

**Photoemission study of Cs-NF<sub>3</sub> activated GaAs(100) negative electron affinity  
photocathodes**

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GaAs based negative electron affinity photocathodes activated with Cs and NF<sub>3</sub> are used as polarized electron sources for linear accelerators. It is generally believed that the activation layer consists of CsF. The activation layers of Cs-NF<sub>3</sub> on GaAs photocathodes are herein investigated using synchrotron radiation photoelectron spectroscopy(SR-PES). F1s, N1s and other core levels are recorded at photon energies ranging from 70eV to 820eV. Surprisingly, a significant amount of nitrogen is observed in the activation layers. Two distinct species of nitrogen are observed, one of which decreases along with the Fluorine signal as the yield of the photocathode decays with time.

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Negative electron affinity (NEA) photocathodes [1] have several important applications including night vision, electron beam lithography, and polarized electron sources for linear accelerators [1-4]. Recently, there is renewed interest in finding efficient photocathodes for fourth generation light sources such as free electron lasers and energy recovery linacs [5,6]. NEA photocathodes are created by depositing a very electropositive substance (e.g., cesium) and a very electronegative substance (e.g., O<sub>2</sub> or NF<sub>3</sub>) on the surface of a III-V semiconductor to lower its vacuum level at the surface below the conduction band minimum in the bulk [1]. By and large, most NEA photocathodes use oxygen and cesium in the activation process. However, in the case of polarized electron sources used in linear accelerators, NF<sub>3</sub> gas is commonly used [4,7].

Most research into the fundamental, atomic understanding of NEA surfaces has focused on the oxygen-activated surface, and relatively little attention has been paid to the NF<sub>3</sub> variant [7]. It has been proposed, however, that the NEA surface prepared with NF<sub>3</sub> is a better candidate for detailed, atomic level surface studies because of its presumably simpler chemistry [7-10]. This is based partly upon the widely-held assumption that the activation layer formed by NF<sub>3</sub> and Cs consists of polar CsF molecules and that NF<sub>3</sub> simply acts as a fluorine delivery agent. Furthermore, it is also assumed that the excess nitrogen does not stay in the activation layer because of the strongly ionic, exclusionary bond formed by cesium and fluorine [11]. The evidence presented in this study contradicts these assumptions.

Although no consensus has been reached on whether a  $\text{NF}_3$  activated or oxygen activated photocathode has a longer lifetime or a higher quantum yield, it has been proven that it is much easier to activate a photocathode with  $\text{NF}_3$  than oxygen [7-11]. In this study, we conduct SR-PES experiments on the Cs- $\text{NF}_3$  activated GaAs photocathode with photon energies up to 1000 eV, which enables us to probe the 1s core levels of both nitrogen and fluorine, two of the key chemical constituents of the system. The experiment is carried out at beam line 10-1 at Stanford Synchrotron radiation Laboratory. A PHI hemispherical electron energy analyzer is used to collect and analyze the emitted photoelectrons. The collection angle for photoemission is normal to the surface.

The samples used are Zn-doped, p-type GaAs(100) wafers obtained from American Crystal Technology with an doping concentration of  $5 \times 10^{18} \text{cm}^{-3}$ . The samples are cleaned using a solution of  $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O}$  in a volume ratio of 4:1:100 [12,13]. The cleaning is carried out in a dry argon environment inside a glove bag connected to our nitrogen-purged load lock chamber into which the sample is transferred. Before activating the photocathode in the UHV chamber, the cleanliness of the sample is confirmed by photoemission spectra of the Ga3d, As3p core levels and valence band [12,13].

The activation and SR-PES are carried out in a UHV chamber with a base pressure of less than  $3 \times 10^{-10}$  torr. A carefully out-gassed Cs getter chromate source is used for Cs deposition [14]. Gaseous  $\text{NF}_3$  is leaked into the chamber through a leak valve. Quantum yield (QY), defined as the ratio of the number of photoelectrons emitted from the sample

into the vacuum to the number of incident photons, is monitored during the activation and PES experiments. A 0.95W He-Ne laser (632nm) is used as a light source in the QY measurement. The body of the vacuum chamber is used as the electron collector and the sample is biased to -9V. During the activation, Cs is deposited on the surface until a maximum in QY is reached. Shortly after the Cs maximum is reached, the NF<sub>3</sub> gas flow is turned on to improve the QY further. It is important to point out that, unlike Cs/O<sub>2</sub> activation, the Cs/NF<sub>3</sub> activation of the cathode is not very sensitive to the NF<sub>3</sub> flux. In Cs/O<sub>2</sub> activation, a higher than optimum oxygen flux will kill the photocathode's QY. But we find no such effect in our Cs/NF<sub>3</sub> activation. A higher NF<sub>3</sub> flux does not affect the cathode QY. After finally ceasing deposition of both Cs and NF<sub>3</sub>, photoelectron spectroscopy of different core level peaks is performed at various photon energies.

Figure 1 shows a typical activation curve, which is a plot of the QY versus time during the activation process. The first plateau in the plot is the maximum QY achieved by dosing Cs only, and the subsequent upturn in QY is caused by the introduction of NF<sub>3</sub> gas at  $2 \times 10^{-8}$  torr. Figure 1 also shows that the QY dips and stabilizes when the NF<sub>3</sub> gas flow is cut off before the Cs is cut off. The QY recovers to the maximum value after the Cs is turned off. The QY increase in a Cs/NF<sub>3</sub> activation is not very sensitive to the NF<sub>3</sub> gas pressure. We perform cathode activations using NF<sub>3</sub> pressures from  $5 \times 10^{-9}$  torr to  $1 \times 10^{-7}$  torr with the same Cs flux. No significant difference in the QY was obtained. This is in sharp contrast to Cs/O<sub>2</sub> activation, where the O<sub>2</sub> pressure has to be carefully matched to the Cs flux and a slight deviation from the optimal O<sub>2</sub> pressure will cause a large QY drop. Overall, a maximum quantum yield between 3% and 5% was achieved in most of

Cs/NF<sub>3</sub> activations performed in these experiments, which is slightly lower than the average QY of a Cs/O activation (~6%) in the same vacuum system. However, the variation in the final QY among all Cs/NF<sub>3</sub> activated cathodes was smaller than that of Cs/O activated cathodes.

After the maximum QY is reached, the N1s and F1s photoemission spectra were taken at 540eV and 820eV photon energy, respectively. These were subsequently repeated every 2 to 3 hours. The Cs 3d core level spectra were taken at both photon energies as well. Figure 2 shows the N1s spectra taken at different times after activation. In sharp contrast to the common assumption that the activation layer consists of only CsF, there is a significant amount of nitrogen in the activation layer. Furthermore, the N1s core level peak splits into two distinct peaks. The intensity of the high kinetic energy peak labeled as “peak 1” dominates the N1s spectrum right after the activation and decays with time. The intensity of the low kinetic energy peak, “peak 2”, does not change with time. After 17.5 hours, the intensities of two N1s peaks are comparable. We also plot the F1s spectra which were taken along with N1s spectra in figure 2. There is only one peak in F1s and the peak intensity also decays with time. To examine the correlation between the N1s peaks and F1s peak, we fit both spectra and plot the normalized intensity of each component vs. time in figure 4. The intensities of the N1s “peak 1” and the F1s peak drop at the same rate for up to 9 hours after the activation. This strongly suggests that the F atoms in the activation layer are bonded to the N atoms (peak 1). Furthermore, the fact that there is only one peak in F1s spectra indicates that the F atoms may not be bonded to the Cs atoms. The NF<sub>3</sub> molecules are not just a fluorine delivery agent as commonly

believed. To estimate the Nitrogen to Fluorine ratio, we normalize the N1s and F1s total peak intensities with the calculated photoelectron cross-section data [15]. The N to F ratio is  $0.3 \pm 0.1$  right after the activation. The peak 2 in the N1s spectra likely belongs to N(+5) chemical species, which can be formed between  $\text{NF}_3$  and other contaminants, such as OH, during gas handling and the activation processes. The Cs 4d core level intensity is also monitored during the cathode activation and degradation processes. No significant change is found in Cs 4d intensity over this 18 hour period under dark conditions.

Therefore, we believe that the decrease of the N1s and F1s intensities is not the result of the activation layer thinning[8,9]; rather, it is likely due to the arrival of surface contaminants (such as OH and CO) which can replace the N-F clusters in the activation layer. The exact decay mechanism of Cs/ $\text{NF}_3$  activated cathodes is beyond the scope of this paper and will be the subject of future research.

As we mentioned above, the existence of N-F clusters in the activation layer can play an important role in NEA GaAs cathode activation and degradation. This may also explain why the  $\text{NF}_3$  based activation is so different from  $\text{O}_2$  based activation. Unlike the oxygen molecule, the  $\text{NF}_3$  molecule is a polar molecule. We speculate that it will align to the field direction under the influence of an electric field. These molecules tend to form a positive dipole layer when it is deposited on the positively charged Cs rich surface [16]. After a layer of such clusters is formed, it may block the further deposition of  $\text{NF}_3$  molecules until a fresh Cs layer is formed. This is not the case for a non-polar molecule like oxygen, which can lead to a large variety of cesium oxide ( $\text{CsO}_x$ ) species [17,18]. Thus, a specific deposition procedure is needed to create the “right type” of cesium oxide

layer on the cathode surface to reduce the work function [17-20]. Furthermore, in the  $\text{NF}_3$  case, once the N-F clusters are trapped in the Cs layers, it will be difficult for them to move within the Cs matrix due to the large size of these clusters. Thus, the dipole layers formed should be thermodynamically stable. However, these clusters are held electrostatically within the activation layer, and no chemical bonds are formed with the Cs atoms. They are still vulnerable to the contaminants, such as CO and OH, which form strong bonds with Cs atoms.

In summary, we investigated the NEA surface of Cs/ $\text{NF}_3$  activated GaAs(100) photocathodes using SR-PES. In contrast to the commonly accepted assumptions, a significant amount of nitrogen does exist in the activation layer. We conclude that majority of the nitrogen atoms in the activation layer are bonded to the fluorine atoms in the form N-F molecules. We observed a strong correlation between the nitrogen and fluorine signal during the degradation of the photocathode.

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### **Figure Captions:**

Figure 1: A typical NF<sub>3</sub>/Cs activation curve of the GaAs cathode. We turn on the Cs flux first. The QY increases and reaches its maximum. Then the oxygen flux is turned on after the QY drops to 2/3 of the maximum reached. The QY increases again and will reach a higher maximum. We then turn off the NF<sub>3</sub> and Cs sequentially.

Figure 2: N1s spectra taken at different time after the activation. There is a significant amount of nitrogen in the activation layer. There are two peaks in all the N1s spectra. The intensity of peak 1 decreases with time and the intensity of peak 2 remains the same.

Figure 3: F1s spectra taken at different time after the activation. There is only one peak in each F1s spectrum and the intensity of F1s peak decreases with time.

Figure 4: We calculated the normalized intensities of N1s peaks and F1s peaks at different times after the activation. There is strong correlation between N1s peak 1 and F1s. This indicates that the F atoms in the activation layer are bonded to the N atoms.







