

# Zinc Oxide-Based Thin-Film Transistor Experiments, Episode II

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## Solid Dielectric Progress

I've managed to cobble together a precursor solution that produces what appears to be reasonable aluminum oxide phosphate (AIPO) film on top some fluoride tin oxide (FTO) coated glass. Two problems have been encountered, one minor, the other significant. The first problem is that the film breaks up wherever it is too thick. This should be able to be fixed by using a makeshift spin coater instead of the “place some solution on slide and manually spread it across the slide” procedure used so far. The second problem is more difficult to address – every single tiny speck of dust that lands on the device before it has been fully baked causes the film to break up around it. In addition, the dust itself may be conductive. It is at this point that some sort of dust-free working space appears to be required. Dust on the semiconductor film is not, in and of itself, a big deal. However, shorts through the dielectric result in inoperable devices.

The procedure used to make the AIPO precursor solution follows.

### Made some aluminum hydroxide

- Combined 0.3 grams of aluminum isopropoxide and 3ml distilled water
- Heated with stirring to 80°C
- Added 2 drops (from a 24-26 drop per milliliter pipette) of 1M nitric acid
- Continued heating (uncovered) and stirring for about an hour
- Result was a somewhat cloudy white translucent gel
- Removed from heat and allowed to cool to room temp

### Made the aluminum oxide phosphate precursor

- Added 1ml of 14% hydrochloric acid to the aluminum hydroxide gel and stirred until dissolved
- Added 3 drops (from a 24 drop per milliliter pipette) of 85% phosphoric acid
- Stirred until the solution was clear

Although I believe the precursor solution made by the above procedure makes, after baking, a AIPO thin film, due to dust I've not yet produced a film I can demonstrate as actually being functional. However, in the interest of documenting the experiments, I've recorded the procedure anyway. The first part of the procedure is based on the information contained in section 5.6.1 of “[Ceramic Processing and Sintering](#)” by Mohamed N. Rahaman. The second part of the procedure is based on the paper “[Solution-Processed Aluminum Oxide Phosphate Thin-Film Dielectrics](#),” by Stephen T. Meyers, et al. Stephen T. Meyers' dissertation, “[Aqueous Chemistries for Oxide Electronics](#)” is listed on Oregon State University's ScholarsArchive. It most likely contains a lot of useful details (as well as costing nothing to obtain), but access to the dissertation is restricted until September 22, 2009.

If you have aluminum hydroxide available, you can substitute a molar equivalent amount of it for the aluminum isopropoxide and skip the first section of the procedure completely (just add it directly to the hydrochloric acid). You may have to stir for a much longer period of time.

Until I decide how to reasonably address the dust issue, and put together a working version of whatever that ends up being, I've decided to try improving the liquid dielectric based devices. Happily, I've had some measure of success here.

## Liquid Dielectric Device Improvements

Devices documented in episode I showed a best case on/off current ratio of about 8 to 1. Since then, the best measured device showed a on/off current ratio of 60 to 1. More significantly, it also showed a small signal voltage gain of approximately 3 when measured with a  $\pm 1.5$ -volt signal centered around a gate bias of 1.5 volts. These devices are still, and will always remain, extremely slow. Their characteristics also shift over time. They are, however, sufficient to construct an astable multivibrator, as is documented in the next section.

Since I've made a variety of changes it is difficult to know which ones are truly significant and which are mainly cosmetic without a lot of additional experiments. The one change that I am absolutely certain is significant is the new dielectric – if only because it is relatively stable for many hours. Other changes include the use of a zinc tin oxide thin film instead of pure zinc oxide thin film, spin coating instead of simply spreading the precursor solution around the slide, and some changes to the construction process intended to make the device easier to construct and more stable. It is difficult to set up definitive experiments due to the variations caused by the strictly manual construction process, and due to the fact that the dielectric is a liquid which is constantly changing. The changes in the liquid dielectric can probably be attributed to oxygen in the atmosphere, evaporation, changes in shape of the dielectric due to wicking and evaporation, and possibly electrolysis effects on both the thin film and the dielectric.

The better liquid dielectric is one of the components of Devcon's "2 Ton Clear Epoxy." The epoxy comes in a single dispenser that contains the two different components. One is clear and colorless, the other is clear and slightly yellow. It is the slightly yellow component that makes a good dielectric. I believe this is the hardening component, but which component is which is not labeled on the package, so I am not absolutely certain of that. I have not tried the hardening component of any other epoxy yet, but I assume the hardening component of any clear epoxy would work about as well. The hardener makes a dielectric with a relatively high resistance and it remains relatively stable for many hours, unlike prepared epoxy or the other various adhesives that, by design, change characteristics very quickly.

I need to point out that according to the MSDS for the epoxy the Devcon hardener contains nonylphenol and aminoethylpiperazine. Aminoethylpiperazine is corrosive and is toxic by contact with skin and by inhalation. Nonylphenol is harmful if swallowed, inhaled, or by contact with skin. The MSDS for the hardener can be found at [http://devcon.com/prodfiles/pdfs/sku\\_msds\\_377.pdf](http://devcon.com/prodfiles/pdfs/sku_msds_377.pdf).

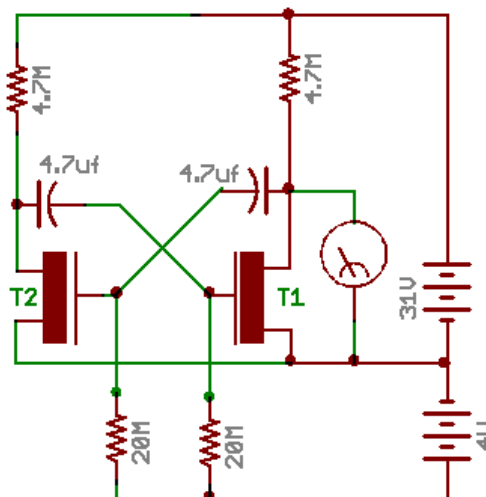
Some experiments with the earlier liquid dielectrics indicated that keeping the liquid off of the source

and drain contacts significantly affected the devices' small and large signal gain. However, several experiments using the new liquid dielectric that I carried out after constructing the astable multivibrator did not show the same effect, so it is unclear just how important it is to keep the liquid dielectric from touching the source and/or drain contacts. The high resistance of the new dielectric may be the reason the effect did not show up in my latest experiments, but that is simply conjecture at this point. There are too many differences from the earlier experiments to draw any definite conclusions beyond the obvious one that some contact of the source and drain using the new dielectric did not significantly affect the gain of the device. More experiments are definitely needed in this area.

Zinc tin oxide makes a much more conductive thin film than zinc oxide, as tin acts as an N dopant for zinc oxide. The zinc tin oxide precursor solution I've been using also works better as a spin coating than the zinc oxide precursor solutions, probably due to the fact that the zinc tin oxide precursor is more viscous. I've tried the same zinc tin oxide precursor solution using the "put solution on slide and manually spread it across the slide" method and spin coating. The devices produced by spin coating show a better on/off ratio and voltage gain. However, since I have been placing the source, drain and gate components on the film by hand there is a large variation in the geometry of each device, so this observation should be taken with a grain of salt or two.

## An Astable Multivibrator

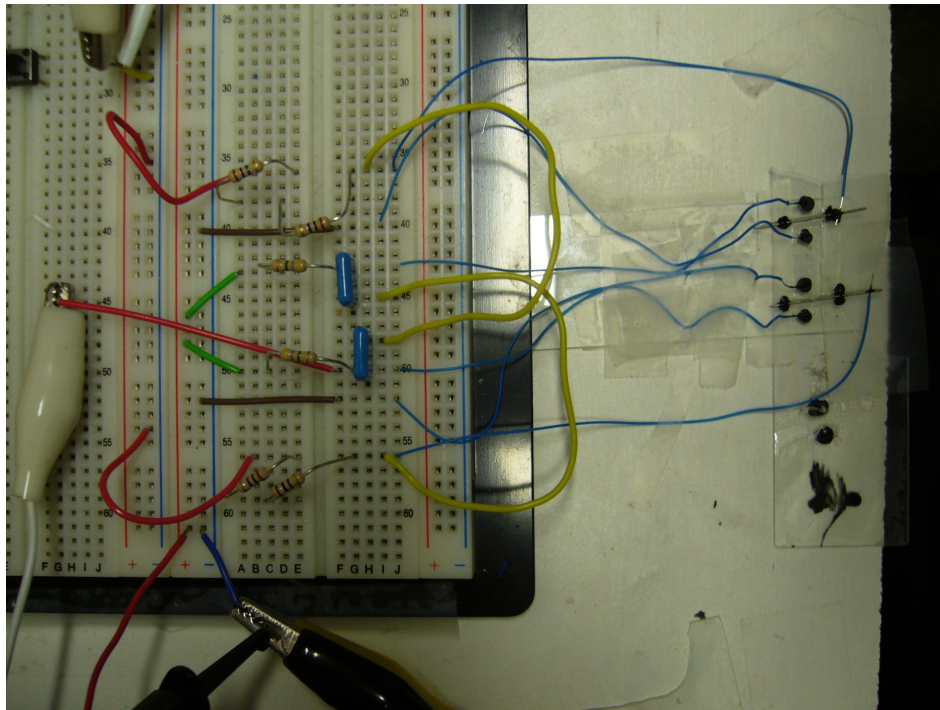
In order to demonstrate fairly conclusively that the devices do exhibit a voltage gain, I've borrowed an idea from Nyle Steiner's flame triode experiment and built an astable multivibrator circuit using two liquid dielectric thin-film devices constructed on a single substrate.



*Figure 1: Astable Multivibrator Schematic*

Figure 1 shows the schematic used to build the astable multivibrator using homemade zinc tin oxide thin-film active devices. Figure 2 shows the entire breadboarded circuit (minus the PC-connected DMM) and the active devices. Figure 3 shows a labeled closeup of the active devices. The four large unlabeled black spots are drops of conductive glue holding the wire segment acting as a gate in place on the scotch tape, and as such they are insulated from the semiconducting film.

film is quite transparent, so it is not really identifiable in the image, but it pretty much covers the entire slide. The slide broke because I did not wait for the hotplate to cool down a bit before removing the slide. This image was taken before the liquid dielectric was added to the devices.

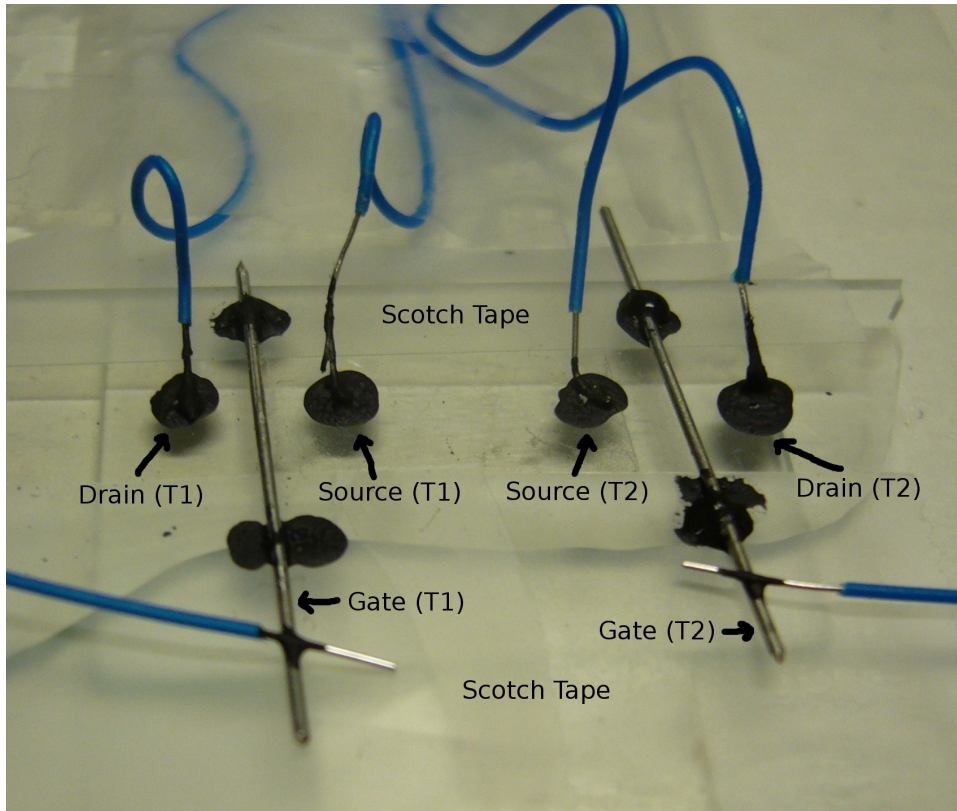


*Figure 2: Breadboarded Circuit and Active Devices*

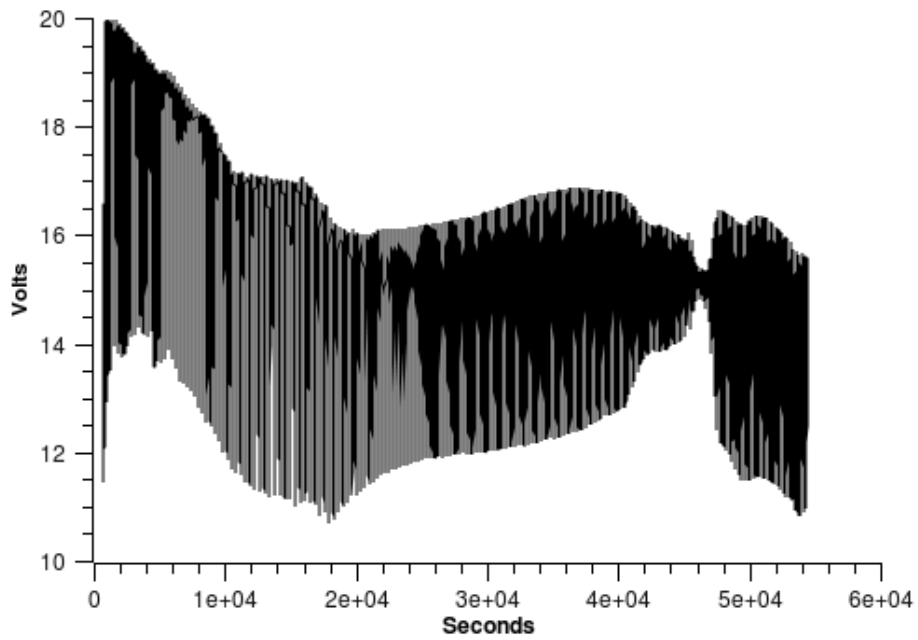
Although several individual devices using the new dielectric built before the astable multivibrator exhibited small signal voltage gain, they did not do so when the gate bias voltage was at or near zero. This observation led me to attempt to bias the devices using a voltage in the middle of their region of greatest gain, rather than simply connecting the 20-megohm resistors (implemented using two 10-megohm resistors in series) to the main 31-volt power supply. In hindsight this may not have been necessary.

The circuit oscillated with a period of approximately 4 to 6 minutes for about 16 hours. Once it started oscillating I did not touch or otherwise make changes to the device until after it stopped.

Figure 4 shows the operation of the astable multivibrator over the majority of its lifetime. It continued operating for about an hour longer than the data in the graph indicates, but the last hour or so of the data was lost when QtDMM crashed. The scale is too large to see the individual oscillations, but it does give a good picture of the overall operation. I assume that the drift in the center voltage of the signal was caused by changes in temperature and in the device's characteristics over time. I do not have any good explanation for the signal's amplitude reduction and recovery near the right side of the graph.



*Figure 3: Zinc Tin Oxide Device Closeup*



*Figure 4: Majority of Operational Lifetime*

Figure 5 and Figure 6 show the first and last hour's worth of data in more detail.

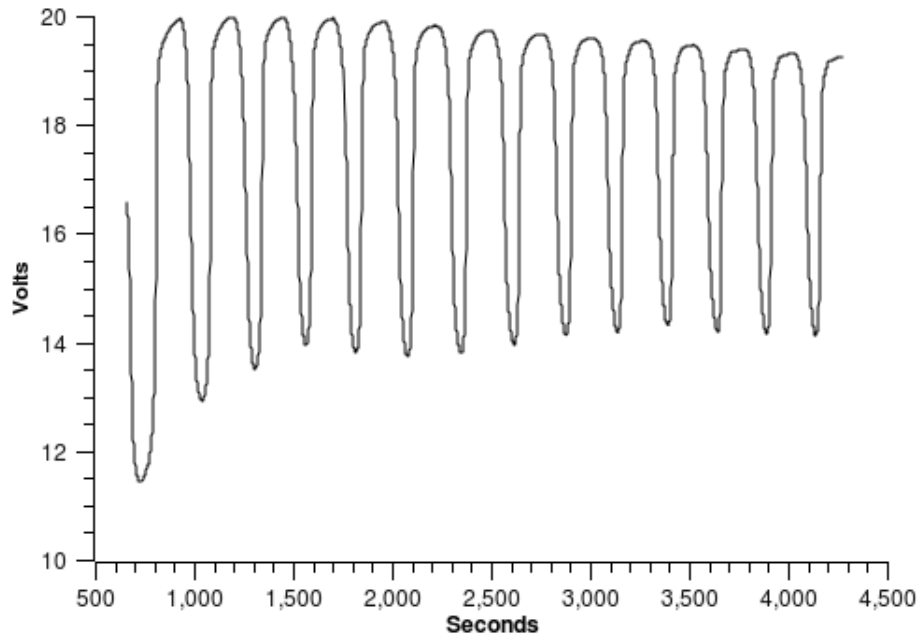


Figure 5: First Hour of Operation

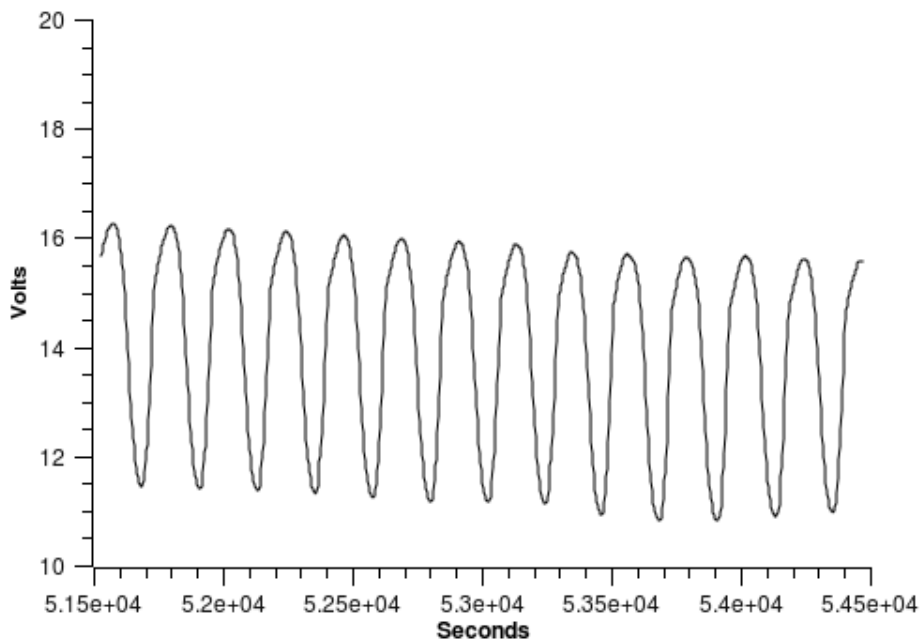


Figure 6: Last Hour of Operation

## Zinc Tin Oxide Procedure

The following procedure was used to produce the zinc tin oxide precursor solution and the coated slide for the astable multivibrator. I don't believe it is a particularly good precursor solution, but it does produce thin films that make devices with better characteristics than the pure zinc oxide thin films used earlier.

### Mixed Up Precursor Solution

*This solution should be used up relatively quickly (within a couple of hours, ideally).*

- 1 gram zinc oxide
- 3 ml 2-propanol
- Stirred until completely dissolved (the solution was clear and colorless)
- Added approximately 0.02 of tin(II) chloride
- Added 10 drops (from a 24-26 drop per milliliter pipette) of 98% acetic acid
- Stirred for half an hour (the solution had a slightly cloudy appearance)

### Spin-Coated the Slide

*Some information about using a brushless PC fan as a spin coater can be found at <http://www.chemistry-blog.com/2007/01/13/pimp-my-spin-coater>. For the one I made, I removed the blades from the fan, enclosed the entire fan in a plastic food container, and used double-sided tape to hold the microscope slide down. I strongly recommend enclosing the entire fan in a solid container in order to keep the slide from flying across the room when the double sided tape fails, as it most certainly will do at some point.*

- Placed microscope slide in the spin coater
- Placed 10 drops of the zinc tin oxide precursor solution on the slide and spread it across the slide
- Placed cover on spin coater and turned on at low setting for 30 seconds.

### Baked the Slide

*If you let the hotplate cool a bit before removing the slide it will significantly decrease the possibility of the slide breaking due to thermal stresses. If only I would remember that.*

- Placed the slide on the hotplate.
- Turned the hotplate to its highest setting (540°C).
- Waited 30 minutes
- Turned off hotplate and removed slide

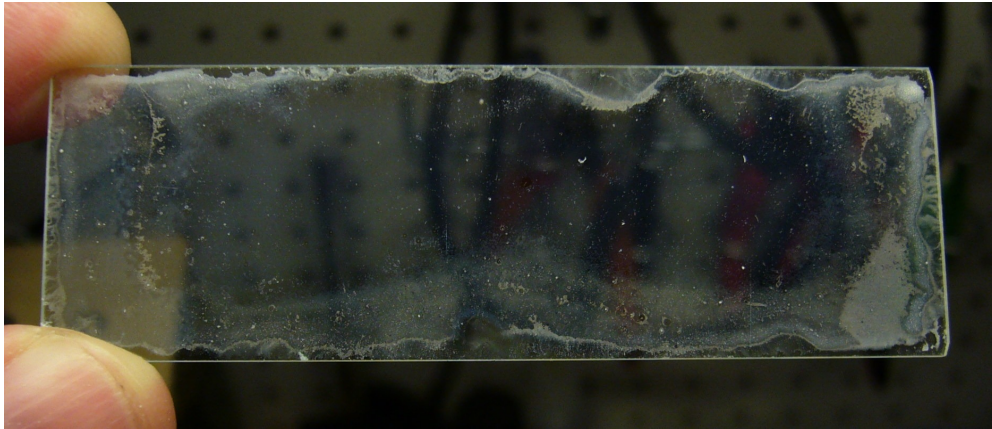
## Possible Future Improvements

Just about everything at this point is subject to significant improvements.

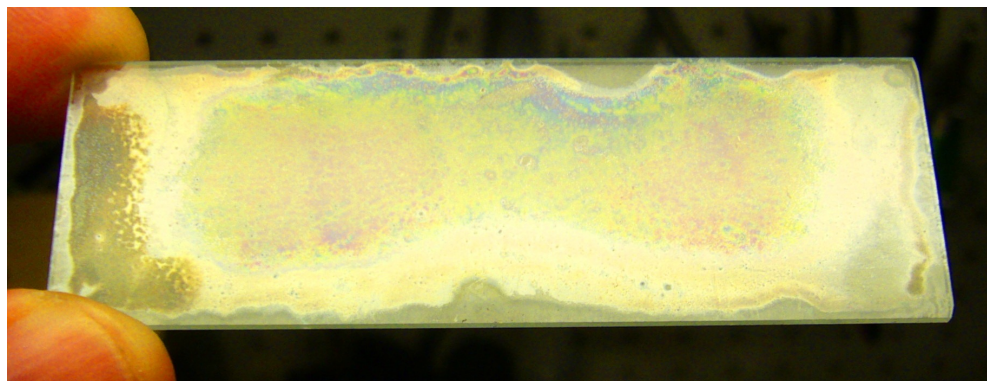
- The precursor solution definitely needs work. There are different published formulas that would probably be better, but I always end up being short one of the ingredients. More experiments to

find a better formula for which I have or can get all of the elements are definitely called for. Also, the ratio of zinc to tin needs to be worked with to find an optimal value, as does the overall dilution of the solution. Finally, there are a lot of other dopants to try out such as indium, gallium, aluminum, boron, etc., and various combinations of the same.

- My slide cleaning technique still needs improvement, as does my spin coating technique. Figure 7 is a picture of one of several coated slides I made shortly after the one used for the astable multivibrator. Figure 8 is the same slide angled slightly so that the reflection interference pattern created by the film can be seen. The saturation has been significantly enhanced so that the relative colors are easier to make out. The interference pattern on a well-coated slide should appear as a single color that changes slightly across the whole of the slide (due to variations in viewing angle). These are, however, much better than the ones made by simply spreading the solution across the slide with the side of a pipette. Quantifying the spin coating speed would be a step in the right direction as well.



*Figure 7: Zinc Tin Oxide Coated Slide*



*Figure 8: Zinc Tin Oxide Coated Slide – Reflection Interference Pattern*

- Some understanding of how baking temperature and time affect the characteristics of the film should be obtained. However, this is difficult to do until the next bullet point is addressed.
- It is difficult to compare devices as they have all been constructed completely by hand, and as



such the various dimensions of the devices vary a lot. I've started experimenting with placing the source and drain contacts by using a stencil. The first attempts all failed because the glue wicked under the stencil, but I've found that if I make the stencil out of the adhesive-backed portion of a Post-it® note the adhesive keeps the glue from wicking under the stencil. Once I have a good repeatable method worked out I should be able to start meaningfully comparing the devices made from different films. Also, I should be able to make a reasonably accurate measurement of the contact resistance presented by the conductive glue contacts.

- At some point in the future I want to try patterning the semiconducting film. It should be possible to make both the active devices and the resistors using the zinc tin oxide thin film and to connect them together using the conductive glue. Capacitors would be more difficult, especially with the large values needed. Unlike tin oxide films, primarily zinc oxide films should be much easier to etch.
- I need a better data recording device and software. It is really annoying when QtDMM crashes as it does not spool the data to disk, so when it crashes the collected data is lost. Also, the DMM I am using goes “crazy” in a couple of specific voltage ranges, oscillating between zero and several small voltages when the input voltage falls within the problematic ranges. Finally, I can only record a single channel. Linear Technology makes some really nice-looking A to D converters that could be hooked up via an Arduino to a computer. Add a D to A converter and device characterization data collection could be fully automated, which would mean a lot less time spent toggling switches or turning variable resistors.