Contrast Inversion of Photoelectron Spectro-microscopy Image

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The contrast of a photoelectron microscopy image depends on the type of excitation photon source and the photoelectron kinetic energy. The contrast inversion observed in the photoelectron image by Hg lamp excitation is due to differences in work functions specific to materials and surface conditions, and the contrast inversion in the case of vacuum ultraviolet light excitation is due to the difference in the valence band density of states. The mechanism of contrast formation in valence photoelectron images is well understood qualitatively as described above, but quantitative evaluations are required for accurate understanding. We investigated the photoelectron image contrast of gold checkerboard pattern printed on the silicon wafer. The intensity of the gold region near the Fermi level is higher than that of the silicon substrate region, while the inverted contrast images were obtained at low kinetic energies. We found that in the case of core and valence photoelectrons, certain contamination degrades the image quality, but in the case of Hg lamp excitation, it increases signal intensity owing to the lowering of work function.

Keywords Momentum microscopy; Photoelectron; PEEM; ARPES; Synchrotron radiation

I. INTRODUCTION

One approach to performing photoemission measurements in small domains of polycrystalline and microcomposite samples is to focus the X-ray beam into a small selected region. The combination of focused soft X-ray beams with a computer-controlled sample positioning system has enabled the scanning micro photoelectron spectroscopy and diffraction measurements from such samples [1]. Hemispherical deflection analyzers (HDA) are widely used for angle-resolved photoelectron spectroscopy (binding energy versus wavenumber \( k \)). In this case, the sample orientation must be rotated to cover a wide solid angle. This requires a longer acquisition time and causes a shift in the measurement position on the sample surface. Consequently, input lenses with deflectors [2–4] and spherical aberration correction mesh lenses [5, 6] were later developed to measure the angular distribution of photoelectrons from a fixed irradiation spot on the sample surface.

Another approach is to use an imaging-type energy analyzer with a cathode lens [7, 8]. Photoelectron spectroscopy resolved in a three-dimensional momentum space with a microscopic field of view is realized by a combination of the so-called momentum microscope [9–15] and a soft X-ray synchrotron radiation source [16, 17]. The full acceptance cone angle of \( 2\pi \) steradian is realized for photoelectron kinetic energies \( E_k \) up to several tens of eV by applying a high accelerating voltage of typically 10 to 30 kV between the sample and the entrance of the objective lens. This approach significantly reduces the time required to retrieve \( x-y \) images and \( k_x-k_y \) patterns. At BL6U of UVSSR synchrotron facility, a single-HDA-type momentum microscope, KREIOS
II. EXPERIMENTAL DETAILS

Details of the momentum microscope experimental station are described elsewhere [18]. In this section, we have reposted some important explanations needed for the following discussion.

A. Beamline optics

BL6U is an undulator-based soft X-ray beamline with an entrance-slit-less design to obtain the high photon flux [2, 3]. The photon energy range is 40–800 eV, with the resolving power $E/\Delta E$ of 5000–10000 and the photon flux of $10^{9}$–$10^{12}$ photons s$^{-1}$. A typical width of an exit slit is 2–50 μm in vertical direction. A refocusing mirror of 1:1 convergence focuses the monochromated soft X-ray onto the sample position. The axis of the photoelectron emission microscope (PEEM) lens was set 68° off from the incident X-ray beam direction. The final footprint of irradiation spot was 300 μm (maximum) in horizontal direction and 2–50 μm in vertical direction. Hg and helium (He) lamps were also equipped and positioned at the 68° off directions from the PEEM lens axis.

B. Momentum microscope

The momentum microscope is a device that combines a PEEM lens, a HDA as an imaging-type energy analyzer, and a two-dimensional position-resolved electron detector. The sample surface is part of the cathode lens together with the entrance of the PEEM as the counter electrode. An extraction voltage of 15 kV was applied to the entrance of the PEEM lens with respect to the common ground (the inner surface of the analysis chamber). An additional bias voltage of $V_{\text{bias}}$ was applied to the sample relative to the common ground, as described later in Figure 4. Photoelectrons with kinetic energy $E_{\text{K}} = eV_{\text{bias}}$ were analyzed.

In the case of microscopy mode, the real space image of the sample surface is transformed to reciprocal space pattern at the HDA entrance aperture position, while in the case of momentum mode, the real space image is formed at the HDA entrance aperture position. The two-dimensional reciprocal space pattern or real space image at the HDA entrance aperture position is reproduced at the exit aperture position. HDA works so that only electrons with a specific energy within the range near the pass energy $E_{\text{p}}$ reach the HDA exit aperture. The electrons that arrive at the HDA exit aperture then pass through a Fourier transform lens. This lens performs a Fourier transform (from reciprocal space to real space or vice versa) in the detector section. Finally, in the case of microscopy mode, the real space image is projected on the screen and captured by a complementary metal-oxide-semiconductor (CMOS) camera. Magnification of the real space image can be varied. The size of field of view can be varied from 10 to 200 μm in diameter.

All measurements reported in this paper were made at room temperature. $E_{\text{p}}$ of the HDA was set to 20 eV in the present work. The work function of the analyzer estimated from the Au photoelectron spectrum at the Fermi level excited by He I was 4.70 eV.

III. RESULTS AND DISCUSSION

A. Core level spectro-microscopy

A gold square island with a width of 1 μm and a thickness of 150 nm was arranged in a checkerboard pattern of 10×10. 10×10 checkerboard patterns of 10 μm in width were arranged in a larger checkerboard pattern of 10×10. Furthermore, 10×10 checkerboard patterns of 100 μm in width were arranged in a larger checkerboard pattern of 10×10. Finally, 10×10 checkerboard patterns of 1 mm in width were arranged in a larger checkerboard pattern of 5×5. The total width is 5 mm. The sample was once sputtered with Ar ions to remove the contamination on the surface and stored in an ultra-high vacuum bank chamber. This sample was routinely used to accurately position the sample and X-ray beam at the focal point of the analyzer and optimize lens parameters.

Figure 1(a) shows a Au 4f photoelectron image of the gold checkerboard pattern observed using excitation photon energy of 120 eV. An exact photon energy was determined by measuring the energy difference of the Fermi level excited by the first and second order light. The exit slit of the beamline monochromator was set to 80 μm. The undulator gap has been changed from the optimum width to reduce unnecessarily strong beam flux intensity. The smallest square (white color) is the gold pattern with 1 μm width. The gold squares excited by the X-ray beam were brightly imaged as expected. The dark parts correspond to the bare Si
substrate region. 161 photoelectron images with binding energies from 82 to 90 eV with the interval of 50 meV were measured and summed. The bias voltage $V_{\text{bias}}$ has been changed within the range of $29.3 \pm 4$ V. Image drift due to bias voltage variation was corrected for each image on summation. There are three defect spots created on the two-dimensional position-resolved electron detector. They are displayed as horizontal dark lines. Accurate aligning of the sample to the PEEM lens axis minimizes image drift.

Figure 1(b) shows Au 4f photoelectron spectra extracted from the 161 photoelectron images by averaging over all regions of the 10-μm gold (A), 10-μm vacant (B), and 100-μm Si substrate (C) squares. A linear background was removed from each spectrum. There is a faint Au 4f signal in the spectrum from region C. The contrast aperture of 4 mm in diameter was used here. By limiting the electrons emitted at the surface normal direction by using a narrower contrast aperture of 100 μm in diameter, the spatial resolution will be improved and the mixing of the Au 4f signals into the spectrum from region C will be suppressed.

B. Valence band spectro-microscopy

The same region was excited by photons with an energy of 60 eV and imaged by valence electrons as shown in Figure 2. 106 photoelectron images with binding energies varying from 10 to −0.5 eV with the interval of 0.1 eV were measured. The photon flux density was high at the center
and low around the upper part. Therefore, we renormalized each image with a spatial distribution averaging over the 106 data to eliminate the non-uniform sensitivity and the background intensity distribution.

Figure 2(a, b) shows a valence band photoelectron image of a gold checkerboard pattern observed with the abovementioned renormalization operation. The three defect spots on the two-dimensional position-sensitive electron detector appear as a pair of black and white dots as a result of the image drift and renormalization operation. Photoelectrons corresponding to the binding energy from 2.0 to 5.0 eV were integrated in Figure 2(a) and those from 6.7 to 9.7 eV were integrated in Figure 2(b). Note that the gold squares excited by the $h\nu = 60$ eV photons were brightly imaged in Figure 2(a), but the gold patterned regions have a lower emission current compared to the Si substrate regions in the case of Figure 2(b). Namely, the contrast between the gold square and Si substrate regions is reversed.

Figure 2(c) shows the valence band photoelectron spectra from the 10-μm gold square (A) and 10-μm vacant square (B) regions. Intensity data of the corresponding regions were extracted from the raw 106 photoelectron images. The Fermi edge of gold appeared at the binding energy of 0 eV in the spectrum corresponding to region A. The energy range for Figure 2(a) corresponds to the Au 5d band from gold checkerboard pattern (A), while the energy range for Figure 2(b) corresponds to the Si 3s band from the substrate surface (B). The contrast inversion observed in Figure 2(b) with respect to Figure 2(a) is explicable by the difference in the density of states between the Au region and the Si region.

Similar measurements were also made even before Ar ion sputtering. Contrast reversal was also observed on the untreated surface, where the Si substrate region was covered with SiO₂ and perhaps some contamination was present in the gold region, but not so significantly as compared to the result of the Ar-ion sputtered sample shown in Figure 2(a). The photoelectron spectra from both gold and Si regions under such a sample condition were diffuse, and the difference in the integrated intensity for the two regions was much smaller.

C. Work function spectro-microscopy

Figure 3(a, b) shows a slightly contaminated gold checkerboard pattern observed using the Hg lamp. Figure 3(c) shows Au photoelectron spectra from 10-μm gold square (A*) and 100-μm vacant square (C*) regions. Asterisks (*) indicate that some contamination remains in the measured area. The lower horizontal axis in Figure 3(c) is a bias voltage $V_{\text{bias}}$ applied to the sample. $V_{\text{bias}}$ was varied from $-0.7$ to $+0.9$ V. This corresponds to the kinetic energy range from $-0.7$ to $+0.9$ eV. Ordinary photoelectron spectroscopy detects photoelectrons with sufficient kinetic energies ($E_K > 0$) to overcome the work function of the analyzer. In the case of this analyzer, the potentials of the electrodes are fixed and the sample bias voltage $V_{\text{bias}}$ is scanned. The sample bias voltage $V_{\text{bias}}$ corresponds to the photoelectrons with the kinetic energy of $E_K = eV_{\text{bias}}$. Difference between the photon energy and the kinetic energy is the work function of the analyzer (4.70 eV). By applying a negative voltage, photoelectrons from a sample with a smaller work function than the analyzer can be analyzed ($E_K < 0$).

The work function of the clean gold single crystal surface depends on surface orientation, i.e., 5.31, 5.47, and 5.40 eV for the (111), (001), and (110) surfaces, respectively [24]. The work function of the gold deposited film on the glass, for example, is smaller, i.e., 4.71 eV [25]. The work function of the Si surface depends on the doping. About 4.8−5.1 eV
(4.5–4.9 eV) is reported for the p-type (n-type) substrate [26]. These values are most often greater than the work function of the analyzer, 4.70 eV, except in some cases of n-type Si substrates. Indeed, the photoelectron intensity from the gold checkerboard pattern largely depends on the condition of the surface. As discussed below, the work function for the gold patterned area and the Si substrate area were 4.20 and 4.05 eV, respectively. The work function of the measured area is much smaller than the work function of the clean Au crystal surface.

The photoelectron corresponding to the sample bias volt-

![Figure 4: The mechanism of the contrast inversion for the gold checkerboard pattern image excited by the Hg lamp. Photoelectron spectra observed using Hg lamp excitation in Figure 3(c) is shown again in Figure 4(a) for easier comparison with Figure 4(b) in the inset (a). (b) Schematic diagram of photoelectron emission using the Hg lamp for excitation. Spectra from the regions A’ and C’ excited by the Hg light with the photon energies of 4.89 eV and 5.48 eV are superimposed. The bias voltage $V_{\text{bias}}$ applied to the sample relative to the common ground (the inner surface of the analysis chamber) was varied. Photoelectrons with the kinetic energy $E_k = eV_{\text{bias}}$ are analyzed. Difference between the photon energy and the kinetic energy is the work function of the analyzer.](image)

age $V_{\text{bias}}$ from $-0.25$ to $-0.35$ V was integrated for Figure 3(a) and that from $-0.45$ to $-0.55$ V was integrated for Figure 3(b). In Figure 3(a), the gold regions A’ appears brighter (white) than the Si substrate regions C’. This is because the total photoelectron current from the gold patterned regions at the Fermi level is higher than that from the Si substrate regions. On the other hand, the gold regions A’ appears darker than the Si substrate regions C’ in the case of Figure 3(b). This is because the work function in the gold pattern regions A’ is larger than that in the Si substrate regions C’.

Contaminated areas are imaged fairly easily by the Hg lamp excitation compared to the Ar-ion sputtered area with less contamination.

Photoelectron spectra observed using the Hg lamp in Figure 3(c) are repeatedly shown in Figure 4(a) for facilitating the understanding of the scheme given in Figure 4(b). Figure 4(b) explains the mechanism of contrast inversion for the gold checkerboard pattern images in Figure 3(a, b) excited by the Hg lamp.

Here we notice that the spectral shape in Figure 4(a) [= Figure 3(c)] is significantly different from that of Figure 2(c). Steep increase in intensity was observed in both spectra with a bias voltage $V_{\text{bias}}$ of 0 eV. In addition, increase in intensity was observed in both spectra at a bias voltage $V_{\text{bias}}$ of ~0.6 V. The energy difference between these two step thresholds is 0.6 eV. The Hg excitation light contains two distinct lines, e.g., 4.89 eV and 5.48 eV separated by ~0.6 eV [27, 28]. Two intensity threshold features are observed at the energies separated by nearly the same energy difference.

Therefore, these features are thought to correspond to the Fermi edge at ~0.19 eV and ~0.78 eV in Figure 4(a) excited by two different Hg excitation lines. Double valence band features shifted by the photon energy difference of the two Hg lines are superimposed in both spectra from the regions A’ and C’. The binding energy axes for two different excitation energies are indicated in the upper part of Figure 4(a) together.

Furthermore, two different cut-off features appeared at different energies in the two spectra in Figure 4(a). The cut-off features are located at the bias voltages $V_{\text{bias}}$ of ~0.50 and ~0.65 V in the spectra for the A’ and C’ regions, respectively. Since the work functions of the two regions differ, the secondary electron cut-off must appear at different bias voltages for the regions A’ and C’ as shown on the left end of Figure 4(a). The estimated work functions are 4.20 and 4.05 eV for the regions A’ and C’ as shown in the upper part of Figure 4(a) together.

IV. SUMMARY

Three-dimensional momentum-resolved photoelectron spectroscopy with a microscopic field of view is achieved...
by a combination of the momentum microscope and a soft X-ray synchrotron radiation source. The contrast of a photoelectron microscopy image depends on the type of the excitation photon source and the photoelectron kinetic energy. The mechanism of photoelectron image contrast formation was investigated using the gold checkerboard pattern printed on the Si wafer. The core-level photoelectron microscopic imaging can provide sharp element-selected spatial information, while the valence photoelectron microscopic imaging opens access to the density-of-states information which is sensitive to the chemical condition of the surface. The intensity of the gold pattern is higher near the Fermi level than that of the Si substrate, while the inverted contrast pattern was obtained at lower kinetic energy (larger binding energy). The contrast inversion observed in the photoelectron image using synchrotron radiation is due to the difference in valence band density of states between gold and the Si substrate. On the other hand, the contrast inversion observed in the photoelectron image using Hg lamp excitation is due to the difference in the work function. Interestingly, the contaminated areas having a lower work function were imaged fairly easily by the Hg lamp excitation compared to the Ar-ion sputtered area with less contamination. In order to study electronic structures of sub-μm region of complex device materials for example by momentum microscope, proper parameter tuning must thus be carefully done by changing the detected binding energies for the different excitation.

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References

[1] F. Matsuı, K. Yasuda, N. Maejima, H. Matsuı, T. Matsushita, and H. Daimon, Jpn. J. Appl. Phys. 58, 110602 (2019).
[2] H. Yamane, F. Matsui, T. Ueba, T. Horigome, S. Makita, K. Tanaka, S. Kera, and N. Kosugi, Rev. Sci. Instrum. 90, 093102 (2019).
[3] F. Matsuı, S. Makita, H. Matsuı, T. Ohigashi, H. Yamane, and N. Kosugi, J. Phys. Soc. Japan 88, 114704 (2019).
[4] F. Matsuı, S. Makita, H. Matsuı, T. Ueba, T. Horigome, H. Yamane, K. Tanaka, S. Kera, and N. Kosugi, e-J. Surf. Sci. Nanotechnol. 18, 18 (2020).
[5] H. Matsuda, H. Daimon, L. Töth, and F. Matsui, Phys. Rev. E 75, 046402 (2007).
[6] H. Matsuda and F. Matsui, Jpn. J. Appl. Phys. 59, 046503 (2020).
[7] R. M. Tromp, Ultramicroscopy 111, 273 (2011).
[8] R. M. Tromp, W. Wan, and S. M. Schramm, Ultramicroscopy 119, 33 (2012).
[9] B. Krömker, M. Escher, D. Funnemann, D. Hartung, H. Engelhard, and J. Kirschner, Rev. Sci. Instrum. 79, 053702 (2008).
[10] M. Escher, K. Winkler, O. Renault, and N. Barrett, J. Electron Spectros. Relat. Phenomena 178-179, 303 (2010).
[11] M. Patt, C. Wiemann, N. Weber, M. Escher, A. Gloskovskii, W. Drube, M. Merkel, and C. M. Schneider, Rev. Sci. Instrum. 85, 113704 (2014).
[12] C. Tusche, A. Krasyuk, and J. Kirschner, Ultramicroscopy 159, 520 (2015).
[13] S. Suga and C. Tusche, J. Electron Spectros. Relat. Phenomena 200, 119 (2015).
[14] C. Tusche, Y.-J. Chen, C. M. Schneider, and J. Kirschner, Ultramicroscopy 206, 112815 (2019).
[15] C. Tusche, Y.-J. Chen, L. Plucinski, and C. M. Schneider, e-J. Surf. Sci. Nanotechnol. 18, 48 (2020).
[16] C. Wiemann, M. Patt, I. P. Krug, N. Weber, M. Escher, M. Merkel, and C. M. Schneider, e-J. Surf. Sci. Nanotechnol. 9, 395 (2011).
[17] C. Tusche, M. Ellguth, A. A. Ünal, C.-T. Chiang, A. Winkelmann, A. Krasyuk, M. Hahn, G. Schönhense, and J. Kirschner, Appl. Phys. Lett. 99, 032505 (2011).
[18] F. Matsui, S. Makita, H. Matsuı, T. Yano, E. Nakamura, K. Tanaka, S. Suga, and S. Kera, Jpn. J. Appl. Phys. 59, 067001 (2020).
[19] H. Yasufuku, M. Okumura, T. Ibe, K. K. Okudaira, Y. Harada, and N. Ueno, Jpn. J. Appl. Phys. 40, 2447 (2001).
[20] C. Kamezawa, M. Hirai, M. Kusaka, M. Iwami, and J. Labis, Appl. Surf. Sci. 237, 607 (2004).
[21] K. Siegrist, V. W. Ballarotto, M. Breban, R. Yongsunthong, and E. D. Williams, Appl. Phys. Lett. 84, 1419 (2004).
[22] T. Sugiyama, M. Aida, N. Ueno, and T. Munakata, J. Electron Spectros. Relat. Phenomena 144-147, 1167 (2005).
[23] N. Barrett, L. F. Zagonel, O. Renault, and A. Bailly, J. Phys.: Condens. Matter 21, 314015 (2009).
[24] B. J. Hopkins, C. H. B. Mee, and D. Parker, Br. J. Appl. Phys. 15, 865 (1964).
[25] A. Novikov, Solid-State Electron. 54, 8 (2010).
[26] K. Burns, K. B. Adams, and J. Longwell, J. Opt. Soc. Am. 40, 339 (1950).
[27] C. J. Sansonetti and J. Reader, Phys. Scr. 63, 219 (2001).

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