

# Theory-based PhotoCathode for LAPPD2

## Godparent "Review" Summary (released)

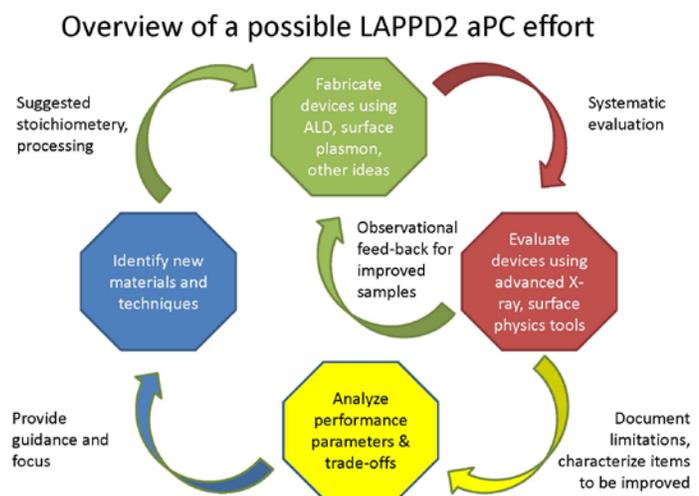
Workshop/Review held: 6-APR-2013

Committee Members: Katherine Harkay, *co-chair* (ANL/ASD), Matt Highland (ANL/MSD), Carol Mertz (ANL/CSE), Carlo Segre (IIT), Charles Sinclair (Cornell), John Smedley (BNL), Gary Varner, *co-chair* (Hawaii)

The committee wishes to thank those who participated in this half-day of presentations and discussion on the role of advanced/theory-inspired PhotoCathode design as part of the second-phase of the Large Area Pico-second Photo-Detector (LAPPD2) project. With the successful demonstration of 8" photocathode deposition at Space Sciences Laboratory at Berkeley using conventional bi-alkali techniques, those activities are now logically and intimately tied into the issues of vacuum handling and sealing, the domain of the established LAPPD2 Packaging committee. While those achievements are a necessary step toward first 8" sealed tubes, to fully realize a revolutionary step forward in photo-detection technology it is strongly desired to continue to apply recent and evolving chemistry and material sciences techniques to very fundamental issues in photocathode fabrication:

1. **What is it in the chemistry and morphology of fabricated photocathodes that dictate their fundamental performance properties, such as Quantum Efficiency, electron emittance, dark current, etc. ?**
2. **What limits these parameters and are there means to enhance them ?**
3. **Are there other materials that can be explored?**
4. **Can the success of ALD or other controlled deposition techniques be exploited to improve control over the fabrication process and achieved results ?**
5. **Is it possible to avoid needing Ultra High Vacuum at all processing/handling steps ?**
6. **Are higher temperature photocathodes possible ?**

The presented material offers a starting place for such a program of exploration within the LAPPD2 project. An outline of such an advanced/theory-inspired Photocathode program is sketched to the right.



It is realized at the outset that resource limitations bound what can be done solely within the context of the LAPPD program. Therefore partnering and coordination with existing efforts will be essential. As denoted, there are 3 core functions: theoretical guidance, fabrication, and evaluation. All three are vital to a successful program. Within the context of known or currently available resources,

1. **Theoretical guidance:** the committee recommends engagement of computational chemistry and fundamental materials experts and other interested parties to implement techniques for identifying and prioritizing new materials and materials processing procedures to be explored. A list is needed of targeted properties, such as QE vs. air-sensitivity vs. dark current vs. emittance, which should be analyzed in terms of tradeoffs for LAPPD in particular, or for the field as a whole.
2. **Fabrication:** it is expected that existing ANL laboratory resources can be utilized to realize new samples for systematic characterization and evaluation. In particular, extension of the existing ALD program to photocathodes is logical. Parallel efforts in Ga-N UV photocathode development at Wash U and collaborative efforts with other university groups in sample preparation are strongly encouraged. Can expertise and advances by ANL's battery group and the Center for Electrical Energy Storage in the development of better cathode materials and material processing techniques (i.e., fabrication of devices using environment-sensitive materials, tailoring interfaces and interactions of materials to control electrochemical processes, engineering scale-up of new material processing technologies, ...) be exploited?
3. **Evaluation:** the efforts at BNL to characterize fabricated devices and provide feedback to both the improvement of fabricated devices, as well as providing hard data to the simulation/study of material fundamental problems is vital. That program is expected to continue independently, though continued, close collaboration is clearly of significant benefit.

We recommend that for a next godparent review that groups seeking resources to contribute to this program make presentations and define their integration and benefits to the program, describe significant outcomes expected and timeframe for achievements.

More detailed comments are included as an Appendix.

## Appendix: Detailed comments from the committee members (unsorted and unedited)

### Charles Sinclair

This was my first “Godfather Committee” meeting, so was partly a learning experience for me. At the end of the meeting, Henry Frisch made a number of remarks. He pointed out that the Theory Based Photocathode effort is not funded as part of the LAPPD project. Thus it does not have a formal managerial structure or set of goals and objectives. Rather it reflects the various interests of a number of people working on photocathode development. These interests cover quite a spectrum, from detecting photons to generating exceptionally bright electron beams for accelerator applications. Lacking a formal funding source, the LAPPD project and the Godfather Committee can only encourage that funding be made available to these efforts from sources like the DOE and laboratory LDRD funds, and suggest areas of study that seem most likely to bear fruit (or possibly that should be abandoned). Thus, this meeting of the theory based photocathode effort was more in the format of a workshop describing work in progress rather than a formal review.

It is clear that the work done by the theory based photocathode effort is quite likely to be of considerable benefit to the LAPPD program. For example, the development of a process to consistently produce very high quantum efficiency (better than about 35 - 40%), large area alkali photocathodes would have major positive implications, in reduced cost and complexity, for the LAPPD project. Reductions in the total time to fabricate such a photocathode could also have a favorable impact, as some of the fabrication prescriptions presently in use are very lengthy. Similarly, learning how to generate high average current electron beams (some 10s of mA) of very high brightness, while not important for the LAPPD effort, would have a dramatic impact on both current and future light sources – perhaps allowing the generation of fully coherent X-ray beams in the 10 to 12 keV range, permitting, for example, phase contrast imaging in the 1 Angstrom range. And who can say what might come from a successful effort with acetylating a  $\text{Cs}_2\text{Te}$  photocathode, or from fabricating a good quality  $\text{Cs}_2\text{Te}_5$  cathode?

My comments below reference information I heard from the various presentations, though not any particular order.

While I agree with Klaus that it would be very interesting to be able to make alkali photocathodes with carefully controlled dopants and dopant profiles, I also believe that the current alkali antimonide results are some distance from producing materials for which it is reasonable to think of controlling dopant densities and profiles. For example, right now many people preparing  $\text{K}_2\text{CsSb}$  photocathodes do not believe (or cannot demonstrate) that they are even making a stoichiometric material. In a situation like this, it is difficult to imagine doing doping studies. At the April 6 meeting, John Smedley reported making  $\text{K}_{2.6}\text{Sb}$  instead of the nominal  $\text{K}_3\text{Sb}$ . At the PPP Workshop at Cornell last October, Cultrera of Cornell showed decidedly non-stoichiometric  $\text{K}_2\text{CsSb}$  cathodes as measured with scanning Auger (which surprisingly had quite high and uniform QE), and S. Schubert (HZB and BNL) reported that they were unable to produce a stoichiometric cathode with different recipes, as determined by XPS studies. The

deviations of stoichiometry shown would represent a very high dopant density if even a fraction of the non-stoichiometric component were an activated dopant.

Given the uncertainty regarding the stoichiometry of the nominally bialkali cathode materials produced, I believe that it would be very useful to characterize the stoichiometry routinely via XPS or scanning Auger, and present the results with a map of the QE with comparable spatial detail. It would be interesting to see what stoichiometry gave the best QE. Klaus's slide 19 showed XPS scans for K, Cs, and Sb that showed a high spatial correlation for the three elements. Unfortunately, there was no quantitative information on the relative abundances of the elements. It would be very useful to have this information, as well as a QE map with comparable spatial resolution.

Presently, many of the cathodes produced show a relatively low QE, compared to the best values reported. It is unclear to me how confidently one can draw good conclusions about photocathodes from low QE results, since there is clearly something "wrong" with these cathodes.

Klaus also made the comment that a good cathode needs a "delta doped" n-type layer at the surface. I have never heard this comment before. What physics is this comment based on? I'm reasonably familiar with the literature on NEA cathodes (principally on III-V materials, but to a lesser extent on the II-V's and ternary compounds like the II-IV-V's), and have never seen any reference to an n-type layer at the surface for NEA cathodes on any of these materials.

I also note that there are a number of different recipes for forming  $K_2CsSb$  in use at different laboratories. I believe there is some merit in attempting to duplicate a demonstrated successful recipe, such as that in Alex Lyashenko's thesis, rather than using seemingly arbitrary temperatures during the bialkali compound formation. When two different labs, using different equipment, begin obtaining highly similar results, it is likely a sign of progress. I also think it would be useful to routinely characterize bialkali cathodes by their spectral response over a reasonably broad range of wavelengths. One could use a Hg lamp, as Lyashenko did, or perhaps a set of narrow band interference filters with a broad spectrum light, but an attempt should be made to use at least several wavelengths. I found doing this, using interference filters giving wavelengths approaching the bandgap, was a very good way to characterize NEA GaAs cathodes, and to support the development of improved processes.

I have to add a bit of personal skepticism regarding doping based on a great many years of preparing NEA photocathodes on GaAs. The standard lore at the time I entered this business, in the mid-1970s, was that a very high level of p-type dopant – on the order of  $10^{19} \text{cm}^{-3}$  – was necessary to achieve a good QE. Over the years, I came to doubt this conclusion, and while at JLab, did a number of experiments making cathodes on much lower doped material. These measurements were made on epitaxial material with very well characterized dopant densities. I made some very high QE photocathodes on these reduced dopant materials. Unfortunately, this work was done at a time when my administrative responsibilities grew considerably, and it never got published. I've always wanted to revisit these results.

I am very impressed with the quality of the X-ray diagnostics that are being brought to bear on the questions of photocathode fabrication – the alkali antimonide cathodes in particular. It would be

interesting to explore a number of questions with this technique, including on cathodes like  $\text{Na}_2\text{KSb}$ , which may not be useful for the LAPPD work, but which might be illuminating from the point of understanding cathode formation and structure. E.g. it was said that in forming  $\text{K}_3\text{Sb}$ , the K completely dissolves the Sb before the formation of the compound, and that this is not the case in forming  $\text{Cs}_3\text{Sb}$ . What about Na or Rb? Why is it that we can apparently form  $\text{K}_2\text{CsSb}$  by adding Cs to  $\text{K}_3\text{Sb}$ , but apparently not by adding K to  $\text{Cs}_3\text{Sb}$ ? Why did Bob Springer's cathodes, made a single step with a nominal  $\text{K}_2\text{Cs}$  alloy, make such reproducibly good photocathodes? (Note that I do not believe he ever measured their QE at wavelengths shorter than green.)

As I have emphasized on multiple occasions, I believe it would be very worthwhile to attempt to reproduce Springer's results. His apparatus was very simple, containing a crucible for evaporating the antimony, and a boat filled with  $\text{K}_2\text{Cs}$ , which is liquid at room temperature. Though I doubt he never measured the vapor pressure of the  $\text{K}_2\text{Cs}$  alloy, or even that the vapor was still in the ratio of  $\text{K}_2\text{Cs}$ , the vapor pressure was apparently high enough at room temperature to form very good photocathodes in a relatively short time – a few minutes. He reproducibly made cathodes with a green QE above 17%. If these cathodes had the same spectral response as those of the PMT manufacturers, or Lyashenko's thesis, then these cathodes are roughly as good as the best alkali cathodes ever reported. I strongly believe that someone should pursue this avenue, as I have personally made a 17+% cathode with his simple apparatus.

Generally speaking, experimental workers in the photocathode field report total pressures only. I believe this is shortsighted. What really matters is the residual gas spectrum. It is very well known that highly vacuum sensitive photocathodes, such as the alkali antimonides and the various NEA cathodes are nearly or completely insensitive to a number of gases –  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{CH}_4$ , all the rare gases, etc., and exceptionally sensitive to others –  $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , etc. It is quite possible to make a decent vacuum (ca.  $10^{-10}$  mbar) and still have unacceptable partial pressures of harmful gases. This point is not moot – some of the alkali antimonide fabrication times are many hours – quite enough for a very low partial pressure of a harmful gas to influence the outcome. It would be beneficial to the field in general, I believe, if experimenters showed the residual gas spectrum in any apparatus in which a photocathode is prepared, stored, or used. And, while I generally avoid endorsing particular commercial products, I note that the Stanford Research Systems 200 amu RGA (with electron multiplier) is by far the best such instrument available, is amongst those with the very lowest cost, and offers superb company support if problems arise.

I strongly agree that minimizing the photocathode roughness is essential to reach the minimum thermal emittance. This has been an issue with the III-V photocathodes for some time now. A very low emittance has been demonstrated for GaAs with low roughness. While it is common for GaAs photocathodes to use a surface  $2^\circ$  off 100 (since this surface is readily available commercially), it is not obvious that this is the best surface from the standpoint of roughness. For example, the 111A surface, while not commonly used, might be a much better choice. I have made good QE NEA cathodes on 111A GaAs (though for a purpose different than low emittance), and perhaps this should be examined for emittance. It is, by the way, not trivial to have the ability to measure emittances as small as those theoretically available from very smooth GaAs.

I do not believe that cathode heating is in general a lifetime limiting phenomena. Cathode heating certainly depends on the amount of incident optical power, and it is straightforward to devise ways to extract relatively small deposited power from the cathode. Obvious stainless steel is not a good substrate for a high average current photocathode. As a demonstration that high currents can be delivered without thermal problems, I note that Cornell University has operated both NEA GaAs and nominal  $K_2CsSb$  cathodes at many 10s of mA average current for hours.

III-V alloy cathodes containing Al may prove problematic if they have to be exposed to air at any point. Many year ago, people generating polarized electron beams attempted to shift the optical wavelength giving maximum polarization by alloying GaAs with Al to shift the bandgap to higher values. These materials were transferred through air, between their fabrication chamber and the electron gun. They showed poor QE, which was ultimately traced to oxidation of the aluminum at/near the surface. Aluminum oxide can't be broken down by the heat cleaning techniques used.

I greatly enjoyed the presentations and format of this meeting. It got me to thinking about some issues I have not thought about for a while. I'm eager to learn of future successes in some of the avenues proposed or presently under study.

## **Carlo Segre**

1. Recent progress - I was impressed with the analytical techniques that have been applied to the photocathode fabrication process. It seems taht much more is known now than in the past and it is encouraging to see that there is substantial understanding of the structure of the  $K_2CsSb$ -type materials and the InGaN-based devices. What is disappointing, however, is that the InGaN materials really do not have good response in the visible light region that is so important for LAPPD and accelerator photocathode sources. Similarly, what is now understood of the fabrication of the  $K_2CsSb$  cathodes seems to set absolute limits on their quantum efficiencies (minimum thickness?) and suitability for accelerator electron sources (surface morphology?).

2. Novel ideas - The talks by Pellin and Nemeth indicate that there are some ways forward to the improvement of quantum efficiencies. The theoretical approach have shown some promise but seems to be a bit hit-or-miss at this time. The idea of using highly conductive metal nanostructures to enhance light absorption in the desired range is promising but untested.

3. The near future - It seems that the LAPPD project needs to move on quickly to fabrication of usable photocathodes to be coupled to the 8" micro channel plate tiles. At the moment, the only game in town for this is to push forward on improvement of the fabrication process for  $K_2CsSb$  photocathodes. It is cleare that the highest efficiencies are achieved with thinner layers of the photocathode. Efforts must be made to optimize the fabrication of the thinnest photocathodes possible and perhaps to test out the Pellin idea to see if it increases quantum efficiency. I would like to see Matt and Razib work on this composite cathode using their 33mm system while Jun keeps pushing on making more uniform QE tiles using the ALD-deposited Sb starting layers. Some small effort might be made in seeking ALD precursors

for K and Cs. It is possible that a fully ALD deposition process could result in a better surface morphology and a more uniformly thin film. Inorganic chemists experienced in making ALD precursors should be engaged in this latter activity.

4. Far future - It is valuable to continue to pursue a theoretical approach to new cathode materials. However, I think a more systematic attack of the problem may yield better results more quickly. I suggest that a list of target properties be assembled (if not already done) and then a small group needs to lay out classes of materials to be investigated theoretically for the suitable properties. One direction to be explored would be novel photovoltaic materials. There may be some which have nearly ideal properties and there is such a large amount of activity in the field these days that it seems like a fertile playground. It is not clear how promising the two materials that Nemeth discussed actually are. I would make some effort to make the MgO/Ag structure, however, if that is not being vigorously pursued at the moment. It is not clear to me how much funding is available for the theoretical studies but some amount should be made available to have manpower available to keep pursuing these long-term goals.

### **Katherine Harkay**

1. Adopting the high-QE bialkali photocathode was clearly the right approach for the first phase of the LAPPD project. However, given the complexity of this system and what seem to be inherent difficulties in tailoring its properties in a reproducible and systematic way despite a concerted effort, this seems to be a good time to step back and consider adding one or more parallel routes. Other systems may lend themselves more readily to tuning the QE or wavelength or to make them less air-sensitive, for example.
2. The most generic way to improve the QE may not involve complex surface chemistry at all, but rather by exploiting surface plasmon-assisted photoemission via a nanostructured surface. The concept is not new, of course, but fabrication considerations for LAPPD may guide which approach is the most promising. Pellin's idea should be pursued for proof-of-principle, as well as other ideas, such as Nemeth's nanorod idea (not presented, but described conceptually in PRL 104, 046801 (2010)). One question that is often raised with any such scheme is whether the nanostructure increases the dark current via field emission. A group at UCLA (Musumeci and Li) fabricated a nano-hole array cathode that they successfully tested in an s-band rf photoinjector. The charge yield was enhanced by two orders of magnitude over a flat surface, and the dark current was reported to be the same as a flat surface. On the other hand, the laser damage threshold was much lower for the nano-hole array and is under study, but this may not be a concern in a detector. Musumeci presented this work at the 2012 Photocathode Physics for Photoinjectors (P3) workshop.
3. Borrowing ideas from other fields and re-purposing them can be quite promising, and tuning one figure-of-merit probably degrades another, so a design effort is best targeted to a relatively narrow set of goals. Also, there is no substitute for testing theoretical concepts by actually fabricating and characterizing them, but funding for materials and equipment is difficult to come by for any high-

risk/high-gain research with a narrow application. Partnering with experts in related materials applications such as photovoltaics or batteries could be quite beneficial in overcoming this barrier, as also suggested by other committee members.

4. I feel that it would be important to specify more definitely a prioritized set of requirements for the advanced photocathode research to focus on. One thing I would like to see is a top-down analysis of trade-offs among the various figures-of-merit: is QE more important than dark current or air-sensitivity or fabrication that is fast & cheap? The surface roughness vs. QE question is already beginning to be addressed by a few groups, but other questions remain open-ended. The analysis should include a list of risks vs. benefits to LAPPD in particular, or the field as a whole, of advances in each category. Such an analysis could benefit the cathode design effort, in particular, where categories of materials could be screened for relevance. It might be useful to find an answer relatively early on as to whether single-crystal or large-grain epitaxial structures are critical to pursue or not.
5. Several speakers emphasized the interesting properties of thin films in photoemission, either in enhancing the QE or tuning the work function. It might be beneficial to seek expertise in the physics of thin films and interfaces and invite them to collaborate.

### **Matt Highland**

One thought that I keep coming back to, which maybe be an area that has already been explored, is the applications of some advanced microscopy to these photocathodes. Some of the AFM results shown indicated inhomogeneity in the microstructure of the films and it seems like it would be very interesting to correlate that with the electronic properties of the material. I believe PEEM was mentioned as a potential technique, but it was pointed out that it was incompatible with these materials. Are there any other viable microscopy techniques such as STM or Electric Force Microscopy that could be used to map the electronic properties on a finer scale? It seems like something along those lines might be helpful. Of course if this is all been done before go ahead and credit it to my lack of familiarity.

### **John Smedley**

One suggestion I have is that we fold our diagnostic info back into our design effort. We clearly have issues - roughness and crystallinity, for example. These issues actually impact our ability to implement the "new ideas" - for example, Klaus's pn junction idea is great - but unless we can better define our layers, there is no way we could do it.

I really like the idea of theory-based photocathodes, but I think that it is appropriate for there to be a "task" assigned to someone to work on bringing designs into fruition. For example, I think I know how to make Klaus's graded density cathode - but we have to address roughness first.

For Carlo's #3 - I'd add sputtering and PLD to ALD as future paths for K<sub>2</sub>CsSb.