Scattering of electrons in image-potential states by steps

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ABSTRACT Image-potential states on several stepped copper surfaces were studied by time, energy, and angle-resolved two-photon photoelectron spectroscopy. For different step densities binding energies and effective masses were determined in the energy-resolved decay rates in the time-resolved mode of two-photon photoemission. The asymmetry with respect to the electron motion up or down the steps of the decay rates is enhanced for less-ordered step arrangements. Elastic intraband scattering strongly depends on details of the backfolding of the bands by the periodic step structure. Elastic intraband scattering is of similar importance as inelastic decay may contribute significantly to the asymmetry of the decay rates.

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1 Introduction

The screening of an external charge in front of a metal surface leads to an attractive force identical to the force exerted by an opposite charge at the same distance inside the metal. In the associated long-range one-dimensional Coulomb-like image-potential a Rydberg-like series of electronic image-potential states forms, which converges to the vacuum level \(E_{\text{vac}}\) [1, 2]. These states are localized in the perpendicular direction, but the electrons can move freely parallel to the surface. In the presence of a band gap in the projected bulk band structure the life-time \(\tau\) of image-potential states is sufficiently long to follow their dynamics by time-resolved two-photon photoemission (2PPE) [3–6]. Decay rates \(\Gamma = \hbar / \tau\) are a measure for the decrease of the population in the image-potential state. Spectroscopic linewidths also contain information on elastic scattering described by an additional pure dephasing rate [4].

For a stepped surface the electrons feel a corrugated potential for the motion parallel to the surface [7, 8]. This may influence the effective mass, leading to enhanced elastic or inelastic scattering, and for a periodic step structure, modifies the bulk and surface band structure through the backfolding of bands [9]. However, it has a much stronger effect on the electron dynamics as demonstrated in previous work on Cu(117) and Cu(119) surfaces [10, 11]. In this work we extend these studies to Cu(115), Cu(111) and Cu(115) to complete the systematic investigation as a function of step density.

2 Experiment

Time and angle-resolved two-photon photoemission [12] permits a detailed study of the properties of image-potential states regarding energy, linewidth and lifetime. Our experiment [4, 13] uses a Ti:sapphire oscillator to generate infrared laser pulses (IR, \(h \nu = 1.53\) eV) with a duration of 25 fs and 550 mW mean power at 86 MHz repetition rate. Ninety percent of the IR intensity is frequency tripled to obtain ultraviolet laser pulses (UV, \(h \nu = 4.59\) eV) with a width of 50 fs and a mean power of 10 mW. Image-potential states are excited by the UV pulse and subsequently ionized by the IR pulse. A delay between the two laser pulses controlled with femtosecond resolution allows for following the population dynamics of the image-potential states. The emitted electrons are analyzed by an electrostatic hemispherical analyzer with respect to energy and direction with an accuracy of 30 meV and 1.5°, respectively. The base pressure during the experiments was better than \(5 \times 10^{-11}\) mbar. Sample preparation of the copper single crystals was done by repeated sputtering and annealing cycles.

The Cu(111) surfaces are vicinal to Cu(001) with step edges running along the [\(\bar{1}10\)] direction. The mean terrace width is \(l/2\) nearest-neighbor distances (2.56Å) and the step height is 1.81Å. Previous scanning tunneling microscopy (STM) investigations [11] showed that the mean terrace width corresponds to 3.6 and 4.0 nearest-neighbor distances for the Cu(117) and Cu(119) surfaces used in our work, respectively. The measured values are used in the context of step density. The nominal orientation is used for the discussion of Brillouin zones, which become unphysically small otherwise. The parallel momentum \(k_{\|}\) is counted positive for emitted electrons moving in the [\(\bar{1}1\bar{2}\)] direction. More descriptive is the notion of electrons going upstairs, or downstairs for the opposite [\(\bar{1}1\bar{2}\)] direction.

3 Results and discussion

3.1 Energies

Two-photon photoemission spectra for stepped copper surfaces are shown in Fig. 1 on a binding energy axis
Two-photon photoemission spectra of image-potential states for various Cu(111) surfaces relative to the vacuum level $E_{\text{vac}}$. The spectra show clear peaks attributed to the $n = 1$ and $n = 2$ image-potential states as well as shoulders attributed to the $n = 3$ and higher states which cannot be resolved energetically. The peaks shift to lower binding energies with increasing step density accompanied by an increased linewidth. The binding energies are compiled in Table 1. The values for the $n = 4$ states are obtained using the measured energy difference of 36 meV to the $n = 3$ states from quantum-beat oscillations [14]. The work functions given in Table 1 were determined from the low-energy cutoff of the spectra (not shown) and the independently measured work function of the analyzer.

The energy values of Table 1 are plotted in Fig. 2 relative to the Fermi energy $E_F$ as a function of the step density. The work function $\Phi = E_{\text{vac}} - E_F$ decreases linearly with a slope of $-57 \pm 3$ meV nm. The lowering of the work function is due to the smoothening of the charge density according to the Smoluchowski effect [15]. The linear decrease is in agreement with a constant dipole potential of the steps, independent of the step density down to a step separation of 2.5 nearest neighbor distances. The dipole moment per step atom is calculated to $-0.038$ Debye which is comparable to the values obtained for Cu(775) [16] and about one order of magnitude smaller than values obtained on stepped Pt or Au surfaces [17].

Figure 2 and Table 1 show that the binding energy of the higher ($n \geq 2$) image-potential states is within the experimental uncertainty of $\pm 5$ meV constant. These states are located at distances away from the surface comparable or larger than the step separation. Therefore they feel only the average potential as measured by the work function for large distances. The $n = 1$ state clearly does not follow the work function decrease as indicated for comparison by the lower linear line in Fig. 2. The energy stays almost constant as would be expected for states localized on the (001) terraces [18]. Localization on the terraces leads to an increase in energy, which can be modeled with a Kronig–Penney type potential. For Cu(1 1 15) the $n = 1$ image-potential state is oriented relative to the (001) terraces (see Fig. 3). The energy difference relative to the shifted vacuum energy for Cu(1 1 15) in Fig. 2 can be used to fit the potential parameter (potential height times width) to 200 meV Å using the model of [19]. The value for the potential parameter is consistent with the one obtained by integration of the dipole potential along the steps [16]. For the other surfaces the energy shift calculated with this potential parameter is too small as shown by the dotted line in Fig. 2. For these surfaces the image-potential states are not localized on the (001) terraces. Rather they are extended over several terrace widths and are oriented relative to the crystallographic sur-

![Figure 1](image1.png)

**FIGURE 1** Two-photon photoemission spectra of image-potential states for various Cu(111) surfaces

![Figure 2](image2.png)

**FIGURE 2** Energies of the vacuum level (work function) and the lowest image-potential states as a function of step density on Cu(111) surfaces

<table>
<thead>
<tr>
<th>Work function $\Phi$ (eV)</th>
<th>Cu(001)</th>
<th>Cu(1 1 15)</th>
<th>Cu(1 1 11)</th>
<th>Cu(119)</th>
<th>Cu(117)</th>
<th>Cu(115)</th>
</tr>
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<tbody>
<tr>
<td>$E_{\text{vac}} - E_F$ (meV)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$n = 1$</td>
<td>4.650</td>
<td>4.625</td>
<td>4.615</td>
<td>4.600</td>
<td>4.590</td>
<td>4.565</td>
</tr>
<tr>
<td>$n = 2$</td>
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<td>574</td>
<td>569</td>
<td>556</td>
<td>545</td>
<td>520</td>
</tr>
<tr>
<td>$n = 3$</td>
<td>184</td>
<td>178</td>
<td>182</td>
<td>176</td>
<td>171</td>
<td>180</td>
</tr>
<tr>
<td>$n = 4$</td>
<td>86</td>
<td>83</td>
<td>84</td>
<td>82</td>
<td>80</td>
<td>85</td>
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<td>Effective mass $m^*/m_e$</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$n = 1$</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>1.0</td>
<td>1.0</td>
<td>–</td>
</tr>
<tr>
<td>$n = 2$</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.1</td>
<td>1.1</td>
<td>1.0</td>
</tr>
<tr>
<td>Decay rate (meV)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$n = 1$</td>
<td>$18 \pm 2$</td>
<td>$30 \pm 4$</td>
<td>$47 \pm 8$</td>
<td>$73 \pm 20$</td>
<td>$73 \pm 20$</td>
<td>$&gt; 130$</td>
</tr>
<tr>
<td>$n = 2$</td>
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<td>$12 \pm 1$</td>
<td>$15 \pm 1$</td>
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<td>$33 \pm 5$</td>
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<tr>
<td>$n = 3$</td>
<td>$1.9 \pm 0.1$</td>
<td>$4.0 \pm 0.2$</td>
<td>$3.9 \pm 0.2$</td>
<td>$5.1 \pm 0.4$</td>
<td>$5.1 \pm 0.4$</td>
<td>$10 \pm 1$</td>
</tr>
<tr>
<td>Pure dephasing rate (meV)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>$n = 1$</td>
<td>$&lt; 2$</td>
<td>$16 \pm 3$</td>
<td>$20 \pm 3$</td>
<td>$40 \pm 2$</td>
<td>$43 \pm 2$</td>
<td>–</td>
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<td>$6 \pm 3$</td>
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<td>$8 \pm 3$</td>
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<td>$&lt; 2$</td>
<td>$&lt; 2$</td>
<td>$&lt; 2$</td>
<td>–</td>
</tr>
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</table>

**TABLE 1** Work function, binding energies, effective masses, decay rates and dephasing rates for image-potential states at $k \parallel = 0$ on stepped copper surfaces
face normal. Therefore the proper band gap for the stepped surface has to be taken into account. The backfolding of the bands into the reduced Brillouin zone of the stepped surface leads to small or vanishing band gaps. The small corrugation of the surface potential experienced by the image-potential states implies that the interaction of the image-potential states with the backfolded bulk bands is quite weak. Therefore it is sufficient to consider only the first Brillouin zone in an extended zone scheme [4, 13]. In this limit the projected band structure is obtained by sampling the first bulk Brillouin zone at the miscut angle relative to the (001) direction. The result is a change of the band gap which leads to an additional increase of the energy as indicated by the dashed line in Fig. 2, which agrees quite well with the experimental data. For Cu(115) the model cannot be applied, because the band gap disappears and the terrace width is too narrow to localize the $n = 1$ image-potential state. We emphasize that a satisfactory, consistent description of the experimental data for all Cu(111) surfaces with $l \geq 7$ can be reached only by including both the change of the band gap and the localization on the terraces.

### 3.2 Dispersion

The peak positions for image-potential states are plotted in Fig. 3 as a function of the polar emission angle for the Cu(1115) surface. All three bands show a parabolic dispersion, however, the minimum for the $n = 1$ band is shifted three degrees to larger emission angles. The dash-dotted line shows the parabola centered around the surface normal of the Cu(1115) surface (at $0^\circ$) and the dashed line the parabola shifted by $5.4^\circ$, corresponding to the surface normal of the Cu(001) terraces. Both alternatives are not compatible with the data. A shift of the band minimum has been observed before for image-potential states on Cu(775) [16] and is attributed to a localization of the state on the flat terraces between the steps. The observed shift is smaller than the miscut angle, which indicates an incomplete localization as reported for occupied surface states [20, 21].

The data of Fig. 3 show besides the parabolic image-potential bands some nondispersing features for emission angles between 20° and 40°. The energies are slightly above the band minima of the image-potential bands and the data points occur around the minima of the expected backfolded bands. Such nondispersing features have been observed for image-potential states on Cu(119) [22] and occupied surface states on stepped Cu(111) surfaces [23, 24]. Several models have been proposed to explain the experimental findings. Since the energies are slightly above the band minima of Cu(1115), localization by disorder is a plausible interpretation [23]. The observation of nondispersing features for positive angles only is in agreement with the asymmetric reflectivity of steps for image-potential states found by STM [25]. The absence of nondispersing features for Cu(111) surfaces with $l \leq 11$ can be understood by the smaller terrace size and the associated smaller terrace-width fluctuations [26].

The dispersion of the image-potential states for the Cu(1111) surface is shown in Fig. 4. Data for Cu(117) and Cu(119) have been presented in a previous publication [13]. The image-potential states show the usual free-electron-like dispersion with effective masses close to the electron mass as listed in Table 1. In the experimental data, bands folded back on the Cu(1111) surface using the potential parameter obtained in the preceding paragraph. This splitting is consistent with the experimental data, but cannot be resolved in the spectra due to limitations in energy and momentum resolution as well as imperfections in the terrace width distribution [11].

### 3.3 Decay rates

The decay rates of the first three image-potential states at the band bottom are plotted in Fig. 5 as a function of step density. The linear increase of the decay rates with step density indicates the opening of scattering channels to bulk states at step edges [25]. The data points for the Cu(115) surface lie significantly above the straight line fits. This surface has no band gap in the projected bulk band structure and the image-potential states are degenerated with bulk bands. Consequently the decay rates become quite large. For the $n = 1$ state the decay rate could not be measured in the time domain and a lower limit was estimated from the linewidth. The decay rates for the nominally flat Cu(001) surface are also found above the straight line fit of Fig. 5. Assuming that the
decay rates would be determined by scattering at step edges only, we would obtain terrace widths between 50 and 100 Å. This estimate is consistent with the observation that the measured work function of the Cu(001) surface is 5 meV below the straight line fit in Fig. 2. This width is certainly below the value obtained for well-prepared low-index copper single crystals. Considering, however, that for our best Cu(001) surfaces we measured about 15% smaller decay rates [27], we estimate that the Cu(001) crystal used in this work may have had a mean terrace width between 300 and 600 Å. The detectable influence on the lifetimes for such low step densities demonstrates again the high sensitivity of the spectroscopy of image-potential states to the quality of the surface.

The lifetimes measured for finite parallel momenta exhibit an asymmetry between the upstairs and downstairs direction [10, 11] with longer lifetimes for electrons moving up the steps. With STM an asymmetric reflectivity of steps for image-potential states was identified [25], which could explain the experimental data for Cu(119) and Cu(1115). However, for Cu(117) and Cu(1111) the asymmetry is significantly smaller. We explain this by the fact that the latter two surfaces exhibit a better order of the step arrangement than the former ones. For Cu(119) and Cu(1115) a single scattering description corresponding to the STM experiment is therefore more appropriate. For the well-ordered step arrays on Cu(117) and Cu(1111) multiple scattering leads to the formation of bands and a reduced asymmetry.

3.4 Interband scattering

Time-resolved two-photon photoelectron measurements for the Cu(1111) surface are shown in Fig. 6 on a logarithmic intensity scale. As indicated in the inset, the data are obtained on the $n = 1$ image-potential band from the band bottom $E_1$ up to the vacuum energy. For energies below 330 meV a rapid linear decrease is seen for positive delays between the UV pump and the IR probe pulse. The corresponding lifetime of 14 fs can only be estimated from the slope, but the shift of the maximum relative to the optimum overlap between the two laser pulses is in good approximation equal to the lifetime when the lifetime is shorter than the temporal resolution [28]. For $E_1 + 370$ meV a second exponential decay is observed with a lifetime corresponding to the one measured on the $n = 2$ band: electrons are scattered from the $n = 2$ band to the $n = 1$ band. This interband scattering contribution can be observed at long time delays, because the lifetime of $n = 2$ states is significantly longer than the lifetime of electrons in the $n = 1$ band [29]. For energies above the bottom of the $n = 2$ band the interband scattering contribution becomes even stronger and a $n = 1$ decay is hardly visible in the spectra of Fig. 6. The $n = 2$ contribution becomes weaker at even higher energies when a third component appears corresponding to the $n = 3$ decay with its typical quantum-beat oscillations [14].

The relative contributions of the interband scattering processes can be obtained by fitting the experimental spectra of Fig. 6 [11]. The results are shown in Fig. 7 for four different stepped copper surfaces. For Cu(117) and Cu(1115) the interband scattering contributions are relatively small and have their maximum close to the bottom of the respective band. For Cu(119) and Cu(1111) the interband scattering from the $n = 2$ band is quite high reaching over 90% for Cu(1111). The maximum contribution is observed for energies above the band minimum $E_2$ at energies depending on the terrace width. These maxima coincide with the intersection of the $n = 1$ band with the backfolded $n = 2$ band (see Fig. 4 and [10]). The periodic step lattice provides an interaction which leads to a mixing of the $n = 1$ and $n = 2$ bands. Therefore, the distinction between $n = 1$ and $n = 2$ bands disappears [9].

The decay rate for the $n = 2$ band at the crossing points between $n = 1$ and $n = 2$ bands is enhanced as can be seen in Fig. 8 for the Cu(1111) surface in agreement with the mixing of both states. The observed decay rate is closer to the value for the $n = 2$ band than the one for the $n = 1$ band. This can be explained by the strong scattering between the two bands, which emphasizes the state with the longer lifetime.
The effect could be enhanced by the asymmetry in the scattering processes as discussed in Sect. 3.3 for the asymmetry of the decay rates in the $n = 1$ band. A similar asymmetry is observed in the interband scattering from the $n = 2$ to the $n = 1$ band. Figure 8 shows that the interband scattering contribution measured on the $n = 1$ band is about a factor of five lower in the downstairs direction compared to the upstairs direction. The electrons scattered to the $n = 1$ band are missing in the population of the $n = 2$ band. Therefore, one would expect a higher decay rate on the $n = 2$ band for the downstairs direction than for the upstairs direction (note that the crossing bands have opposite group velocity). The experimental data for the decay rate in the $n = 2$ band in Fig. 8, however, show no significant asymmetry between the upstairs and downstairs direction for energies $E - E_2 < 0.13$ eV. For higher energies the decay rate in the upstairs direction is lower compared to the downstairs direction as observed for the $n = 1$ band [10, 11]. The apparent difference in the interband scattering probability could then be attributed to the asymmetry of the intraband scattering in the $n = 1$ band, which was used to explain the asymmetry of the decay rate for energies below $E_2$ in Sect. 3.3.

3.5 Pure dephasing rates

In the preceding sections the importance of the elastic scattering processes has been demonstrated. Elastic intraband scattering cannot directly be observed in time-resolved spectroscopy, because the net population within the band does not change. The observed asymmetries in the decay rates or interband scattering probabilities could also be due to preferential intraband scattering in either upstairs or downstairs direction [25]. Elastic intraband scattering events do not influence the decay rate, but lead to an increased linewidth in energy-resolved spectra [30]. Figure 9 shows the measured linewidth as a function of pump-probe delay for several Cu(111) surfaces. The linewidth first decreases linearly and saturates for long delays. The saturation value is determined by the pure dephasing rate, which describes the loss of phase coherence by elastic scattering events. The widths of the Gaussian envelopes of the laser pulses and the energy resolution of the analyzer contribute also to the measured linewidth and are known from independent measurements. The linear decrease of the linewidth with delay contains information about the decay rate [30]. The data of Fig. 9 show clearly an increase of the dephasing and decay rate with step density. The values for the pure dephasing rate are given...
in Table 1. For the stepped surfaces the pure dephasing rates are only slightly smaller than the decay rates. This supports the previous statement that elastic intraband scattering is an important process. Similar observations have been made for single adatoms on copper surfaces [31, 32].

Extending the measurements of the elastic scattering rate to higher energies above the band bottom would be quite interesting to unravel an asymmetry with respect to the step direction. For adatoms a strong increase of the elastic scattering cross section with energy has been found [31, 32]. Spectra for several time delays at a fixed emission angle of 30° are shown in Fig. 10 for the Cu(1 1 1) surface. As illustrated by the band structure in the top panel, four different bands are sampled in the spectra. The relative intensity changes with time delay as expected from the lifetime of the \( n = 1 \) and \( n = 2 \) bands. The overlapping peaks prohibit a reliable linewidth analysis as a function of time delay.

4 Summary and conclusions

Two-photon photoemission of image-potential states on stepped copper surfaces revealed a wealth of detailed information. Work function, binding energies and decay rates show a systematic dependency on the step density. The breaking of the symmetry by the steps leads to an asymmetry in the decay and interband scattering rates. This asymmetry is correlated with the order of the step arrangement. For well-ordered surfaces multiple scattering reduces the asymmetry, whereas for less-ordered surfaces the asymmetry of the single scattering events is enhanced. For perfect surfaces the scattering in the direction perpendicular to the steps should be dominant. The frizziness of the steps on real copper surfaces [33, 34] leads to scattering contributions in any direction. For adatoms the scattering can be assumed to be isotropic [31, 32, 35, 36]. It would be interesting to study the anisotropy of the scattering by the steps in measurements for different azimuthal orientations. Elastic interband scattering strongly depends on details of the backfolding of the bands by the periodic step structure and can, therefore, not be understood on the basis of step density alone. As for the case of adatoms [31, 32] elastic intraband scattering is of similar importance as inelastic decay. For stepped surfaces this process may contribute significantly to the asymmetry of the decay rates, but an asymmetry of the elastic intraband scattering could not be determined experimentally in this work.

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