20], (511) [20], (977) [18,19,26] and (771) [22,24] surfaces. This cleaning procedure may however not suffice to completely remove carbon impurities. From
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hydrogen sticking probability data, we observe that indeed extra cleaning measures are required for our cylindrical single crystal. This requirement was also found by several other authors [28–30]. In such cases, the combination of an oxygen treatment for the removal of carbon, followed by excessive hydrogen dosing to remove oxygen can be a solution.

We discuss here our results on the structure of surfaces in the Ni[110] zone, obtained after a cleaning procedure using oxygen and hydrogen. In chapter 4, a schematic representation of an ideal fcc cylindrical single crystal with a [110] axis is shown. The indicated principal surfaces are separated by stepped surfaces with a smoothly varying average terrace length. The expected relative location of some of these stepped surfaces is also indicated in that figure. Deviations from these structures are possible due to improper cutting in the preparation of the crystal and reconstructions, e.g. step bunching and faceting. Previously, it was shown that the angles of the (100) and (110) surfaces relative to the four (111) surfaces had the expected values of $55^\circ$ and $35^\circ$ respectively over the whole length and circumference of the cylinder. It confirmed that the crystal is truly a single crystal without planar defects and shows the absence of miscuts [31]. In this study, the same nickel cylindrical single crystal is further analysed based on the quality of the diffraction patterns and the size and energy dependence of the spot splitting observed in the LEED images.

5.2 Experimental

The sample used was a nickel (5N low carbon) cylindrical single crystal, polished along its outer surface and with its axis along the [110] direction (Surface Preparation Labs, Zaandam, the Netherlands). The cylinder has an outer diameter of 20 mm, an inner diameter of 16 mm and a length of 14 mm.

The crystal was cleaned by Ar$^+$ sputtering at 0.8 kV and subsequent annealing at 900-930 K. Oxygen was dosed during annealing ($2 \times 10^{-8}$ mbar for 30 s) followed by elaborate reduction ($\text{H}_2$, $1 \times 10^{-6}$ mbar, 3 min.). Annealing was continued for 3 minutes after the reduction step. Cooling proceeded at an average speed of approximately 45 K/min. After cleaning and cooling down, no surface impurities could be detected using Auger electron spectroscopy (AES).
All experiments were conducted using a four-grid MCP LEED (OCI Vacuum Microengineering BLD800IR). A commercial camera was used to record the images. The electron beam diameter was found to be around 0.3 mm by measuring the current to a tungsten wire of known diameter spot-welded at the crystal’s base and in line with the crystal’s outer edge while moving it through the electron beam. With these dimensions, our LEED electron beam covers approximately 1.7° of the circumference of the crystal. In all experiments, the electron beam’s angle of incidence was chosen to be along the macroscopic normal of the surface. The crystal temperature was, unless noted otherwise, between 90 K and 300 K, at which no nickel mobility can be expected [18]. A more detailed description of our UHV-supersonic molecular beam apparatus can be found in ref. [31].

5.3 Analysis methods

Because of the cylindrical shape of the sample, its surface structure will vary slightly within the area probed by the LEED electron beam. To minimize this inherent convolution, an electron beam diameter as small as possible must be used. A microchannel plate (MCP) LEED allows for the use a small electron beam diameter (here approximately 0.3 mm) because the strongly increased detection sensitivity strongly reduces the required intensity of the incident electron beam [32,33]. A less intense electron beam can be focused to a smaller spot.

The use of MCP LEED, however, may give rise to a projection error [34]. Contrary to the hemispherical display of a conventional LEED apparatus, MCP LEED uses a planar display (see figures 5.1 a) and b)). To obtain an identical image of the diffraction pattern, the electron trajectory must be modified in MCP LEED (figure 5.1 b)). In some MCP LEED apparatuses this correction is absent, leading to distorted patterns as depicted in figures 5.1 c) and d). The origin of distortions in our LEED patterns was confirmed to be this projection error by successfully modelling the diffraction pattern of the (111) surface at several incidence energies using equations 1 and 2.
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Figure 5.1: Schematic representation of various forms of LEED apparatus. Electron trajectories are indicated by arrows. a) Conventional LEED set-up with hemispherical display. b) MCP LEED with electron trajectory correction. c) MCP LEED without electron trajectory corrections. Geometry parameters $r$ and $d$ are described in the text. d) MCP LEED image of the (111) surface at 615 eV, recorded with a LEED apparatus as depicted in c).
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\[ x_b = \frac{x(r + d)}{\sqrt{r^2 - x^2 - y^2}} \]  \hspace{1cm} (5.1)

\[ y_b = \frac{y(r + d)}{\sqrt{r^2 - x^2 - y^2}} \]  \hspace{1cm} (5.2)

Here, \( r \) and \( d \) are the apparatus geometry parameters indicated in figure 5.2 c). The variables \( x \) and \( y \) are the coordinates in the LEED pattern calculated from an Ewald construction for a conventional LEED geometry with radius \( r \). Finally, \( x_b \) and \( y_b \) are the coordinates in the distorted MCP LEED image.

Similarly, distorted LEED images can be corrected using equations 3 and 4.

\[ x = \frac{x_b r}{\sqrt{x_b^2 + y_b^2 + (r + d)^2}} \]  \hspace{1cm} (5.3)

\[ y = \frac{y_b r}{\sqrt{x_b^2 + y_b^2 + (r + d)^2}} \]  \hspace{1cm} (5.4)

When this correction is applied to the diffraction patterns from our sample, we find the expected straight rows of spots, with split spots for stepped surfaces (see figure 5.2).

The absolute distance between the spots in a split spot is characteristic for an average step density and depends only on the incident electron energy and set-up geometry. The dependence on these parameters can be cancelled by dividing the spot splitting \( \Delta \) by the row spacing \( l \) indicated in figure 5.2. Values of this spot splitting over row spacing ratio have been tabulated by Van Hove and Somorjai for a range of surfaces [35].

The spot splitting over row spacing ratio can be predicted from the Ewald construction shown in figure 5.3 [33], which essentially is a 3-dimensional analogue of the Bragg law. For stepped surfaces, the Ewald construction contains reciprocal lattice planes for the step periodicities and rods for the periodicities within the terraces.
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Figure 5.2: a) Original and b) corrected LEED pattern from the (111)15°[100] surface at 150 eV. $\Delta$ and $l$ are the spot splitting and row spacing, respectively.

Because the terrace is not infinitely large, the terrace rods are not infinitely small, \textit{i.e.} blurred in the direction perpendicular to the step edges. Coincidence of the Ewald sphere, and the terrace rods and step planes determines the diffraction angles (see figure 5.3). From the Ewald construction it is clear that the spot splitting can be calculated using equation 5.

\[
\Delta = r\sin\alpha = r \frac{q}{k_0}
\]  

Here, $r$ is the radius of the LEED (see figure 5.1 c)), $\alpha$ is the angle between the specular beam and the closest intersect between the Ewald sphere and the step reciprocal planes, $q$ is the step reciprocal plane spacing and $k_0$ is the wavenumber of the electrons. Similarly, the spot row spacing is proportional to the row spacing of the terrace rods.

\[
l = \frac{rv}{k_0}
\]
Figure 5.3: Ewald sphere construction of a (111) vicinal surface for normal beam incidence. a) side view. b) top view (analogue to experimental viewing direction). The parameters $q$, $k_0$, $\beta$, $\alpha$, and $v$ are used to calculate the spot splitting over row spacing ratio (see text). The black arrows indicate the directions of the diffracted beams.

Here, $l$ is the row spacing, and $v$ is the row spacing of the terrace rods. From equations 5 and 6, it is clear that the spot splitting over row spacing ratio observed on the LEED screen is equal to the step plane spacing over terrace rod row spacing ratio.

$$\frac{\Delta}{l} = \frac{q}{v} \quad (5.7)$$

For monoatomic height steps, $q$ can be calculated using equation 8.

$$q = \frac{2\pi}{b} = \frac{2\beta}{m} \quad (5.8)$$
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In equation 8, \( b \) is the average distance between step edges, hence \( b^{-1} \) is the step density, showing its relation to the LEED pattern. The step height is indicated as \( m \), and \( \beta \) is the rotational angle of the crystal relative to the principal plane that defines the terrace type (e.g. (111), (100) or (110)). Knowing that the row spacing in reciprocal space is given by \( \frac{2\pi \sqrt{2}}{a} \), with \( a \) being the lattice parameter, the spot splitting over row spacing ratio is given by equation 9.

\[
\frac{\Delta l}{l} = \frac{\beta}{m \sqrt{2}} \quad (5.9)
\]

In order to identify facets, one can also use the Ewald construction to calculate the positions of the spots observed on the screen. From figure 5.3, it is clear that the center of a split spot will appear close to the direction in which the terrace diffracts. Therefore, it suffices to calculate the pattern as if there are no steps, only an infinite terrace rotated away from normal incidence by angle \( \beta \). In figure 5.3, this means that only the intersect of the center of the terrace rods with the Ewald sphere has to be calculated. Using the geometry as described in figure 5.3, the intersect coordinates are given by equations 10 to 12.

\[
x_t = n v \\
y_t = \frac{p}{\cos \beta} - \frac{z}{\tan(0.5\pi - \beta)} \\
\left(1 + \frac{1}{\tan(0.5\pi - \beta)}\right)z_t^2 - 2\left(\frac{m}{\tan(0.5\pi - \beta)} + k_0\right)z_t + \frac{m^2}{\cos^2 \beta} + x_t^2 = 0 \quad (5.12)
\]

Here, \( n \) is an integer and \( p \) is the spacing of terrace rods within a row. The vector that defines the diffraction beam is now \((x_t, y_t, z_t - k_0)\). To calculate the position at which this beam would be visible on the screen, one only has to rescale the vector such that: \( z_t - k_0 xu = r + d \). Therefore, the position of the beam on the screen is
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given by equations 14 and 15.

\[
x_b = \frac{x_t x(r+d)}{z_t - k_o} \\
y_b = \frac{y_t x(r+d)}{z_t - k_o}
\] (5.13) (5.14)

Using equations 13 and 14, one can find the terrace type of a facet. In combination with the spot splitting, the Miller index of the facet can be identified.

The step height(s) present in a sample can be determined from the energies at which the (00) spot appears as a doublet or a singlet. For this the formula of Henzler is used [36]:

\[ E_{00} = \frac{150s^2}{4d^2} \] (5.15)

Here \(d\) is the step height and \(s\) is an integer for the singlet appearance energies and a half-integer for doublet appearance energies. By comparing the experimental energies where doublets and singlets are observed to the values predicted by the Henzler formula for monoatomic and double steps, step doubling can be clearly identified.

5.4 Results and discussion

5.4.1 (111) vicinal region

As can be seen in the example in figure 5.4, the surface region close to (111) shows the expected hexagonal pattern of split spots. The absence of extra spots or streaks indicates no faceting is taking place. When moving from (111) towards (311) however, streaking starts to appear at approximately 12° from (111). The origin of the streaks will be discussed in the section of the (311) vicinal surfaces. Rotating from
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Figure 5.4: LEED pattern of the (111)\textdegree[100] surface at 350 eV.

(111) towards (331), streaking is observable at approximately 6° from (111). This will be discussed in the section of (110) and (331) vicinal surfaces.

In order to quantify the step density along the circumference of the crystal, the spot splitting over row spacing ratio was determined. Using a dataset recorded at 150 eV, the results shown as dots in figure 5.5 were obtained. Shown as solid lines are the theoretical curves expected for steps of monoatomic height. Clearly, the spot splitting behaves as expected for the (111) vicinal surfaces. The excellent agreement between the data and the theoretical prediction indicates that the surface either has the expected average step density, or contains areas with the expected step density larger than the LEED coherence length. For the latter, an additional diffraction pattern superimposed on the expected pattern should be observed. As no extra spots or streaks are found in the (111) vicinal region, it can be concluded that no step doubling has occurred.

To corroborate the evidence for the absence of step doubling, the step height was determined at several angles from the energy dependencies of the (00) spot splitting behaviour. In figure 5.6, the expected and observed energies at which the (00) spot appears as a singlet or a doublet are compared. Expected values for monoatomic
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Figure 5.5: Spot splitting over row spacing ratio as a function of the angle of the circumference relative to the location of the (111) surface. Dots: experimental values. Solid line: prediction assuming monoatomic height steps. Thick grey stripes: areas where streaking in the LEED pattern is observed. The location of some relevant surfaces discussed in the text are indicated at the top of the graph.

and diatomic steps are shown as open and filled squares, respectively. The integer or half integer \( s \) shown on the \( x \)-axis cannot be determined experimentally. For the experimental values it is therefore chosen such that optimal agreement between data and theory is obtained for the first data point. The open circles represent the best fit of our data to the theoretical values for monoatomic height steps and the filled circles the best fit of our data to theoretical values for double height steps. Clearly, our data only matches the predictions based on a monoatomic step height. No triplets were observed in the LEED patterns while scanning the incidence energy. As a triplet can originate from a doublet contribution of a monoatomic stepped region and a singlet contribution from a step doubled region, this absence again leads to the conclusion that the (111) vicinal surface region contains steps of monoatomic height.

5.4.2 (100) vicinal region

A similar situation is found for the surface region close to (100). Here, the typical square geometry of split spots is observed. When moving from (100) towards (311), some streaks start to appear at approximately 10° from (100).
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Figure 5.6: Theoretical and observed spot splitting behaviour of the (00) spot. The x-axis contains the integer and half integer values $s$ from the Henzler formula [36]. Filled squares: expected successive singlet and doublet appearance energies for double height steps. Empty squares: expectation for monoatomic height steps. red circles: (111)10°[100]. blue circles: (111)10°[110], overlain with both sets of expected values.

In figure 5.5, it can be seen that the spot splitting to row spacing ratio agrees very well with the values predicted assuming monoatomic step height. From the absence of extra spots and the spot splitting behavior of the (00) spot (not shown), which again compares very well with the expected behavior, it is concluded that the (100) surface region has monoatomic height steps.

5.4.3 (311) vicinal region

Although the (311) surface itself shows the ideal LEED pattern, its vicinal surfaces show some streaking, especially at lower incident energies. The amount and degree of structure in the streaking varies from experiment to experiment, indicating that the exact preparation conditions influence the crystal surface’s final structure.

When the (211) surface, which shows particularly strong streaking, is studied while the sample is heated from 220 K to 600 K, the streaking disappears. While cooling at the slightly reduced cooling rate of 35-40 K/min, the streaking reappears
Figure 5.7: LEED images of the (111)20°[100] surface at 150 eV. From left to right: pattern before heating and while cooling down from 600 K. The full picture indicates which section of the patterns is compared.

with higher intensity and more structure than it initially contained (see figure 5.7). The spot splitting remains unaffected during both heating and cooling, its size indicating monoatomic height steps. The resulting pattern, shown also in figure 5.7, contains extra spots separated by half the distance of the spot splitting (after projection error correction).

No fractional order spots are present in the direction along the steps, indicating that no reconstructions other than step bunching or faceting are taking place. However, perpendicular to the steps, extra spots emerge within streaks. Qualitatively, such extra spots can be explained either by faceting or an adsorbate overlayer pattern. However, quantified from the Ewald sphere construction, neither a (111) vicinal facet nor a (100) vicinal facet can cause the vague second and third spots from the bottom in figure 5.7. For an adsorbate overlayer to cause the observed extra spots, the spacings between all spots in the direction perpendicular to the steps must be equal after projection error correction. Indeed, it is found for all (211) vicinal surfaces investigated that all spots are spaced by half the distance of the spot splitting. This spacing indicates that the periodicity of the overlayer is twice the length of the expected step to step distance, in accordance with step bunching.
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Our observations can be explained as resulting from a surface with patches of clean, single atom height steps mixed with patches of a step-doubled surface with an overlayer pattern originating from an adsorbate bound to steps. The existence of separate patches of the clean, unreconstructed surface is indicated by the unaffected spot splitting during heating and cooling. In the case of a transition from a surface with monoatomic step height at high temperatures to a random, partially or completely step doubled surface at low temperatures, the average step density within the coherence length of the LEED electrons would drop gradually. This would result in a spot splitting that gradually becomes smaller while cooling, which is not observed. For this reason, we favour the interpretation of mixed patches of single and double atomic height steps, which contribute independently to the observed LEED pattern.

Because of its ability to induce step doubling at extremely low coverages [18], oxygen may be the cause of the observed overlayer pattern. The other main contaminants that could cause a step overlayer pattern observable in LEED at the investigated temperatures are C, S and CO. However, studies of the reconstruction behaviour caused by these contaminants seem to indicate no step bunching [25,37–40].

An oxygen overlayer could be formed by segregation of subsurface oxygen [26] that the hydrogen treatment used as part of the cleaning procedure was unable to remove. Although we have tried, no residual surface oxygen could be detected by temperature programmed reaction for m/z 19 and 20 after dosing deuterium on a surface expected to have residual adsorbed oxygen. D₂O and HDO would be expected to be formed slightly below 200 K [41,42]. The detection sensitivity of this measurement may be too low, however, as step doubling may be caused by very small amounts of oxygen [18] and our angle-resolved TPD experiments probe a very small surface area of the single crystal [31]. To confirm that oxygen is able to cause the observed LEED pattern, oxygen (1 × 10⁻⁸ mbar for 30 s) was re-dosed at 400 K directly after the normal cleaning procedure followed by hydrogen reduction (5 × 10⁻⁷ mbar for 1 min) to remove oxygen adsorbed at the terraces. The LEED pattern of the resulting surface is shown in figure 5.8. Clearly, the pattern is very similar to the pattern shown in figure 5.7, yet the step bunching and overlayer pattern are even more pronounced.
Figure 5.8: LEED image of the (111)22°[100] surface at 150 eV after oxygen dosing (1 × 10⁻⁸ mbar for 30 s) at 400 K followed by hydrogen reduction (5 × 10⁻⁷ mbar for 1 min) to remove oxygen adsorbed at the terraces.

From figure 5.5, it is clear that at least patches of monoatomic height steps exist over the whole (311) vicinal region. The observation of separate patches of single and double step height regions is in contrast with findings of the group of Sibener [43], who found oxygen-induced step doubling to occur without long range correlations. As already suggested in that paper however, a small terrace length like in the (311) vicinal region, may result in a much stronger step-step interaction than for the (977) surface used by the group of Sibener. This could lead to clustered areas of step doubling.

When rotating from the (311) surface towards (100), less streaking is observed than around the (211) surface. For the (911) surface, located in this region, Dorsett et al. [21] reported that a small amount of oxygen on the surface induced no step doubling, only a narrowing of the terrace length distribution. Therefore, streaking is not expected to be an indication of step doubling in this region.
5.5. CONCLUSION

5.4.4 (331) and (110) vicinal region

The region of the (331) and (110) vicinal surfaces shows large variations in quality of the LEED pattern. For the (110) and (331) surfaces, a clear pattern without streaking is found. In between however, streaking is so profound that it hinders the spot splitting analysis. When rotating from (331) towards (111), streaking is less pronounced.

For the spot splitting analysis in the region between (331) and (110) two different spot splittings can be tracked, depending on whether the surface is considered as having a (110) terrace with (111) steps or as having a (110) terrace with (111) steps. For the latter, spot splittings could not be determined over the whole range due to the strong streaking. However, the data that could be recorded indicates the expected spot splitting (see figure 5.5).

The observed streaking in the LEED patterns could be the caused by an oxygen overlayer similar to the (211) vicinal surfaces. Such surface oxygen could cause a missing row reconstruction, as shown by Haase et al. for Ni(771) [22]. However, the fractional order spots or streaks that one would expect to see because of this reconstruction are not observed. Due to the hampered ability to analyse LEED patterns in this region, other types of reconstructions can not be disproven.

5.5 Conclusion

From a LEED study on a nickel cylindrical single crystal with its axis along the [110] direction, it is shown that the low step density regions of the crystal contain the expected surface structure with steps of monoatomic height. For the intermediate step density regions, streaking is observed, which may indicate reconstructions and/or the presence of oxygen on the steps. For the (211) vicinal surfaces, adsorbate-induced step doubling may cause patches with two-atom heigh steps. This behaviour is thought to be caused oxygen adsorbed on the steps. To improve the surface quality in this region of our cylindrical crystal, an optimization of the cleaning procedure will be required. In the highest step density regions, around (311) and (331), only the expected surface structure with monoatomic height steps is found.
BIBLIOGRAPHY

Bibliography


