The surface activation layer of GaAs negative electron affinity photocathode activated by Cs, Li and NF$_3$

Y. Sun[1, a)], R.E. Kirby[2], T. Maruyama[3], G. A. Mulhollan[2], J. C. Bierman[2] and P. Pianetta[1]

[1] *Stanford Synchrotron Radiation Lightsource, Menlo Park, California 94025, USA*

[2] *Saxet Surface Science, Austin, Texas 78744, USA*

[3] *SLAC National Accelerator Laboratory, Menlo Park, California 95025, USA*

The lifetime of GaAs photocathodes can be greatly improved by introducing Li in the Cs+NF$_3$ activation process. The surface activation layer of such photocathodes is studied by synchrotron radiation photoemission and is compared with GaAs photocathodes activated without Li. The charge distributions of N, F and Cs experience significant changes when Li is added in the activation. In addition, the presence of Li causes NF$_x$ molecules to take an orientation with F atoms on top. All these changes induced by Li hold the key for the lifetime improvement of GaAs photocathodes.

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a) Corresponding Author. E-mail: ssun@slac.stanford.edu

GaAs negative electron affinity (NEA) photocathodes have been used in many applications as efficient electron emitters due to their high quantum efficiency (QE).[1-7] Cs and NF_3 are widely used to activate GaAs, especially for polarized electron sources used in accelerators.[4, 7] However, GaAs photocathodes are sensitive to contaminants so they need to be operated in the very best vacuum environment. This limits the use of GaAs photocathodes in the current generation of accelerators employing RF guns, which generally have a more severe environment than DC guns. Mulhollan et al. found that by adding Li to the Cs+NF_3 activation process, the immunity of GaAs photocathode from contaminants can be enhanced,[8] but the role of Li was not well-understood. In addition, Li and F interaction is of general interest in many applications, such as the role LiF plays in the improved electron transfer from cathodes to organic light emitting diodes.[9] In this work, synchrotron radiation photoemission is used to study the GaAs photocathode surface activation layer formed by Li, Cs and NF_3. The changes brought by the addition of Li are more complicated than simple hole-filling as originally expected.[8] The interaction between Li and NF_x causes the NF_x molecules to take a F-on-top orientation with charge moving towards N. At the same time, two different types of Cs and Li are observed and they are situated at different vertical locations in the activation layer.

The samples used were Zn-doped, p-type GaAs(100) wafers obtained from American Crystal technology with a doping concentration of 5×10^{18} cm^{-3}. The samples were chemically cleaned in 9% HCl solution for 30s in an argon purged glove bag, then annealed at 400°C in the UHV chamber for 20 min to remove the surface elemental arsenic produced in the chemical etch.[10] The activation process follows the general Cs+NF_3 activation procedure but with four Li doses introduced at different times during

the activation, as described in ref. 8. Photoemission spectra were collected by a PHI hemispherical electron energy analyzer at beam line 8-1 (hv: 30-170eV) and beam line 10-1 (hv: 200-1000eV) of Stanford Synchrotron Radiation Lightsource (SSRL) and were normalized by photon beam flux. Unless stated otherwise, spectra were collected at normal emission (0°). Photoemission peaks were fitted using the program developed by A. Herrera-Gomez,[11] with the spin orbital splitting of Cs 4d fixed at 2.28eV.

The F 1s and N 1s spectra for a Cs+Li+NF_3 activated sample are shown in figure 1(a) and 1(c), respectively. Spectra for a Cs+NF_3 activated sample are also plotted for comparison. In an earlier study of GaAs photocathodes activated by Cs and NF_3, Liu et al. observed the existence of both N and F in the activation layer and concluded that Cs atoms do not completely break NF_3 molecules into N and F atoms to allow formation of the CsF compound. Instead, N and F are still bonded together as N-F clusters.[12] We observed the same thing for Cs+NF_3 activated samples. Although we believe that the N-F cluster is simply the NF_3 molecular form because NF_3 is inert at room temperature,[13] we decided not to draw such a conclusion at this point simply based on the atomic ratio between N and F (0.3±0.1) alone. We use NF_x to represent the N-F cluster. Similarly, NF_x is also found on Cs+Li+NF_3 activated samples because both N 1s and F 1s peaks are observed and the ratio between N and F does not differ much from Cs+NF_3 activated ones. However, the peak positions of F 1s and N 1s are notably different from Cs+NF_3 activated samples, with F 1s moving towards lower kinetic energy (higher binding energy) by 1.0±0.2 eV and N 1s moving towards higher kinetic energy (lower binding energy) by 0.3±0.1 eV. The peak shifts indicates that the presence of Li changes the charge distribution of NF_x, making N more electronegative and F more electropositive.

The change of F can also be seen in the valence band region plotted in figure 1(b), where the peak related to F 2p shifts towards lower kinetic energy for $Cs+Li+NF_3$ activated samples. From figure 1(a) and 1(c), we also observe that the activation layer can retain more NF_3 when Li is added in the activation under comparable NF_3 dosage (27.3L NF_3 for $Cs+Li+NF_3$ activation and 28.8L NF_3 for $Cs+NF_3$ activation for the spectra shown).

N 1s and F 1s spectra were also collected at off-normal emission angles, which are more surface sensitive than those collected at 0°. N 1s was taken at hv=500eV and F 1s was taken at 790 eV so that the photoelectrons had similar kinetic energy (around 100eV) and consequently, similar mean free paths. For $Cs+Li+NF_3$ activated samples, the ratio of the intensity at 60° to the intensity at 0° is calculated as 0.28 for F 1s and 0.18 for N 1s. For $Cs+NF_3$ activated samples, the ratio is 0.23 for F 1s and 0.26 for N 1s. Because the intensity from atoms buried deeper in the layer should be attenuated more at more surface sensitive 60° emission angle, we can conclude that for $Cs+Li+NF_3$ activated samples, F atoms are above the N atoms, while for samples activated without Li, there is no clear indication that a preferred orientation for NF_x exists.

The Cs 4d spectra for samples activated with and without Li show conspicuous differences, as shown in figure 1(d). While for $Cs+NF_3$ activated samples, only one Cs 4d doublet is seen, the Cs 4d line shape for $Cs+Li+NF_3$ activated samples is more complex and needs to be numerically deconvolved. The results of the Cs 4d fitting are shown in figure 2(a), where the complex line shape is shown to be caused by an additional doublet, labeled as Cs2. The Cs2 component, situated at 1.2±0.1 eV away from the component Cs1, should be more electropositive than Cs1 because it has lower kinetic energy. At the more surface sensitive off-normal emission angles, the relative intensity of Cs2 becomes

larger while that of Cs1 becomes smaller, indicating that Cs2 atoms are above Cs1 atoms. For Cs+Li+NF$_3$ activation samples, examination of the Li 1s spectra in figure 2(b) reveals two types of Li, Li1 and Li2, with an energy difference of 1.7±0.2 eV. Li2 has a lower kinetic energy (higher binding energy), thus should be more electropositive than Li1. In the mean time, Li2 should be situated above Li1 because the relative intensity of Li2 is larger at the more surface sensitive off-normal emission angles.

Because the intensity from atoms buried deeper should be attenuated more at more surface sensitive off-normal emission angles, the intensity ratios between peaks at off-normal angles and peaks at 0° for Cs1, Cs2, Li1, Li2 and F (calculated from F 2p) should provide clues for the vertical locations of those atoms in the activation layer. We examined those ratios at 15°, 30°, 45° and 60° emission angles and they demonstrate consistent angular dependence, with results at 60° showing the clearest difference between different types of atoms. The intensity ratios between 60° peaks and 0° peaks for four independent experiments are plotted in figure 3, with the x-axis as the experiment number. The overall trend is clear: Cs2 is on top; F and Li2 are on fairly the same level below Cs2; Cs1 is below F and Li2; finally, Li1 is at the bottom of the activation layer.

Figure 4 is a schematic drawing to show the activation layer on a GaAs substrate activated by Cs+Li+NF$_3$. NF$_3$ molecules are drawn to represent NF$_x$ cluster discussed in the text. The lateral relationship between the atoms is not the focus in this drawing because we are not able to obtain such information in our photoemission measurements. The relative vertical placements of Cs1, Cs2, Li1, Li2 atoms and NF$_x$ molecules should be fairly accurately depicted based on the results obtained through our angular analysis.

The obvious differences between the GaAs photocathodes activated with and without Li probably come from the interaction between Li and NF_x. When Li atoms are adsorbed on the GaAs substrate (Li1 component), they donate charge to the substrate atoms and become positively charged. The positively charged Li atoms (Li^{y+}, $0<y<1$) can interact with NF_x to form a Li^{y+}--NF_x complex. Grandinetti et al. believed that the Li^+--NF_3 complex is stable in their calculations.[14] Further theoretical work by Pei et al. also predicted the stability of Li^+--NF_3 complex.[15] For the configuration where Li^+ directly interacts with the N atom of NF_3, the overall charge of the NF_3 molecule is drawn towards the direction of Li, thus making the N atom more electronegative and the F atoms more electropositive.[15] In our study, positively charged Li atoms on the GaAs surface interact with the N atoms of NF_x, orient them with N on bottom and F on top and shift the charge distribution towards N. The more positively charged F atoms in NF_x further attract electron charges from the top layer of Cs (Cs2) and Li (Li2), making them more electropositive. In Pei's work, the interaction and stability of M^+--NF_3 drop when M is Na and drop further when M is K.[15] This trend explains why such interaction is not observed for GaAs activated with $Cs+NF_3$ because the large size of Cs atoms prevents effective orbital overlapping between Cs and N or F atoms,[16] and consequently, no stable Cs--NF_x complex is formed.

The interaction between Li and NF_x causes NF_x to take a F-on-top orientation and shifts the charge away from F atoms, which further attracts charge from Cs2 atoms on top of the activation layer. It is known that metallic Cs is a good getter material, but Cs^+ is not. Therefore, the positively charged Cs atoms on top of the activation layer, labeled as Cs2, can reduce the sticking coefficient of contaminants from the surrounding

environment, compared with the more electron rich Cs atoms on top of Cs+NF$_3$ activated photocathodes. This reduction of contaminants adsorption, together with the stabilizing effect induced by Li and NF$_x$ interaction, is probably the key to the improved immunity from contaminants and enhanced lifetime of the Cs+Li+NF$_3$ activated photocathodes. More work is planned to study the changes on the surface when activated GaAs photocathodes are exposed to contaminating gases to examine the roles that Li plays in the performance improvement of GaAs photocathodes.

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Figure Captions:

Figure 1. (a) F 1s, (b) valence band, (c) N 1s and (d) Cs 4d spectra for GaAs photocathodes activated by $Cs+NF_3$ and $Cs+Li+NF_3$. F 2p feature is labeled in (b).

Figure 2. (a) Cs 4d, (b) Li 1s spectra (dots) and their numerical fittings (solid lines) for a GaAs photocathode activated by $Cs+Li+NF_3$. Spectra taken at normal emission (0°) are shown at the bottom and spectra taken at 60° off normal are shown at the top.

Figure 3. The ratio between the peak intensity at 60° off normal and the peak intensity at normal emission (0°) for Cs1, Cs2, Li1, Li2 and F. Results for four independent experiments are shown.

Figure 4. Schematic diagram of the activation layer showing the vertical locations of Cs, Li and NF_x on an activated GaAs photocathode surface.
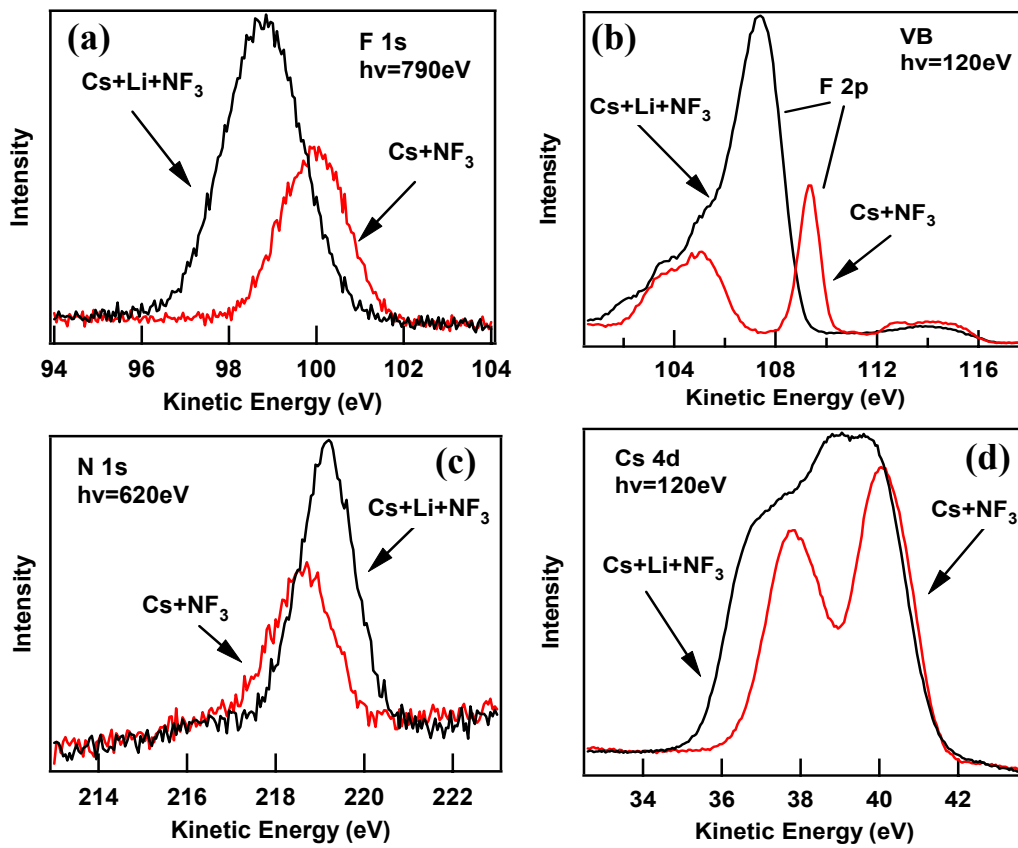
(a) Cs+Li+NF₃ — F 1s hv=790eV — Cs+NF₃

(b) Cs+Li+NF₃ — VB hv=120eV — F 2p — Cs+NF₃

(c) N 1s hv=620eV — Cs+Li+NF₃ — Cs+NF₃

(d) Cs 4d hv=120eV — Cs+Li+NF₃ — Cs+NF₃

Figure 1

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(a) Cs 4d, hv = 120eV, with labels Cs2, Cs1, at 60° and 0°, Kinetic Energy (eV)

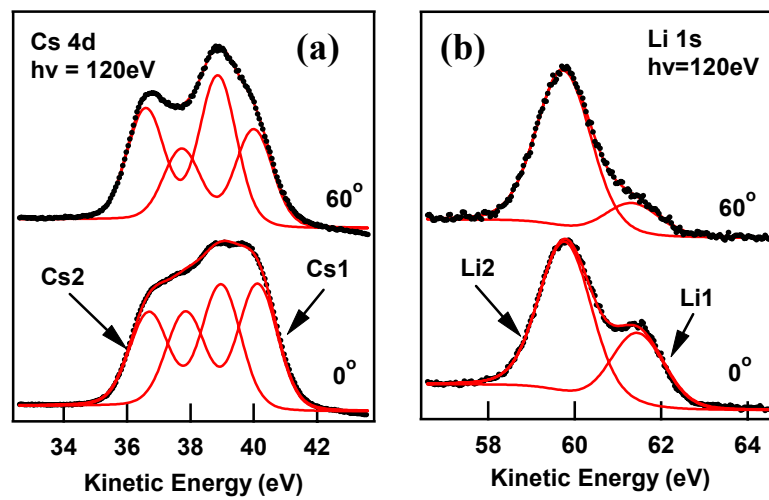**(b)** Li 1s, hv=120eV, with labels Li2, Li1, at 60° and 0°, Kinetic Energy (eV)
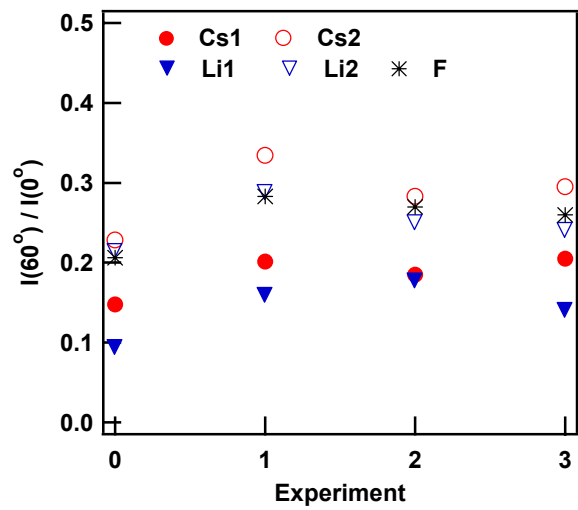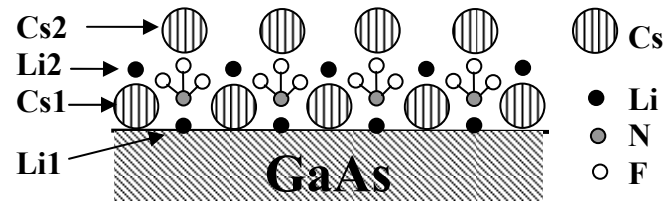
Figure 2

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Figure 3

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Figure 4

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