Tailoring the emissive properties of photocathodes through materials engineering: ultra-thin multilayers

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Abstract

We report on an experimental verification that emission properties of photocathodes can be manipulated through the engineering of the surface electronic structure. Ultrathin multilayered MgO/Ag(001)/MgO films were grown by pulsed laser deposition, tuning the thickness n of the flanking MgO layers to 0, 2, 3, and 4 monolayers. We observed an increase in quantum efficiency and simultaneous decrease in work function with layer thickness. The scale and trend direction of measurements are in good but not excellent agreement with theory. Angle resolved photoemission data for the multilayered sample $n = 3$ showed that the emission profile has a metallic-like momentum dispersion. Deviations from theoretical predictions [K. Németh *et al.*, PRL 104, 046801 (2010)] are attributed to imperfections of real surfaces in contrast with the ideal surfaces of the calculation. Photoemissive properties of cathodes are critical for electron beam applications such as photoinjectors for Free Electron Lasers (FEL) and Energy Recovery Linacs (ERL). An ideal photoemitter has a high quantum efficiency, low work function, low intrinsic emittance [and long lifetime](#). It has been demonstrated here that emission properties may be systematically tailored by control of layer thickness in ultrathin multilayered structures. The reproducibility of the emission parameters under specific growth conditions is excellent, even though the interfaces themselves have varying degrees of roughness.

Keywords

Pulsed laser deposition, RHEED, epitaxy, photocathode, work function, quantum efficiency

Graphical Abstract

1. Introduction

Much of the development of photocathode materials has been aimed at the growth of photoemissive thin films with low work function (WF), and high quantum efficiency (QE) [1]. It has been shown, both theoretically and experimentally, that metal-insulator junctions can lead to the modification of the WF for coverages of a few monolayers (ML) of metal oxides on metallic substrates [2-6]. Reduction of WF and increase of QE can be achieved simultaneously by coating metal surfaces with Cs, CsBr, Y and Mg [7-11]. Cs ion implantation on Cu, Ag, and Au has been shown to reduce the WF and increase QE while still retaining the robustness of the metal; nonetheless, the crystalline quality of the substrate is sacrificed [12]. Since low intrinsic emittance beams play an increasingly important role for some photoinjector driven applications, maintaining a high quality surface can be advantageous in avoiding emittance degradation [13].

A theoretical model by Németh, et al. [2] describes the density functional theory (DFT) simulation of a multilayered structure MgO/Ag(001)/MgO in the configuration of 4 ML of Ag(001) flanked by n ML of MgO. This model indicates that 2 or 3 ML of MgO can reduce the emittance of an electron beam, because the surface band structure exhibits a narrowing of the range of surface-parallel momenta near the Γ -point neighboring the Fermi level. Since the surface-parallel momenta of the electrons are conserved in prompt emission, the angular spread of emitted electrons (and so the intrinsic beam emittance) is reduced. In addition, this and another similar model [5] predict a WF drop of 1-1.5 eV from that of 4 ML of Ag(001). Measurements using atomic and Kelvin probe force microscopies (AFM and KPFM) show that even a one layer deposition of MgO on a Ag(001) single crystal substrate produces a WF drop of 1.1 eV (1 ML) and 1.4 eV (2 ML) from that of the bare substrate [3,4]. Recently, an effort to quantify the effect on emittance of a single 4 ML coating of MgO on Ag(001) was carried out using Angle Resolved Photoelectron Spectroscopy (ARPES) by Droubay, et al. [14]. The photon energy was not optimized, so the emittance of the coated sample was larger than from the substrate alone. However, an enhancement of the photoemission intensity at the Γ -point near the Fermi level was observed for the coated versus the uncoated Ag(001) substrate.

Here the dependence of emission behavior on the thickness of the MgO layers of multilayered MgO/Ag/MgO structures was examined. The high quality multilayer films were fabricated using pulsed laser deposition. Reflection High-Energy Electron Diffraction (RHEED) [15-17] and Photoelectron Spectroscopy (PES) [18,19] were used to monitor the formation of the highly oriented, crystalline, multilayer films, and verify the chemical structure of each. The Kelvin Probe technique was used to determine any changes in the work function as a function of the thickness of the MgO layers. QE was measured in vacuum by grounding the samples, illuminating them with UV light and collecting the photocurrent using an anode at 450 V. ARPES was used to measure the angular emission profile of the multilayer $n = 3$.

2. Materials and Methods

Pulsed Laser Deposition (PLD), a state-of-the-art ultra-high vacuum film synthesis technique [20-23], was used for growth of all films described here. The laser fluence for all instances was 5-6 J/cm². Substrate heating was performed using a continuous wave CO₂ laser (10.6 μ m) that impinges on the back of the substrate through a zinc-selenide window. Film growth monitoring was carried out using in-situ RHEED. The deposition rate was calibrated before growth of each film using a quartz crystal microbalance (QCM) with an uncertainty of less than 10% of the film thickness. Thickness measurements were independently verified using ellipsometry showing a small average discrepancy of ± 0.03 Å. It was found in a separate study that the roughness of the deposited surfaces was reproducibly dependent on the substrate temperature during deposition. The surfaces of the films for different layer thicknesses were consistent in quality from sample to sample.

3. Results and Discussion

3.1 Synthesis and Structural Characterization

The multilayer MgO/Ag/MgO structures, in the (001) orientation, were fabricated on smooth epitaxial 40 nm Ag buffer films deposited on MgO(001) in order to substitute more expensive commercially available single crystal metallic substrates. Multilayers consisted of a 4 ML Ag interlayer flanked by $n = 2, 3, 4$ MgO monolayers, where the nominal monolayer thicknesses (i.e. half of the lattice parameter) are: 2.106 Å and 2.045 Å for (001) MgO and Ag, respectively [2]. The deposition temperature was 130 °C and the chamber base pressure was $\sim 5 \times 10^{-9}$ Torr for all films.

After growth, the films were initially characterized in order to study their structural properties. During growth the films were monitored in situ using RHEED in order to examine their crystalline structure. An example of multilayer evolution (for $n = 3$ ML) during growth, examined by RHEED, is shown in Figure 1. Figure 1 (a) shows the pattern of the Ag/MgO(001) growth platform. Thin rods and Kikuchi lines as well as the absence of transmission-like features indicate that the film has become a terraced 2-dimensional surface [6,15]. The RHEED system was calibrated using the pattern from MgO(001) (not

shown). The calibration showed that the lattice constant for the Ag/MgO(001) pattern was $4.01 \pm 0.03 \text{ \AA}$, $\sim 2\%$ smaller than the nominal value of $4.09 \text{ \AA}$ for bulk Ag(001) [2]. Figure 1 (b)-(d) show RHEED patterns of the sequential deposition of MgO (3 ML), Ag (4 ML), MgO (3 ML) on Ag/MgO(001). Epitaxial growth is manifested by the absence of polycrystalline features (rings and/or curved rods) [15-17]. The appearance of distinctive horizontally collinear features is indicative of transmission diffraction from 3D surface features [17], thus it is clear that the films grew in the form of highly ordered epitaxial islands. All patterns were taken along the [100] azimuth of MgO(001).

Figure 1. RHEED patterns during deposition of multilayer $n = 3$ ML: (a) Ag/MgO(001) support, (b)-(d) multilayer progression.

The multilayer surfaces were then imaged by STM in order to confirm the results from RHEED. Figure 2 depicts the STM images corresponding to the multilayer $n = 3$ ML described in Figure 1. Figure 2 (a) confirms the highly ordered, terraced surface finish of the Ag/MgO(001) growth platform, and Figure 2 (b)-(d) shows the formation of the multilayer as epitaxial nano-islands. The average and rms surface roughness for the Ag/MgO(001) support were measured to be $0.42 \pm 0.03 \text{ nm}$ and $0.52 \pm 0.04 \text{ nm}$, respectively. The average and rms surface roughness for the multilayer surface $n = 3$ ML were measured to be $0.56 \pm 0.03 \text{ nm}$ and $0.71 \pm 0.03 \text{ nm}$, respectively. Roughness was sampled over $100 \times 100 \text{ nm}^2$ areas.

Figure 2. Ex-situ STM at different stages of growth of multilayer $n = 3$ ML as shown in Figure 1: (a) Ag/MgO(001), (b)-(d) multilayer progression.

In addition to the characterization of the physical structure by RHEED and STM, ex-situ PES was used to track the chemical structure of the multilayered films at different stages of deposition. Figure 3 shows Al K_{α} PES spectra of the evolution of deposition for the $n = 3$ ML example in Figures 1 and 2; starting from the Ag/MgO(001) single crystal surface through the sequence MgO ($n = 3$ ML), Ag (4 ML), MgO ($n = 3$ ML). The stages of deposition can be observed in the modulation of the Mg 2s and 2p peaks as their intensities increase and decrease according to the surface finish at any given step. A small shift of 0.4-0.6 eV toward higher kinetic energy (lower binding energy) was observed in the Mg core levels.

This is likely the result of the electron density displacement from Mg-O bonds due to the formation of interfacial states with Ag-O bonds. RHEED patterns, STM images and XPS spectra collected for multilayers $n = 2$ ML and 4 ML showed similar results and trends, which indicate the growth of epitaxial and stoichiometric films with surface roughness less than 1 nm over sampled areas of $100 \times 100 \text{ nm}^2$.

Figure 3. PES spectra showing the stages of deposition of MgO/Ag/MgO on Ag/MgO(001). The formation of the multilayer is evidenced by the increase (decrease) of intensity of the Mg (Ag) peaks.

3.2 Photoemissive Properties

In order to test the theoretical model by Nemeth *et al.* [2], the films were characterized as photoemitters by measuring their WF and QE. The theoretical model was reproduced in order to verify that the calculation was not dependent on the particular model used. In addition, an initial measurement of angular emission is provided for the multilayer with $n = 3$ ML.

Relative work function measurements of multilayers $n = 2, 3$ and 4 ML were made using the Kelvin Probe technique [24]. The probe tip WF was calibrated using commercially available HOPG and high purity (99.97%) polycrystalline Nb foil. Figure 4 shows the relative WF, $\Delta\Phi$, of multilayers with respect to Ag/MgO(001) as a function of multilayer thickness (n). A monotonic decrease in the WF with multilayered film thickness (given as the number of MgO monolayers) was observed. For comparison, Density Functional Theory (DFT) calculations are plotted as well.

The WF for multilayers $n = 2, 3$ and 4 ML was calculated using the software QuantumWise Atomistic Toolkit with Virtual NanoLab, which uses the formalisms of linear combination of atomic orbitals (LCAO) and the generalized gradient approximation (GGA) [25]. We used the PW91 functional with cutoff at 1360 eV for bulk and 1000 eV for slabs. The atomic grids were $23 \times 23 \times 23$ (bulk), $16 \times 16 \times 1$ (slabs). Geometric optimization yielded maximum stress values of 0.001 eV/Å and lattice vectors within 4% of their nominal value, similar to previous results [2]. Our DFT calculations and those from reference [2] for these films suggest an initial sharp drop in WF of close to 1 eV for the multilayer system with $n = 1$ ML of MgO; this reduction is almost the same for 2, 3 and 4 MgO ML. The measurements presented here show a somewhat linear decrease $\Delta\Phi$ of -0.34 eV, -0.60 eV and -0.89 eV (± 0.07 eV) for $n = 2, 3$ and 4 ML, respectively. As suggested by the RHEED patterns (Figure 3), the multilayers must have a roughness, consisting of islands of material of varying height and perhaps, finish (Ag or MgO). It is suggestive that the monotone WF drop is correlated with the surface coverage, which is likely due to the average contact potential difference (CPD) measurement under the macroscopic 2 mm diameter tip. The effect of roughness thus results in the unexpected benefit of providing the means for finer control of the WF change with multilayer thickness than predicted by DFT calculations of perfect surfaces. We expect that a more realistic theoretical description of the multilayers will require the inclusion of interface roughness.

Figure 4. WF measurements of multilayers $n = 2, 3, 4$ for the orientations compared to our DFT calculations and those from [2].

The reduction in the WF suggests an increase in QE for a fixed photoexcitation energy, as deeper binding energy states can be probed. Figure 5 shows measurements of QE versus WF for Ag(001), multilayer ($n = 2, 3, 4$ ML) and polycrystalline Mg surfaces. The measurements were conducted at 25 °C in a vacuum environment at $\sim 10^{-4}$ Torr using a white light source (Hg-arc lamp) with filters to select 254 nm and 313 nm wavelengths. The samples were grounded and illuminated while the photocurrent was collected by an electrode at a voltage of 450 V using a pico-ammeter. The background signal was recorded to be 1-2 orders of magnitude weaker than the photocathode current. In order to compare the photoemissive performance of the multilayered films, the WF and QE of Mg (a high QE alkaline earth metal routinely used as a photocathode coating and even in bulk as a photocathode itself [26-29]), were measured as well. The QE scales in the plots were adjusted to align the values of Mg for 254 nm and 313 nm wavelengths in order to facilitate visual comparison between the QE of thin films and Mg. The increase in the QE of the multilayers is attributed to the reduction in WF with film thickness. For both wavelengths used, the increase in QE ranged from about half to one order of magnitude. At 313 nm the rise in QE was not enough to reach the level of Mg. However at 254 nm, the increase in QE for multilayers $n = 3$ and 4 ML was more substantial, reaching the level of Mg within error.

Figure 5. Plots of QE vs WF of Mg, Ag/MgO(001) and multilayers $n = 2, 3, 4$ ML using 254 nm and 313 nm wavelengths.

We measured the ARPES spectrum of a multilayer as an initial attempt to determine the angular emission profile of the multilayers. The spectrum of the multilayer $n = 3$ ML was obtained using synchrotron radiation with photon energy of 22 eV at pass energy of 5 eV at the U13UB beamline from NSLS at BNL. The Fermi level was measured at 17.4 eV using a metallic Ag(001) surface for calibration. The samples were aligned at fixed azimuthal orientation in order to collect energy distribution curves (EDCs) at various positions of the polar angle (θ) ranging from 0° to 45°. The low-binding-energy region (0-2 eV) was modeled with Gaussian fits of 0.85 eV FWHM for each EDC. The background was modeled as an exponential decaying curve. Due to its complex structure, the density of states of the Ag 4d core level (roughly 4.5 eV to 8.5 eV), was approximated with a 4-Gaussian envelope. Figure 6 shows the momentum-transformed dispersion of the peak-fit positions within the first 2 eV. The dispersion observed resembles that of narrow metallic surface bands due to the average over relatively ordered islands and grains, as seen in Figures 1 and 2. This behavior has been previously observed for surfaces with

similar physical structure [14,30,31]. We expect these ARPES spectra to be consistent given the reproducibility of the various surfaces studied here.

Figure 6. Positions of peak-fits from ARPES spectra near the Fermi level of the multilayer $n = 3$ ML. This is approximately an average over the band structure of the islands on the surface.

4. Conclusion

To conclude, we have provided evidence showing one can control the photoemissive properties of photoemitters by engineering their physical and hence, electronic structure. It was shown that simultaneous and gradual decreases in WF and increases in QE are dependent on the thickness of MgO/Ag(001)/MgO multilayers. Using UV-ARPES we have shown that the angular profile of emission of the $n = 3$ ML multilayered exhibits a metallic-like dispersion. Demonstration of the ability to tailor emission properties via the precision deposition of thin crystalline layers is an encouraging result that supports efforts to fabricate *designer* photocathodes for increased performance in photoinjector applications.

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6. References

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