FULL-HEMISPHERE VALENCE BAND PHOTOEMISSION SPECTRA CALCULATED FOR THE IDEAL Si(001)-SURFACE

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Angle resolved photoemission spectra from the Si(001)-surface have been calculated within the highly accurate one-step model. These spin integrated constant final state spectra for the valence bands have been investigated as a function of the emission direction of electrons. Especially, differences between right and left circularly polarized light in the spectra have been considered. A strong circular dichroism is found depending on the orbital composition of the contributing initial states. From various photoelectron patterns over the full 2π hemisphere an example for a p-orbital dominated binding energy is presented and discussed.

Up to date theoretical photoemission spectroscopy in the valence band regime relies on the calculation and interpretation of single spectra. For some emission angles and photon frequencies the theoretical spectra are compared with experimental angle resolved spectra to decide on the correctness of the underlying bandstructure or potential model. Within that procedure the information that a two-dimensional pattern according to the emission angle would offer about the importance of various spots and their mutual relevance is lost. The reason for limiting the theoretical efforts with this respect was given in the past by the amount of available computer power. We know about no full hemisphere one-step calculations for the photoemission from the valence bands. However, actually those limits are no longer unsurpassable. In addition, also the experiment increasingly takes care of the two-dimensional shape of the emission pattern[1,2].

The investigation of circular dichroism in core level photoelectron spectroscopy recently has found interest also for non-magnetic materials[3–5]. Especially, an azimuthal peak rotation is identified if photoelectron patterns of left and right circularly polarized radiation are compared. With a simple quantummechanical argument for single scattering at high energies that peak rotation is explained by the angular momentum of the final state electron which shifts the emission direction away from the straight line between the emitter and scatterer[4]. Those results form the original motivation of this work, i.e. to investigate the valence band spectra and to look for evidence of the same mechanism in this energy regime. Surely, one cannot expect simple results as in the core level photoemission, because the overlap of wavefunctions of different orbitals will deteriorate the picture of one definite angular momentum in the initial state. As long as further analytical evidence is not detected the first step for this goal would be to calculate a reasonable number of photoemission patterns for both polarizations. Besides the special question of peak rotation the aim of the paper lies in the general discussion of the two-dimensional valence band photoemission patterns. The Si(001)-surface with ideal termination is chosen for its general interest. Neglecting surface reconstruction may appear adequate within this first step, especially as the reported theoretical dichroism for core levels was found to be insensitive to reconstruction[5].

The one-step formulation of the photocurrent starts with the golden rule. We consider left (right) circularly polarized light with vector potential $\mathbf{A}_+(\mathbf{A}_-)$ and intensities $I_+(I_-)$. In the case that the light propagates antiparallel to the z-axis the corresponding vector potential is taken as $\mathbf{A}_\pm = const(1, \pm i, 0)$ in a right handed coordinate system. Similar to the spin case[6] symmetry imposes certain restrictions also for the spinless case. Especially, locations with a vanishing asymmetry function

$$\Delta I(\mathbf{q}_\parallel, \mathbf{k}_\parallel) := \frac{I_+ - I_-}{I_+ + I_-} \qquad (1)$$

can be predicted. The surface parallel components of the light and electron wave vectors are denoted by $\mathbf{q}_\parallel$ and $\mathbf{k}_\parallel$, respectively. The Golden-Rule formula, see also Eq. 3, with the vector potential appropriate for an arbitrary circular polarization, leads to the proportionality

$$\Delta I(\mathbf{q}_\parallel, \mathbf{k}_\parallel) \propto \mathbf{q} \cdot [\bar{\mathbf{p}} \mathrm{x} \bar{\mathbf{p}}^\star] \qquad (2)$$

with transition amplitude $\bar{\mathbf{p}} := < \Phi_{final} \mid \mathbf{p} \mid \Psi_{initial} >$. Consequently, the dichroism is represented by a pseudoscalar showing the symmetry of the surface group and transforming with change of sign under a mirror. Especially, it vanishes if $\mathbf{q}_\parallel$ and $\mathbf{k}_\parallel$ both are situated on a mirror plane. In the following, we consider normal incidence of the light which results in vanishing dichroism along the [110] and [$1\bar{1}0$] emission directions, the mirrors of the (001)-surface of silicon.

Our numerical procedure for calculating the valence band photoemission spectra uses

$$I \propto Im \sum_{i,j} < \Phi^{\star}_{LD}(E, \mathbf{k}_{\|}) \mid \mathbf{p} \cdot \mathbf{A} \mid \psi_i > G_{i,j}(E - \hbar\omega, \mathbf{k}_{\|}) \times < \psi_j \mid \mathbf{p} \cdot \mathbf{A} \mid \Phi^{\star}_{LD}(E, \mathbf{k}_{\|}) > \tag{3}$$

with $G_{i,j}(E, \mathbf{k}_{\|})$, as the halfspace Greens function of the valence states in a layer orbital LCAO basis i, j[7]. The final state corresponds to $\mid \Phi^{\star}_{LD}(E, \mathbf{k}_{\|}) >$, an inverse LEED state for the detected electron. It is constructed from the complex bandstructure of a pseudopotential representation inside the crystal. The surface is terminated by a step like solid–vacuum barrier potential. The wavefunction of the final state results from matching the bulk to the vacuum solutions. The matrix elements $< ... \mid \mathbf{p} \cdot \mathbf{A} \mid ... >$ are obtained by direct integration in position space of the orbital functions and the final state wavefunction without any decomposition of the latter. Good lattice points are used.

The spectra are calculated in the constant final state scheme (CFS), i.e. the outgoing inverse LEED state is kept constant through scanning the photon frequency simultaneously with the binding energy. This is also a spectral measurement technique, though not a fast one. However, since finally we want to determine the hemispherical emission from a thin shell of binding energies within the experimental energy resolution through a fixed photon frequency, we need only a fixed kinetic energy as well for the final state. In Fig. 1 the CFS spectra for a series of azimuthal angles are displayed. The final state energy of 30 eV is typical for the vacuum ultraviolet (VUV) radiation used in valence band spectroscopy. The polar angle of 40° is chosen to discuss a prominent peak of the two-dimensional emission pattern. That peak arises around -2 eV in the CFS spectra. Actually, there is appreciable intensity down to -12 eV which may be interpreted similarly to the following procedure, but we will consider in the following only the main peak. It does not disperse as strongly with azimuth as many other peaks, which makes it easier to identify a peak rotation. In the case of core levels one is concerned with one fixed binding energy, but here one has to decide which energy should be chosen in a dispersing peak. Additionally, the angle of the peak rotation, if any, which is deduced from the simple core level picture, may show different values for the various parts of a composite peak containing different orbitals with varying phase. Under these circumstances it is adequate to consider the whole bulk of a spectral peak and determine its average rotation. The plot of the difference, lcp minus rcp spectra, shows a dominance of lcp (rcp) around 65°(30°) azimuth which might be associated with a peak rotation of about 30°, but a difference curve may separate the peaks of two curves to another distance. Anyway, it may be used as a measure to quantify the rotation which is seen rather qualitatively in the direct lcp towards rcp comparison. A better identification will be found in displaying the whole two-dimensional pattern.

The one-dimensional density of states (DOS) as projected along the k_z-axis is plotted in Fig. 2 for a surface and a volume block. A block means an ensemble of 4 successive Si(001)-layers which as a whole show fourfold symmetry in the bulk but not at the surface even in the ideal case. The energy interval of (-2.2,-1.8) eV covered in this figure contains mainly p_x, p_y orbitals. Note the high density values on the border of the Brillouin zone, which is parallel to the direction of the cube face diagonals of the crystal. This spectral density is partly reproduced in the hemispherical photoemission patterns shown in Figs. 3-5. The same binding energy interval as before was chosen. The intensities are calculated in a scan of 5° steps with respect to azimuth and polar angle as shown in the upper part of each figure and are interpolated for an pattern and a contour plot as shown in the lower part. The lattice drawn within the latter corresponds to the reciprocal lattice of the surface parallel planes, i.e. the DOS of Fig. 2 is related to a single square of a lattice mesh. In Fig. 3 and Fig. 4 one finds that the photoemission intensity is clearly associated with the DOS. The corresponding emissions near the pole are lacking, because for the chosen perpendicular light incidence the matrix elements suppress those transitions as can be estimated by the simple approximate rule of taking $\mathbf{A} \cdot \mathbf{k}$ as transition amplitude. Analogous influence of the two-dimensional spectral distribution on the photoemission intensity can be observed in a multitude of further patterns not shown here.

Going from Fig. 3 to Fig. 4 one seemingly detects a clockwise peak rotation of about 25° through replacing lcp by rcp light. This rotation is associated with the strong peak at 40° polar angle and near 60° azimuth in the lcp plot of Fig. 3. It consists of p_x, p_y emissions, the order of magnitude of the rotation being in agreement with the core level findings. However, the above mentioned regions of high DOS bound the appearance of photoemission peaks such that the rotation angle is hidden. No quantitative simple relation could be detected up to now. The properties of the asymmetry function are in accordance with the group theoretical requirements as displayed in Fig. 5 by the difference function. The emission intensity vanishes on both mirror planes of the crystal, i.e. on the k_x, k_y-axes. It should be noted that there is no mirror along the cube axes, i.e. on the lines $k_x = \pm k_y$ in this crystal. However, if the dominant emission did arise solely from the surface plane which indeed has this symmetry, then such a mirror should have been observed in photoemission. Thus the symmetry of structures within the two-dimensional emission pattern could help to decide on their origin, i.e. to identify surface states, if the surface states are composed of only first layer bonds. In the difference pattern the peak rotation is apparent once more, it seems to be enhanced by about 10° in this mode of representation.

In conclusion, the two-dimensional representation of the photoemission patterns bears valuable information in addition to a purely spectral analysis. The presented calculations seem to be the first of this type for the valence band regime and show that such calculations are feasible. An interesting feature is observed by the peak rotation of circular dichroism which shows properties similar to those in core level spectroscopy, but affected by the density of states.

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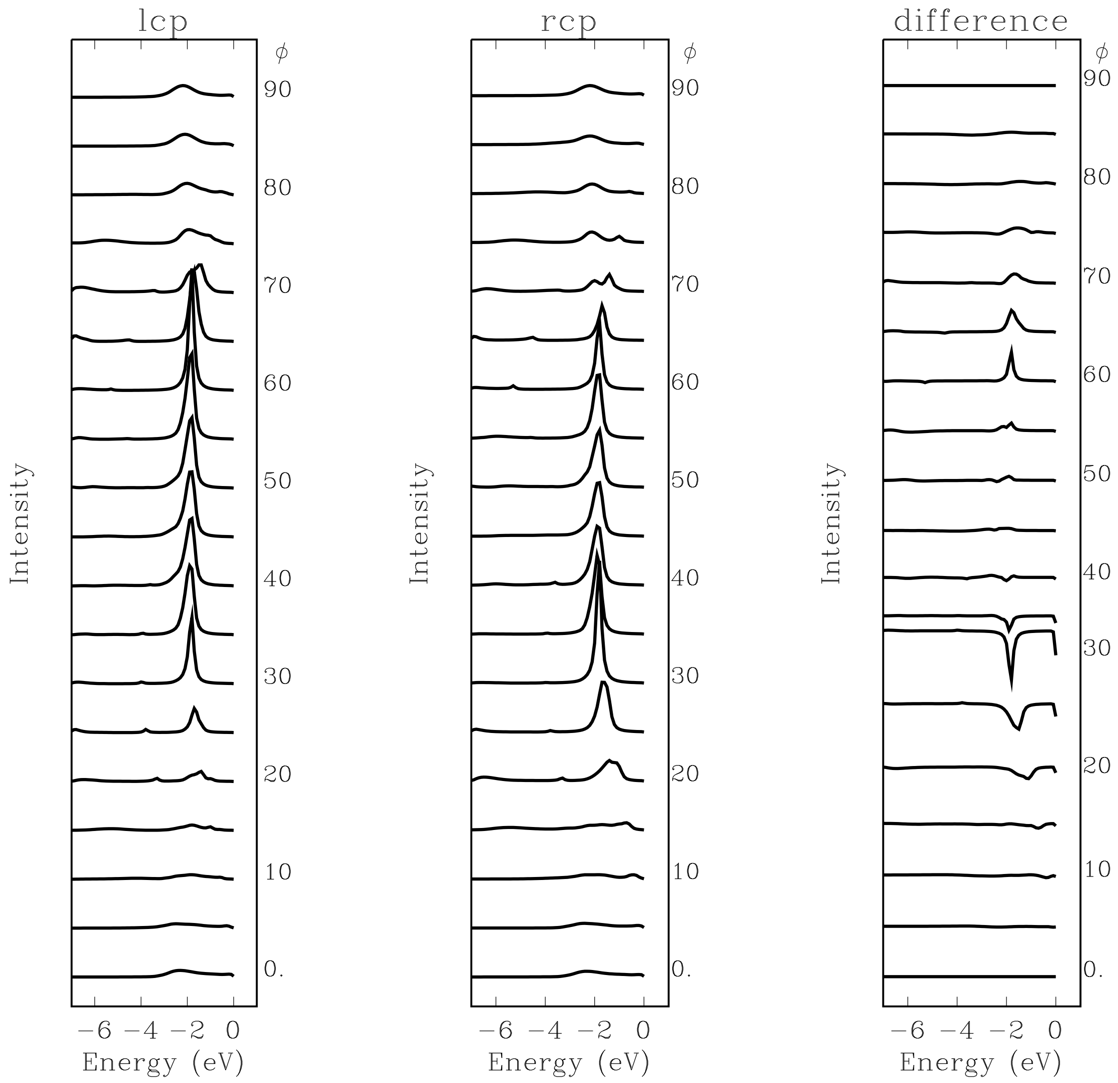

FIG. 1. CFS spectra for 30 eV energy and 40° polar angle of the final state. The parameter denotes the azimuth, lcp (rcp) applies to left (right) circularly polarized light perpendicularly incident onto the surface. The difference between the lcp and rcp curves is displayed in the rightmost panel.

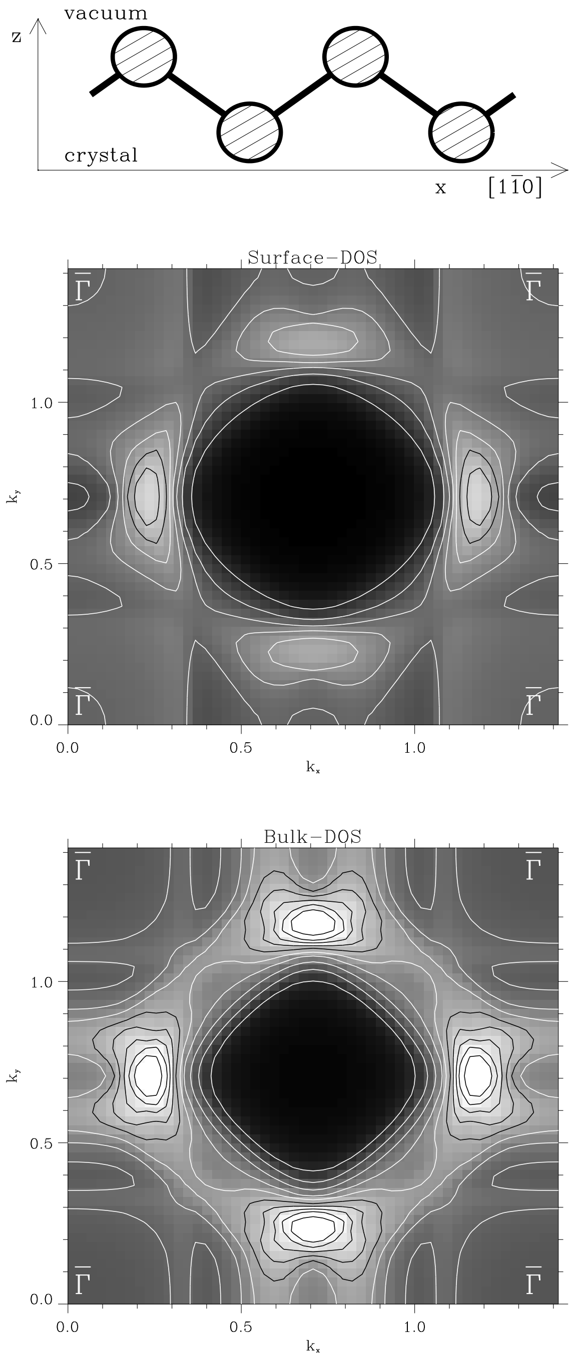

FIG. 2. One-dimensional DOS projected along k_z onto the (k_x, k_y)-plane of the reciprocal lattice unit cell for the surface block (upper panel) and bulk block (lower panel). The energies are collected from the interval (-2.2, -1.8) eV. The direction of the chains containing the bonds between first and second layer atoms is depicted at the top.

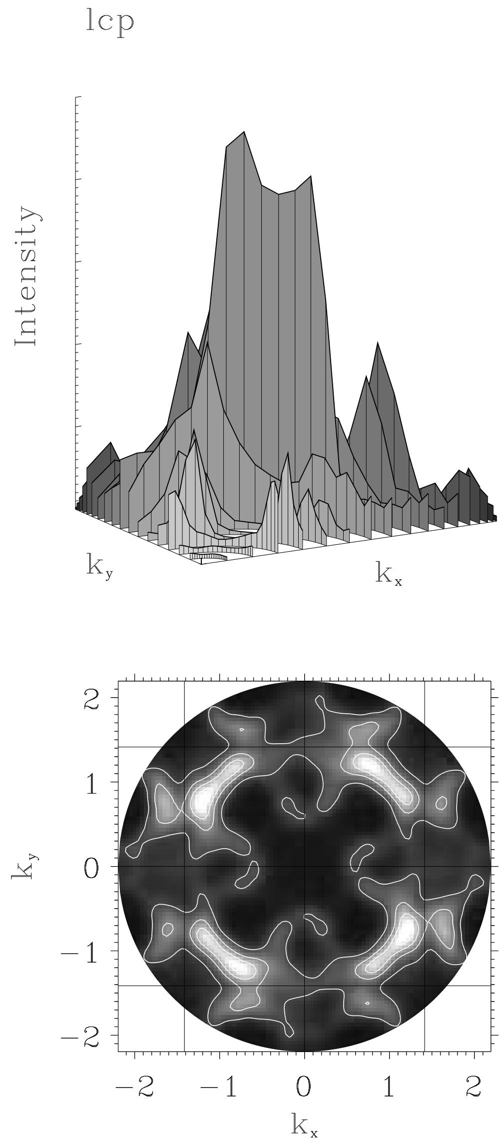

FIG. 3. Intensity distribution in the first quadrant (upper panel) and the full hemisphere (lower panel) for left circularly polarized light. Polar angle and azimuth are scanned in steps of 5°. The center with 0° polar angle corresponds to normal emission, the azimuth counts from the k_x-axis, i.e. the $[1, \overline{1}, 0]$ direction.

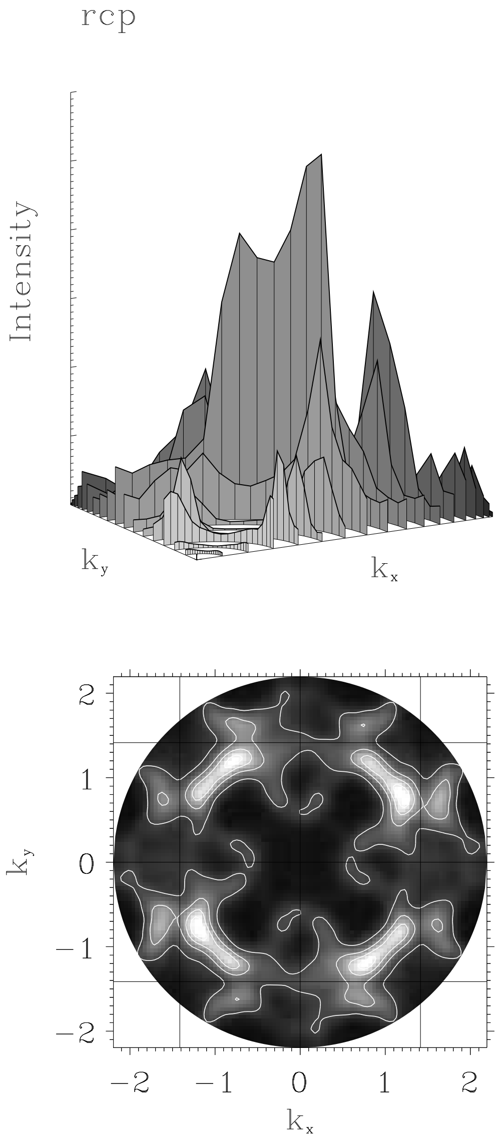

FIG. 4. Same as Fig. 3 but for right circularly polarized light.

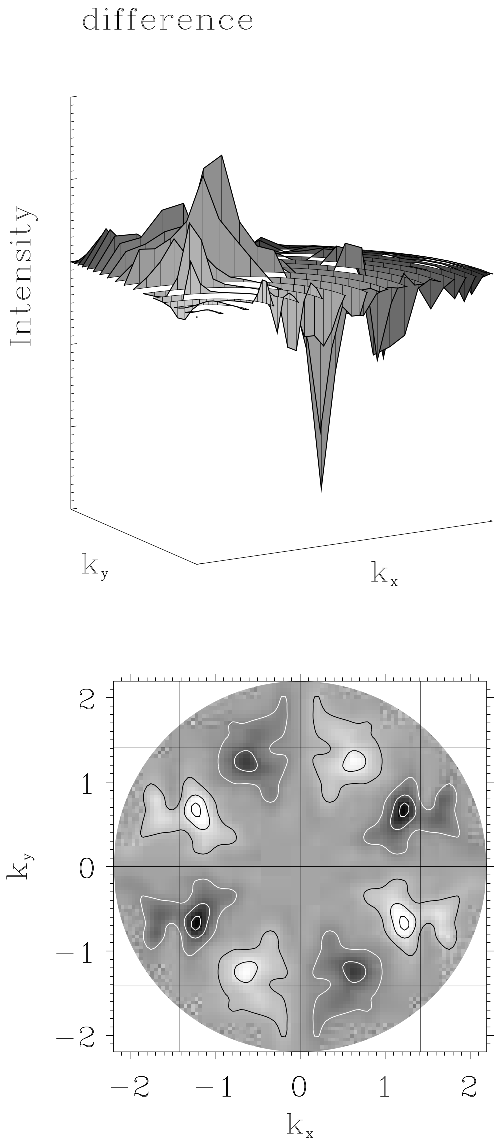

FIG. 5. Difference between the lcp and rcp intensities plotted in Figs. 3 and 4.