

# PREPARATION OF POLYCRYSTALLINE AND THIN FILM METAL PHOTOCATHODES FOR NORMAL CONDUCTING RF GUNS\*

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## Abstract

A comparison of quantum efficiency (QE) and work function (WF) measurements of polycrystalline and thin film metal photocathodes for use in normally conducting RF (NCRF) guns, similar to the S-band gun under development for the CLARA project at Daresbury, are reported. Cu and Nb thin films were grown on a Si substrate by magnetron sputtering and subsequently prepared by annealing and Ar ion sputtering. To determine the surface chemistry, X-ray photoelectron spectroscopy (XPS) was employed. QE measurements were enabled using a 265 nm UV LED. WF measurements were carried out using a Kelvin probe. Annealing the Cu thin film to 250°C yielded a QE of  $1.2 \cdot 10^{-4}$ ; one order of magnitude higher than the QE for sputter cleaned and post annealed polycrystalline Cu. The optimum QE measurement for Nb thin film was  $2.6 \cdot 10^{-4}$ , which was found to be comparable to the results obtained for cleaned bulk Nb. Analysis of XPS data of these metals suggest surface composition and surface chemistry are main contributing factors to the QE and WF.

## INTRODUCTION

Our interest in metal photocathodes stems from the installation of VELA (Versatile Electron Linear Accelerator) at Daresbury Laboratory (DL) [1]. As with many NCRF guns, VELA injector uses a metal photocathode for its fast response that allows for much shorter pulses, and it's relative insensitivity to the vacuum environment. VELA gun uses a Cu disk photocathode, integrated onto the back wall of the Cu cavity; this yields a QE of approximately  $10^{-5}$ . Now the interest has turned to investigating alternative metals to Cu, with potentially better photocathode performance. The metal photocathodes will be installed in NCRF guns such as VELA and also high repetition rate guns for future 4<sup>th</sup> generation light sources test facility such as the Compact Linear Accelerator for Research and Applications (CLARA) [2], a proposed Free Electron Laser test facility, which will require a fast response time cathode with a reasonable QE.

A range of polycrystalline metals have already been investigated and several metals have been identified as

yielding reasonable QE values (greater than  $10^{-5}$ ), namely Mg, Pb, Zr, Nb and Ti [3]. The next stage is to study the properties of these metals when deposited as thin films. The use of thin films could potentially evade problems of RF breakdown that commonly occur in adjoining metal disks to the Cu cavity [4].

This study will report a comparison of QE, work function and chemical composition of Cu and Nb thin films versus bulk metal cathodes.

## EXPERIMENTAL PROCEDURE

Magnetron sputtering has been used to deposit metal thin films on Si(100) substrates; this is a preliminary experiment, and so for operational photocathodes an appropriate substrate material will be chosen. The Si substrates were cleaned and degreased in ultrasonic bath of acetone, IPA, methanol and then finally washed in deionised water. Nb and Cu were sputtered onto the Si substrate; Kr sputter gas was used at 3 mbar and the magnetron was operated at a DC power of 600 W.

As was the procedure for the polycrystalline cathodes, the thin films were then carefully inserted into a sample holder and then cleaned in an ultrasonic bath of acetone for 10 minutes before analysis.

An ESCALAB Mk II XPS instrument has been adapted for the purpose of preparing and analysing the cathode samples. For this experiment, surface analysis techniques were used to obtain measurements of QE, WF and surface chemical composition. The following measurements were carried out in the analysis chamber of the ESCALAB Mk II at a pressure of approximately  $10^{-10}$  mbar.

A 265 nm LED with 12 nm bandwidth was used for excitation of the cathodes. The intensity of the LED was calibrated using a UV sensor. The resulting drain current from the cathode was measured using a pico-ammeter.

The KP Technology UHVKp100 equipment installed in ESCALAB Mk II is used to create a potential difference between the cathode and the tip of the Kelvin probe, and thus infer a work function with a resolution of less than 3 meV. X-Ray Photoemission Spectra were measured Al  $K\alpha$  illumination and the emitted electrons energy analysed with a hemispherical analyser. The XPS system has an energy resolution of approximately 1.1 eV and a spatial resolution of 100  $\mu\text{m}$ . This technique is used to qualitatively and quantitatively assess the cathode chemical composition.

\* The work is part of EuCARD-2, partly funded by the European Commission, GA 312453.  
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## RESULTS AND DISCUSSION

Table 1: Summary of XPS Measurements

Metal	XPS		Metal
	O1s	C1s	
<b>Cu Bulk</b>			
Received	40.4	59.0	0.6
Ar <sup>+</sup> Sputter	0	0	100.0
Anneal 250°C	6.1	0	93.9
<b>Cu Film</b>			
Received	23.5	67.8	8.7
Anneal 250°C	20.2	61.7	18.1
<b>Nb Bulk</b>			
Received	47.8	48.6	3.6
Ar <sup>+</sup> Sputter	16.2	21.0	62.8
<b>Nb Film</b>			
Received	63.1	25.3	11.6
Anneal 250°C	61.5	4.3	34.2
Anneal 300°C	55.8	15.9	28.2
Ar <sup>+</sup> Sputter	9.6	0	90.4

### Copper Photocathodes

XPS data shown in Table 1 summarises the degree of contamination on the cathode surfaces with C and O at various stages of this investigation. All samples as received have significant amounts of O and C on the surface. A closer look at the Cu region scan in Fig. 1 specifies the oxidation state. CuO is characterised by high intensity shake up satellites that occur at approximately 9 eV higher binding energies than the main Cu 2p peaks [5], which is evident for both Cu samples, but is less pronounced in the Cu thin film. It is to be expected that the cathodes will contain surface impurities as indicated by the XPS data, due to exposure to atmosphere prior to installation.

Bulk Cu was then sputtered with Ar<sup>+</sup> at 5 keV for 10 minutes and then post annealed to 250°C for 30 minutes. This treatment, as evidenced in Table 1, is a highly effective method of removing contaminants.

The Cu thin film was not sputtered with Ar<sup>+</sup> for fear of removing the film entirely, but was annealed to 250°C for 30 minutes. Although the quantities of O and C did decrease, annealing alone is not effective in significantly reducing contamination levels at the surface. A closer look at the Cu region spectra shows that the small CuO satellites present as received have diminished upon annealing. It is impossible to distinguish between Cu metal and Cu<sub>2</sub>O from Cu region scan, however, the significant levels of O 1s present would suggest that the oxidation state has changed from CuO to Cu<sub>2</sub>O.

The QE for both bulk and thin film Cu (see Table 2) as received was comparable. Upon sputtering and post annealing the QE increased by an order of magnitude for Cu bulk; this increase in QE can be attributed to the increase in purity of the cathode surface. For the thin film, the QE increases by two orders of magnitude, despite the persisting presence of O and C. The effect of annealing

the Cu thin film was to change the oxidation state this appears to be responsible for the difference in QE.

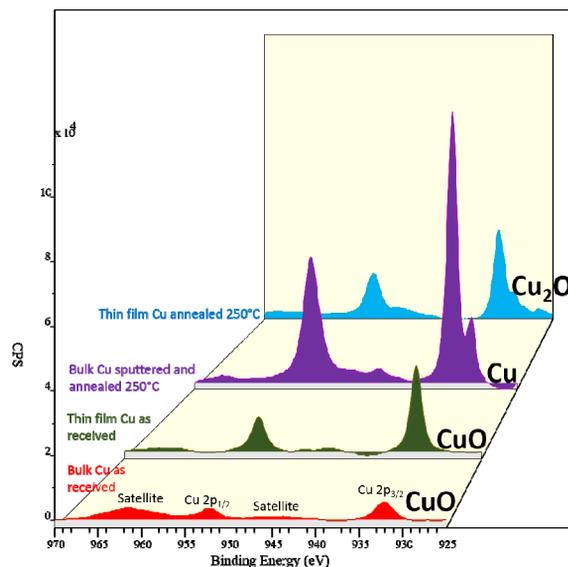


Figure 1: Cu 2p region scan for bulk and thin film as received, sputtered and annealed.

WF is a measure that is sensitive to surface contaminants, and so a variation is to be expected during sample cleaning. Typically, there is a charge double layer at the surface of a clean metal resulting from the truncation of the three dimensional bulk [7]. Any contamination on the surface will modify this double layer and hence the apparent WF; which in the case of O and C contaminants will be expected to increase. O and C contaminants will be expected to modify the double layer in such a way as to increase the

Table 2: Summary of QE and WF Measurements

Metal	QE (%)	Literature WF(eV)[6]	Measured WF (eV)
<b>Cu Bulk</b>			
Received	$5.0 \cdot 10^{-6}$	4.65	5.4
Ar <sup>+</sup> Sputter	$1.1 \cdot 10^{-5}$		5.3
Anneal 250°C	$1.7 \cdot 10^{-5}$		5.2
<b>Cu Film</b>		4.65	
Received	$1.5 \cdot 10^{-6}$		5.1
Anneal 250°C	$1.2 \cdot 10^{-4}$		4.7
<b>Nb Bulk</b>		4.3	
Received	$3.9 \cdot 10^{-7}$		5.3
Ar <sup>+</sup> Sputter	$1.9 \cdot 10^{-4}$		4.7
<b>Nb Film</b>		4.3	
Received	$7.8 \cdot 10^{-7}$		4.4
Anneal 250°C	$2.5 \cdot 10^{-5}$		4.9
Anneal 300°C	$5.7 \cdot 10^{-6}$		5.1
Ar <sup>+</sup> Sputter	$2.6 \cdot 10^{-4}$		4.8

WF. This effect has been observed for both thin film and bulk Cu cathodes; as the oxide and carbonaceous layers decreased, so too does the WF.

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## Niobium Photocathodes

As with the Cu samples, the Nb cathodes were highly oxidised as received. This is evidenced in the observed shift in the Nb 3d doublet in Fig. 2. For both samples, the 3d peaks are shifted by 5.5 eV to a higher binding energy indicative of Nb<sub>2</sub>O<sub>5</sub>.

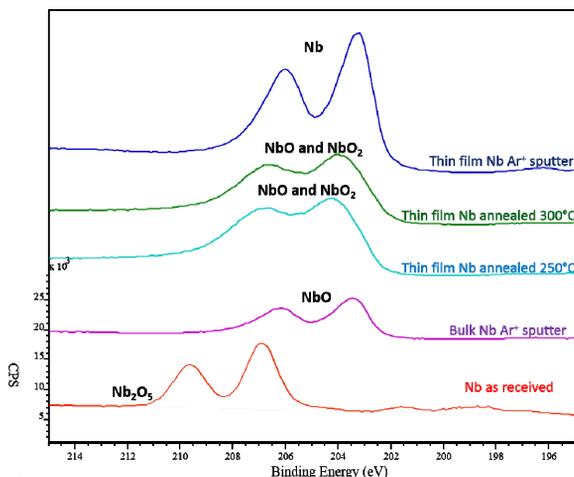


Figure 2: Nb 3d region scan for bulk and thin film as received, sputtered and annealed.

Bulk Nb was sputtered with Ar<sup>+</sup> for 10 minutes at 5 keV. The effect of this is to breakdown the Nb<sub>2</sub>O<sub>5</sub> layer, revealing NbO; this is evidenced in the shift in the Nb 3d peaks; 3d<sub>5/2</sub> from 207 eV (corresponding to Nb<sub>2</sub>O<sub>5</sub>) down to 203.4 eV. Sputtering Nb bulk has removed much of the O and C contamination from the surface, potentially leaving a mixture of Nb and NbO.

As with the Cu thin film, the Nb film was annealed. The effect was to reduce much of the carbon from the surface so that only traces remain. Quantitative data shows no change in the amount of O, but the region spectra reveals a change in the oxidation state (see Fig. 2). The resulting surface suggests the possibility of a compound of intermediate stoichiometries which we will call NbO<sub>x</sub>. If we take the Nb 3d<sub>5/2</sub> peak for example, it has shifted to a binding energy of 204.2 eV; this is in the middle of where one might expect to find NbO<sub>2</sub> and NbO which occur at 206.2 eV and 203.6 eV respectively. The effect of annealing is to decompose Nb<sub>2</sub>O<sub>5</sub> to NbO<sub>2</sub> and eventually NbO depending on the duration and temperature of annealing [8].

Additional annealing to 300°C decreased the amount of O further, but also led to an unexpected increase in carbon and a decrease in Nb signal. The thin film was eventually sputtered for several minutes at a lower energy of 3 keV to remove the oxide layer. The Nb 3d<sub>5/2</sub> peak is now shifted to 203.2 eV, showing that pure Nb now dominates the surface chemistry.

Both Nb thin film and bulk cathodes have comparably low QE values as received due to the high levels of surface contamination. After sputtering the Nb bulk sample, the QE increased by three orders of magnitude.

Annealing the thin film to 250°C produced NbO<sub>x</sub>, the effect of which was to increase the QE by two orders of magnitude. Sputtering the film removed further O leaving NbO on the surface, resulting in another increase in QE by one order of magnitude. Annealing to 300°C increased the carbonaceous layer presumably due to recontamination from the vacuum as a result of outgassing of heated components, the effect of which has been to lower the QE by one order of magnitude.

The WF of bulk Nb is 1 eV higher than the quoted literature value due to the oxide and carbonaceous layers observed in the XPS spectra. After removing some of these contaminants by sputtering, the WF decreases as expected. The changes to the WF for the thin film were not expected; the as received measurement was very close to the literature value, however, subsequent heating has increased rather than decrease the WF.

## CONCLUSION

The aim of the study was to conduct a preliminary set of experiments to compare QE and WF measurements of thin films versus polycrystalline bulk metals. Using data from XPS, the effect of surface composition and chemistry has been investigated. Though Ar<sup>+</sup> bombardment of Cu and Nb is an effective means of removing surface contamination, this is not always sufficient to yield higher QE values. Heating the samples changes oxidation states, which can increase QE by up to 2 orders of magnitude. Future work will involve further investigation of a range of metallic thin films.

## ACKNOWLEDGMENT

The work is part of EuCARD-2, partly funded by the European Commission, GA 312453.

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