JLab Technical Note
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Polarized Source Group

Active Area Definition of GaAs Photocathodes via Anodization

An informal guide to the process of anodizing GaAs photocathodes to define the active area in support of longer operational lifetime in the JLab polarized electron sources.

Motivation

Longer operational lifetime of the photocathode.

The electron optical properties of the electrode structures of the 100 keV photoemission electron sources on the CEBA accelerator at Jefferson Laboratory are such that electrons originating from a large radius on the photocathode will follow significantly different trajectories than electrons emitted from the central region. These extreme trajectories lead to a high probability that these electrons will strike the walls of the vacuum chamber at the exit of the source or the first few meters of the beamline. The electron stimulated desorption of various species (primarily hydrogen) into the source vacuum will lead to accelerated deterioration of the quantum efficiency (QE) of the photocathode due to "ion back-bombardment" [1].

The growth of an anodized surface over a large radius portion of the photocathode to inhibit the formation of a high QE is a useful technique to suppress the generation of electrons in this large radius region. Scans of the QE over the surface of an anodized photocathode have shown a suppression of the QE in the anodized region by a factor of at least 10^3. This technique has been in use at Jefferson Lab since early in 1998 [2]. A mask is used to precisely define which regions of the photocathode are anodized and thus unable to emit electrons via photoemission.

Until ~2 years ago, the anodization was accomplished using a mask which consisted of a small region of glue as developed by J. Scott Price. Concerns over the possible contamination of the GaAs photocathode from such glue, led to the development of the vacuum mask anodization technique by Paul Rutt.

The process of anodizing GaAs photocathodes is relatively simple in terms of the equipment and time required, but requires a good degree of care to prevent inadvertent contamination of the active area. Detailed contamination studies outside of the active area have not been performed, but experience suggests that contamination will usually present itself as a rough (i.e. not mirror-like) surface in the anodized region or at the edges of the active area. The concern at this point is that the composition of the rough surface is not well known. This uncertainty may present operational challenges when such a photocathode is used in a high voltage electron source.

[1] Mainz work by Kurt et.al.
[2] BTLLPEG minutes (?).

Equipment and Supplies Required

Consumable Supplies Required

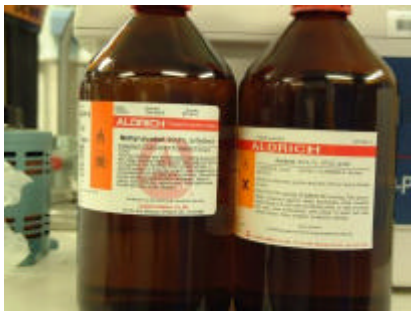
The following consumable supplies are required. A small quantity of these supplies are stored in a locked cabinet in the Test Lab offline chemical room along with the required equipment listed later in this document. Combination is **11-21-15**. Additional quantities of these supplies are stored in the first bay behind the acid storage building with access at that area obtained via members of the safety group.

1) An unopened 1 liter bottle of high purity methyl alcohol [3]. Due to the hydroscopic nature of methyl alcohol, one is specifically cautioned against using a previously opened bottle,

2) 500 ml of high purity Acetone [4] which has been stored in a controlled manner to prevent any from of contamination since the bottle was first opened (use a fresh bottle if you have *any* doubts),

3) 100 ml of high purity Trichlorethylene [5] which has been stored in a controlled manner to prevent any form of contamination since the bottle was first opened (use a fresh bottle if you have *any* doubts),

4) Approx. 5 ml of high purity phosphoric acid [6] which has been stored in a controlled manner to prevent any form of contamination since the bottle was first opened (use a fresh bottle if you have *any* doubts).



5) A supply of high purity de-ionized water such as that available from the Millipore-RO machine in the Test Lab offline chemical room

6) Powder-free gloves such as those suitable for use with UHV vacuum system components.

7) A gold or platinum filament of 0.1 mm diameter (min.) and ~8 mm length. While it may be possible to obtain several uses from such filaments, their use is typically limited to one anodization session to prevent contamination.

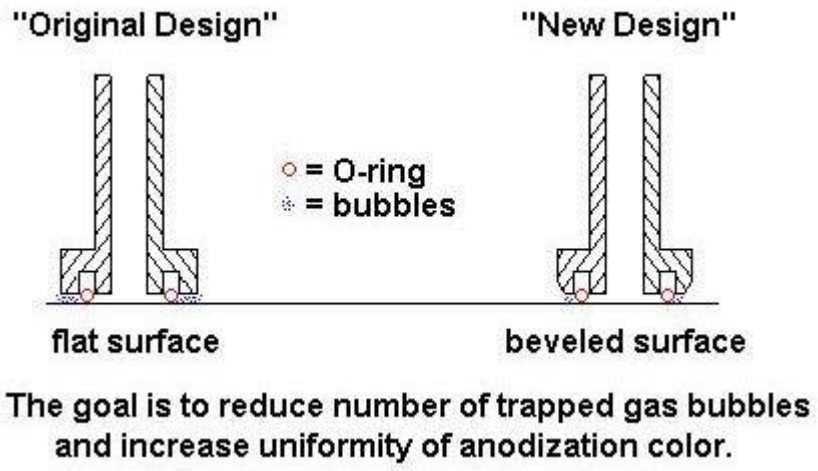
8) Glass cover slides, Quickstick[7] glue, Al foil, and a clean (i.e. fully degreased!) single edge razor blade to chip a small piece of this very brittle) glue.

[3] Aldrich Chemical # 322415 or equiv.
[4] Aldrich Chemical # 270725 or equiv.
[5] Aldrich Chemical # 251402 or equiv.
[6] Baker Chemical # xxxxxx or equiv.
[7] Quickstick is the South Bay Technologies trademark for glycol pthalate wax: an acetone soluble wax. Available from South Bay Technologies, 1120 Via Callejon, San Clemente, CA 92672, 714.492.2600. Also available as Crystalbond.

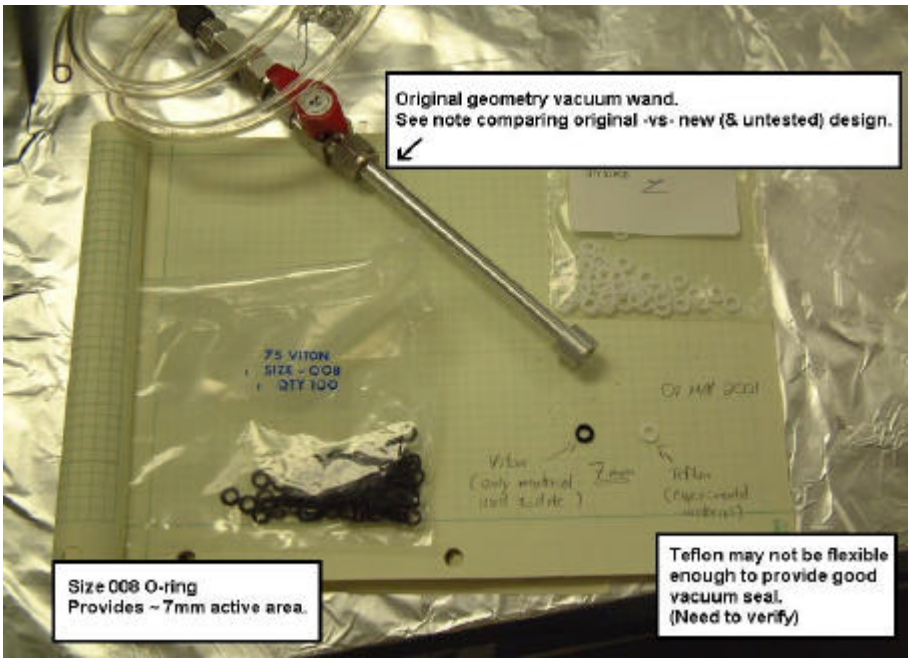
Equipment Required

The following equipment is required. Please note that this equipment is typically stored in a locked cabinet in the Test Lab offline chemical room. Lock Combination is **11-21-15**.

1) Photocathode anodization fixture [8] and a ring stand to support the fixture. Please note that there are presently two sets of three fixtures that provide an active area of 5 mm, 7mm, or 9 mm. The photocathodes are typically anodized with a 7 mm active area at present.



2) The appropriate size of viton o-ring [9, 10, 11] to fit the anodization fixture being used. A new, clean o-ring must be used for each anodization process. They are to be cleaned prior to use via several minutes of ultrasonic cleaning in methyl alcohol, followed by three rinses in de-ionized water, and a careful drying.

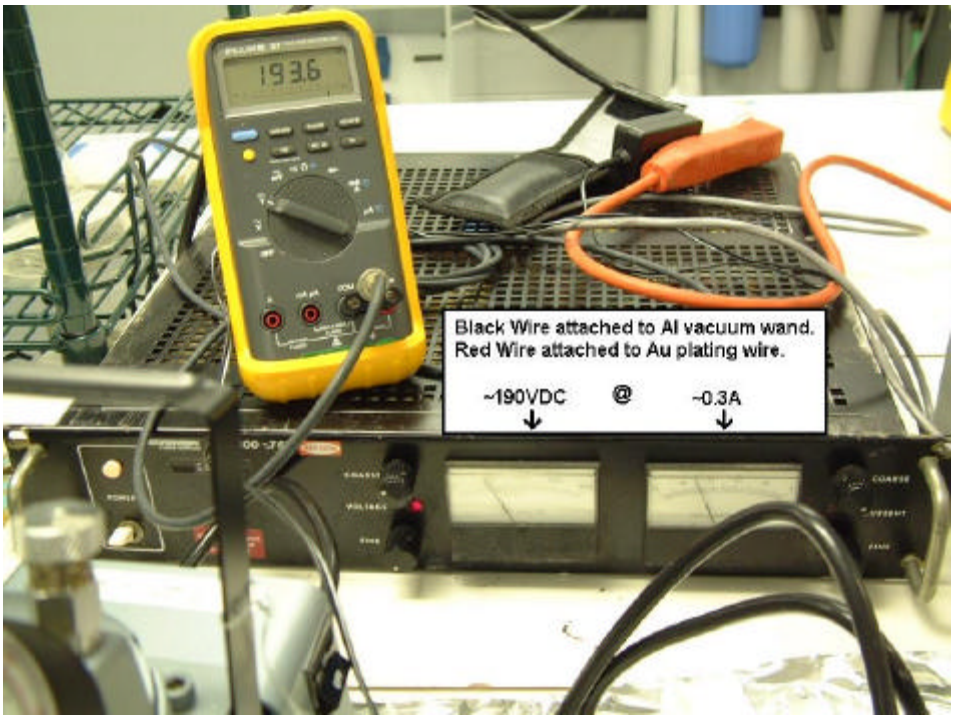


[8] Jlab drawing 39300-C-0165
[9] McMaster-Carr 9464k105 or equiv.
[10] McMaster-Carr 9464k12 or equiv.
[11] McMaster-Carr 9464k14 or equiv.

3) An oil-free vacuum pump [12] capable of generating at least 10mm Hg of vacuum.

4) A hotplate.

5) A DC power supply capable of providing 250 V @ ~300 mA.



6) Twice as many 50 ml glass beakers as the number of photocathodes to be anodized and two 250 ml beakers. It is very important that these beakers be properly cleaned [13].

> **Appendix D: Glassware Cleaning Procedure**
> Start with all new glassware.
> Ultrasonically clean each item three times using a solution of Alconox in de-ionized water.
> Rinse each item out with methanol.
> Leach each item with boiling de-ionized water and cover with clean aluminum foil.
>
> Please note that once a beaker has been properly cleaned, it may be reused several times permitted that is properly wrapped and stored between uses. A beaker may be reused if the same chemicals are used in it each time.

7) Properly cleaned tools to handle the photocathodes. A box with clean tweezers and other tools is available with the other equipment in the Test Lab offline chemical room.

8) A method of measuring the pH (~2.6) of a solution of H_20 and dilute phosphoric acid. An electronic meter dedicated to this task is available in the cabinet in the Test Lab offline chemical room.

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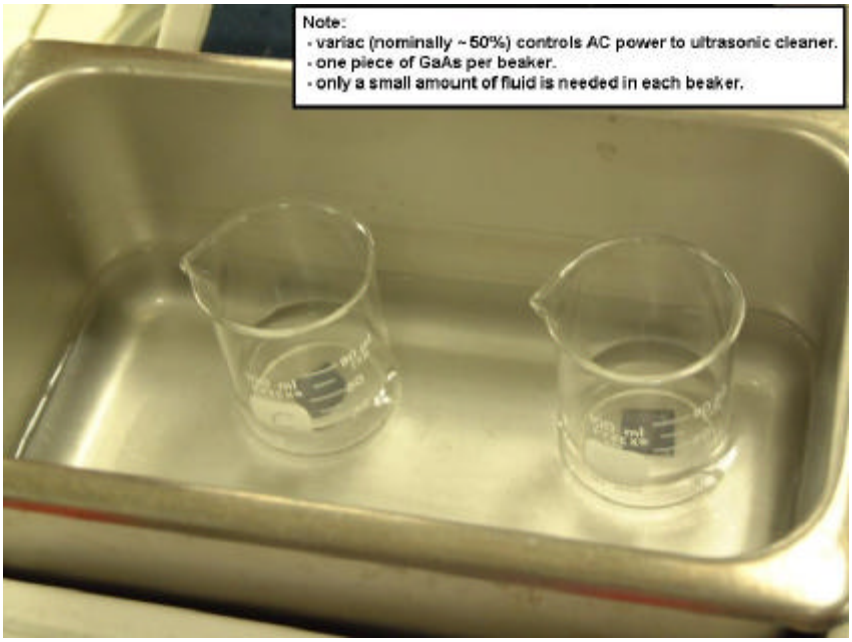
[12] McMaster-Carr 4176k11 or equiv.
[13] *Appendix D: Glassware Cleaning Procedure* contained in Cleaning and Anodizing GaAs, NPL Tech note 90-3A, B.M. Dumham (1992).

Preparations Before the Anodization Process

The following steps need to be completed before the start of the anodization process:

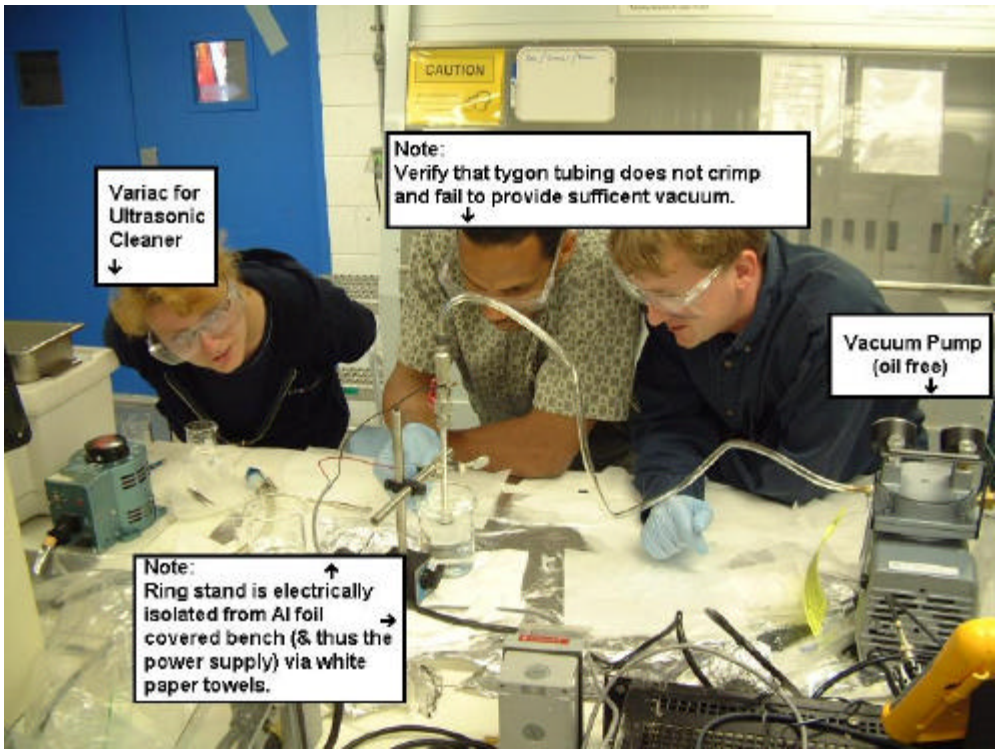
9) Prepare ~400 ml of H_2O + phosphoric acid solution. Add ~2 to 3 drops of phosphoric acid to ~400 ml of de-ionized water from the Millipore-RO water system. Please note that the phosphoric acid is not likely to mix well with the water unless the mixture is stirred well for ~30 sec. Use the pH meter to measure the pH of the solution, the goal is to obtain a solution with a pH of 2.6 +/- 0.1. If the pH is less than 2.5, then pour off ~200 ml of the solution and add de-ionized water until the pH is 2.6. If the pH is above 2.7, then add phosphoric acid 1 drop at a time, stir well for ~30 seconds then re-measure the pH.

10) Rinse the photocathodes one time each with acetone and methyl alcohol.



11) Dry the photocathodes off in a stream of dry nitrogen gas. Verify that the photocathodes are free from any visible signs of contamination. Re-clean in methyl alcohol and carefully dry off again if you suspect any surface contamination.

12) Place a sheet of Al foil onto the workbench to provide a clean work area. Cover with a couple layers of lent free clean room paper. Setup the ring stand, vacuum pump, anodization fixture + o-ring, and beaker of dilute phosphoric acid solution.



13) Cover the surface of the hotplate with clean Al foil. Form a small "boat" of Al foil to hold a glass cover slide. Place a clean cover slide in the boat. Now place the boat and cover slide onto the hotplate. Heat the cover slide (`5 minutes at a setting of ~5) and place a small chip of the Quickstick glue onto the cover slide. The glue should melt and flow within ~10 sec.

14) Place the photocathode onto the cover slide + glue and remove the assembly from the heat by removing the Al foil "boat" from the hotplate. Allow items to cool for several minutes.

Attaching the photocathode to a glass cover slide in this manner serves two purposes. First, it makes photocathode more robust for handling. This is less of an issue for 650 micron thick substrates then for the 325 micron substrates which historically have a ~20+% breakage rate. Second, it protects the rear surface of the photocathode from anodization. This is thought to be important based on the observation that indium does not appear to "wick" onto an anodized GaAs surface as well as surface without anodization. The photocathode is Indium soldered to a stalk for thermal transfer and mechanical stability reasons.

The Anodization Process

1) Center vacuum mask on photocathode.

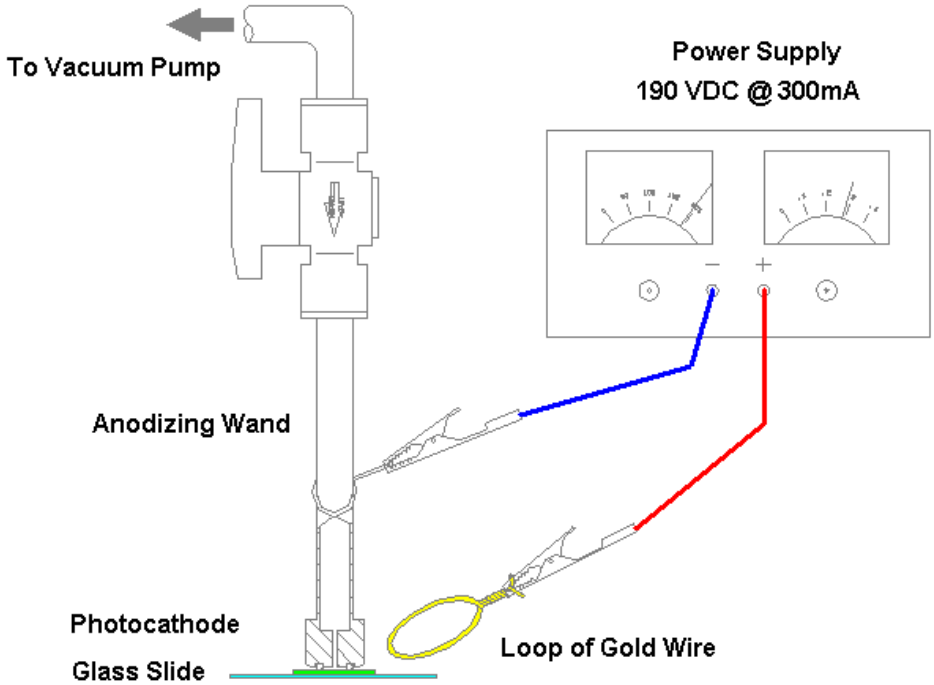
2) Invert anodization fixture + photocathode and attach to ring stand.

3) Insure the ring stand is electrically isolated from the workbench using a couple layers of the lent free clean room paper.

4) Connect the negative lead of the power supply (shown here as the blue wire) to the Al anodizing fixture.

5) Lower the anodization fixture + photocathode to depth of ~2 cm in the dilute phosphoric acid solution.

6) Connect the positive lead of the power supply (shown here as the red wire) to the gold electrode and bring this electrode to the edge of the photocathode without touching it.



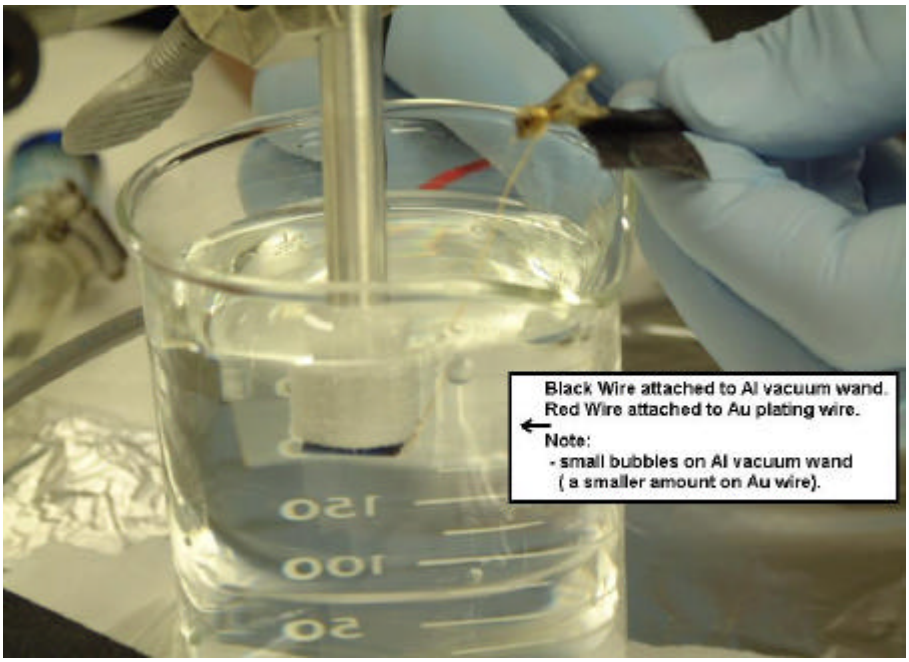
7) Turn on the power supply to ~20 V. Note bubble formation on photocathode and gold electrode wire.

8) Ramp up voltage in steps of 25 V with ~10 sec. duration at each step. Bubbles released from the phosphoric acid + water solution may become trapped between the vacuum mask holder and the photocathode. Such bubbles appear to partially "shield" the photocathode from the anodization process. If all large radius regions of the photocathodes are anodized to at least 100 V, such non-uniformities are not thought to present any significant operational concern.

9) At each voltage, position the Au electrode near each of the four corners without touching the photocathode. Hold the gold wire in each position until the color of that corner is consistent with the color associated with the power supply's anodizing voltage as listed in table on the following page.

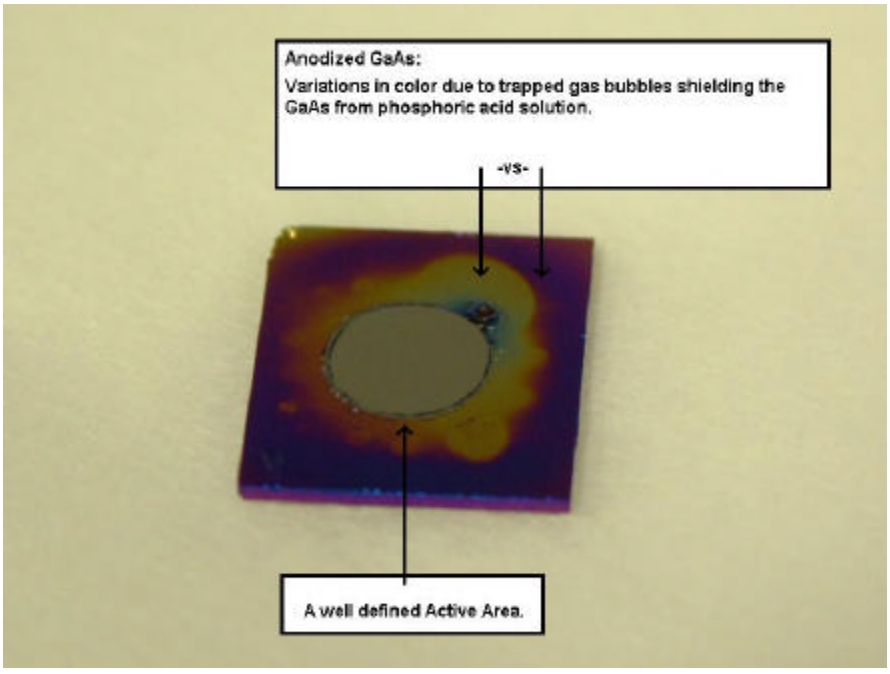
10) If the bubble formation becomes large enough to block direct view of the wafer, carefully remove the anodizing fixture from, and then re-insert into, the phosphoric acid solution. This along with gentle agitation of the solution around the wafer may reduce the quantity of bubbles on the surface.

11) Upon completion of the anodizing process clean beakers and tools with three rinses of fresh de-ionized water from Millipore-RO system. Cover items with lent free clean room paper and wrap in clean Al foil. Clean the workbench area and return supplies and bulk solvents to the appropriate storage cabinet. Pour used solvents into the appropriate used chemical bottles, marked with one X. The dilute phosphoric acid solution may be poured down the drain accompanied by running water.



Anodiztion voltage	Thickness of anodization[14]	Color
50 V	800 A	Barely visible
100 V	1900 A	Straw yellow
150 V	2700 A	Deep blue
200 V	3600 A	Deep yellow.

Table 1. Anodization layer thickness and color vs. voltage



[14] B. Swartz, F. Ermanis, and M.H. Brastad, The Anodization of GaAs and GaP in Aqueous Solutions, J. Electrochem. Soc., p 1088 - 1097 (1976)