FINAL REPORT

Single crystal metal photocathodes: Benchmarking performance against *Ab initio* theory

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Executive summary

The results generated by this short-term research project have contributed significantly to our overall understanding and practical implementation of metal photocathodes. First, the research work has verified the direct connection between the energy-momentum dispersion of the emitting bulk band states and the mean transverse energy (MTE) and quantum efficiency (QE) of the electrons emitted from solid-state photocathodes. Second, and more importantly, the work has shown that the density of the recipient vacuum states must be included in any description of the emission properties of photocathodes. Third, amongst the primary crystal faces of Cu, only Cu(100) is found to be a good single-crystal photocathode material in the 260-270nm wavelength range, which includes the fourth harmonic of Nd:YAG lasers. Finally, measurements on Mg(0001) indicate that UV transparent oxide surface layers may increase (decrease) the MTE of electrons emitted at low (high) excess energies.

Single-crystal Cu photocathodes

The spectral characterization of single-crystal Cu photocathodes was performed at Lawrence Berkeley National Laboratory (LBNL) using a photocathode characterization system in a UHV (~10^{-10}torr) vacuum chamber with a 250-280nm (4.43-4.96eV) UV radiation source based on a Ti:sapphire laser system. To ensure photoemission from a pristine crystal surface, the photocathode samples were subjected to several cycles of Ar^+ ion bombardment and temperature annealing until a strong low energy electron diffraction (LEED) pattern from the required crystalline surface was observed. Auger spectroscopy was used to confirm the cleanliness of the prepared Cu crystal surfaces.

The measured spectral dependence of the MTE for a Cu(100) at 300K is shown in Fig. 1 together with a new theoretical formulation of one-step photoemission that has been developed using the exact one-dimensional quantum solution for transmission through and over a triangular barrier evaluated by R.G. Forbes and H.B. Deane [*Proc. R. Soc. A* **467**, 2927 (2011)]. This analytical solution has been extended into the transverse dimension, using conservation of transverse

momentum in electron emission, to include parabolic electronic bands with cylindrical symmetry; that is, with a longitudinal effective mass m_z differing from the transverse effective mass m_T isotropic in the plane of the crystal emission face. In addition to including the local density of the emitting states (multiplied by the appropriate Fermi-Dirac population distribution) in the photoemission simulation, we have also now included the vacuum density of states; that is, the density of the recipient states for the emitted electron.

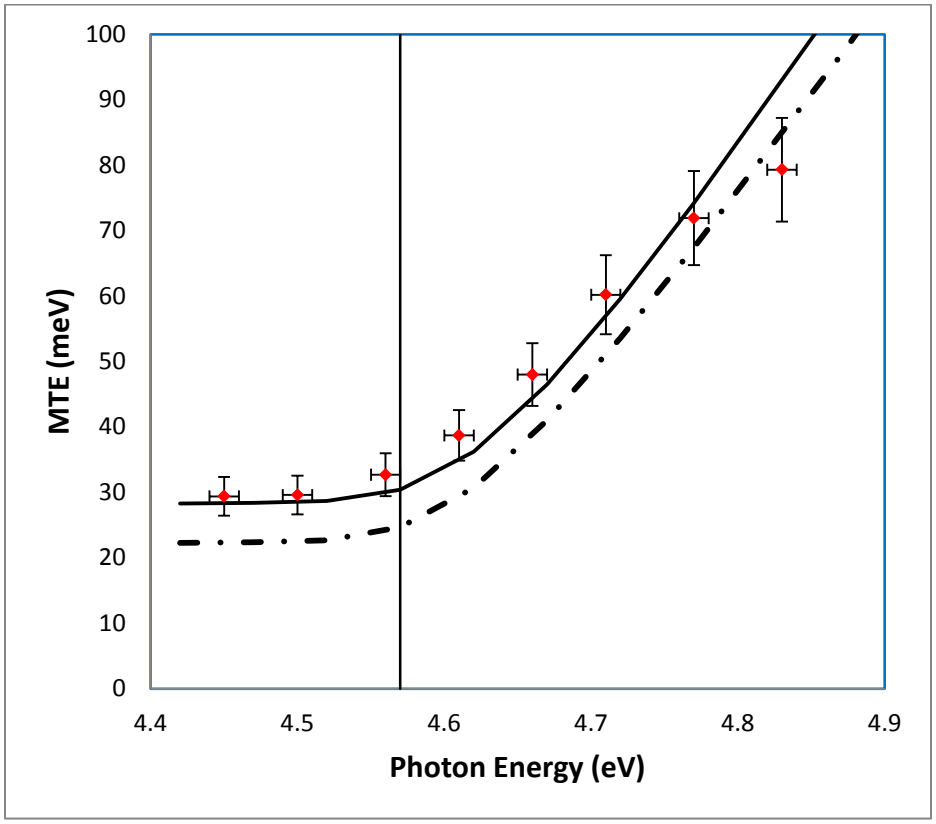

Figure 1
Measured MTE (data points) as a function of incident UV photon energy for a clean Cu(100) photocathode at 300K: Bold solid line is a zero free parameter one-step photoemission simulation including the vacuum density of states and using ϕ = 4.57eV (thin vertical line); Bold dot-dashed line represents the one-step photoemission simulation result without the vacuum density of states.

The one-step photoemission simulation (bold solid line) is clearly in very good agreement with the experimental variation of the MTE with incident photon energy (data points). The simulation employs $m_z = 0.45m_0$ and $m_T = 0.89m_0$ (where m_0 is the free electron mass), and an effective Fermi energy of 14eV, all obtained from a parabolic band fit to a density functional theory (DFT) calculation of the Cu band structure around the emitting bulk band states. With the vacuum density of states omitted (bold dot-dashed line), the one-step simulation significantly underestimates the MTE. The somewhat lower than expected data point at $\hbar\omega$ = 4.83eV is likely due the difficulty of extracting an accurate value of the MTE for large electron beam spot sizes on the employed micro-channel plate detector.

The value of 4.57eV for the work function ϕ of the Cu(100) face used in Fig. 1 was obtained using a power law fit to the measured QE as a function of the excess photoemission energy $\Delta E = \hbar\omega - \phi$. As shown in Fig. 2, the spectral dependence of the simulated QE (bold line), which is normalized to the measured value at a photon energy $\hbar\omega = 4.77$eV, is also in very good agreement with the experimental measurements (data points) and illustrates the effect of the 300K Boltzmann tail in the electron distribution when ΔE is less than 0.1eV. The theoretically predicted dependence, $QE = A(\Delta E)^{2.75}$ where A is a constant, allows for an asymptotic extraction of ϕ for $\Delta E > 0.15$eV (dotted line) using $(QE/A)^{0.364} = \hbar\omega - \phi$. The fact that the QE does not depend on ΔE^2, as in prior photoemission analyses, is due to the density of states of both the emitting bulk band and recipient vacuum states – the joint density of states for the one-step photoemission transition.

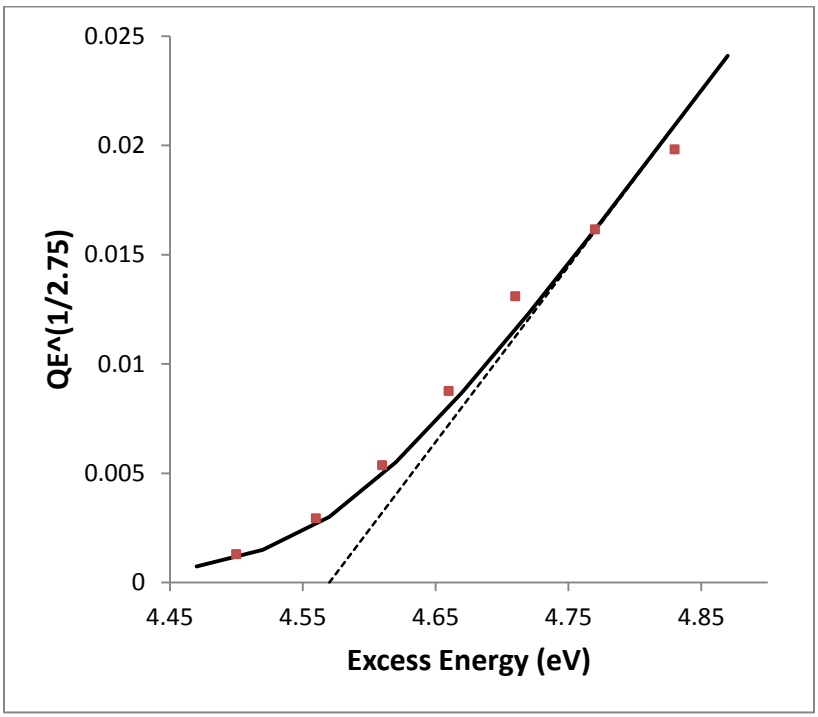

Figure 2
Measured QE (data points) to the $0.364 = (2.75)^{-1}$ power as a function of incident UV photon energy for a clean Cu(100) photocathodes at 300K: Prediction of the one-step photoemission simulation fit to the measured QE at $\hbar\omega = 4.77$eV (bold solid line) and linear fit to high excess energies for extraction of $\phi = 4.57$eV (dotted line).

In addition, for the Cu(100) photocathode, measurements of the MTE and QE were made at 30K. In agreement with the one-step simulation, MTE values as low as 6meV were obtained at an excess energy of 0.11eV, albeit at a significantly reduced QE of $\sim 10^{-8}$ due to the much decreased Boltzmann tail population at higher ΔE where the emission probability is increased.

Measurements of the spectral emission properties of a Cu(110) photocathode were also attempted. Unfortunately, the significantly higher chemical reactivity of this Cu crystal face

caused the work function to change during the course of experimentation; that is, the Cu(110) surface suffered contamination despite the good UHV conditions. Nonetheless, no MTE values below 33meV were measured at 300K and this corresponds very well to the expected minimum value of 33.8meV for $\Delta E < 0$ evaluated using the new one-step photoemission model with $m_z = 0.59m_0$, $m_T = 1.15m_0$, and an effective Fermi energy of 12eV extracted from a parabolic band fit to the DFT calculated Cu band structure around the emitting bulk band states.

For the Cu(111) surface, the hole in the Fermi surface in this crystal direction precludes emission from the bulk electronic states for photon energies less than about 5.4eV, despite the work function value of 4.94eV, and hence is outside the 4.43-4.96eV tuning range of the UV radiation source at LBNL. Electrons are expected from the Cu(111) surface state at slightly lower photon energies and its emission properties are known [*Appl. Phys. Lett*. **93**, 183505 (2008)].

Together, these results indicate that Cu(100) is the most practical low index Cu single-crystal photocathode. At an incident photon energy of 4.66eV, the fourth harmonic of a Nd:YAG laser, a clean room temperature Cu(100) photocathode should have a MTE of 50meV and a QE of $\sim 2\times10^{-6}$. At the fourth harmonic of a Yb:fiber laser system operating at 1030nm, the MTE will be around 90meV, but the QE increases by an order of magnitude to $\sim 2\times10^{-5}$.

Single-crystal Mg photocathodes

Investigation of the spectral properties of single-crystal Mg photocathodes at LBNL were not attempted due to the small (4.43-4.96eV) spectral range of the available UV radiation source which does not include the expected ~3.8eV work functions of Mg crystal faces. Nonetheless, a preliminary characterization of a Mg(0001) photocathode has been performed using the photocathode characterization system at the University of Illinois at Chicago (UIC), which incorporates a UV radiation source with a 3.0-5.3eV tuning range, but does not have the capability to clean the photocathode surface and does not operate under UHV conditions. As a result, the 10-20Å thick native oxide on the photocathode surface was not removed; that is, a Mg(0001)/MgO photocathode was characterized. As MgO has a band gap of ~7eV, the oxide layer should transmit the incident UV radiation without significant absorption, which implies that the observed photo-emitted electrons originate from the metal.

The measured spectral dependence of the MTE for the Mg(0001)/MgO photocathode at 300K is shown in Fig. 3 (data points) together with the dependence expected from the one-step photoemission simulation for the near parabolic primary emission band for a Mg(0001) photocathode (bold line), for which $m_z = 0.21m_0$, $m_T = 0.82m_0$, and the Fermi energy is 1.05eV. The MTE simulation, which assumes a work function of 3.4eV extracted from a power law dependence of the QE on $\hbar\omega$ (as in Fig. 2 for Cu(100)), predicts a distinct peak when the excess photoemission energy ΔE is equal to the Fermi energy of the emission band. This is not observed in the experimental data, which has a distinctly different spectral trend.

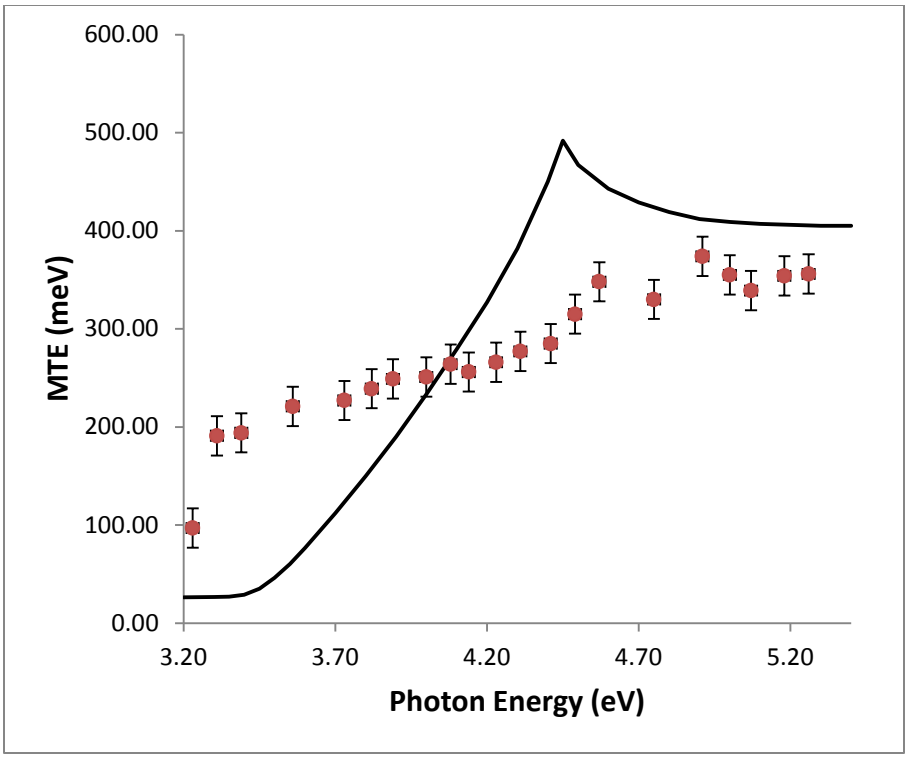

Figure 3
Measured MTE (data points) as a function of incident UV photon energy for a Mg(0001)/MgO photocathode at 300K: Bold solid line is a one-step photoemission simulation from the primary bulk emission band ($m_z = 0.21m_0$, $m_T = 0.82m_0$, and a Fermi energy of 1.05eV) with $\phi = 3.4$eV.

The properties of the surface oxide layer likely offer the explanation for the observed discrepancy between experiment and theory, although comparison with emission from a clean Mg(0001) surface will be required. At low excess photoemission energies ΔE, the emitted electrons are expected to be subject to scattering with optical photons in the MgO layer as they move through it from the metal to the vacuum. This would negate the transverse momentum conservation implicit in the one-step photoemission simulation and result in an increase in the MTE – an effect that has already been postulated for PbTe(111) and doped oxide photocathodes. As ΔE increases, the optical photon scattering effect is reduced as the electrons' time of flight through the oxide layer decreases. As a result, the oxide layer becomes more of a passive quantum barrier which will preferentially decrease the transmission of electrons with higher transverse momenta, thereby causing a reduction in MTE (compared to theoretical expectations) at high ΔE values.

At incident photon energies of 4.5-5.0eV, the DFT calculated bulk band structure of Mg suggests that there should be resonances with two unoccupied upper conduction bands for emission from the (0001) surface. The MTE measurements in Fig. 3 appear to show features consistent with such resonances, which would verify that the emitted electrons do indeed come from the bulk Mg metal.

Personnel and Future Activities

All the experimental measurements were performed by Dr. S. Karkare and Gowri Adhikari, a female graduate student in the Physics Department at the University of Illinois at Chicago (UIC). The results they obtained for the Cu(100) photocathode that show the importance of including the density of the recipient vacuum states in any analyses of photoemission will be presented at the *Photocathode Physics for Photoinjectors* (P3) workshop to be held at Los Alamos, NM, in October 2018. A publication on this fundamental result is also planned, possibly for the journal *Nature*.

It is expected that the collaboration between the UIC group and Prof. Karkare, now at Arizona State University, will continue into early 2019 in order to complete the work on clean single-crystal Mg photocathodes, using the same UHV electron beam analysis system and a UV radiation source with a wider tuning range.