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Spatial variation of the surface state onset close to three types of surface steps on Ag(111) studied by scanning tunnelling spectroscopy

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Abstract. A regular step, a dislocation slip step and a step formed by the emergence of a split edge dislocation (SED) to the surface influence the local density of states close to the onset of the surface state as investigated by scanning tunnelling spectroscopy at low temperature. The onset of the surface state shifts close to the regular step and the dislocation slip step by approximately 15 meV towards the Fermi energy. Additional maxima above the onset are only observed if a second step leads to confinement. In both cases, the conductivity decreases close to the step. However, an increase in conductance above the surface state onset is observed close to the SED step. Furthermore, a variety of additional states are discernable. Thus, different types of steps lead to markedly different changes in the local electronic structure on surfaces.

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Contents

1. Introduction

Defects are of utmost importance for the understanding of phenomena within the area of material science. In particular, dislocations that mark the border between the displaced and not displaced parts of a crystal play a central role in the mechanical and electrical properties of crystalline solids. Consequently, they have been investigated in detail for more than 50 years [1]. Although most investigations have focused on bulk properties, dislocations also play a significant role in a number of surface-related phenomena. If the Burgers vector of a bulk dislocation has a nonzero component along the surface normal, a bulk dislocation intersecting the crystal surface will result in a surface step that ends at the dislocation. These steps are very important, e.g., for the control of growth and solidification processes. If the dislocation is split into partial dislocations, a surface step may evolve between the partial dislocations, even if the total Burgers vector is in parallel to the surface. In fcc crystals, splitting into two partials, which have fractional screw character, is energetically favourable. We have shown before that on Ag(111) an edge dislocation that splits according to the reaction $\frac{1}{2}[1\bar{1}0] \rightarrow \frac{1}{6}[1\bar{2}\bar{1}] + \frac{1}{6}[2\bar{1}1]$ leads to such a partial step that can be imaged by scanning tunnelling microscopy (STM) [2].

Also, surface states situated in the large sp-band gap of the projected bulk band structure along the Γ–L line on fcc(111) surfaces of noble metals [3] govern a variety of surface processes including diffusion [4], epitaxial growth [4, 5], equilibrium crystal shapes [6], reconstructions [7], atom sticking [8], surface chemistry [9], molecular ordering [10] and screening of defects at surfaces [11]. Recently, we demonstrated that they also influence adatom island decay [12].

STM and scanning tunnelling spectroscopy (STS) are particularly sensitive to these surface states that dominate in the zone between the tip and the surface [13, 14]. These techniques map the local electronic density of states (LDOS) in real space and allow us to probe the interplay of surface electronic and geometric structures with high resolution. Spatial variations in the LDOS of a surface near the Fermi energy E_F can be approximately mapped out by measuring dI/dV spectra at different locations [15]. dI/dV spectra have allowed the observation of electrons in surface states and of their interactions with adsorbates [16, 17], steps [16], [18]–[22] and other structures [16, 23], giving a measure of the surface state dispersion, as well as an insight into the interaction between surface state electrons and scattering sites on the surface [16].

In this paper, we investigate the interaction of surface state electrons with three types of surface steps: a regular step, a slip dislocation-induced step of regular step height (named dislocation slip step) and the emergence of a split edge dislocation (SED) to the surface with varying step height (named SED step). The latter differs from a regular surface step not only
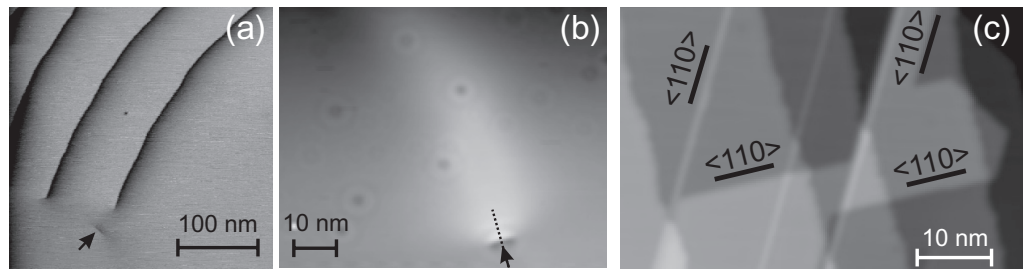
Figure 1. Large-scale STM images of surface steps on Ag(111): (a) several regular steps emerging at screw dislocations and one SED step (arrow); differential imaging mode so that the image appears to be illuminated from the left, −0.49 V, 3.5 nA, room temperature; (b) the SED step (arrow) disappearing into bulk; black spots are CO molecules as confirmed by a CO adsorption experiment [25], 130 meV, 1.6 nA, 5 K; mirror planes of edge dislocations are in parallel to arrows in (a) and (b) as indicated by dashed lines in (b); (c) the region with regular steps following no specific surface direction, here from top to bottom, and with dislocation slip steps running along the closed packed ⟨110⟩ directions of the surface, 203 mV, 0.43 nA, 5 K.

in the continuously varying increase in step height, but also because it is the indication of a two-dimensional (2D) defect perpendicular to the surface [2].

First, we present the dI/dV spectra measured close to the SED step. We then compare these spectra to those measured close to a regular step, a pair of two regular steps, and a dislocation slip-induced straight step. This comparison shows that a variety of additional states and a largely increased conductivity are only observable close to the SED step. We conclude that the difference is related to scattering at the subsurface part of the edge dislocation.

2. Experimental procedure

The experiments were performed in ultrahigh vacuum with several low-temperature STMs of the same type as described in [24]. The single crystalline Ag(111) surface is cleaned by several sputtering and annealing cycles. Measurements are carried out at 5–7 K apart from figure 1(a) imaged at room temperature. The topographic images are taken in constant current mode. The dI/dV spectra are recorded in the lock-in technique of the ac tunnel current driven by an up to 4 mV signal added to the junction bias with a frequency between 330 and 740 Hz. Tips are gently brought into contact with the surface till no features apart from the surface state onset are visible in spectra taken on terraces far away from any defect. This precaution ensures that tip states are not at the origin of the observed spectra.

The error bars on peak positions include (a) different fits to the onset and (b) determination of the onset positions in different spectra taken at the same spot of the surface.

3. Results

In figure 1, we present large-scale images of the types of steps investigated here. Figure 1(a) shows a large-scale image of a nonperfect region of an Ag(111) surface. From our previous work [2], we know that the two steps emerging in the lower left part of the image mark the

emergence of screw dislocations. The arrow points to an SED step. In figure 1(b), the distortion caused by the SED step slowly diminishes towards the upper part of the image, indicating the subsurface displacement of the atoms that in this case slowly diminish into the bulk. The step that marks the emergence of the edge dislocation is mirror symmetric with respect to the two emergence points, as indicated by the mirror plane (dashed line). At 7 K, the partials of an edge dislocation have a distance of ≈ 8 nm at the surface [2]. Between the two emergence points of the partials, a step of reduced height (1/3 or 2/3 of the total step height) is formed. Here, the step height is 0.07 nm, i.e. about one-third of an intrinsic surface step on Ag(111). Both, distance and height, are in excellent agreement with the theoretical calculations in [2].

The regular steps in figures 1(a) and (c) do not follow any specific surface direction and are curved or wavy. In contrast, dislocation slip steps strictly follow the $\langle 110 \rangle$ directions of the surface (figure 1(c)), because they are induced by a slip along those (111) planes that are not in parallel to the surface. These planes intersect the surface along the $\langle 110 \rangle$ direction. Both types of steps, regular and dislocation slip, have the same step height of 0.24 nm. They might cross, as seen in figure 1(c). They do not displace atoms from bulk sites.

Before discussing the dI/dV spectra near the steps, we recapitulate the electronic structure of Ag(111) close to E_F on a defect-free terrace. On defect-free regions of the surface, the only feature in dI/dV spectra is usually the onset of the surface state marked by a sharp cusp in the dI/dV spectra at the bottom of a surface state band, at which the conductivity doubles (figure 2(a)). According to photoemission data, the surface state onset of Ag(111) lies at (-74 ± 5) meV [26] at our measurement temperature or at (-63 ± 1) meV at 30 K in a more recent measurement [27] corresponding to -67 meV at our measurement temperature according to [26]. According to STS data [19, 23], it is situated at $-(65 \pm 3)$ meV modified by the Stark shift [28]. With our setup, the surface state onset extends from $V_{bot} = -75$ mV to $V_{top} = -62$ mV with $V_{SS} = -69$ mV, within the range of previous measurements. The width of the onset of $\Delta V = 13$ mV includes temperature and modulation broadening. Considering these, we determine a lifetime of > 80 fs [22], which is lower than the best limit determined so far of 120 fs [29]. The lifetimes determined in this way always present a lower limit because of instrumental broadening. The noise level (i.e. unwanted variation in tip–sample distance at constant parameters) of our instrument is thus somewhat higher than in [29]. We will thus only qualitatively discuss the relative broadening of the onsets.

We now investigate changes to dI/dV spectra close to an SED step. Because of its mirror symmetry (see figure 1(b)), we concentrate on one side of it (figure 2(b)). The emergence of the partial leads to a smooth increase in step height up to a third of the regular step height on Ag(111) (figure 2(c)).

The spectra taken across the SED step and along it (figure 2(d)) differ considerably from spectra on the defect-free surface (figure 2(a)). The onset of the surface state shows a slight shift on both sides of the step. Its intensity is lower on the lower side of the step than on the upper side of the step (compare e.g. spectra (1) and (3)). This is the opposite trend to the one observed close to regular steps [30]. Most importantly, all spectra show additional features above the surface state onset. These additional states add up to a greatly enhanced conductivity as compared to the unperturbed surface. Near the defect, the conductivity is up to ten times larger above the onset, while it only about doubles on the perfect surface (figure 2(a)). For example, in between 100 and 200 mV, the conductivity is 2.9 nA V^{-1} on the infinite surface, but 10 nA V^{-1} for spectrum 5 (as calculated from the absolute values). Both spectra are acquired with the same tip and the same set point parameters of 0.2 V and 0.7 nA. This enhanced conductivity is in total higher on the
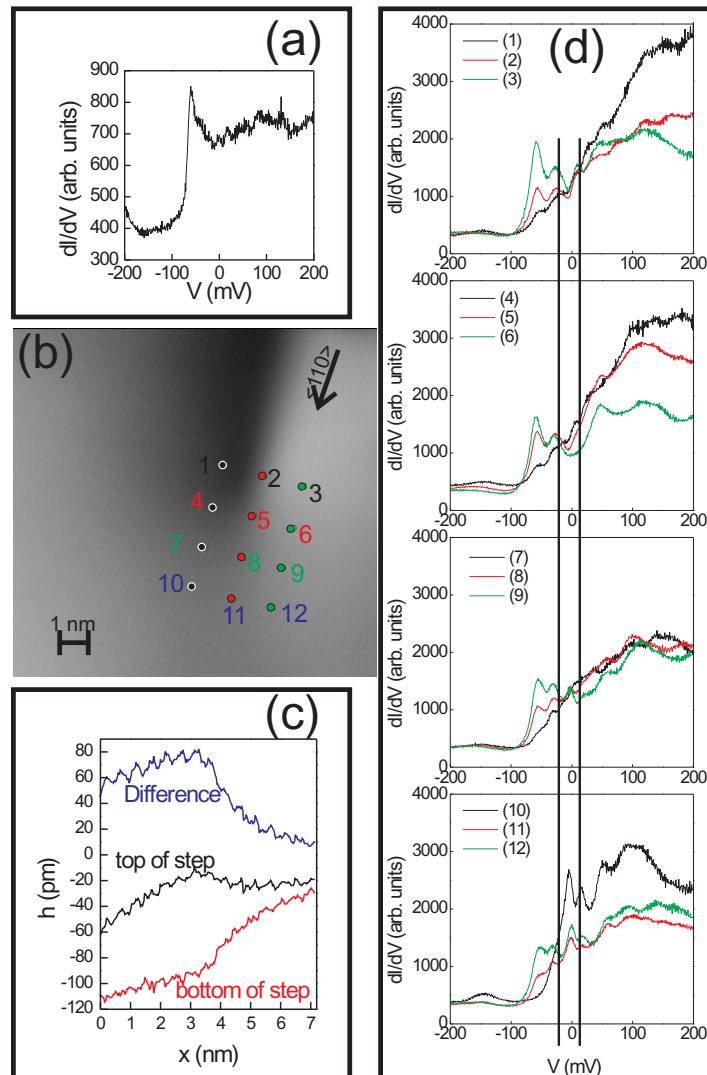
Figure 2. (a) dI/dV-spectrum displaying the surface state onset at -69 mV on a defect-free Ag(111) surface; (b) STM image of lower half of an SED step, -0.2 V, 0.68 nA, 7 K; (c) profile along both sides of SED step in (b) in parallel to the indicated $\langle 110 \rangle$ direction; (d) dI/dV spectra measured where indicated in (b) (distance between the measurement points is 1 nm); spectra within one panel correspond to spectra from the same row; vertical lines mark the second and third maximum in the top most panel and serve to guide the eye; all spectra were acquired with the same tip and set point; $V_{mod} = 4$ mV.

lower side of the step and decreases with increasing distance from the step (on both sides of the defect, not shown).

Concentrating on the first few maxima, which can be easily resolved, we observe that the positions of the additional maxima are situated at the same energy for the spectra taken on a line perpendicular to the step (the same panel in figure 2(d)) and vary only in intensity. In contrast, spectra taken in a parallel row to the step exhibit shifts in energy of the maxima (e.g. the third maximum as indicated by the vertical line in figure 2(d)).
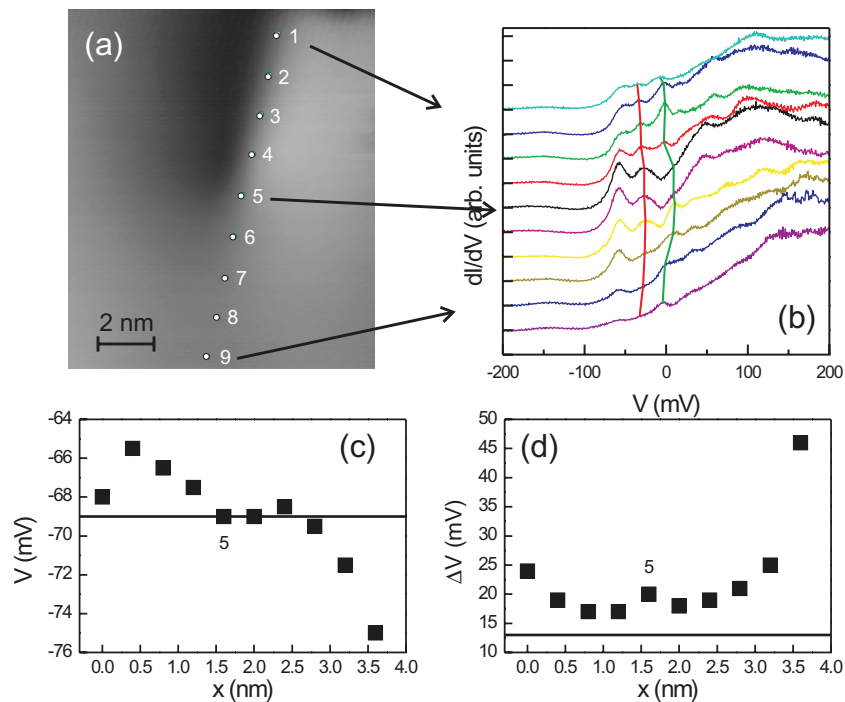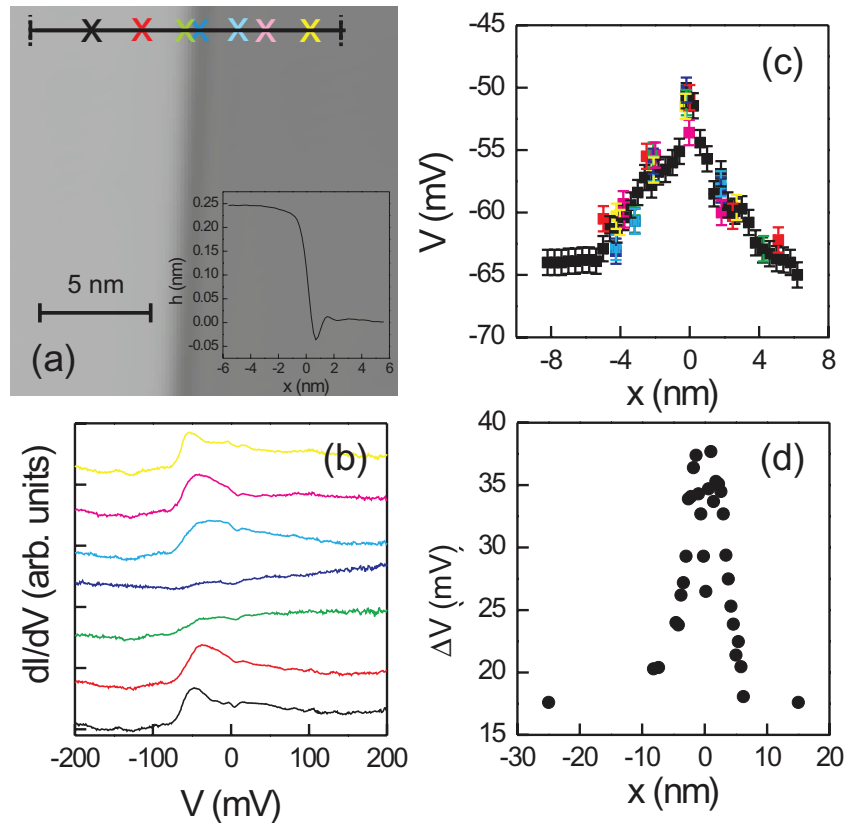
Figure 3. (a) STM image of the same SED step as in figure 2, 7 K; (b) dI/dV spectra along a line in parallel to the step where indicated in (a); spectra displaced along abscissa for better visibility; lines are a guide to the eye for the second and the third maximum as determined from the derivative of the curves; (c) the position of the surface state onset; spectra taken at point 5 in (a) are marked; (d) the width of the surface state onset; vertical lines in (c, d) indicate values for the defect-free terrace extracted from figure 2(a); $V_{mod} = 4$ mV.

We thus concentrate, for a further analysis, on spectra recorded on a single line in parallel with the SED step taken over a larger region than in figure 2. As the maxima are more clearly resolved on the upper side of the step (here the right-hand side), we discuss the spectra taken on this side of the step besides their overall lower intensity (figures 3(a) and (b)).

The surface state onset shifts in total by approximately 10 meV. It is closest to the value on regular terraces for spectra 5 and 6 (figures 3(c) and (d)), i.e. close to the inflection point of the step (cf figure 2). At this point it also shows the highest intensity. The onset shifts closer to the Fermi energy for increasing step height and away from it for decreasing step height (figure 3(c)). The width of the surface state onset is broader than on the pristine Ag(111): in all spectra, at least by 4 mV and up to three times as broad (figure 3(d)).

We identify up to seven increases/maxima in the region between the surface state onset and 150 meV (figure 3(b)), after which the differential conductance saturates. It is not always possible to assign the peaks of the different spectra univocally to each other, but there are some clear shifts in energy and obvious changes in intensity as indicated by the lines in figure 3(b) for the second and the third maximum. The variation in both, energy and intensity, is thereby of the same order as for the surface state onset. The second onset is situated approximately 30–40 meV above the surface state onset and shows similar intensity behaviour to the surface state onset. However, its maximum shifts for decreasing step height into the opposite direction by up to
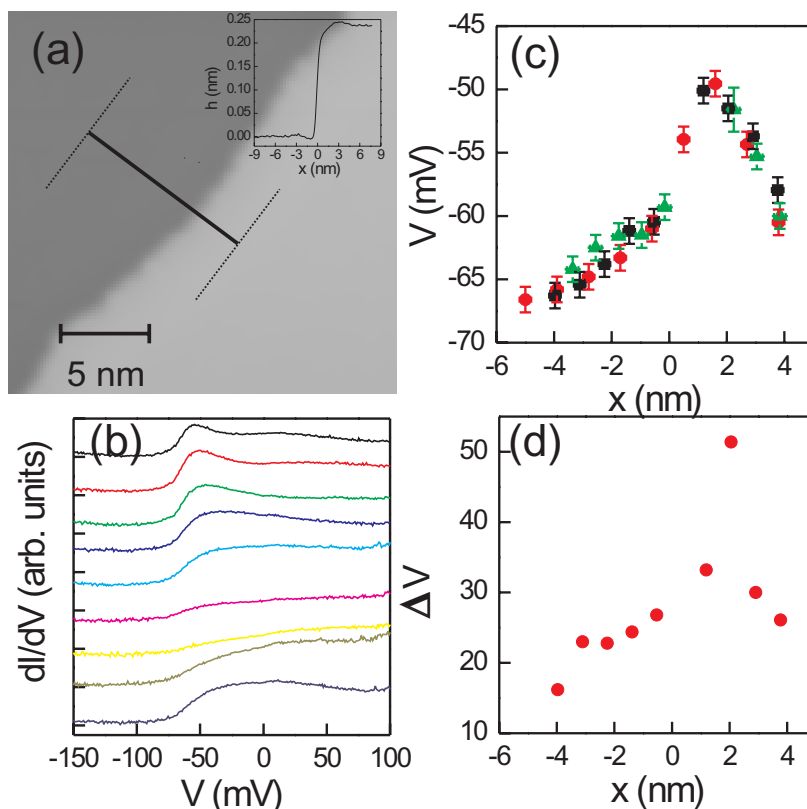
Figure 4. (a) STM image of the dislocation slip step; inset: line scan across the step, 5 K; (b) dI/dV spectra taken at a distance of 1 nm along a line perpendicular to the dislocation step where indicated in (a); spectra displaced along the abscissa for better visibility; $V_{mod} = 1.4$ mV; (c) the position of the onset of the surface state; different symbols for different measurement series; (d) the width of the surface state onset.

≈ 10 meV. The positions of the other maxima shift by up to 16 meV for different positions along the step. We propose that these maxima are related to scattering of bulk electrons at the subsurface part. In the following, we test this hypothesis by the investigation of purely surface defects.

In order to exclude that the spectra result simply from an interference of electrons scattered at different parts of the dislocation-related step, we now present spectra taken at other types of steps. We start by discussing spectra taken close to a dislocation slip step (figure 4(a)). Such a step represents the line defect of the highest possible symmetry because it is atomically straight (along the ⟨110⟩ surface direction). Similar spectra for a pair of such dislocation slip-induced straight steps were presented before with a different focus [20].

The step of 0.24 nm in height (line scan in figure 4(a)) leads to an attenuation of the surface state intensity (figure 4(b)) and to a shift in the surface state onset from −65 to −50 meV (figure 4(c)). The total shift in the surface state is thus of the same order of magnitude as the one close to the SED step. However, it only shifts towards the Fermi energy. The deviation from the surface value extends from the step around 5 and 6 nm to the upper and lower terraces, respectively. Note a slight asymmetry in the shift on the two sides of

Figure 5. (a) STM image of the regular step, $-200\,\text{mV}$, $1\,\text{nA}$, $5\,\text{K}$; inset: line scan across the step; (b) dI/dV spectra taken at a distance of $1\,\text{nm}$ along a line perpendicular to the regular step where indicated in (a); spectra displaced along the abscissa for better visibility; $V_{\text{mod}} = 2.9\,\text{mV}$; spectra from the top to the bottom are measured from top left to bottom right in the STM image; (c) the position of the onset of the surface state; different symbols for different measurement series; (d) the width of the surface state onset.

the step. This asymmetry reflects different reflectivities of an ascending versus a descending step [20].

Onsets extracted from several series of spectra taken at different positions along the step are shown in figure 4(b) and demonstrate that the position of the surface state onset here depends only on the distance from the step, contrary to the SED step discussed above. The width of the onset varies between 20 and 38 meV (figure 4(d)). Most importantly, no additional maxima are observed above the surface state onset and the conductivity decreases close to the dislocation slip step in contrast to the largely increased conductivity close to the SED step. A simple scattering of surface state electrons at the discontinuation of the surface by a step can thus not explain the spectra close to the SED step.

Another possible explanation for the specific features of the SED step is different phase shifts of the scattered electrons at different parts of this step of continuously varying height. This explanation can be ruled out by spectra recorded close to a regular step [30]. Characteristic of such a step is an atomic-scale roughness. This roughness consists of straight segments along close-packed directions of the surface separated by kinks (figure 5(a)). If the additional

maxima of the SED step resulted from different phase shifts during scattering and subsequent interference, additional maxima should be observed here, because different scattering distances as induced by the kinky nature of the step have a similar effect as different phase shifts at constant distance.

The step of 0.24 nm in height (figure 5(a)) leads to an attenuation of the surface state (figure 5(b)) and to a shift in the surface state onset from −67 to −50 meV (figure 5(c)), very similar to the dislocation slip step shown in figure 4. Note that the shift is not continuous, but the shift to 60 meV is over a distance of 4 nm, while the shift to 50 meV extends over a distance of 2 nm only. The asymmetry between the ascending and the descending step is more marked than for the dislocation slip step. Both observations are attributed to the curved appearance of the step and result from scattering at kinky parts of the step. The width of the onset varies between 16 and 51 meV (figure 5(a)) and thus does not differ considerably for straight and curved steps.

Again, several series of spectra taken at different positions along the regular step are shown (figure 5(b)) and demonstrate that the position here depends mainly on the distance from the step, in contrast to the SED step discussed above. As for the dislocation slip step, no additional maxima are observed above the surface state onset and the conductivity is not increased. Thus, superposition of electrons scattered with different phase shifts is unlikely to be the origin of an increased conductivity close to the edge dislocation.

An increased conductivity has been shown to result from confinement [31]. Although it is not obvious how confinement could result from an SED step, we finally discuss whether the increased conductivity close to the SED step is possibly due to such confinement. For this purpose, spectra are recorded across a terrace limited by two regular steps (figure 6(a)). It has been shown before that the confinement of surface state electrons in such a geometry shifts the surface state onset and leads to quantum well states above the onset [22]. The terrace shown in figure 6(a) has a local width of 7.4 nm. Indeed, the confinement of the surface state electrons between the two regular steps leads to a second maximum in the dI/dV curves above the surface state onset at around 0 eV (figure 6(b)). The surface state is shifted in energy in accordance with [22] and varies between −52 and −58 meV. The first quantum well state shifts between −4 and 9 meV. As expected for confined states, the intensity of both the states varies along the terrace, the second state with double periodicity (figure 6(d)). The energy variation of the second state is indeed comparable to the one of the additional states near the SED step. However, the increase in conductivity induced by this single extra maximum is much less than the one observed close to the SED step. Confinement can thus not explain the increase in conductivity close to the SED step.

4. Discussion

Table 1 summarizes the values extracted from the spectra close to the different types of steps. All properties are similar for the two types of single steps, the regular step and the dislocation slip step, and thus a small step curvature does not influence these parameters measurably.

Concerning the width of the surface state onsets, they are broadened for all of the investigated steps with respect to the width on an infinite terrace. The width is inversely proportional to the lifetime of the electrons; thus the lifetime is reduced. Considering the modulation voltage and the measurement temperature, this would correspond, e.g., to a reduction of the lower limit of the lifetime from 52 to 24 fs for the dislocation slip step, i.e. the lifetime is approximately halved. However, an increase in surface state onset width close to
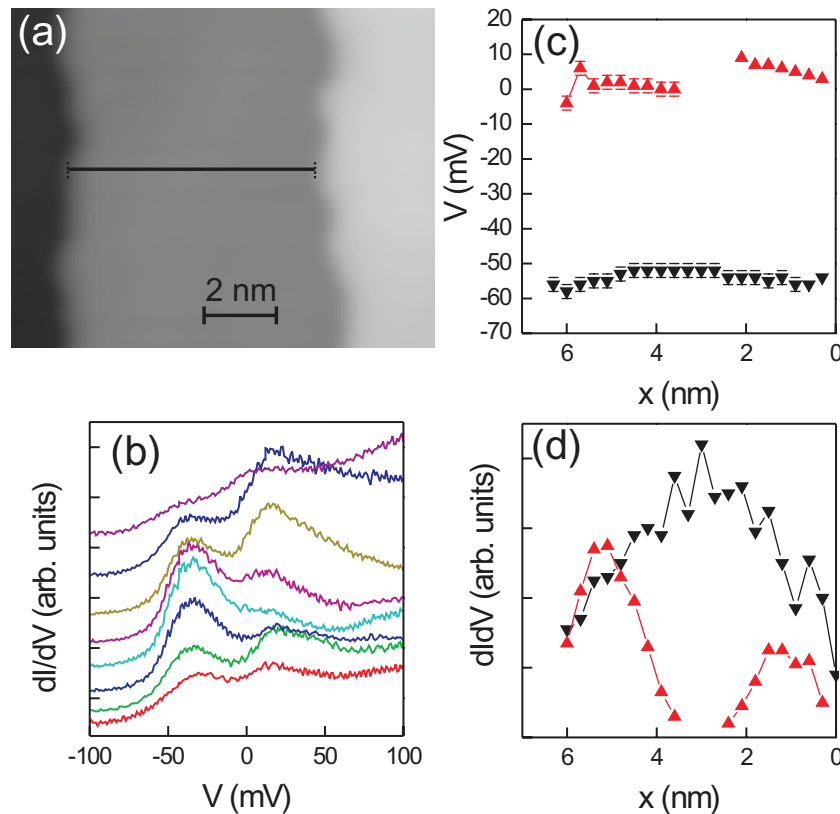
Figure 6. dI/dV-spectra in between two regular steps: (a) STM image, -51 mV, 1.2 nA, 7 K, terrace width: 7.4 nm; (b) seven spectra out of 18 taken along the line indicated in (a); (c) position of surface state onset (down triangle) and second onset (up triangle); (d) intensity of onsets, same symbols as in (c); $V_{mod} = 4$ mV.

Table 1. Surface state properties close to different step types; V_{SS}: surface state onset; ΔV: width of onset; $\frac{I}{I_{bulk}}$: relative increase in conductance; N: number of onsets.

Location	V_{SS} (meV)	ΔV (meV)	$\frac{I}{I_{bulk}}$	N
Defect-free terrace	-69	13	2	1
Dislocation slip step	$-64 \ldots -50$	$20 \ldots 38$	< 2	1
Regular step	$-67 \ldots -50$	$16 \ldots 51$	< 2	1
Pair of regular steps	$-58 \ldots -52$	$20 \ldots 42$	4	2
SED step	$-75 \ldots -65.5$	$17 \ldots 46$	up to 9	up to 7

steps was calculated even for infinite lifetime [22]. This geometric effect contributes also to the increased widths. The somewhat larger increase for the curved step might be attributed to this geometric effect. We thus do not attempt to extract lifetimes and only conclude that the lifetime is reduced by similar amounts for all defects. This reduction is conventionally explained by the scattering of the surface state electrons into bulk states without momentum conservation. On a perfect terrace, it has been shown that such intra-band transitions are responsible for only about 80% of the surface state decay [14], because surface states and bulk states are orthogonal.

Bulk and surface states are no longer orthogonal at a step because of the reduced symmetry near the defect. Thus, scattering from surface state electrons into bulk states, which usually violates momentum conservation, is possible even when it is elastic. By this scattering mechanism, the electrons can interact with bulk states with momenta from the entire Brillouin zone. This reasoning is independent of the exact geometry of the step. Indeed, the lifetime is reduced by approximately the same amount in all of the cases investigated here.

Also, the surface state onset is displaced from the one on the perfect terrace in all cases. While steps of regular height shift the surface state by $\approx$15 meV towards the Fermi energy, the SED step has two different effects depending on the exact position at which the spectra are recorded. The sign of the shift changes at the inflection point of the step. Geometrically, the surface distortion is changed into a visible step at this inflection point (see figures 2(b) and (c)). The observed shift thus implies that distortion of the surface lowers the surface state energy, but a discontinuation, even a small one, has the opposite effect. The former is in agreement with calculations for strained Ag on Si(111)-7×7, which showed a shift in the surface state onset to higher energies for small tensile strain [32]. The latter is in agreement with earlier work on regular steps [22] and results from a finite and energy-dependent reflectivity of the steps on Ag(111) [20]. The smaller shift as compared to the steps of regular height is consistent with the reduced step height.

The spectra close to the SED step are furthermore different from the others in increasing the relative conductance via a series of additional states. Furthermore, the overall conductivity is higher than on the perfect surface. The simplest explanation for the additional peaks in the spectra close to the SED step is a superposition of scattered electrons with different phases at different parts of the dislocation. Different phases thereby result from different scattering centres because of different geometry. One could imagine that an oscillatory surface state pattern is achieved. However, in view of the spectra close to the curved regular steps presented above, this explanation is rather unlikely.

Charge redistribution at regular surface steps leads to localized step states reported first on Ag(111) and Au(111) [30]. Their intensity leads likewise to an increased LDOS of occupied states near the bottom of the step, but a corresponding decrease in the LDOS of unoccupied states near the top in relation to the unperturbed electron density found on a terrace [30]. The intensities here show the opposite trend and thus the spectra observed here are not consistent with such a step edge state.

Instead, we argue that the spectra reflect not only the scattering of the surface state electrons at the defect but also the one of bulk electrons. For this interpretation, it should be kept in mind that an edge dislocation is a bulk defect and the SED leads to displacement of atoms from their bulk position on an area perpendicular to the surface and of the width of the observed step on the surface. Thus bulk electrons can form standing waves between this defect and the surface as observed before for subsurface cavities [33]–[37] and subsurface point defects [37]–[39]. The spectra close to the SED step are thus a superposition of a surface state onset, changed by the existence of the step, and bulk electrons that are scattered back to the surface at the subsurface part of the edge dislocation. The exact shape of the spectra demands sophisticated calculations [40], including the anisotropy of the Fermi surface [41]. Such calculations are not yet available for extended subsurface defects, as investigated here.

The bulk nature of the additional states is supported by the spectra. The difference in bulk and surface states is usually discussed in terms of dimensionality and of $k_{\parallel}$ dispersion.

The spectra are not sensitive to $k_\parallel$ dispersion. Concerning the difference in bulk and surface states in terms of dimensionality, it is the onset region of an electronic band that is most sensitive to its dimensionality. While 2D systems, such as surface states, have a step-like DOS at the onset of the band, 3D electron systems have a vanishing DOS at the electronic band origin, and increase with the square root of the energy. The overall increase in the additional states and following approximately an inverse parabola are consistent with the 3D character of the bulk states. Because of the pseudo gap near the $\bar{\Gamma}$ point, the integrated density of bulk states is not continuous over the energy range investigated, thus explaining the stepwise increase in intensity.

5. Conclusion

In conclusion, we have presented dI/dV spectra on the Ag(111) surface close to three types of steps: regular surface steps, slip dislocation-induced surface steps of regular height and an emerging SED-induced step. Steps of continuous height shift the position of the surface state onset towards the Fermi energy and reduce the conductivity. The SED step leads to a smaller shift in the surface state onset. In contrast to the regular steps, the shift is away from the Fermi energy for the distorted part of the SED step. Furthermore, such a step greatly enhances the conductivity. We interpreted our results as a superposition of the surface state electrons scattered at the step at the surface and the bulk state electrons scattered at the part of the dislocation that is subsurface.

We believe that this observation will be important for the understanding of different surface-related phenomena that depend on electron density such as e.g. nucleation of molecules at steps [42] or surface reactions. Furthermore, it might be possible to extract the properties of the subsurface part of the edge dislocation from such spectra if supported by theory.

Acknowledgment

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