Quantum efficiency enhancement in CsI/metal photocathodes

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Abstract:

High quantum efficiency enhancement is found for hybrid metal-insulator photocathodes consisting of thin films of CsI deposited on Cu(100), Ag(100), Au(111) and Au films irradiated by 266 nm laser pulses. Low work functions (near or below 2 eV) are observed following ultraviolet laser activation. Work functions are reduced by roughly 3 eV from that of clean metal surfaces. We discuss various mechanisms of quantum efficiency enhancement for alkali halide/metal photocathode systems and conclude that the large change in work function, due to Cs accumulation of Cs metal at the metal-alkali halide interface, is the dominant mechanism for quantum efficiency enhancement.

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1. Introduction

In order to meet requirements for next-generation free electron laser (FEL) and synchrotron-based light sources, and to enable dynamic transmission electron microscopy

(DTEM) [1, 2], robust new photocathode materials are needed. Current photocathode materials with high quantum efficiency (QE), such as Cs:GaAs cathodes, are highly sensitive to low concentrations of background gases, and thus require extreme vacuum conditions $\sim 10^{-11}$ Torr for long-term operation [1]. Even under extreme vacuum conditions, the lifetime of currently used photocathodes is limited.

Metal photocathodes have excellent tolerance to common background gases, are robust toward pulsed laser excitation and display long operational lifetimes. However, bare metal photocathodes have relatively high work functions (>4 eV) and low QE, typically on the order of 10^{-5} to 10^{-4} [1,3], which results in the requirement of a UV drive laser with high average power and hence limited application. In order to overcome limitations of metal photocathodes, several approaches have been explored. These include incorporation of nanostructured features, such as gratings and nanohole arrays, to couple light efficiently into the metal and induce surface-plasmon enhanced electric fields [4,5], utilizing ultrathin oxide layers to reduce work function [2], and deposition of alkali halide films to increase QE [6-10]. Alkali halide thin film deposition has been proven to be one of the most effective ways to lower work function and increase QE of metal photocathodes.

Quantum efficiencies of metal single crystals (for example, Cu, Cr and Mo) can be greatly enhanced by the deposition of alkali halide films, such as CsBr [6-8], followed by UV irradiation. Three mechanisms have been proposed for the observed QE enhancement in CsBr covered metals: (i) a decrease in work function of the hybrid-metal alkali halide system compared to the bare metal. Work function is reduced by deposition of the alkali

halide film itself and is further reduced following laser irradiation. (ii) direct photoemission from the intraband states (F centers) created during laser irradiation might contribute to part of the QE enhancement. (iii) formation of a thin Cs layer at the metal-alkali halide interface or at the hybrid photocathode surface. Thin Cs layers are commonly used to enhance photoemission from a variety of photocathode materials.

Recently, much higher QE enhancement and significantly greater work function reduction has been found for a CsI thin film, compared to a CsBr film, on Cu single crystal substrates [9]. Direct photoemission from the Cu *3d* band, for the CsI thin film, and electrons emitted from the intraband states were considered as possible contributions although several key mechanistic questions remain. In order to determine the dominant QE enhancement mechanisms, we explore the deposition of CsI thin film on noble metal substrates (Cu(100), Ag(100), Au(111) and a Au film on Si). We find that the major mechanism for QE enhancement is a dramatic work function reduction, due to accumulation of Cs metal at the metal/CsI interface. For Cu and Au substrates, much of the d-band electron density is available for photoemission, using 4.66 eV photoexcitation, as work functions are reduced to near 2 eV. We find that F centers (intraband states) do not contribute significantly to photoemission enhancement of CsI/metal photocathode systems.

2. Experimental details

All single crystal metal substrates were repeatedly Ar ion sputtered and annealed (560 °C for Cu, 200 °C for Ag and Au) in ultrahigh vacuum until X-ray photoelectron spectroscopy data displayed only substrate core-levels. Gold films of 100 nm thickness

were deposited on clean Si substrates by argon plasma sputtering. CsI thin films were then grown on the clean substrates by heating 99.999% pure CsI powder in an effusion cell to 410°C in a separate growth chamber. A quartz crystal microbalance positioned near the growth location was used to calibrate the film growth rate. No reaction of CsI with any of the metal substrates is observed. The coated sample was then irradiated by an unfocused 266 nm pulsed laser (pulse width ~ 400 picoseconds, repetition rate of 20 kHz, beam diameter of 1.5 mm) for several hours, to induce laser activation. Laser activation (LA) required between 5 and 10 hours in vacuum, at a laser power of 12 mW, depending upon metal substrate type for nominal 8 nm thick films. Base pressure increased only slightly to 2×10^{-9} Torr during LA.

Relative photoelectron yields and kinetic-energy distributions were obtained using a photoelectron spectrometer with hemispherical analyzer (Kratos Axis HS) and the same 266 nm laser as used in the activation process but with a greatly reduced average power (20 μ W). Work functions were determined from the photoemission spectra by subtracting the width of the energy-resolved photoemission peak, at the base, from the photon energy (4.66 eV) and correcting for the instrument resolution. X-ray photoelectron spectroscopy (Al K α x-rays) was used to confirm film thicknesses and characterize iodine and cesium concentrations during the laser activation process. The QE of laser activated CsI/Cu was determined by measuring the photoelectron current using an electrometer. Quantum efficiency of laser activated CsI thin films on Cu was determined, as a function of CsI film thickness (ranging between 6 and 40 nm).

3. Results and discussion

Figure 1 displays the QE for 8 nm CsI films on four different substrates: Cu (100), Ag(100), Au(111) and a Au film on Si as a function of laser activation time. Significant QE enhancement is induced by LA for CsI on all the four different substrates. QE after LA varies on the different substrates, especially for CsI on Cu(100), which results in the highest photoelectron yield. QE after LA for CsI on the other three substrates are nearly the same. No significant difference was observed between single crystal Au(111) and the polycrystalline gold metal film substrate (Au film on Si). The time needed for full LA varied with each metal substrate requiring approximately 3 hours for CsI on Ag(100), 7 hours for CsI on Cu and 10 hours for CsI on Au.

Figure 2 shows the photoemission kinetic energy spectra for bare metal substrates and laser activated CsI on the four different substrates as a function of LA time. These photoemission spectra regardless of substrate show similar features. Each spectrum broadens significantly as LA proceeds, for all four CsI/metal systems, which indicates a reduction in the work function resulting from LA. In addition, for all substrates, a dominant low kinetic energy feature develops as LA proceeds. This feature dominates the kinetic energy spectra and photoelectron yield in fully laser activated CsI/metal systems.

Table I displays initial and final work functions and quantum efficiencies for CsI on Cu(100), Ag(100), Au(111) and a Au film on Si. A significant work function reduction and QE enhancement was observed for CsI deposited on all the substrates. CsI on Cu(100) results in the lowest final work function (~ 1.7 eV) and highest final QE (7.5×10^{-3}). Slightly greater work functions of 1.9, 2.0 and 2.1 eV are observed for

CsI/Au film/Si, CsI/Au(111), and CsI/Ag(100) with QEs of 3.1×10^{-3} , 2.7×10^{-3} and 2.8×10^{-3} , respectively.

The results of hybrid CsI/metal photocathodes strongly contrast those of CsBr/metal [6-9] as CsI/metal photocathodes have significantly higher quantum efficiencies following laser activation. Figure 3 presents the energy diagram of the CsI/Cu system. As a result of the large work function reduction induced by LA, electrons located in the Cu *d*-band can be directly emitted following excitation by 4.66 eV photons. Direct photoemission from the electron dense *d*-band greatly enhances the photoemission QE at 4.66 eV for laser activated CsI/Cu. However, for CsBr/metal systems the work function is not reduced sufficiently, even after prolonged laser activation, to enable direct electron emission from the Cu *d*-band.

Table II displays work function reduction, relative photoelectron yield and laser activation (LA) time for CsI on Au(111) with different film thicknesses (6, 10, 20 and 40 nm). The term relative photoelectron yield refers to the photoelectron yield after LA with respect to that of a 6 nm CsI film on Au(111). Photoelectron yield decreases monotonically with film thickness, and drops 90% as film thickness varies from 6 to 40 nm, whereas final work function values after LA increase from 1.85eV to 2.2eV. The LA time needed to achieve full activation increases with film thickness.

Figure 4 displays a time sequence of the photoelectron spectra for 8 nm CsI on four different substrates: Cu(100), Ag(100), Au(111) and the polycrystalline Au film on Si. Photoelectron spectra both before and after laser activation are displayed. In addition, spectra obtained 10 hours after laser activation is completed, and then “reactivated” for

one (CsI/Ag) or three hours (CsI/Cu(100), CsI/Au(111) and CsI/Au film) is presented in Figure 4. The data show a clear decrease in photoelectron yield 10 hours after laser irradiation is completed. This indicates that the conditions necessary for large quantum yield enhancement are transient at room temperature, over the course of hours, even under ultrahigh vacuum conditions. In all cases, the enhanced QE could be nearly fully recovered by additional laser activation.

We note that the relative loss of QE enhancement, over 10 hours following the conclusion of laser activation, is substrate dependent. The greatest loss is observed for CsI/Cu(100) followed by CsI/Ag(100) and CsI/Au(111) and finally the CsI/Au thin film on Si. Furthermore, the rate of loss, immediately following conclusion of laser activation, is also substrate dependent, with faster loss rates observed for CsI/Ag(100) than for CsI/Au systems. It is clear that the differences in relative QE loss and rate of QE loss must be due to chemical and/or physical differences at the CsI/metal interface. These results would not vary between the four systems if Cs metal accumulated on the CsI surface.

We can draw several conclusions from analysis of the above data. The large reduction in work function is highly correlated with QE enhancement. If the work function of the hybrid CsI/metal photocathode is sufficiently large, following LA, electrons can be directly emitted from the substrate metal *d* band and easily escape the CsI overlayer into the vacuum (mean free path for a < 2 eV electron is roughly 20 nm in CsI). Photoemission from the electron dense d-band is likely an important contribution to the QE enhancement for CsI on Cu and Au as previously suggested [9]. When the work

function is decreased to near 2 eV, Cu $3d$ and Au $5d$ electrons can be directly emitted following excitation by 4.66 eV photons. This mechanism results in the appearance of the intense low kinetic energy features displayed in Figure 2, as both Cu $3d$ and Au $5d$ band are located ~ 2.0 eV below the Fermi level, E_F [14]. We note that if the metal d band is the only electron source for the large QE enhancement, then the QE enhancement behavior for CsI on Ag should be different because the Ag $4d$ band is located 4.0 eV, rather than 2.0 eV, below E_F , [14] implying that strong d -band emission from Ag is less likely. While photoemission from CsI/Ag(100) is significantly reduced from that of CsI/Cu(100), under similar conditions, it is nearly as intense as from CsI/Au systems in contrast to this prediction. Nonetheless we expect photoemission from CsI/Ag(100) to increase sharply with the large reduction in work function, that accompanies LA as is observed.

The large work function reduction for CsI on metal substrates, induced by LA, is most likely caused by Cs metal accumulation into an ultrathin layer [9]. Regarding Cs accumulation during LA, there are two hypotheses. Hypothesis 1: Cesium accumulates on the top of the CsI layer. If this is true and the CsI valence band contributes strongly, a thicker layer should have higher quantum yield. As noted previously, this is not observed (see Table II). Hypothesis 2: Cesium accumulates at the interface between the metal substrate and the cesium iodide. If this is true, then the thicker layer should reduce the quantum efficiency due to reduced electron transport through the thicker film. Hypothesis 2 is consistent with all data reported in Table II. Very low coverage of Cs on metal substrates (less than 0.5 monolayer) is known to reduce the metal work function to as low as 1.6 eV [15-17].

In total, the results, including work function decreases, thickness studies, relative loss of QE enhancement and the rate of QE loss at the conclusion of laser activation, argue strongly for a model where Cs metal accumulates at the interface between the metal and alkali halide film (Hypothesis 2). For example, the QE enhancement of laser activated CsI/Cu(100) decreases significantly over the course of several hours in vacuum. If Cs atoms do accumulate at the interface, then accumulated Cs atoms might migrate into the CsI film lattice or diffuse away from the irradiated area following laser activation. We note that the rate of QE loss and the time required for asymptotic laser activation (Figure 2) varies significantly with noble metal substrate. Moreover, the activation time varies with the substrate. CsI on Ag activates fastest, followed by CsI on Cu and CsI on Au. These observed differences likely result from Cs accumulation chemistry due to specific interactions between each metal substrate and the generated Cs layer. Furthermore, alkali metal atoms accumulated on the alkali halide surface (the interface between alkali halide and vacuum) are known to desorb readily at room temperature to maintain alkali halide stoichiometry under UV irradiation [18-20]. This fact, while not confirmed specifically for Cs metal on CsBr or CsI, strongly suggests that the alkali halide remains stoichiometric at the alkali halide/vacuum interface and that Cs metal accumulates at the metal/alkali halide interface.

Intraband states (e.g. F center defects) created by laser activation could possibly contribute to the QE enhancement in alkali halide/metal systems [6,8,10]. F center states are located at 3.37 eV and 1.9 eV below the bottom of conduction band of CsBr [10,11] and CsI [12,13] respectively (below the respective Fermi levels by roughly 1.0 and 1.3 eV). Since both F bands are located below the respective metal Fermi levels, we expect F

center states to be “full” for activated alkali halide/metal systems. In other words, anion vacancies, created by photoemission from F center states, should be refilled by electrons from the metal Fermi level. Thus, in principle, photoemission from F centers, could be efficient provided certain conditions are met. Namely, there must be a sufficient number of F center states created by laser activation, their optical cross section must be high, and electron refilling of the anion vacancy must be rapid.

It does not appear, from our experimental data, that these conditions are met. There are few F centers created in the thin film volume as the maximum density is very likely below 1% of total anion sites. A very low total number of F center states are therefore expected in the thinnest alkali halide films tested. While the thinnest CsI film studied in this work is 6 nm, we have investigated 3 nm films previously [9] and obtained similar results, i.e. very high QE enhancement. The 3 nm films support only 6 or 7 monolayers of CsI such that even fewer F centers likely exist per unit area. Although there should be more total F centers created in thicker films, the data in Table II show a decrease in photoelectron yield for thicker films, rather than the increase that would be predicted if F centers contributed significantly. The last argument also applies to any other intraband defect states (e.g. H, H aggregate, M, or I, centers) that could possibly contribute to the QE enhancement mechanism. Therefore, intraband states, created by LA, are not a significant source of electron photoemission at 4.66 eV from hybrid alkali halide/metal photocathodes.

4. Conclusions

Cesium metal very likely accumulates at the metal/alkali halide interface during laser activation of hybrid CsI/metal photocathodes. The large work function reduction due to Cs accumulation during laser activation is therefore the dominant factor for the very high QE enhancement in CsI/metal systems. Direct electron emission from the metal *d*-band, made possible by the large work function reduction, is likely responsible for the high QE enhancement of laser activated hybrid CsI/metal photocathodes. F center emission can only contribute very modestly to QE enhancement and, more generally, intraband states created during LA are not a significant source of photoemission.

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Figure 1. Quantum efficiency of 8 nm CsI covered Cu(100), Ag(100), Au(111) and Au film on Si as a function of laser activation (LA) time. The measurements were taken using a 266 nm pulsed laser source with average power of 20 μW and the activation utilized the same laser with average power of 12 mW . The maximum QE for each sample was determined by photoelectron current measurement and all curves were normalized according to the obtained maximum QE.

Figure 2. Photoelectron yield (in counts per second, CPS) for 8 nm CsI on Cu (100), Ag(100), Au(111) and Au film on Si with different laser activation (LA) times compared to bare substrates. The measurement was made using a 266 nm pulsed laser source with average power of 20 μW and the activation utilized the same laser with average power of 12 mW .

Figure 3. Energy diagrams of clean Cu metal, a thin film of CsI on Cu metal (CsI/Cu) and a laser activated thin film CsI on Cu metal (CsI/Cu+LA). E_F , E_V , and F denote the Fermi level, the vacuum level and the F center level in CsI. The photon energy (4.66 eV) is represented by the arrows and $h\nu$. The position and width of the Cu d -band is represented by the gold rectangle while the green and dashed purple rectangles indicate the CsI valence and conduction bands. The Fermi and d -band levels rise toward the vacuum level as the work function is reduced, first by addition of a thin film of CsI (middle panel) and then by laser activation of the (CsI/Cu) system (right panel). A 4.66 eV photon is capable of inducing photoemission from the Cu d -band for the laser activated (CsI/Cu) system.

Figure 4. Photoelectron yield (in counts per second, CPS) versus photoelectron kinetic energy for 8 nm CsI on Cu (100), Ag(100), Au(111) and Au film on Si. Black spectra: after laser activation; Red spectra: laser activation stopped for 10 hours in vacuum; Green spectra and Blue spectra: additional laser activation for 1 hour and 3 hours, respectively.

Table I. Work function reduction and quantum efficiency enhancement for 8 nm CsI on Cu(100), Ag(100), Au(111) and Au film on Si.

	Initial work function (eV)	Final work function (eV)	QE before LA ($\times 10^{-3}$)	QE after LA ($\times 10^{-3}$)*
CsI/Cu(100)	4.65	1.7	0.050	7.5
CsI/Ag(100)	4.26	2.1	0.16	2.8
CsI/Au(111)	5.1	2.0	0.079	2.7
CsI/Au film		1.9	0.10	3.1

* QE obtained by photoelectron current measurement

Table II. Work function reduction, relative photoelectron yield and laser activation (LA) time as a function of CsI film thickness on Au(111).

Thickness (nm)	Final work function (eV)	Relative Photoelectron yield*	LA Time (h)
6	1.85	1.0	11
10	1.85	0.95	14
20	2.0	0.35	18
40	2.2	0.1	24

* Relative photoelectron yield refers to photoelectron yield after LA compared to 6 nm CsI film covered Au(111)

Hybrid Photocathodes of CsI thin films on noble metals show high quantum efficiency

Quantum efficiencies of ~1% are observed for the CsI/Cu(100) system (6 nm film)

Hybrid photocathodes hold promise for light sources and dynamic electron microscopes