Enhanced photoemission from localized inhomogeneities on Cu(001) characterized by laser-assisted photoemission electron microscopy and low-energy electron microscopy

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(Received 19 October 2006; revised manuscript received 12 December 2006; published 20 February 2007)

Multiphoton photoelectron emission from a state-of-the-art prepared Cu(001) surface has been investigated with photoemission electron microscopy. Randomly distributed, spatially confined regions (about 1 μm in diameter) of intense electron yield (hot spots) are observed. The hot spots give rise to distortions of the corresponding low-energy electron microscopy image. They are identified as polycrystallinelike protrusions embedded in the surface. The density of these inhomogeneities is about 2×10^{-4} μm^2 and cannot be manipulated by ion bombardment or by homoepitaxial growth. The response of hot spots to illumination under ultraviolet light produced by an arc lamp and illumination by blue and infrared femtosecond laser light for different polarizations is recorded from the same surface region, allowing for a direct comparison. Hot spots respond very efficiently and even stronger to *s*-polarized light as compared to *p*-polarized light, and show apparently a nonresonant behavior with respect to the exciting wavelength. We discuss some of the conceivable mechanisms underlying this anomalous photoemission, also in view of the particular characteristics that are specific to our experimental setup. Our data are not compatible with an interpretation which relies exclusively on the excitation of (localized) surface plasmon modes, but rather with a nonresonant near-zone light field enhancement.

DOI: 10.1103/PhysRevB.75.085430 PACS number(s): 79.60.Bm, 68.37.Nq, 68.37.Xy

INTRODUCTION

Photoemission has and still does provide valuable information on band structures and electron dynamics at solid surfaces.[1–3] It has earlier been recognized[4–6] that localized, rough, and perturbed regions of single-crystal surfaces (which, in practice, are always present) give rise to spatially inhomogeneous photoemission with anomalously high electron yields (hot spots), which mask the genuine surface properties. Therefore, emission from these hot spots has been discarded in the data analysis.[3] The origin of this anomalously high electron yield from these spatially confined regions has been attributed to electrical field enhancement at "tiplike" morphologies,[4,5] reminiscent of early experiments on electrical breakdown between flat electrodes in vacuum,[7] or recently, to an enhancement mediated by the excitation of localized surface plasmons, similar to that observed in metallic clusters.[8] In the past, the use of spatially integrating techniques, to detect "hot spots" has been a difficult task. However, the development of photoemission electron microscopy (PEEM), which provides a two-dimensional map of emitted photoelectrons, allows one to readily visualize the presence of inhomogeneous photoemission.[9]

The aim of our study was to investigate the morphology associated with the presence of hot spots on Cu single-crystal surfaces. We also provided information as to the underlying mechanism of photoemission from these spatially confined regions, using low-energy electron microscopy (LEEM) as a structural probe in combination with laser-light-assisted PEEM.

EXPERIMENTAL SETUP

The LEEM and/or PEEM (Elmitec), operating at a base pressure of 3×10^{-10} mbar, was coupled to a conventional Hg discharge ultraviolet (UV) lamp with an energy cutoff at $\sim$5.1 eV and an 80 MHz pulsed Ti:sapphire laser (Tsunami) for electron excitation. The laser system provided pulses with a Gaussian section profile focused to 80 μm in diameter onto the sample and with a duration of about 100 fs. The wavelength was tunable from 720 nm (1.72 eV) to 900 nm (1.38 eV), and from 370 nm (3.35 eV) to 420 nm (2.95 eV), with peak power on the sample of less than 5 MW/cm^2. The incident angle of the light from all sources was 74° off the surface normal. Linear light polarization was tuned from *s* to *p* by wide-band half-wave plates, and the laser pulse power density varied by a set of neutral filters. The field of view (FoV) of the microscope was tuned from 2.5 to 100 μm in diameter, whereby lateral spatial resolutions of 10 and 25 nm were achieved in LEEM and PEEM imaging modes, respectively. A high voltage of 20 kV was applied between the anode and the sample in order to guide the electrons without distortion through the optics of the microscope. The images were recorded with a charge-coupled device camera and digitized for further analysis. In the PEEM mode, the brightness of a pixel was proportional to the electron emission yield.

The Cu(001) single crystal (Mateck) was oriented with an accuracy of 0.2°. Prior to preparation in ultra high vacuum (UHV), the sample was desulfurized by heating at 1170 K under H_2 flow for two months. The surface was cleaned *in situ* by repeated cycles of 800 eV Ar^+ ion sputtering and annealing to 750 K until a sharp low-energy electron diffraction (LEED) pattern was observed. Deposition of Cu onto the sample was carried out *in situ* by means of a heated pyrolitic bore nitride crucible charged with desulfurized Cu. The present experimental setup did not allow for direct control of surface cleanliness by Auger electron spectroscopy. *Ex situ* experiments with the same sample revealed no contamination after preparation along the described lines.

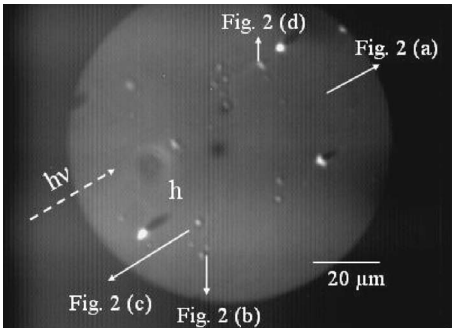

FIG. 1. PEEM image observed under electronic excitation with UV light produced by a Hg arc lamp. FoV=100 μm. The dashed arrow indicates the direction of incident light. The regions marked correspond to the area from which the LEEM images presented in Fig. 2 have been taken. The two dark spots in the center of the image result from damage of the fluorescent screen of the microscope.

EXPERIMENTAL RESULTS

Figure 1 shows a large-scale PEEM image recorded using unpolarized UV radiation for electronic excitation produced by a Hg arc lamp. The FoV is about 100 μm in diameter. (The two dark spots in the center of the image result from damage of the fluorescence screen.) Because the photon energy, 5.1 eV, is higher than the work function of Cu(100), 4.6 eV,[10] the photoelectron emission observed by this source corresponds to a single-photon process. The PEEM image shows a relatively weak nearly uniform emission from the surface, highlighted by randomly arranged spatially confined regions of enhanced electron yield, so-called hot spots,[6,9] whose extension appears to be $\sim 1-3$ μm^2. The increase of the one-photon photoemission yield from these sites indicates that their work function is lower as compared to that of the Cu(001) surface. Recently, Cinchetti *et al.*[11] investigated the variation of the photoelectron yield with the orientation of a polycrystalline copper surface having an overall work function of 4.3 eV. Thus, observed regions that correspond to the hot spots can be regarded as regions with significantly distorted structures with respect to the underlying (001) crystal lattice.

The light source is directed toward the sample at a glancing angle. Therefore, a pronounced shadow pattern is observed at the back side with respect to the light direction of some hot spots, which indicates that the hot spots are, morphologically, made up of protrusions embedded in the Cu(001) surface. The geometrical light limit places the upper height of these structures to a few micrometers. In the vicinity of some structures, less than or comparable to the light wavelength (243 nm), we observe also a modulation of the photoemission signal, most likely as the result of diffraction.[12,13] We note that besides the lower work function associated with the protrusions, its geometrical form also favors an enhanced photoemission signal due to the absence of the "escape cone" associated with planar surfaces.[14]

The PEEM image allows one to distinguish additional topographical structures, marked with the letter "h" in Fig. 1. The darker gray contrast with slightly increased emission at its back side indicates that this distinct element reflects a deep hole in the surface. This is confirmed through homoepitaxial growth experiments observed in LEEM.[15]

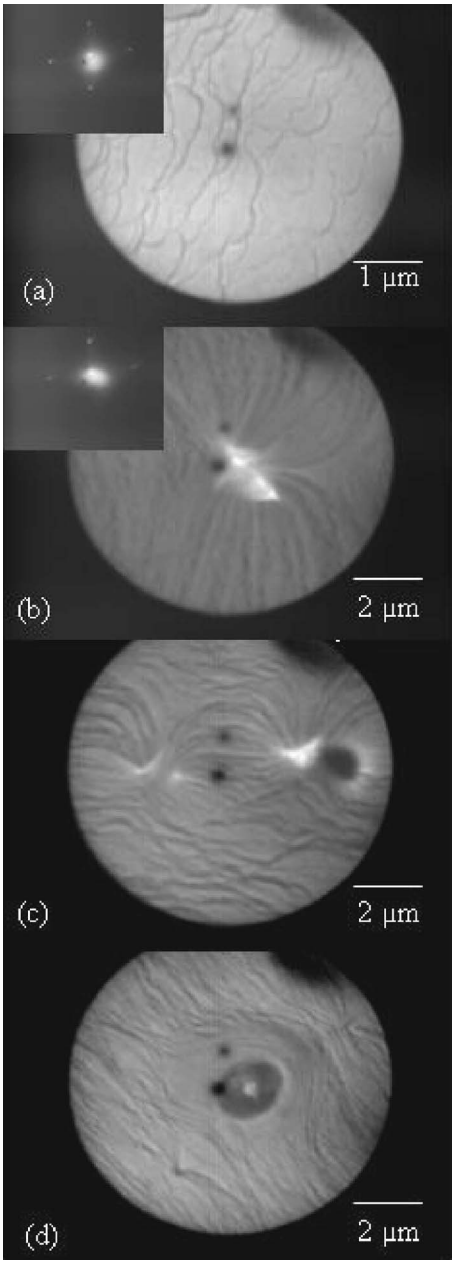

FIG. 2. LEEM images of (a) terrace-step morphology on Cu(100) (LEED pattern as insert), (b) surface area containing defects that provoke distortions of the image with bright contrast, (c) defect region with bright and dark contrast, and (d) defect region that produces dark contrast. The incident electron energies are around 3 eV.

Figure 2(a) shows a typical LEEM image of the Cu(001) surface. Defect-free terraces extending over 200 nm are separated by residual steps of monoatomic height. This image reflects the morphology that corresponds to the homogeneous photoemission observed between hot spots, depicted in Fig. 1. The steps of monoatomic height are not resolved in PEEM. We note that such an image is "typical" in the sense that, after preparation of the crystal in UHV, this morphology

is almost always observed at every macroscopic position on the sample, off visible scratches. However, by changing the position of the impinging electron beam by only a couple of micrometers from the region that produces Fig. 2(a), we often observe distorted LEEM (and LEED) images, such as shown in Fig. 2(b). Strongly curved bunches of steps are pinned at large defects, which appear "bright" in the image. This misrepresentation is the signature of a distortion of the electrical field applied for imaging felt by the electrons due to surface protrusions (or holes),[16] similar to the "focusing effect" that has been reported in LEEM from engineered surfaces[17] with abrupt height changes in the morphology. It is, in fact, these large-scale defects that produce distortions of the LEEM images, which give rise to the strongly enhanced photoemission yields, i.e., the hot spots detected in PEEM.

Figures 2(b)–2(d) illustrate that distorted regions of the surface with "large-scale" defects may appear differently in the LEEM images, depending on the microscope settings and the type of defect (void or hill), in line with the theory developed in Ref. 18. In fact, slight defocusing or "going through focus" may lead to significant contrast variation and even to contrast reversal from bright to dark. A detailed analysis of this complex contrast behavior would require specific assumptions on the size and shape of the defect.[18] We may, nevertheless, distinguish between "void" or "hill" configurations by observing the behavior of these defects in the growth of Cu on Cu in the step flow mode.[15] The LEED pictures taken from these surface regions do not show extra spots. This indicates that the defects are made up of very small facets and can be regarded as polycrystallinelike protrusions embedded in the Cu(001) surface.

The size of these large-scale defect regions can roughly be estimated from their appearance in the LEEM images, thus in the (sub-) micrometer range. Their density amounts to $(2-3)\times 10^{-4}$ μm^2, but it is worth noting that they are not uniformly dispersed on the surface and that there are vast regions free from such structural inhomogeneities.

An important finding is our observation that the density of these large-scale defects cannot be changed by creating structural disorder through ion bombardment[19] nor through homoepitaxial growth at low surface temperatures.[20] Ion bombardment or growth does create structural disorder at a scale of about 4–40 nm (Refs. 19 and 20) on the terrace-step regions, as also witnessed by LEEM. PEEM does not indicate the appearance of additional hot spots, but a random modulation of the homogeneous emission between them, hardly discernable, if at all. This might be a very weak sign of the idea expressed by Aeschlimann *et al.*[6] that roughness allows for a coupling to (localized) surface plasmons, which thereby produces an increase of the emission yield. The structural disorder produced by ion bombardment or growth can be removed by annealing to 750 K, and the morphology depicted in Fig. 1 is restored. Thus, the structural disorder that can be reversed by annealing is not at the origin of the large-scale defects. It appears that these energetically very stable inhomogeneities are inherent to the sample and most likely the result of structural imperfection created in the production process of the single crystal, such as dislocations. In fact, similar observations as those reported here have also been made on a different Cu(001) sample and on a Cu(111) crystal.[21]

In order to provide additional information concerning the underlying mechanism associated with the anomalous photoemission from hot spots, we have used laser light for electronic excitation. This allows us to investigate the response to different wavelengths and polarizations not accessible by using the Hg arc lamp.

Figures 3(a) and 3(b) show the PEEM images observed using the femtosecond laser beam in the blue spectral range, at around 3.17 eV; Figs. 3(c) and 3(d) represent images observed under infrared illumination, at around 1.65 eV, with *p*-[(a) and (c)] and *s*-[(b) and (d)] polarized light, respectively. These images have been recorded from the *same* surface area that has been illuminated by UV light and produced the photoemission map shown in Fig. 1. We may therefore directly compare the response of the morphological elements to UV, blue, and infrared light illumination, and to light polarization.

Numerically, the observed electron emission produced by blue and infrared light should correspond to a two- and a three-photon process, respectively, via the generalized Einstein equation. It is seen that the image produced by *p*-polarized blue laser light [Fig. 3(a)] is identical to that observed by excitation with the UV lamp [Fig. 1] with the exceptions that, generally, hot spot intensities are strongly enhanced (some of them more than 10^3 times) and that the diffraction fringes are more pronounced as compared to excitation with the UV lamp. The change to *s* polarization of the blue laser beam [Fig. 3(b)] leads to the following changes in the photoelectron image: (i) The uniform emission from the regular step-terrace regions of the surface disappears; (ii) the intensity of most of the hot spots increases; and (iii) some spots observed with *p* polarization disappear, while others appear.

While, as expected, the emission yield is larger for *p*-polarized light with respect to *s*-polarized light,[3] the intensity increase of the hot spots with *s* polarization is quite surprising, but has been observed before.[9,11,22] Change (iii) suggests that light coupling to the defect is presumably sensitive to its shape and size.[22]

This is compatible with the results obtained using illumination by infrared light, see Figs. 3(c) and 3(d). First, one notes that three-photon photoemission from the unperturbed terrace-step regions is not active with the absorbed power densities used, for both *s* and *p* polarizations, as reported previously.[23] Structural changes created by ion bombardment or homoepitaxial growth (see above) in these regions do not alter this observation. Nevertheless, hot spots are visible under excitation by infrared light, although their number is smaller than that observed under UV or blue laser light excitation. The dependence on polarization is similar to that observed using blue light: The defect structures couple stronger to *s*-polarized light, which is reflected in the increased number of active emission sites and enhanced hot spot intensities as compared to *p*-polarized light. A particular detail extracted from the images is the observation that perturbed regions smaller than about 0.5 μm in diameter are predominantly active under excitation by *p*-polarized light.

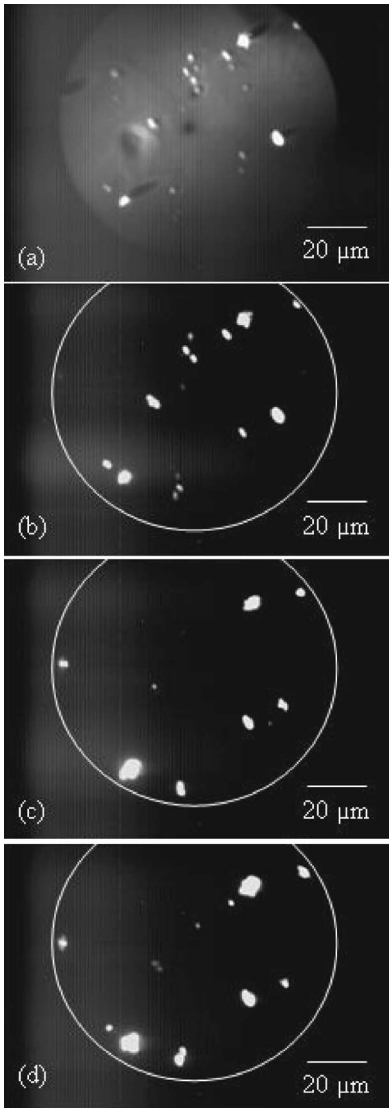

FIG. 3. Multiphoton PEEM images (FoV=100 μm, depicted by the white circle) recorded from the same surface region as in Fig. 1 using electronic excitation by femtosecond laser light: (a) blue laser light, 3.17 eV, 390 nm, 0.4 MW/cm^2, and p polarization; (b) same with s polarization; (c) infrared laser light, 1.65 eV, 750 nm, 2.5 MW/cm^2, and p polarization; (d) same with s polarization. The dark region in the bottom part of image Fig. 3(a) is not illuminated by the focused laser beam, which is only about 80 μm in diameter at the surface. The very intense hot spots appear deliberately overexposed in order to also detect weak emitting sites.

DISCUSSION

The nature of the photoexcitation process that led to the appearance of hot spots under pulsed laser illumination has been discussed[6,24,25] and is actively under debate.[25] We limit our discussion to the information inferred from the observations reported here and to particular characteristics that are specific to our experimental setup.

PEEM images produced via excitation by the UV lamp correspond to a one-photon process and the inhomogeneous emission can be traced back to the local variation of the work function. A similar reasoning should also hold for excitation with blue laser light, except that the signal is produced by the nonlinear two-photon process. In general, in nonlinear photoemission, the electron emission yield scales as I^n. The laser intensity I necessary to produce a given electron yield increases by orders of magnitude with the number of photons n absorbed.[26] The intensity dependence determined under blue light excitation from the uniform emission regions associated with the terrace-step morphology gives, in our case $n=2.1\pm0.3$, which, given the relatively large error bar, can be regarded as the indication of a two-photon process.[27] Interestingly, the *same* exponent n has been determined from hot spot regions as well.

The two-photon photoemission process from the regular terrace-step configuration reduces significantly by tuning the polarization from p to s.[3] The hot spot intensities show just the opposite behavior. We note, however, that this surprising observation may have a simple "geometrical" origin in the sense that the polarization vector, defined with respect to the macroscopic surface plane, could be "seen" differently by the protrusions embedded in the regular surface.

An intriguing finding is the fact that we observe hot spot emission also with infrared radiation as an exciting source.[6,25,28] The absence of emission from the regular terrace-step structure at the laser intensities used is in line with a previous observation[23] and therefore excludes the activation of the three-photon photoemission process. If we assume that the photoemission from hot spots in this spectral range is governed by a power-law dependence, the exponent n amounts to $n=2.3\pm0.3$, which, despite the large error bar, favors $n=2$ instead of $n=3$, if one admits that the exponent is an integer number, as it normally should be. Indeed, the action of surface and interface plasmons (in specially designed morphologies) may result in a reduction of the number of photons n needed to be absorbed for electron emission.[29] In any case, the absence of photoemission from an unperturbed surface region implies that there must be additional sources that enabled photoemission under infrared light excitation from hot spots.

First, we note that the design of the microscope requires applying a voltage of 20 kV to the sample, which translates to an electrical field of $E=5\times10^6$ V/m. The Schottky correction to the zero-field work function amounts to about 0.06 eV, using $\Delta\phi=(eE/4\pi\varepsilon_0)$, where $\Delta\phi$ is the lowering of the work function, e the elementary charge, E the surface electrical field, and ε_0 the vacuum permittivity.[30] We may assume that the local electrical field is enhanced at the protrusion associated with hot spots. For illumination under infrared light, and keeping in mind that $n\approx2$, an enhancement factor larger than 700 has to be provided by these defects in order to provide sufficient lowering of the work function. In fact, such field enhancement factors have been reported from tiplike morphologies on nominally flat electrodes.[31] However, experimentally, when we decrease the electrical field at the sample by an order of magnitude by varying the distance between the sample and the anode, we do not observe visible changes in the hot spot characteristics. This indicates that the electrical field of the microscope used for imaging does not significantly influence the photoemission process.

The electrical field of the laser may also be enhanced at tiplike morphologies. It has been shown previously[6] that the

relatively low laser intensities used in our investigation do not provide conditions for tunneling ionization through the lowering of the surface potential barrier by its own light field induced on the surface. There is, however, the possibility of a near-zone laser field enhancement[24] (which can be regarded as a lightning rod effect[4,5]) and the laser field enhancement mediated by the excitation of (localized) surface plasmons, that have been evoked in order to explain the appearance of hot spots.[6,24] These scenarios are actively under debate.[11,24,25]

At first, we note again that the images shown in Fig. 3 are recorded from the same surface region, so that the response of protrusions to different wavelengths and polarizations can be directly compared. Specifically, presumed localized plasmon excitations are associated with the same defects with respect to their size and shape under various experimental parameters. It is seen that, for both polarizations, the vast majority, with few exceptions, of hot spots are active under blue and infrared laser light excitations. This finding suggests that plasmon excitation shows an unusual nonresonant behavior with respect to the exciting wavelength, which, in fact, has been predicted for percolated, semicontinuous metal films.[32] For spatially separated, isolated structures, which we have here,[33] well-defined resonances are expected and have been observed.[8] There is, however, still the possibility that "the spectral gap" at around 2 eV (620 nm) imposed by our laser system fortuitously omits the expected resonance (but then for all defect sizes and shapes), and that the spectral ranges accessible to our experiment cover only the "wings" of the resonance. However, within both accessible ranges, we do not observe differences in the hot spot characteristics. This indeed suggests a truly nonresonant behavior. In this case, our data favor the interpretation in terms of the near-zone field enhancement,[24] a mechanism that is nonresonant.

The sites of anomalous photoemission have been identified as spatially separated protrusions. This suggests that the morphology of active sites can be described by a distribution of cluster configurations[34] rather than by models assuming self-affine topographies.[35] For independent prolate ellipsoids with their major axis being parallel to the surface, the maximum response is expected for *s*-polarized light, as observed for the majority of hot spots in our case.

A close inspection of PEEM images taken at high magnification reveals that most of the defect regions with sizes smaller than about 0.5 μm couple almost exclusively to *p*-polarized light in the infrared regime, but to both *s* and *p* under blue light illumination, just as it is for larger sized defects in the infrared and blue light ranges. This indicates that small defects must have, in terms of an ellipsoidlike structure, their major axis off the plane of the surface.[34] The component susceptible to respond to *s*-polarized light is not detectable with infrared light illumination because the overall coupling of these small structures should decrease with increasing light wavelength. We note that these indirect conclusions drawn concerning the shape of the defects from an assumed localized plasmon excitation are subject to the fact that "macroscopically" defined light polarization vectors can be transposed to that seen by the defect structure, as discussed above.

Besides the presence of inhomogeneities associated with hot spots, structural disorder has been created by ion bombardment or growth at a scale of 4–40 nm on the terrace-step regions between them. These structural modifications of the pristine areas do not amplify photoemission at variance with the findings reported in Ref. 6. There, the roughness induced has not been characterized. We suppose that the roughness created in our case is smaller, so that the coupling to (localized) surface plasmon is weak.

CONCLUSION

PEEM allows directly identifying that a state-of-the-art prepared, seemingly pristine Cu(001) surface comprises spatially confined regions of very intense electron yield. These hot spots distort the corresponding LEEM image, but can, nevertheless, in combination with PEEM and LEED observations, be identified as "polycrystallinelike" protrusions embedded in the terrace-step morphology of the surface. The density of these hot spots cannot be modified by ion bombardment or by homoepitaxial growth. Hot spots appear to be inherent defects of the single crystal. We have been able to investigate the response of surface inhomogeneities in the same area of the surface to different excitation sources. The majority of these structural inhomogeneities provide intense electron emission through excitation by both unpolarized UV light produced by an arc lamp supplying a small photon density and polarized laser light in the blue and infrared spectral ranges. In many cases, hot spots respond more strongly to *s*-polarized light (defined with respect to the macroscopic surface plane) than to *p*-polarized light. The influence of the high electrical field used for imaging in our microscope on the photoemission characteristics is shown to be negligible. The mechanism of the emission process associated with hot spots has been discussed in terms of a local lowering of the work function, the near-zone laser field enhancement, and the excitation of localized surface plasmons. No coherent picture that describes *all* our observations, specifically that most of the hot spots can be excited with UV, blue, and infrared light, can be reached in terms of an interpretation that relies exclusively on the excitation of localized surface plasmons. The observed nonresonant behavior favors a mechanism that involves a near-zone laser field enhancement, in combination with a lowering of the work function. Also, creating structural disorder by ion bombardment or growth does not amplify photoemission from terrace-step regions, indicating a weak coupling to surface plasmons. We hope that our detailed characterization will stimulate theory. Because we find that the density (and shape) of hot spots cannot be manipulated by "classical surface science" tools, it would be interesting to investigate the photoemission process of specially tailored Cu nanostructures with controllable size and shape.

ACKNOWLEDGMENTS

We thank Z. Korczak, L. Douillard, and F. Charra for their contributions at the initial stages of this project. We gratefully acknowledge the technical assistance by F. Merlet.

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