

METAL PLASMONIC NANOSTRUCTURES FUNCTIONALIZED BY ATOMIC LAYER DEPOSITION OF MgO FOR PHOTOCATHODE APPLICATIONS

S.V. Baryshev, S. Antipov, A.D. Kanareykin, Euclid Techlabs LLC, Solon, OH 44139
M.R. Savina, A.V. Zinovev, Argonne National Laboratory, Argonne, IL 60439
E. Thimsen, University of Minnesota, Minneapolis, MN 55455

Abstract

To create high current, long lasting electron sources capable of providing sub-ps bunches, new photocathode concepts are sought. Most recently, plasmonic nanostructured metal surfaces or flat metal surfaces activated by an ultrathin MgO are under great attention. We report on a photocathode design combining these two approaches. It consists of plasmonic Ag nanoparticles (NPs) functionalized by 3 MgO monolayers (MLs). Ag NPs were synthesized by an aerosol method and MgO was grown by atomic layer deposition (ALD). The NPs geometry was tuned to obtain broadband >50% absorption in the entire blue range as evidenced by UV-vis. spectroscopy. The work function (WF) of 3 MgO MLs/Ag NPs multilayer was reduced by 1 eV compared to bare NPs, from 5 to 4 eV, as evidenced by UPS and Kelvin probe. Reduction by 1 eV is maximal for this pair of materials, and agrees well with experimental and theoretical findings. While the effect on WF is indeed significant, a special handling protocol for Ag before depositing MgO is a must. It would preserve a clean Ag surface with a WF of nearly 4 eV to achieve 3 eV upon ALD of MgO. This and other issues are under study to promote photocathode applications.

INTRODUCTION

New developments in photocathode technology can significantly improve the beam quality in photoinjectors used at accelerator R&D facilities, current and future light sources. There are four key performance requirements for any photocathode: (1) quantum efficiency (QE), i.e. the fraction of electrons emitted from the surface per incident photon; (2) thermal emittance ($\Delta x \times \Delta p_x$) of the photoelectrons, i.e. angle divergence of generated electron beam/pulse from a specific spot area; (3) response time (τ), and eventually (4) lifetime of the photocathode and its robustness with respect to vacuum quality. The next generation of electron photoinjectors requires high quantum efficiency with controlled emittance and a fast response time. It would be beneficial to have new cathodes operating in visible light as oppose to UV. Many applications require an average current $>1\text{kA}/\text{cm}^2$.

Semiconductor cathodes yield high quantum efficiency but are not prompt with response time more than 1 ps. Besides that, semiconductor cathodes are not very robust: they require 10^{-10} Torr vacuum and their performance degrades due to poisoning in a month time [1]. At this moment, there are no materials that can meet all four high performance requirements. There is a definite need for novel concepts to synthesize materials for the next

generation photocathodes. The creation of a principally new, robust (vacuum vs. life time), high efficiency, tunable wavelength, ultrafast photocathode would preserve major achievements and address current challenges.

We propose to fabricate an ultrathin photocathode comprised of metal plasmonic particles which surface is functionalized by a few atomic monolayers of MgO or BaO. Plasmonic particles can be engineered to provide high absorption in a target spectrum range, for example in visible. Simultaneously, polar MgO and BaO lower the work function hence increasing QE. In present paper, we report on a scalable synthetic route to the multilayered structure MgO on Ag nanoparticles and results on its optical properties and work function.

CONCEPTUAL DESIGN

The proposed cathode design consists of plasmonic nanostructures comprised of noble metal (Ag or Au) particles functionalized by a highly polar, ultrathin (<2 nm) layers of alkaline earth metal oxides BaO or MgO – see Fig. 1.

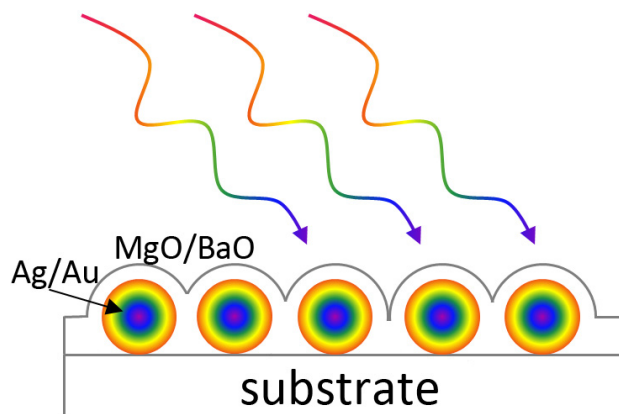


Figure 1: Nanoparticle antennas on a substrate covered with an ultrathin polar metal-oxide layer.

The localized surface plasmon resonances (LSPR) of noble metal nanostructures is used to tune the absorption maximum to enable emission via excitation at different wavelengths spanning the visible region of the spectrum (3.0 eV to 1.8 eV). Maximization of light absorption increases the quantum efficiency of the cathode. Tuning can be done varying the composition, size, shape and local dielectric environment [2].

Content from this work may be used under the terms of the CC BY 3.0 licence (© 2014). Any distribution of this work must maintain attribution to the author(s), title of the work, publisher, and DOI.

However, the native work functions of Au and Ag require relatively large photon energies in the UV for electron emission, 5.2 eV and 4.5 eV respectively. The energy of excited plasmon can be efficiently transferred to a single electron, but this energetic electron would have insufficient energy to overcome the work function at the native metal surface to be emitted into the vacuum. Hence, the challenge is to lower the work function with a robust coating. Natural considerations suggest that metal-oxide coatings need to be employed to establish a dipole electric field at the surface to promote emission in the visible (<3 eV). For the coating to act as a dipole, it must be ultrathin ($d < 2$ nm) and conformal on the noble metal nanostructure. MgO or BaO are to reduce the work function of Au or Ag particles by, at least, 1 eV. Oxides of group 2A metals (Mg and Ba) are expected to be much more stable than group 1A metal-oxides (Cs-O).

Since the structure is metallic and the emission of a photo-excited electron from a metal is a surface phenomenon, the response time is expected to be ultrafast, in the <100 fs regime.

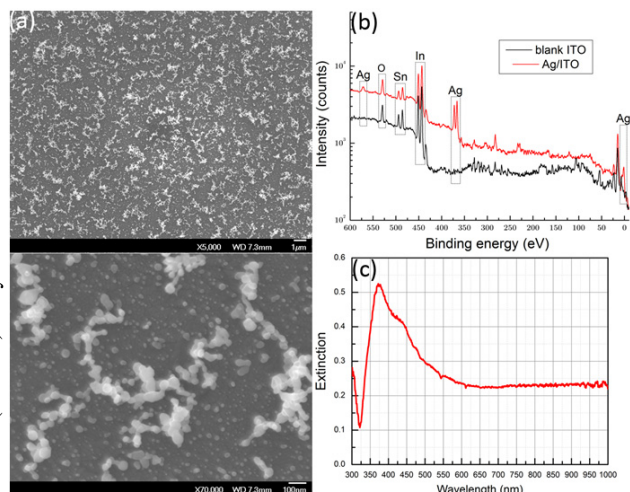


Figure 2: Plan-view SEM images of Ag nanoparticles supported on ITO; (b) XPS spectrum of Ag nanoparticles deposited on an ITO substrate by the aerosol method and the background spectrum from a blank ITO substrate; (c) Typical optical response of the synthesized Ag nanoparticles.

SAMPLES AND METHODES

Silver plasmonic nanoparticles were synthesized and deposited in a single step process by a custom built hot-wire aerosol reactor, in a system similar to one described in Refs. [2]. This is a dry process that produces nanoparticles with very clean surfaces, critical for electron emission. At the same time, it provides arbitrary oriented particles (polycrystalline matrix) as opposed to epitaxial growth that has been typically utilized for synthesis of similar multilayer systems to achieve significant reduction in the work function [3, 4]. Metallic silver feedstock was heated in a hot wire source to a

temperature where a small amount of vapor was generated above the source. This vapor was entrained in an inert gas flow at room temperature and a pressure of approximately 1 bar. Away from the hot wire, the metal vapor rapidly cools resulting in nanoparticle nucleation and formation. A temperature gradient exists between the hot wire and the water-cooled substrate that produces a thermophoretic force directing the particles to deposit on the substrate. The resulting aerosol was passed over a cooled Sn:In₂O₃ coated glass (ITO) substrate and the particles deposited by thermophoresis. The resulting deposit contained some large aggregates and many small nanoparticles. Sample scanning electron microscope (SEM) plan view images are provided in Fig. 2a. Chemical purity of the silver was confirmed by the X-ray photoelectron spectroscopy (XPS) in a custom instrument [5]. The XPS spectrum of Ag nanoparticles deposited on ITO versus a spectrum of bare ITO is illustrated in Fig. 2b. The existence of a surface plasmon resonance was confirmed by UV-vis. extinction spectroscopy, which measures absorption versus wavelength across the spectrum (ultraviolet to infrared). A typical UV-vis. extinction spectrum of the as-deposited samples is presented in Fig. 2c. It is seen that the final Ag nanoparticle matrix has a strong (>50%) broadband (with FWHM 350 to 500 nm) absorption. A clear plasmon peak was observed at 373 nm, which was consistent with the expectation for the population of isolated smaller silver nanoparticles; the broadband offset is attributed to the larger aggregates.

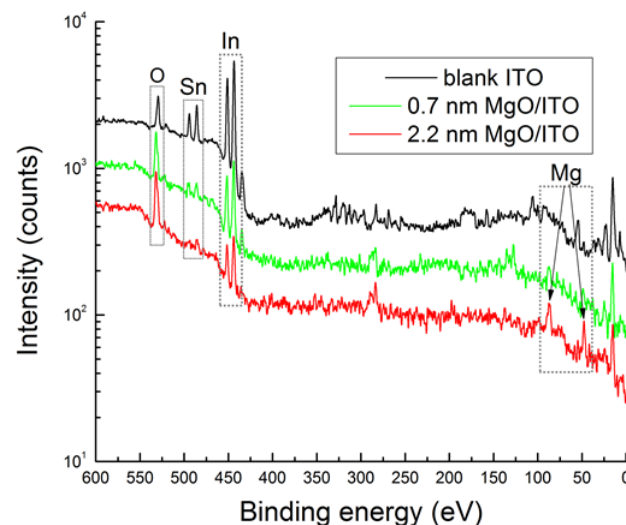


Figure 3: XPS spectra of MgO deposited on ITO substrate by ALD.

ALD of MgO was accomplished in a commercial ALD reactor Savannah S200, Ultratech. Control over the thickness was achieved through *in situ* quartz microbalancing. This was done in conjunction with *ex situ* ellipsometry measurements of ultrathin layers thickness on witness coupons.

Chemical composition and crude thickness estimation was cross validated by XPS. In Fig. 3, three XPS spectra are illustrated. Black is from a bare ITO substrate, and green and red spectra are from 0.7 and 2.2 nm MgO films on the ITO substrate, respectively. It is clearly seen that signals from major constituents of the ITO, Sn and In, attenuate as the MgO thickness gradually increases. The effect is especially strong for Sn, which is a 3% impurity in the In_2O_3 host matrix. For 0.7 nm MgO, the Sn signal almost disappears. For a 2.2 nm film, photoelectrons originating from ITO are almost halted at the simultaneous onset of characteristic 2s and 2p Mg peaks for a 2.2 nm film. Considering the relatively low XPS sensitivity to Mg and the mean escape length of photoelectrons in XPS is 2-3 nm, the red spectrum (lowest in Fig. 3) suggests that MgO was synthesized, and confirms the thickness calibration.

WORK FUNCTION MEASUREMENT

To investigate the effect of ultrathin MgO on Ag work function MgO/Ag samples were analyzed by ultraviolet photoelectron spectroscopy (UPS) by the same XPS instrument which makes use of UV source instead X-rays, and by a Kelvin probe by a commercial instrument KP6500 from McAllister Technical Service.

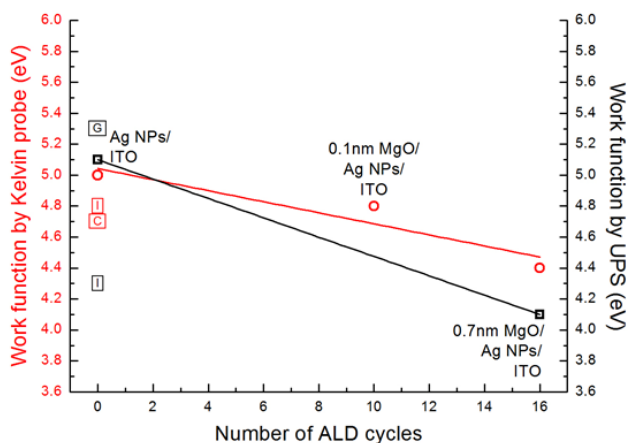


Figure 4: Work function data as measured by Kelvin probe (in red, left scale) and UPS (in black, right scale); star symbols are bare ITO WF reference data from the Kelvin probe and UPS. Framed symbols I, G, C correspond to ITO, gold, and copper respectively.

Kelvin probe is a noncontact method to measure WF using a small tip made of a chemically stable material with a precisely known WF. The WF of the sample of interest is determined versus WF of the tip using equation for contact potential difference, $\text{CPD} = (\text{WF}_{\text{tip}} - \text{WF}_{\text{sample}})/e$.

UPS relies on recording the kinetic energy distribution of secondary photoelectrons generated by primary UV light. The WF from UPS is calculated as follows: $\text{WF} = h\nu - \Delta\text{KE}$; where $h\nu$ is the energy of the incident light [in eV]; ΔKE is the kinetic energy window [in eV], a measure of the kinetic energy range within which photoelectrons are emitted. In this context, the WF is a measure of the energy loss by a photoelectron as it overcomes the surface potential barrier. The deduced WFs are plotted in Fig. 4 (for black symbols and line, refer to the right scale). As seen we achieved the drop in the work function of 1 eV. Overall, the Kelvin probe measurements confirmed the UPS findings while suggesting a more moderate effect in terms of lowering the WF. Such a difference is expected, because it is known that the Kelvin probe is less sensitive to changes in the chemical state of surfaces.

CONCLUSION

A scalable approach to synthesize high QE photocathodes with low WF via aerosol deposition and atomic layer deposition was proposed. It is demonstrated that polar 2A metal-oxide ultrathin films activate the surface of a metallic nanostructures by reducing its work function by approximately 1 eV.

REFERENCES

- [1] D. H. Dowell *et al.*, Nucl. Instrum. Methods Phys. Res. A **622**, 685 (2010).
- [2] E. Thimsen, Chem. Mater. **23**, 4612 (2011).
- [3] T. König *et al.*, J. Phys. Chem. C **113**, 11301 (2009).
- [4] T. C. Droubay *et al.*, Phys. Rev Lett. **112**, 067601 (2014).
- [5] A. V. Zinovev *et al.*, Surf. Sci. **600**, 2242 (2006).