

SYNTHESIS OF ULTRA-THIN SINGLE CRYSTAL MgO/Ag/MgO MULTILAYER FOR CONTROLLED PHOTOCATHODE EMISSIVE PROPERTIES

Daniel Velázquez, Rachel Seibert, Zikri Yusof, Jeff Terry, Linda Spentzouris
IIT Physics Department, Chicago, IL, 60616, USA

Abstract

Photocathode emission properties are critical for electron beam applications such as photoinjectors for free electron lasers (FEL) and energy recovery Linacs (ERL). We investigate whether emission properties of photocathodes can be manipulated through the engineering of the surface electronic structure. The multilayers described here have been predicted to have emission properties in correlation with the film thickness. This paper describes how ultra-thin multilayered MgO/Ag/MgO films in the crystallographic orientations (001) and (111) multilayers were synthesized and characterized. Preliminary results of work function measurements are provided.

Films were grown by pulsed laser deposition at 130 °C for the (001) orientation and 210 °C for the (111) orientation at a background pressure of $\sim 5 \times 10^{-9}$ Torr. Epitaxial growth was monitored in-situ using reflection high-energy electron diffraction, which showed single crystal island growth for each stage of the multilayer formation. Photoelectron spectroscopy was used to track the chemical state transition from Ag to MgO during the deposition of successive layers. The Kelvin probe technique was used to measure the change in contact potential difference, and thus work function, for various MgO layer thicknesses in comparison with bare single crystal Ag(001) and Ag(111) thin films. The work function was observed to reduce with increasing thickness of MgO from 0 to 4 monolayers as much as 0.89 eV and 0.72 eV for the (001) and (111) orientations, respectively. Photoelectron spectra near the Fermi level revealed electron density shifts toward zero binding energy for the multilayered surfaces with respect to the clean Ag surfaces.

INTRODUCTION

Much of the development of photocathode materials has been aimed to the growth of photoemissive thin films with low work function (WF), and high quantum efficiency (QE) [1]. It has been shown, in some cases, that metal-insulator junctions can lead to the modification of the WF for coverages of a few monolayers of metal oxides on metallic substrates, both theoretically and experimentally [2-5]. Reduction of WF and increase of QE can be achieved simultaneously by coating metal surfaces with Cs or CsBr [6,7]. Cs ion implantation on Cu, Ag and Au has also been shown to also reduce the WF and increase QE while still retaining the robustness of a metal, nonetheless, sacrificing the

crystalline quality of the substrate [8]. However, the production of electron beams suitable for new photoinjector technologies in many instances requires low emittance beams from the cathode itself [2]. Therefore, the cathode intrinsic emittance plays an increasingly important role in new electron beam source designs [1].

A theoretical model by Nemeth et al. [2] describes the density functional theory (DFT) simulation of a multilayered structure MgO/Ag(001)/MgO in the configuration of 4 monolayers of Ag(001) flanked by n monolayers (ML) of MgO, where n is a small integer. This model indicates that it is possible to reduce the emittance of a photoemitted electron beam as the surface band structure exhibits a narrowing the density of states near the Γ -point neighboring the Fermi level when the thickness n of the MgO layers is 2 or 3 monolayers. In addition, this and other similar model [3] predict a work function drop of 1 eV to 1.5 eV from that of a bare Ag(001) surface. Measurements using atomic and Kelvin probe force microscopies (AFM and KPFM) show that even the deposition of MgO on a Ag(001) single crystal substrate produces a work function drop of 1.1 eV (1 ML) and 1.4 eV (2 ML) from the work function of the silver substrate, for 1 and 2 monolayers respectively [4,5].

More recently, an effort to quantify the effect on the emittance of 4 monolayers of MgO deposited on a Ag(001) substrate was carried out by Droubay et al. [9] who used Angle Resolved Photoelectron Spectroscopy (ARPES) to show that there was an enhancement of the photoemission intensity at the Γ -point near the Fermi level for the MgO coated Ag(001) in comparison with the uncoated Ag(001) substrate. Nonetheless, the ARPES spectrum for the MgO coated surface also exhibited the presence of sharp side bands near the Brillouin Zone boundaries which had the effect of increasing the total intrinsic emittance to 0.97 $\mu\text{m}/\text{mm}$ from 0.47 $\mu\text{m}/\text{mm}$ for the bare Ag(001) surface.

In this paper we present test results of multilayered MgO/Ag/MgO films as photoemitters. These multilayers were synthesized by Pulsed Laser Deposition (PLD) and characterized by Reflection High-Energy Electron Diffraction (RHEED) and Photoelectron Spectroscopy (PES) to show the formation of the crystalline and chemical structure of the multilayered films. It was found that there was a gradual decrease of the relative work function for MgO coated Ag surfaces in the (001) and (111) crystallographic orientations with respect to that of uncoated surfaces as the thickness of the flanking layers increased.

EXPERIMENTAL DETAILS

Films were prepared by PLD using a custom-built UHV system. Upon deposition, the films were extracted from the PLD chamber to perform ex-situ XPS and work function measurements in separate experimental chambers. The XPS system uses a Al-K α source and a cylindrical mirror analyser for angle integrated photocurrent detection. The approximate resolution of the XPS system including the source, detector and electronics is roughly 0.9 eV. The description of the Kelvin Probe technique and the system used for work function measurements have been previously described [10].

RESULTS AND DISCUSSION

Deposition: Characterization of Crystalline and Chemical Structure

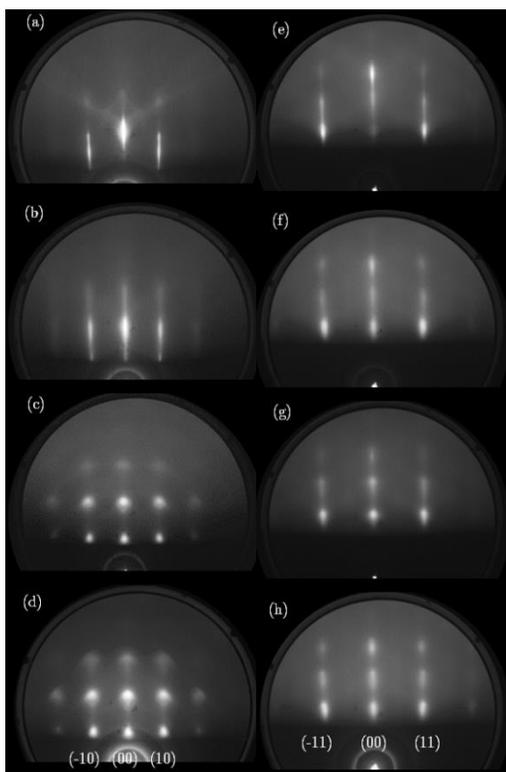


Figure 1: RHEED patterns depicting the progression of multilayer formation: (a) Ag/MgO(001), (b) MgO/Ag/MgO(001), (c) Ag/MgO/Ag/MgO(001), (d) MgO/Ag/MgO/Ag/MgO(001), (e) Ag/Si(111), (f) MgO/Ag/Si(111), (g) Ag/MgO/Ag/Si(111), (h) MgO/Ag/MgO/Ag/Si(111). For each orientation the initial Ag film is ~ 40 nm thick and each successive layer is 3, 4, 3 monolayers thick in the sequence MgO, Ag, MgO.

For deposition of multilayered films, 40 nm single crystal Ag(001)/MgO(001) and Ag(111)/Si(111) films were used in place of single crystal substrates. Sequential deposition of MgO, Ag, MgO followed. Growth of all films was performed at fixed temperatures of 130 °C and

210 °C for (001) and (111) orientations, respectively, at pressures of $\sim 5 \times 10^{-9}$ Torr. The film thickness was calibrated in every instance prior to deposition using a quartz crystal microbalance [11]. Multilayers consisted of a 4 monolayer Ag interlayer flanked by a discrete number, $n = 2, 3, 4$, of MgO monolayers (ML). Figure 1 shows examples of RHEED patterns during the progression of multilayer deposition in the crystallographic orientations (a-d) (001) and (e-h) (111). In both cases the thickness of the MgO flanks was $n = 3$ ML. As observed in the RHEED patterns, taken along the [100] azimuth, the roughness of the films increases as deposition progresses. This is evidenced by the appearance of horizontally collinear features which are indicative of transmission diffraction, thus it is clear that the films, in both orientations, grew in the form of highly ordered epitaxial islands of different heights. This is further supported by the absence of polycrystalline features (rings and/or curved rods) [12].

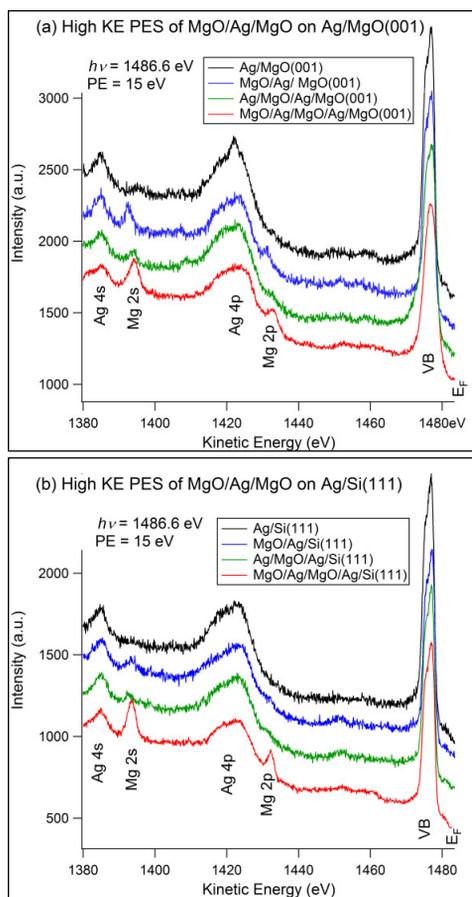


Figure 2: PES spectra showing the stages of deposition of MgO/Ag/MgO on (a) Ag/MgO(001), and (b) Ag/Si(111). The formation of the multilayer is evidenced by the increase (decrease) of intensity of the Mg (Ag) peaks.

Ex-situ PES was used to characterize the chemical structure of the multilayered films. Figure 2 shows high kinetic energy PES spectra of the evolution of deposition starting from the bare Ag single crystal surface through

the sequence MgO ($n = 3$ ML), Ag, MgO ($n = 3$ ML) for both orientations, (001) and (111). The stages of deposition can be more easily observed in the modulation of the Mg 2s and 2p peaks as their intensities increase and decrease as expected. A small shift of 0.4-0.6 eV toward higher kinetic (lower binding energy) can be 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 originating from Ag-O bonds. Similar observations were made for multilayers characterized by $n = 2$ ML and $n = 4$ ML.

Work Function Measurements

Work function measurements of (001) and (111) oriented multilayers for $n = 2, 3, 4$ ML of MgO were made for sets of films in each orientation using the Kelvin Probe technique. The measurements were referenced to the contact potential difference between the probing tip and 40 nm single crystal Ag(001) and Ag(111) films for the corresponding orientations. Figure 3 shows the work function change of the multilayer structures with respect to the uncoated Ag surfaces. For both orientations, to some degree, a monotonic decrease in the work function of the multilayered films was observed that correlated with the number of deposited MgO monolayers.

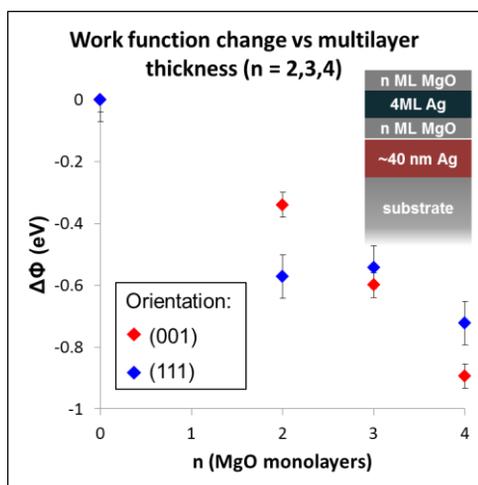


Figure 3: Relative work function measurements of multilayers $n = 2, 3, 4$ for the orientations (a) (001) and (b) (111). The monotone decrease in the work function is likely due to the partial surface coverage of the Ag surfaces by different multilayer thicknesses.

Theoretical predictions for the (001) orientation indicated an initial sharp drop in work function of close to 1 eV for the multilayer system with $n = 1$ ML of MgO, which remains at a similar value for up to 4 MgO monolayers [2]. Our measurements show a rather linear decrease with work function changes of -0.34 eV, -0.60 eV and -0.89 eV (± 0.07 eV) for $n = 2, 3$ and 4, respectively. As suggested by the RHEED patterns (Figure 1), the multilayers consist of islands of varying height and perhaps, finish (Ag, MgO). This variation of

the surface coverage results in a monotonic work function drop which is likely due to the averaging of the contact potential difference (CPD) measurement [13,14] under the macroscopic 2 mm diameter tip. The work function for the (111) orientation decreased in a similar manner to the (001) orientation with changes of -0.57 eV, -0.54 eV and -0.72 (± 0.09) for multilayers with $n = 2, 3$ and 4 monolayers, respectively. No theoretical prediction was found in the literature for this system, although, DFT simulations of polar MgO/Ag(111) surfaces [15] show an increase in the local density of states near the Fermi level in comparison with an uncoated Ag(111) surface. This is similar to the theoretical model for the (001) orientation [2].

CONCLUSION

We have presented initial studies of the formation of multi-layered MgO/Ag/MgO ultra-thin films in the (001) and (111) orientations. These preliminary studies revealed a correlation between the multilayer thickness and the reduction in work function with respect to uncoated Ag surfaces in the (001) and (111) orientations. These studies are the preamble to upcoming studies aimed at the demonstration of the systematic control of work function, quantum efficiency and angular emission through the engineering of the photocathode surface.

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