Nonparametric Modeling of Face-Centered Cubic Metal Photocathodes

Tuo Li\textsuperscript{1} and W. Andreas Schroeder\textsuperscript{2}

\textsuperscript{1}Uptake Technologies, Inc., 600 W Chicago Ave Ste 620, Chicago, IL 60654, USA
\textsuperscript{2}Department of Physics, University of Illinois at Chicago, 845 W. Taylor Street, Chicago, IL 60607-7059, USA

(Dated: March 27, 2018)

Face-centered cubic (FCC) is an important crystal structure, and there are ten elemental FCC metals (Al, Ag, Au, Ca, Cu, Pb, Pt, Rh, and Sr) that have this structure. Three of them could be used as photocathodes (Au, Rh, Pt, and Pd have very high work functions; Ca and Sr are very reactive). Au has high work function, but it is included for the sake of the completeness of noble metals’ photoemission investigation. In this paper, we will apply the nonparametric photoemission model to investigate these four remaining FCC photocathodes; two noble metals (Cu and Au), two \( p \)-block metals (Al and Pb). Apart from the fact that the direct photoemission is dominant for most FCC photocathodes, photoemission from a surface state has also been observed for the (111)-face of noble metals. The optical properties of the (111) surface state will be extensively reviewed both experimentally and theoretically, and a surface state DFT evaluation will be performed to show that the photocathode generated hollow cone illumination (HCI) can be realized.

Keywords: DFT Calculations, Face-Centered Cubic, Hollow Cone Illumination, Photoemission, Photocathodes, Statistical Modeling

I. INTRODUCTION

Noble metal photocathodes with low emittance (high brightness) are nowadays routinely used as electron sources for laser-driven high-gradient guns \cite{1-9}. That is because these metals are resistant to corrosion, easy to fabricate, reliable and tolerant to contamination, and have uniform emission, high operating life time and a fast response time. The other principal reason for the wide use of noble metals as photocathodes is, of course, the wealth of available information about them. For example, the electronic properties of noble metals have been thoroughly investigated by cyclotron resonance, XPS experiments, X-ray emission experiments, ARUPS experiments and de Haas-van Alphen measurements \cite{10,12}. Each experimental method mentioned above has been extensively applied to the field of photoemission physics and the results have been found to fit a consistent and entirely reasonable picture of the metal’s Fermi surface.

The disadvantages of noble metal photocathodes are their low QE (of the order of \( 10^{-4} \)) and the need for a UV drive laser (> 4.60eV), which limits these photocathodes for applications requiring less than \( 1 \)mA average current \cite{13}.

In recent years, axial hollow cone illumination has gained great interest at high resolutions in conventional transmission electron microscopes since it eliminates phase contrast artifacts from an image, thus making high resolution electron microscopy (HREM), bright-field imaging and dark-field electron microscopy (DFEM) much more reliable \cite{14,15}. The current method of producing HCI employs annular condenser apertures, circular condenser apertures, or an electronic cone illumination method, which impose several instrumental limitations. It is therefore important to consider an alternative method of producing hollow cone illumination which minimizes such limitations and enables the corresponding microscopy to be performed routinely. Aside from the needed instrument improvements, it is inevitable that the standard methods of producing cone illumination mask the electron beam and therefore decrease its brightness.

In this sense, a photocathode that directly generates the required hollow-cone beam for HCI would be quite attractive.

In Section \textsuperscript{11} we will conduct the nonparametric DFT-based analysis for Ag, Cu and Au. In Section \textsuperscript{11} we will present HCI based on Ag(111) single crystal emission, and show the schematic procedure to generate a ‘cone-like’ electron beam. As \( \Delta p_T \) data on photoemission from the Ag(111) face surface state is lacking in the photocathode community, our DFT calculation \cite{17-20} fills this vacancy. Emphasis will be placed on a discussion of the surface state photoemission and the resulting \( \Delta p_T \) analysis and results obtained with it. In Section \textsuperscript{1V} the DFT-based photoemission analysis is used for the evaluation of the emission properties of surface states.

II. DFT-BASED PHOTOEMISSION ANALYSIS

The first Brillouin zone (BZ) of an FCC lattice has a truncated octahedron shape as shown in Fig. \textsuperscript{1}. Noble metals only have one free electron per atom, so that the BZ is only half filled. The structural and electrical properties of both the bulk and surfaces of noble metals were previously investigated theoretically and experimentally \cite{11,22,23}. The calculated band diagrams for copper and gold are shown in Fig. \textsuperscript{2}. The relatively flat bands lying about 2eV below the Fermi surface are associated principally with \( d \) atomic states, whereas the bands

\[ \textit{ljizanchen1986@gmail.com} \]
lying at higher energy are associated principally with \( s \) and \( p \) atomic states. The \( d \) bands are fully filled and the \( s \) bands are half-filled; thus, the volume contributed by the \( d \) bands is enclosed by the Fermi surface formed by the \( s \) bands. The equivalent Fermi surface radius then equals the average of \( \Delta_1 \) (\( \Gamma \rightarrow X \)) and \( \Sigma_1 \) (\( \Gamma \rightarrow K \)) radii of the Fermi energy surface, values for which are shown in Table. I both from Ref [21] and our DFT calculations. The unequal (100) face and (110) face radii indicate a distortion of the nominally spherical noble metal Fermi surface. In addition, contact is established between the Fermi surface and the BZ boundaries in the \(<111> \) directions (\( \overline{\Gamma \overline{L}} \)). These contact areas correspond to the energy gap at the zone boundary along the high symmetry line \( \Lambda \). To further examine the consistency of the Fermi surface calculations by DFT, the effective masses \( (m^*) \) corresponding to the (001), (110) and (111) faces are determined using \( m^* = \left( \frac{\partial^2 E(p)}{\partial p^2} \right)^{-1} \). The noble metal’s Fermi surface is constructed of three major parts; a ‘Dog’s bone’ orbit from the contours in the (111) plane, a ‘Neck’ orbit from contours in the (110) plane (the hexagonal face), and a ‘Belly’ orbit from the contours in (100) plane [24].

These three orbits are shown in Fig. 3 and the results from the effective masses calculations corresponding to the orbits are listed in Table. II. It can be seen that Ag, whose Fermi surface is closest to a perfect sphere, has effective mass values close to \( m_0 \), while Cu whose Fermi surface is furthest from a perfect sphere has an

![FIG. 1. FCC Brillouin zone](image)

![FIG. 2. Silver, Copper and Gold band structures along high symmetry points and lines. The Fermi level is shifted to zero energy and labeled with dashed line. In [001] (\( \Gamma_1 \rightarrow X \)) and [110] (\( \Gamma_1 \rightarrow K \)) direction, \( \Delta_1 \) band and \( \Gamma_1 \) band cross Fermi level respectively. In the [111] (\( \Gamma_1 \rightarrow L \)) direction, \( \Lambda_1 \) is 0.77 eV below the Fermi level.](image)
effective mass much less than \( m_0 \). The DFT evaluated effective masses are all within 10% of the experimental values. Unlike potassium whose band structures could be completely defined by the electron energy \( (E) \) versus momentum \( \vec{p} \) diagram calculated along the principal crystal directions, the distorted spherical Fermi surfaces of the noble metals suggests that a DFT-based emission analysis will be required to evaluate their \( \Delta p_T \).

![Diagram of Fermi surfaces of Ag, Cu, and Au](image)

**FIG. 3.** Fermi surface of Ag, Cu, and Au in first Brillouin zone. The polyhedron (black solid lines) represents the first Brillouin zone of FCC. It consists of an almost perfect ‘belly’ sphere, centered at high symmetry point \( \Gamma \), which connects to the \( L \) points along the [111] direction. Two projections of the noble metals reciprocal lattice show the shape of Cu and Au Fermi surfaces. The orbits considered are labeled by light blue lines: (a) dog’s bone orbit, (b) neck orbit, and (c) central belly orbit.

The results of evaluating the photoelectric work functions of noble metals with respect to crystal orientation using the thin-slab method [34], are shown in Table. III. The calculated work functions are within 10% of experimental values [33, 35], with any absolute discrepancies being in the vicinity of 0.1eV. Nonetheless, for these metals the calculated theoretical values are consistent and appear to be reliable; indeed, they are in very good agreement with experimental values. For bulk Au, a \( h\omega=5.36 \) eV (231 nm) photon energy is the minimum energy required to overcome the photoelectric work function barrier. Due to this high work function value, there are no literature values of the rms transverse momentum \( \Delta p_T \) value for photoemission from Au with an excess energy greater than zero. For Cu and Ag, a \( h\omega=4.75eV \) (261nm) UV laser can be used to photoemit from the (100) and (110) crystal faces. The \( \Delta p_T \) of an electron beam emitted from polycrystalline Cu and Ag surfaces irradiated by the 4.75eV picosecond laser pulses has been measured by the solenoid scan technique, and the measured \( \Delta p_T \) values for polished Ag and Cu photocathodes are 0.235\( \sqrt{m_0}eV \)

**TABLE II.** The effective mass of Ag, Cu and Au (in units of \( m^*/m_0 \)).

| face  | DFT | Expt. |
|-------|-----|-------|
| Ag (001) | 1.00 | 1.03±0.01b |
|   (110) | 0.35 | 0.39±0.01b |
|   (111) | 0.89 | 0.94±0.01b |
| Cu (100) | 0.47 | 0.49±0.02a |
|   (110) | 0.50 | 0.53±0.02a |
|   (111) | 0.42 | 0.45±0.02a |
| Au (001) | 0.96 | 0.99±0.01c |
|   (110) | 0.45 | 0.48±0.01d |
|   (111) | 1.03 | 1.08±0.01c |

aReference [12]
bReference [27]
cReference [26]
dReference [28]

**TABLE III.** The work function of Ag, Cu, and Au (in units of eV).

| face  | Expt. | DFT |
|-------|-------|-----|
| Ag (001) | 4.64  | 4.64±0.05 |
|   (110) | 4.52  | 4.53±0.05 |
|   (111) | 4.75d | 4.83±0.05 |
| Cu (100) | 4.59b | 4.64±0.05 |
|   (110) | 4.48b | 4.52±0.05 |
|   (111) | 4.94d | 5.02±0.05 |
| Au (001) | 5.47c | 5.52±0.05 |
|   (110) | 5.37c | 5.36±0.05 |
|   (111) | 5.31c | 5.50±0.05 |

aReference [29]
bReference [30]
cReference [31]
dReference [32]
and 0.130√m₀eV, respectively. The polycrystalline nature of the measured noble metal photocathodes implies a crystal orientation randomness to the samples, so that the strict theoretical expression for ∆₁ average must be expressed as

$$\Delta P_{T,\text{average}} = \sum_{i,j,k} x_{ijk} \Delta P_{T,(ijk)},$$

where $x_{ijk}$ is the weight of (ijk) crystal orientation and $\sum x_{ijk} = 1$. The general $x_{ijk}$ distribution of FCC polycrystalline is displayed in FIG. 4, which indicates that (100) and (110) are the two prevalent crystal faces and, hence, are expected to dominate the photoemission from polycrystalline noble metals [33]. Therefore, it is possible to consider an average ∆₁ using an analysis that is restricted to (001) and (110) face emission.

TABLE IV. DFT evaluated photoemission properties of Cu and Au.

| Metal | face | $\Delta P_{T,DFT}$ (√m₀eV) | $\Delta P_{T,0}$ (√m₀eV) | $A_{T=0K}$ |
|-------|------|--------------------------|------------------------|------------|
| Ag    | (100) | 0.202                    | 0.235                  | 0.860      |
|       | (110) | 0.202                    | 0.235                  | 0.860      |
| Cu    | (100) | 0.170                    | 0.191                  | 0.445      |
|       | (110) | 0.198                    | 0.288                  | 0.444      |
| Au    | (100) | 0.208                    | 0.278                  | 0.425      |
|       | (110) | 0.168                    | 0.361                  | 0.245      |

The DFT-based photoemission model described in the previous papers [33][34] is used to evaluate ∆₁ for Ag, Cu, and Au. The results for photoemission from the (001) and (110) faces of Cu and Au are shown in FIG. 5. The spatially-averaged values of ∆₁ extracted from the excess energy contours are calculated using $\hbar \omega = 4.75$ eV for Cu and $\hbar \omega = 5.77$ eV for Au, and the results are listed in TABLE IV. The theoretical data is a good fit to $\Delta P_T = A \sqrt{m_0 (\hbar \omega - \phi)}$, giving the A values within 79% of 0.577 for Ag all cases expect Au(110) where A value within 42% of 0.577. In the $\Delta P_T(\hbar \omega, T_c)$ plot (FIG. 5(c)), the rms transverse momentum is evaluated under 0 K, 300 K and the melting point, where the melting temperature for Cu (Au) is 1363K (1336K) [33]. As would be expected, the increase in $\Delta P_T$ due to electron temperature increase is weak (strong) for Au (Cu) which has the large (small) excess photoemission energy; both metals have inward bent ‘electron-like’ energy states. Owing to the high degree of symmetry of Fermi surface in the FCC Brillouin zone, a relatively isotropic transverse momentum distribution is dominant in the prevalent crystal orientations.

III. PHOTOEMISSION FROM THE SURFACE STATE

Previous literatures have indicated that there are surface states in the Surface Brillouin Zone (SBZ) for Ag(111), Cu(111) and Au(111) [3][4][8][42]. Due to the presence of a crystal surface, bulk-forbidden electronic single-particle states may arise leading to a band in the corresponding projected bulk band gap. These so-called surface states are highly localized perpendicular to the surface, and form a quasi two-dimensional electron band. Typically, surface states exist if their character is similar to a bulk state, but shifted in energy by the surface perturbation. Because the occupied part of the surface state is far away from the surface Brillouin-zone (SBZ) boundary, its dispersion can be regarded as identical for all in-plane directions. As shown in FIG. 6 the SBZ is a two dimensional hexagonal structure for the (111) FCC crystal face ($k_z = 0$), and it is centered at Γ point with ΓM and ΓK directions as $k_x$ and $k_y$, respectively; that is to say, the surface state disperses with momentum parallel to the surface $p_x$ and $p_y$ but not with perpendicular momentum $p_z$ (momentum is restricted with the in-plane vector $p_T = p_x + p_y$). According to Ref. [33], [44], and [3], it is the surface state which can play an essential role in noble metal (111) face photoemission because, for a clean (111) surface, the photoemission intensity reaches a peak at $E_F - E_{ss,min}$, where $E_{ss,min}$ is the surface state band energy minimum [25]. Surface states can therefore dominate emission from the (111) faces of noble metals.

A successful method of distinguishing surface state and bulk photoemission features and determine the former’s properties is to use a DFT-based surface band calculation within the slab model to extract the slab’s band structure and inspect its energy dispersion properties, and thereby find the surface state band that is located between Fermi level and bulk bands. First, a (111)-face supercell comprising the multi-layer slab and suitable vacuum region needs to be constructed. Second, band structure calculation along the ΓM and
FIG. 5. The results from the DFT-based photoemission analysis for the (001)/(110) face of Cu and Au. (a) Crystal momentum map of the electronic states (shaded regions) below the Fermi level (solid line) that may photoemit within $p_{T,max} = \sqrt{m_0\Delta E}$ (dashed lines) for the transverse (010)/(001) and (110)/(110) crystal directions. (b) Transverse momentum distribution of the photoemitted electrons in the (010)/(001) and (110)/(110) directions. (c) Incident photon energy dependence of the rms transverse momentum $\Delta p_T$ for electron temperatures $T_e \to 0$ (data points with solid line fit); $\Delta p_T = A\sqrt{m_0\Delta E}$, $T_e = 300$K and the melting points of each metal (dot-dashed lines), together with the expected form of $\Delta p_T = \sqrt{(\hbar\omega - \phi)/3}$ (dashed line).

$\Gamma\bar{M}$ directions is performed. Third, the bulk bands are projected onto the $k_x-k_y$ plane and plotted together with surface bands to determine the allowed surface states. As the surface energy dispersion relations are described
in the surface Brillouin zone (See Fig. 6), in order to estimate where a surface state is, one can project the bulk bands into the two-dimensional Brillouin zone and then look for gaps that might accommodate such a state among the bulk states. The surface bands are the highest-energy partially occupied bands that fall below the Fermi level \( E_F \) only for limited regions of the momentum-space. The electronic states of these surface bands are usually well localized in the vicinity of the surface. The electrons occupying such a region of allowed \( k_x - k_y \) space require the least energy to overcome the summation of the work function and transverse energy required to escape the material as photoelectrons. When the laser photon energy is high enough to liberate these electrons but insufficient to reach the next energy band, an electron beam suitable for HCI can then be generated by emission from the single assessed surface state.

For Ag(111), there is an \( s - p \) gap at \( \Gamma \), where a Shockley-type surface state was observed by R. Paniago, G. Nicolay et al [3, 4, 42]. The \( L \)-gap \( s - p \) surface state dispersion was obtained by measuring the energy of the surface state as a function of the external electron angle \( \theta \). In contrast to the experimental investigations, we use a well-converged basis set and a \( \delta \)-mesh of 17\times17\times1 points in the two-dimensional irreducible Brillouin zone and modeled the surface by employing a periodic slab of 9 atomic layers separated by 15 \( \AA \) of vacuum. The thin slab band calculation [34] is implemented by quantum-ESPRRESSO using the local-density approximation [45] pseudopotential. Results of the band structure calculation along the \( \Gamma \) direction for the 9 layer slab of Ag(111) is shown in Fig. 7(b). In order to be consistent with the experimental measurement unit, we plot the band dispersion in terms of \( E(\vec{k}) \). In Fig. 7(b), the blue solid lines give the slab’s band dispersion by DFT at \( T_e = 0 \), and the Fermi level has been adjusted to zero (dashed line), the allowed surface surface is highlighted by the red circle. In Fig. 7(a), we compare my DFT calculation (solid green line) with the experimental Ag(111) surface state measurement of Nicolay [3] (blue solid line) and by Paniago [4] (red solid line). The DFT calculated surface state is between the two experimental surface states, which again demonstrates that there is a good agreement between experiment and theory.

The surface state, with its parabolic dispersion about the \( \Gamma \) point of the SBZ, is 62 meV below the Fermi level by emission from the single assessed surface state. An intrinsic emittance calculation

\[
\frac{(p_x^2 + p_y^2)}{2m_0} + \phi_{(111)} + \frac{p_z^2}{2m_0} = h\omega + E(p_x, p_y),
\]

where \( p_x \) and \( p_y \) are the transverse momentum components \( (p_T = \sqrt{p_x^2 + p_y^2}) \), \( p_z \) is the longitudinal momentum in vacuum and \( E(p_x, p_y) \) is initial electron state energy. An intrinsic emittance calculation
FIG. 7. Energy dispersion relation for the Ag(111) Surface state. Results of the band-structure calculation along the $\Gamma M$ direction for a 9-layer slab of Ag(111). The Fermi level has been adjusted to zero level. The left panel shows the comparison between the DFT calculated surface band (blue solid line) with the experimental measured surface bands. The blue solid line is Nicolay’s result (red solid line); the red solid line is Paniago’s result (green solid line). The right panel shows the surface dispersion and the surface state is highlighted by red circle.

FIG. 8. (a) Ag(111) surface state constant energy contour with $\Delta E = 35 \text{ meV}$. The outmost red contour is the two dimensional surface state Fermi surface contour with radius $0.220 \sqrt{m_0 eV}$. The innermost blue contour is the $E_F - \Delta E$ constant energy contour with radius $0.190 \sqrt{m_0 eV}$. (b) Ag(111) surface state transverse momentum distribution with $\Delta E = 35 \text{ meV}$. Dashed line Gaussian fits are guides to eyes.

may thus be obtained from the transverse momentum distribution of photoemitting energy contours. After application of Eq. [3] the resulting transverse momentum distribution displayed in Fig. [8(b)] shows the $L$-gap surface state photoemission. The $\Delta p_T$ of the ‘ring-like’ emission peaks is $0.029 \sqrt{m_0 eV}$ for $\Delta E = 35\text{ meV}$. It can be seen that the transverse momentum distribution is symmetrical with respect to $\Gamma$ and has maxima close to $p_F$, which is consistent with experimental measurements.

As the emitted transverse momentum distribution is in the form of a ring with a radius $k_F = 0.077 \AA^{-1}$, its
IV. SUMMARY AND DISCUSSION

This paper describes the emission properties of three noble metals (Ag, Cu, and Au) and the emission from the surface state. The Fermi surface, effective mass, and band structures for the (100), (110), and (111) faces are evaluated to confirm and supplement the current dataset regarding the electronic properties of the four FCC metals. The nonparametric model discussed can be generalized, implemented, and extended toward applications such as material design, data analysis, and multivariate modeling. A surface state DFT evaluation has performed to show that the photocathode generated hollow cone illumination (HCI) can be realized through Ag(111) single crystal with 0.03 eV excess energy. In case of $n_0 > m_e$, the minimum energy required to photoemit from the surface state, $E_{(111)}$, is the sum of FCC (111) face work function $\phi_{(111)}$ and the (111) Fermi level transverse momentum offset $p_T^2/2m_0$. The $\Delta p_T$ of the ‘ring-like’ emission from Ag(111) surface state peaks is 0.029 $\sqrt{m_0 eV}$.

ACKNOWLEDGMENTS

The authors are indebted to Juan Carlos Campuzano, Christopher Grein, Randall Meyer, Alan Nicholls, and Serdar Öğüt for their valuable discussions. This work was partially supported by the Department of Energy (Contract No. DE-FG52-09NA29451), Futurewei Technologies, Inc., and Uptake Technologies, Inc.

[1] J. A. Berger, B. L., Rickman, T. Li, A. W. Nicholls, and W. A. Schroeder, Applied Physics Letters 101, 194109 (2012)
[2] J. F. Schmehle, J. E. Clendenin, D. H. Dowell, and S. M. Gierman, International Journal of Modern Physics A 22, 4069 (2007).
[3] G. Nicolay, F. Reinert, S. Hfner, and P. Blaha, Physical Review B 65 (2001), 10.1103/PhysRevB.65.033407.
[4] R. Paniago, R. Matzdorf, G. Meister, and A. Goldmann, 336, 113.
[5] Z. M. A. El-Fattah, M. Matena, M. Corso, M. Orama, J. E. Ortega, and F. Schiller, Physical Review B 86, 121407 (2012).
[6] S. LaShell, B. McDougall, and E. Jensen, Physical review letters 77, 3419 (1996).
[7] T. C. Hsieh, P. John, T. Miller, and T.-C. Chiang, Physical Review B 35, 3728 (1987).
[8] L. Brigo, L. Petersen, H. Brune, and K. Kern, Surface science 417, L157-L161 (2000).
[9] N. V. Smith, Physical Review B 32, 3549 (1985).
[10] J. F. Koch, R. A. Strawling, and A. F. Kip, Physical Review 133, A240 (1964).
[11] R. Courths and S. Hufner, Physics Reports 112, 53 (1984).
[12] A. S. Joseph, A. C. Thorsen, E. Gertner, and L. E. Valby, Physical Review 148, 569 (1966).
[13] D. H. Dowell, T. Bazarov, B. Dunham, K. Harkay, C. Hernandez-Garcia, R. Legg, H. Padmore, T. Rao, J. Smedley, and W. Wan, Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment 622, 685 (2010).
[14] W. Krakow and L. A. Howland, Ultramicroscopy 2, 53 (1976).
[15] C. Dinges, H. Kohl, and H. Rose, [Ultramicroscopy 55, 91 (1994)]
[16] Y. Kondo, T. Ito, and Y. Harada, Japanese Journal of Applied Physics 23, L178 (1984).
[17] T. Li, in University of Illinois at Chicago Physics Fest 2015, Chicago, IL (2015) p. 22.
[18] B. W. A. Schroeder and T. Li, in Center for Free-Electron Laser Science, German Electron Synchrotron (DESY), Hamburg, Germany (2015) p. 40.
[19] B. W. A. Schroeder and T. Li, in Femtosecond Imaging and Spectroscopy (FEIS-2) 2015 (Michigan State University, 2015).
[20] A. Schroeder, B. Rickman, T. Li, and J. Berger, in P3 2014: Photocathode Physics for Photoinjectors (Lawrence Berkeley National Laboratory, 2014) pp. https–drive.
[21] P. T. Coleridge and I. M. Templeton, Physical Review B 25, 7818 (1982).
[22] C. N. Berglund and W. E. Spicer, Phys. Rev. 136, A1030 (1964).
[23] R. A. Ballinger and C. a. W. Marshall, Journal of Physics C: Solid State Physics 2, 1822 (1969).
[24] N. E. Christensen, physica status solidi (b) 31, 635 (1969).
[25] A. Schroeder, B. Rickman, T. Li, and J. Berger, in P3 2014: Photocathode Physics for Photoinjectors (Lawrence Berkeley National Laboratory, 2014) pp. https–drive.
[30] C. Fall and A. Baldereschi, *Ab initio study of the work functions of elemental metal crystals*, Tech. Rep. (1999).

[31] H. B. Michaelson, *Journal of Applied Physics* **48**, 4729 (1977).

[32] H. Farnsworth and R. Winch, *Phys. Rev.** 58**, 812 (1940).

[33] C. S. Barrett and T. B. Massalski, *Structure of metals*, Vol. 92 (McGraw-Hill New York, 1966).

[34] C. J. Fall, N. Binggeli, and A. Baldereschi, *Journal of Physics: Condensed Matter* **11**, 2689 (1999).

[35] H. B. Michaelson, *J. Appl. Phys.* **48** (1977).

[36] T. Li and W. A. Schroeder, arXiv preprint arXiv:1704.00194 (2017).

[37] T. Li, *Photoelectric Emission Properties of Photocathode Materials*, Ph.D. thesis (2016).

[38] T. Li, B. L. Rickman, and W. A. Schroeder, *Journal of Applied Physics* **117**, 134901 (2015).

[39] J. A. Berger, B. L. Rickman, T. Li, A. W. Nicholls, and W. Andreas Schroeder, *Applied Physics Letters* **101**, 194103 (2012).

[40] T. Li, B. L. Rickman, and W. A. Schroeder, *Phys. Rev. ST Accel. Beams* **18**, 073401 (2015).

[41] L. Cohen, W. Klement, and G. Kennedy, *Physical Review* **145**, 519 (1966).

[42] S. D. Kevan and R. H. Gaylord, *Physical Review B* **36**, 5809 (1987).

[43] L. Bürgi, L. Petersen, H. Brune, and K. Kern, *Surface science* **447**, L157 (2000).

[44] G. Hörmandinger, *Phys. Rev. B* **49**, 13897 (1994).

[45] D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990).

[46] Z. Wang and T. Li, “Methodology to improve the anomaly detection rate,” (2017), uS Patent 20,170,099,208.