Influence of surface structural disorder on linewidths in angle-resolved photoemission spectra

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By combination of high-resolution photoemission data and linewidth analysis of low-energy electron diffraction spots we are able to derive a semiquantitative understanding of how disorder (induced by argon-ion bombardment and subsequent insufficient annealing) broadens photoemission peaks. At the example of surface states on Cu(100) and Cu(111) we demonstrate how the linewidth may be extrapolated to ''perfectly'' ordered surfaces in favorable cases. We also present experimental evidence that disorder-induced broadening is dominated by defect scattering of the photohole and is inversely proportional to the effective masses. Extrapolated ''intrinsic'' linewidths (full width at half maximum) are $\Gamma_i \leqslant (21 \pm 5)$ meV at $\bar{\Gamma}$ on Cu(111), $\Gamma_i \leqslant (20 \pm 3)$ meV at $\bar{M}$ on Cu(111), and $\Gamma_i \leqslant (13 \pm 4)$ meV at $\bar{M}$ on Cu(100). [S0163-1829(97)00432-3]

I. INTRODUCTION

A reasonably sharp and well-defined peak in an angle-resolved ultraviolet photoemission spectrum can be associated with a quasiparticle state of a definite excitation energy and lifetime.[1–5] It is, therefore, of considerable basic interest to measure as accurately as possible the intrinsic spectral function of photoemission lines. However, the ''intrinsic'' line shape and linewidth, respectively, are generally obscured by the limitations of sample preparation, experimental parameters with respect to both energy and angular resolution, the influence of the finite sample temperature, and eventually additional effects. Only if these problems can be clearly identified and may be accounted for in a quantitative manner, will any attempt to obtain information on the ''intrinsic'' spectral function be reasonable. Several recent publications consider the actual state of the art.[6,7] In summarizing the present discussion we must state that, in general, angle-resolved photoemission peaks neither reflect the ''intrinsic'' line shape nor the corresponding linewidth. Only experiments performed with extreme experimental care and a profound understanding of the mechanisms influencing the line shape may promise some progress in this field.

In the present work, we focus on surface order and we report an empirical study of the influence of surface disorder as induced by argon-ion bombardment of the sample and insufficient subsequent annealing. The relative amount of surface disorder is characterized by the linewidth of low-energy electron diffraction (LEED) spots representing the particular surface. Disorder-induced broadening has been recognized already very early.[2,8] The message of this paper is that experiments which control ''disorder'' semiquantitatively allow an extrapolation to ''perfect'' order in favorable cases.

II. EXPERIMENTAL DETAILS

The UHV chamber (1×10^{-10} mbar) is equipped with a cold-cathode discharge lamp for excitation of unpolarized rare-gas resonance radiation, an electrostatic hemispherical electron energy analyzer (energy resolution $\Delta E = 12$ meV, angular resolution $\Delta\theta = \Delta\varphi = \pm 0.7°$ with respect to polar angle θ and azimuth φ), facilities for sample cooling and heating, an argon-ion gun for sample cleaning, and a spot-profile-analysis (SPA) LEED system.[9]

The Cu(100) and Cu(111) samples were oriented to $\pm 0.25°$, polished mechanically to 0.1 μm, and finally polished electrochemically. Afterwards, they were cleaned by cycles of argon-ion bombardment (600 eV, 10–20 μA/cm^2) and annealing at temperatures $T \leqslant 700$ K.

Angular distributions can be measured by rotating the sample by the angle θ around an axis A through the sample surface, while the angle between incident radiation and detected electron is kept fixed at $\alpha = 45°$. Note that the axis A is oriented within the plane defined by incident photon and electron take-off direction, respectively; for details see Fig. 1 of Ref. 10. Also the manipulator provides rotation of the sample around its surface normal. This arrangement allows a very accurate adjustment to particular points of the surface Brillouin zone.

III. RESULTS AND DISCUSSION

To demonstrate the effect of insufficient sample surface order we have first studied the well known[2–4,11] Shockley state appearing in normal emission on Cu(111) at about 0.4 eV below the Fermi energy E_F. In the experiments the sample was first cleaned by argon-ion bombardment and annealed for about 2 min at temperatures between $T_A = 420$ and 700 K. Then normal-emission spectra were collected with the sample at $T = 300$ K. Two effects are observed: with decreasing annealing temperature the surface-state emission peak is broadened more and more asymmetrically, with the larger half width at half maximum at the side with lower binding energy $|E_i|$, and the peak maximum continuously shifts into the direction of E_F at $E_i = 0$. This effect is well known[2] already. Two sample spectra from our work are reproduced in Fig. 5 of Ref. 7 and we therefore do not reproduce similar data here again.

This surface state has an upward dispersion with increasing $\mathbf{k}_\parallel$ into direction of E_F. Therefore, both the observed asymmetric broadening and the shift in peak maximum indicate a relaxation of the sharpness of $\mathbf{k}_\parallel$, leading to an integration over $E(\mathbf{k}_\parallel)$ in some area of the two-dimensional Bril-

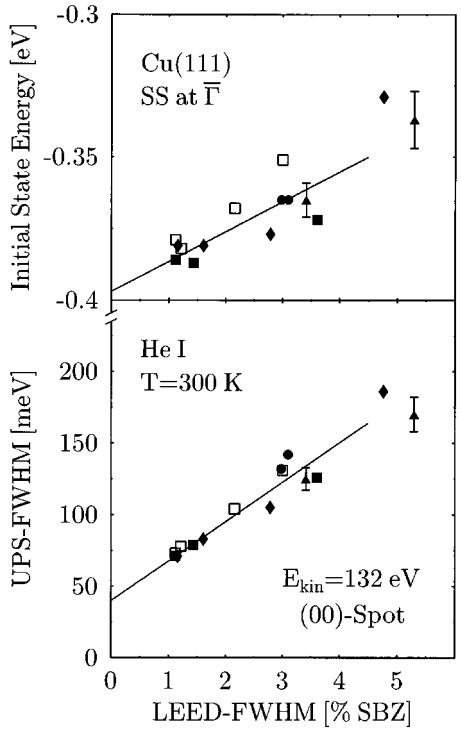

FIG. 1. Top: Peak maximum energy of the Shockley surface state observed at $\overline{\Gamma}$ on Cu(111) in its dependence on surface disorder as monitored by the width of the corresponding LEED spots. Bottom: Observed photoemission peak width against width of LEED spots.

louin zone around $\overline{\Gamma}$ at $k_{\parallel}=0$.[12] Geometrical disorder on the surface also weakens the $k_{\parallel}$ conservation in diffraction experiments, resulting in a reduced coherence length and a concomitant broadening of the LEED spots. Using a high-resolution SPA-LEED system[9] we therefore also measured the full width at half maximum (FWHM) of the (0,0) spot. Figure 1 combines both data sets such that for one and the same sample the experimental photoemission linewidth and the experimental width of the LEED spot are displayed in the lower panel. The upper panel shows the experimental photoemission peak maximum plotted versus the width of the LEED spot as taken from the same sample. The data points refer to different annealing temperatures, between 700 K at the left and 420 K at the right side of Fig. 1. The most important message of Fig. 1 is that ultraviolet photoemission spectroscopy (UPS) FWHM and LEED-FWHM are correlated linearly. This allows a straightforward linear extrapolation to LEED-FWHM$\rightarrow$0 and yields $\Gamma_{meas}=39$ meV at a ''perfectly ordered'' surface. If we correct the data points for the finite resolution of the SPA-LEED system (0.4%) we obtain a slightly larger number of $\Gamma_{meas}=45$ meV.

It is not obvious why a relation between the width of a photoemission peak and the width of a LEED beam should exist at all. Can we rationalize the observed linear relation? Clearly both broadening effects are related to surface disorder. Let us remember how the LEED spot profile varies with incident electron momentum $k_{\perp}$ for a surface with randomly spaced steps.[13,14] In the limit in which all atoms are found in perfect lattice sites, the spot profile is bimodal, with a central specular component of instrument-limited width (in the case of perfectly ordered smooth terraces) and a broadened diffuse component arising from surface roughness. The central spike dominates at values of $k_{\perp}$ for which constructive interference occurs between adjacent terraces separated by a step (''in-phase''). The width of the spike is reciprocally related to the degree of long-range lattice order.[13] The broadened component dominates at values of $k_{\perp}$ for which destructive interference occurs between adjacent terraces separated by a step (''out-of-phase''). The width of the diffuse component is reciprocally related to the average step separation.[13,14] For a predominantly rough surface the whole spot profile broadens[15,16] (instead of splitting into central spike and diffuse peak as one observes for a comparatively smooth surface) and the details of the resulting profile depend on both the remaining terrace widths and step-height distributions. It is a nontrivial inverse problem to derive detailed quantitative information on the various types of surface defects from the analysis of LEED profiles.[13–16] This type of analysis requires systematic studies over a sufficiently large range of $k_{\perp}$, and this was not the purpose of our experiments. We use the width of the LEED profile taken at a $k_{\perp}$ just in between in-phase and out-of-phase condition as an empirical parameter to characterize the surface disorder. As Fig. 1 demonstrates, this pragmatic approach yields a linear relationship to the width of the photoemission peak in its dependence on the (identical) surface disorder. While our procedure does not reveal quantitative details of the actual surface roughness, it allows a straightforward extrapolation to ''perfectly'' ordered samples. This extrapolation allows us to estimate quantitatively the contribution of surface disorder to the photoemission linewidth and allows us to derive an upper limit for the ''intrinsic'' width determined by the reciprocal lifetime of the photohole.

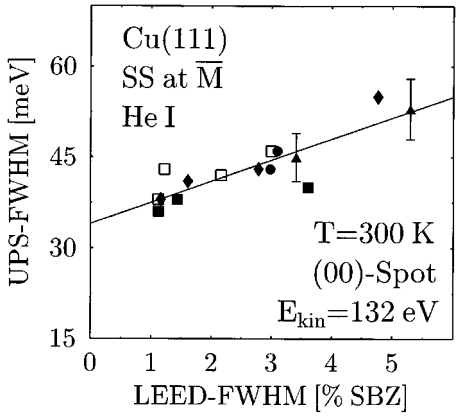

FIG. 2. Photoemission peak width of the Tamm-type surface state observed at $\overline{M}$ on Cu(111) in its dependence on surface disorder as characterized by the width of the corresponding LEED spots.

Another well-known d-like Tamm surface-state exists on Cu(111) around the $\overline{M}$ point of the surface Brillouin zone.[3,4,10,11] We plot the data analogous to those of Fig. 1 for the $\overline{M}$ state in Fig. 2. Again, we observe an almost linear correlation between UPS-FWHM and LEED-FWHM. Annealing temperatures range from $T_A=700$ K (left side) to $T_A=420$ K at the right side. However, the slope observed in Fig. 2 is smaller by almost one magnitude as compared to Fig. 1. Extrapolation to zero on the abscissa yields $\Gamma_{meas}=35$ meV, including the finite transfer width of our SPA-

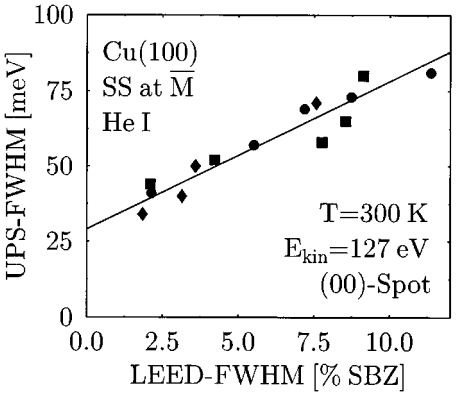

FIG. 3. As in Fig. 2 but for the Tamm state at $\overline{M}$ on Cu(100).

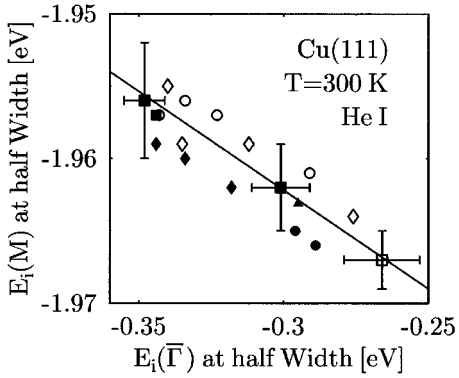

FIG. 4. Initial state energies (at the energy side of dispersion with $k_\parallel$) where the surface-state photoemission peaks observed on Cu(111) at $\overline{M}$ (ordinate) and $\overline{\Gamma}$ (abscissa) have just half the intensity of the peak maximum.

LEED equipment. To collect additional empirical knowledge, we have also investigated a d-like Tamm state known to exist on Cu(100), around the $\overline{M}$ point of the corresponding surface Brillouin zone.[2,3,11] The results are combined in Fig. 3. Again, we observe an almost linear correlation, with an extrapolated UPS width of $\Gamma_{meas}=30$ meV. The slope observed in Fig. 3 is comparable in magnitude to that of Fig. 2.

The latter results seem surprising at first. All information available on surface states supported on Cu (Refs. 2, 3, and 11) agrees that Shockley states tend to penetrate several layers into the bulk and are pinned largely by the properties of the gaps in the bulk band structure. In contrast Tamm states are localized essentially within the topmost layer. Insufficient annealing of the surface intuitively means that the outermost planes of the surface will be the most disordered. This sample picture suggests that either Shockley and Tamm states are affected similarly (if disorder extends several layers deep), or that Tamm states are disturbed even more (if disorder is largest in the first layer). However, the results presented in Figs. 1–3 tell us just the opposite.

Closer inspection of the two surface states on Cu(111) reveals that they differ drastically in their effective masses m^*. Both disperse parabolically according to the equation

$$E_i(\mathbf{k}_\parallel)=E_0+(\hbar^2/2m^*)(\mathbf{k}_\parallel-\mathbf{k}_0)^2, \qquad (1)$$

where $\mathbf{k}_0$ refers to $\overline{\Gamma}$ and $\overline{M}$, respectively. While at $\overline{M}$ we observe $m^*/m_0=-2.86\pm0.20$ (Ref. 10) in units of the free-electron mass m_0, at $\overline{\Gamma}$ we have $m^*/m_0=0.41\pm0.02$.[17,18] As mentioned already, disorder tends to relax $\mathbf{k}_\parallel$ conservation, leading to an effective integration of $\mathbf{k}$ vectors. With respect to the surface states studied in the present work, this integration should lead to increased broadening with decreasing effective mass. To consider this effect more quantitatively, we checked for a correlation between broadening, disorder, and effective mass. As a significant measure of broadening, we consider E_i [on the side to which Eq. (1) disperses] at which the emission line has reached half the intensity of the peak maximum. Figure 4 displays our results, where one data point refers to one and the same sample, and abscissa and ordinate give the half-amplitude energies for the $\overline{\Gamma}$ and $\overline{M}$ states, respectively, observed on this Cu(111) surface. Data points at the upper left of Fig. 4 refer to $T_A=700$ K, while the largest disorder occurs at the lower right ($T_A=420$ K). Again, we recognize an almost linear correlation. The slope of this curve is -6.9 ± 0.7 which agrees perfectly with the effective mass ratio $m^*(\overline{\Gamma})/m^*(\overline{M})=-7.0\pm0.5$.

Our results thus clearly prove that $k_\parallel$ integration is the dominant effect of disorder with respect to the linewidth. This is also consistent with our observation that the energies E_i of half amplitude on the side opposite to the dispersion of $E(k_\parallel)$ does not depend within error bars on the degree of disorder. In an early pioneering work Kevan[12] demonstrated that the FWHM of the $\overline{\Gamma}$ surface state on Cu(111) does not depend on photon energy, at least between $\hbar\omega=11$ and 21 eV. This observation rules out any dominant effect of the electron in the photoemission final state. The electron in the initial state cannot be scattered elastically by defects since no empty states are available below E_F. Therefore, our experiments must be explained by scattering of the photohole. Disorder supplies a broad distribution of $k_\parallel$ vectors available for elastic scattering of the hole. If $k_\parallel$ is the most probable scattering value Eq. (1) shows that energies around $E=(\hbar^2/2m^*)k_\parallel^2$ are scattered into the detector. Since one and the same disordered surface supports both the $\overline{M}$ and the $\overline{\Gamma}$ surface state on Cu(111), the same $k_\parallel$ contributes to the scattering in both bands and this explains why the ratio of broadening (Fig. 4) is given by the inverse ratio of the corresponding effective masses.

Kevan[12] had proposed momentum broadening induced by scattering at surface defects in order to explain an unexpected broadening of the $\overline{\Gamma}$ surface state on Cu(111) when approaching the Fermi energy in spectra taken in off-normal direction. More recent work[17,18] has shown that his observations are dominated by insufficient angular resolution which also tends to integrate over $\mathbf{k}_\parallel$. However, our results give experimental proof that momentum broadening by defects may be dominantly operative and that it is important even at $\mathbf{k}_\parallel-\mathbf{k}_0=0$, compare Eq. (1). In this case, defect scattering means that $\mathbf{k}_\parallel$ is changed while $|\mathbf{k}_\parallel|$ remains constant, with a resulting loss of phase coherence of the hole state.

Our results obtained at room temperature for the $\overline{\Gamma}$ state yield an extrapolated width $\Gamma_{meas}=45\pm5$ meV. If we assume quadratic addition of experimental resolution ($\Delta E=12$ meV) and ''intrinsic'' width Γ_i, we obtain $\Gamma=43\pm5$ meV. Recent work[17,18] has shown that the contribution of the phonon-hole coupling to the linewidth adds linearly accord-

ing to the equation $\Gamma = 2\pi b k_B T$, with $b = 0.137 \pm 0.015$.[18] If we subtract this contribution we end up at a linewidth $\Gamma_i \leqslant 21 \pm 5$ meV at $\bar{\Gamma}$ on Cu(111). If we apply the same type of correction to the Tamm states at M, we obtain as an upper limit for the ''intrinsic'' widths, the numbers 20 ± 3 meV at M on Cu(111) and 13 ± 4 meV at M on Cu(100). At $\bar{\Gamma}$ our extrapolated result $\Gamma_i \leqslant 21$ meV is somewhat smaller than $\Gamma_i \leqslant 30$ meV as observed by McDougall, Balasubramanian, and Jensen.[17] This is surprising at first, since they used a spectrometer with a much better angular resolution than available in our experiment. However, it is well known that Cu single crystals even of the best quality available exhibit a mosaic spread of at least $\pm 0.2°$,[19] which also induces broadening by integration over $\mathbf{k}_\parallel$ (Refs. 7 and 20) even in the case of infinitely good angular resolution. We suggest that our extrapolation to minimum surface disorder eliminates most of the effect due to mosaic spread.

If the final-state hole is filled by radiationless processes phase-space arguments predict a vanishing linewidth on approaching E_F,[21] with a quadratic energy dependence $(E_F - E_i)^2$. This expectation is not reflected in the extrapolated data presented above. There are two possible explanations available. Either d holes and s,p-like holes (both are located in gaps of the surface-projected bulk band structure) decay at different rates. Or, perhaps more probable, effects related to sample imperfection are still operative, and these tend to broaden the $\bar{\Gamma}$ state more (by a factor of about 7) than the M states due to the different effective masses. In agreement with Ref. 6 we recognize that much improved sample quality is required to solve this and related problems.

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