Process 2.3

Sol-gel PZT

1.0 Process Summary

1.1 The sol-gel PZT process is a method for spin-on deposition and crystallization of thin-film lead zirconate titanate (0.53/0.47).

2.0 Material Controls & Compatibility

2.1 The number one consideration for any researcher considering this process is the inclusion of **lead** (Pb). For many of the tools in the Nanolab, lead is a contaminant and inclusion of PZT in your film stack will prevent your wafers from entering many tools.

2.2 Crystallization of PZT is achieved using rapid thermal annealing. Improper crystallization will result in formation of non-piezoelectric pyrochlore-phase PZT.

2.3 It is advisable to avoid high-temperature (>300^{o}C) processing post-crystallization as elevated temperatures will affect the PZT film.

3.0 Applicable Documents

3.1 (axcelis) Fusion M200PCU photostabilizer system

3.2 (headway1/headway2) Headway photoresist spinner

3.3 (msink2) Msink2 PR strip sink (general purpose)

3.4 (msink6) VLSI MOS Clean

3.5 (msink8) Non-MOS Clean

3.6 (msink16/msink18) General purpose sink

3.7 (msink20) Diamond seeding and the lift-off process (general solvent sink)

3.8 (primeoven) HMDS

3.9 (rtp1) AccuThermo AW610 RTP for III/V or PZT

3.10 (tystar2/tystar3/tystar4) dry/wet oxidation & anneal atmospheric

4.0 Definitions & Process Terminology

4.1 Piezoelectric effect: accumulation of mechanical strain due to imposed electrical charge, or of charge due to imposed mechanical strain, that occurs due to asymmetry in certain chemical compounds.

4.2 PZT: lead zirconate titanate, most often of chemical formula $Pb[Zr_{0.53}Ti_{0.47}]O_3$. PZT is a ceramic compound that exhibits strong piezoelectric properties.

4.3 Pyrolysis: chemical decomposition due to heating.

4.4 Rapid thermal processing: rapid heating, on the order of several hundred degrees

4.5 Perovskite: a specific crystalline structure exhibited by piezoelectric PZT

4.6 Pyrochlore: the non-piezoelectric phase of PZT

5.0 Safety

5.1 While the lead in PZT is comparatively stable, the lead precursor, Lead (II) Acetate Trihydrate, is quite toxic. Care should be taken to avoid the generation of dust while working with the precursor chemicals. Standard PPE (triple-polymer gloves, apron, and face shield) should always be used when mixing or working with the sol-gel solution or any of the component chemicals.

5.2 Sol-gel solution has a strong odor due to large quantities of acetic acid present. All mixing should be performed at one of the general purpose sinks (msink16/18) and any bottles of solution should be kept tightly closed when not in use.

5.3 Pyrolysis of PZT requires the use of high-temperature hot plates. PEK-tipped wafer tweezers will melt if used to transfer wafers during the pyrolysis steps.

6.0 Process Data

6.1 See: Yiping Zhu *et-al*, "A piezoelectric unimorph actuator based tip-tilt-piston micromirror with high fill factor and a small tilt and lateral shift." In: *Sensors and Actuators A: Physical* 167.2 (June 2011), pp 495-501. DOI:10.1016/j.sna.2011.03.018

7.0 Process Explanation

7.1 The sol-gel PZT process consists of the following steps: substrate preparation, sol-gel precursor solution preparation, sol-gel PZT deposition, PZT wet-etch patterning, and PZT polling.

7.1.1 Substrate preparation. In order to ensure growth of perovskite PZT, a specific substrate stack is required. A layer of wet thermal oxide and a thin Ti/Pt electrode layer provide the proper epitaxial substrate for the growth of good-quality PZT.

7.1.2 Sol-gel solution preparation. The sol-gel deposition process uses a solution of lead, titanium, and zirconium precursor chemicals. This solution must be mixed by the researcher prior to usage, and requires a fairly substantial amount of preparation time. The recipe produces approximately 540ml of solution, or enough to produce a couple of dozen sol-gel wafers. While this quantity may seem excessive, scaling the recipe down to smaller batches is not recommended due to the difficulty in precisely measuring smaller quantities of the component liquids. However the solution *may* be stored for some time (a couple of months, at least, though exact "shelf life" has not been determined) in the photoresist storage refrigerator in the 381 service chase.

7.1.3 Sol-gel deposition. Deposition of sol-gel begins with the precursor solution. Using a pipette and a wafer spinner, a thin (~92nm) layer is applied to substrate and subsequently pyrolized using a series of hotplates. The resulting film, however, is amorphous, and must be crystallized. Rapid thermal processing is essential, here, as the pyrochlore phase of PZT forms at lower temperatures than the perovskite phase. This deposition, pyrolysis, and crystallization process is repeated for a maximum of five layers.

7.1.4 PZT patterning. Patterning of sol-gel PZT is best accomplished by wet etching. An ambient bath of 10:1 BHF is used as the primary etchant but tends to leave a residue behind. As a result, a secondary, cleaning etch of $HCl:H_2O$ 2:1 at 45^oC is required to remove this residue from the substrate.

7.1.5 PZT polling. Because sol-gel-derived PZT is inherently polycrystalline, it must be "polled" electrically. This process forces the crystalline domains to align and greatly increases the performance of the resulting film. Polling, however, should be performed as a *last* step in processing, as any heated steps in the process flow will tend to cause a partial loss of

polling. Additionally, for the polling to be effective, the PZT must also be heated above its glass transition temperature.

7.2 Two of the most important aspects of a successful sol-gel run are *patience* and *cleanliness.* Do not try and rush the mixing steps, *especially* the cool-down step, as this will cause partial crystallization of the solution prior to deposition. Let the solution settle after-filtering and before deposition, as this will help to remove any bubbles that are present. Ensure that the substrate onto which you are spinning sol-gel is as clean as possible in order to ensure good epitaxial growth.

8.0 Process Procedure

8.1 Wafer preparation

8.1.1 Start with prime-grade, **four inch** wafers. SOI is recommended if released devices are planned.

8.1.2 Thermal growth of 1um of wet oxide using tystar2/tystar3/tystar4

8.1.2.1 Standard pre-furnace sink cleaning in msink8, msink6.

8.1.2.2 Wet oxide growth of 1um of wet thermal oxide using standard furnace recipe

8.1.3 Lower electrode deposition via outsource

8.1.3.1 20nm of Ti followed by 200nm of Pt

8.1.3.2 Must be **sputtered**, not evaporated

8.2 Sol-gel solution mixing at msink16/msink18. All steps performed while covered. Yields approximately 540ml.

8.2.1 Combine 9.92g zirconium (IV) propoxide and 5.45g titanium (IV) isoproxide. Mix for five (5) minutes.

8.2.2 Add 10.3g acetic acid. Mix for five (5) minutes.

8.2.3 Add 16g isopropyl alcohol. Mix for five (5) minutes.

8.2.4 Add 16.86g lead (II) acetate trihydrate.

8.2.4.1 Using a hotplate, heat to 90^{o}C while mixing

8.2.4.2 Turn off hotplate, allow solution to cool to room temperature

8.2.4.3 At msink20, sonicate solution for five (5) minutes

8.2.5 Add 15g acetic acid and 5.6g DI water. Mix five (5) minutes

8.2.6 Add 16g isopropyl alcohol. Mix five (5) minutes

8.2.7 Add 10.5g acetic acid. Mix five (5) minutes

8.2.8 Add 5g isopropyl alcohol. Mix for **12-24hrs**.

8.2.9 Let solution settle. Using a 0.2um filter, filter solution into large-size Nalgene bottle.

8.3 Sol-gel dispensing, pyrolysis, and crystallization

8.3.1 Sol-gel dispensing at headway1/headway2

8.3.1.1 Clean and prep wafers using acetone, IPA, DI rinse followed by N2 or SRD dry.

8.3.1.2 Filter solution using 0.2um syringe filter and syringe. Dispense into petri dish, cover and wait 5 minutes.

8.3.1.3 Using pipette, dispense enough sol-gel to cover the wafer. Wait 10-15s to allow any bubbles time to settle/pop.

8.3.1.4 Spin wafer for 3s at 500 rpm (1000 rpm/s ramp)

8.3.1.5 Spin wafer for 30s at 3,000 rpm (1000 rpm/s ramp)

8.3.2 Hot plate pyrolysis (two hot plates required)

8.3.2.1 Bake wafer for one (1) minute at 200^{o}C

8.3.2.2 Bake wafer for five (5) minutes at 400^{o}C

8.3.2.3 Bake wafer for one (1) minute at 200^{o}C

8.3.2.4 Cool wafer for five (5) minutes on Technicloths

8.3.3 Crystallization in RTP1

8.3.3.1 Set O_2 to 40-50mm, wait 3 minutes

8.3.3.2 Run the following RTP1 recipe:

8.3.3.2.1 Delay 10s

8.3.3.2.2 Ramp 20s to 200^{o}C

8.3.3.2.3 Steady 30s at 200^{o}C

8.3.3.2.4 Ramp 8s to 700^{o}C

8.3.3.2.5 Steady 60s at 700^{o}C

8.3.3.2.6 Ramp 40s to 500^{o}C

8.3.3.2.7 Steady 30s at 500^{o}C

8.3.3.2.8 Ramp 100s to 200^{o}C

8.3.3.2.9 Delay 60s (can remove once at 200^{o}C)

8.3.4 Repeat 8.3.1-8.3.3 a total of **five** (5) times for a total of ~460nm of PZT.

8.4 Sol-gel wet etching at msink16/msink18

8.4.1 Wafer litho/prep

8.4.1.1 Standard acetone, IPA, DI, SRD rinse

8.4.1.2 2hrs (minimum) dehydration bake @ 120^{o}C in OvenVWR

8.4.1.3 HMDS application via primeoven (recipe 0 preferred)

8.4.1.4 Apply 1.1um of i-line resist. Expose and develop per i-line standard

8.4.1.5 Using axcelis, run recipe A to crosslink the i-line resist.

8.4.2 Timed etch

8.4.2.1 BHF 10:1 at room temperature

8.4.2.1.1 Etch until film is cloudy and white (will take 1-3 minute)

8.4.2.1.2 Rinse with DI

8.4.2.2 HCl clean (residue)

8.4.2.2.1 Solution of HCl:H_2O 2:1 at 45^oC

8.4.2.2.2 Etch until white film is gone and clear/shiny lower electrode remains (10-15s)

8.4.3 PR strip via long soak in msink2

8.5 Sol-gel polling (final processing step post-release)

8.5.1 Heat device on hot plate to device temp of >90^oC

8.5.2 Apply 20Vdc for several minutes

8.5.3 Turn off hot plate and allow to cool while still applying voltage

9.0 Troubleshooting Guidelines

9.1 PZT has "streaks." This is most-often caused by bubbles in the sol-gel. Allowing more time after dispensing and before spinning will help to minimize this.

9.2 PZT is "cloudy." This can be caused by contamination, or by bubbles, and is indicative of a poor-quality PZT film. A good-quality film should be mirror-like in appearance (see Figure 1).

9.3 PZT exhibits a color gradient across the wafer. This is expected. Due to the spin-on nature of the PZT film, there will inherently be thickness-variations across the wafer. However, the edge regions of the wafer are typically not usable, anyway, so this non-uniformity is less of a problem.

10.0 Figures & Schematics

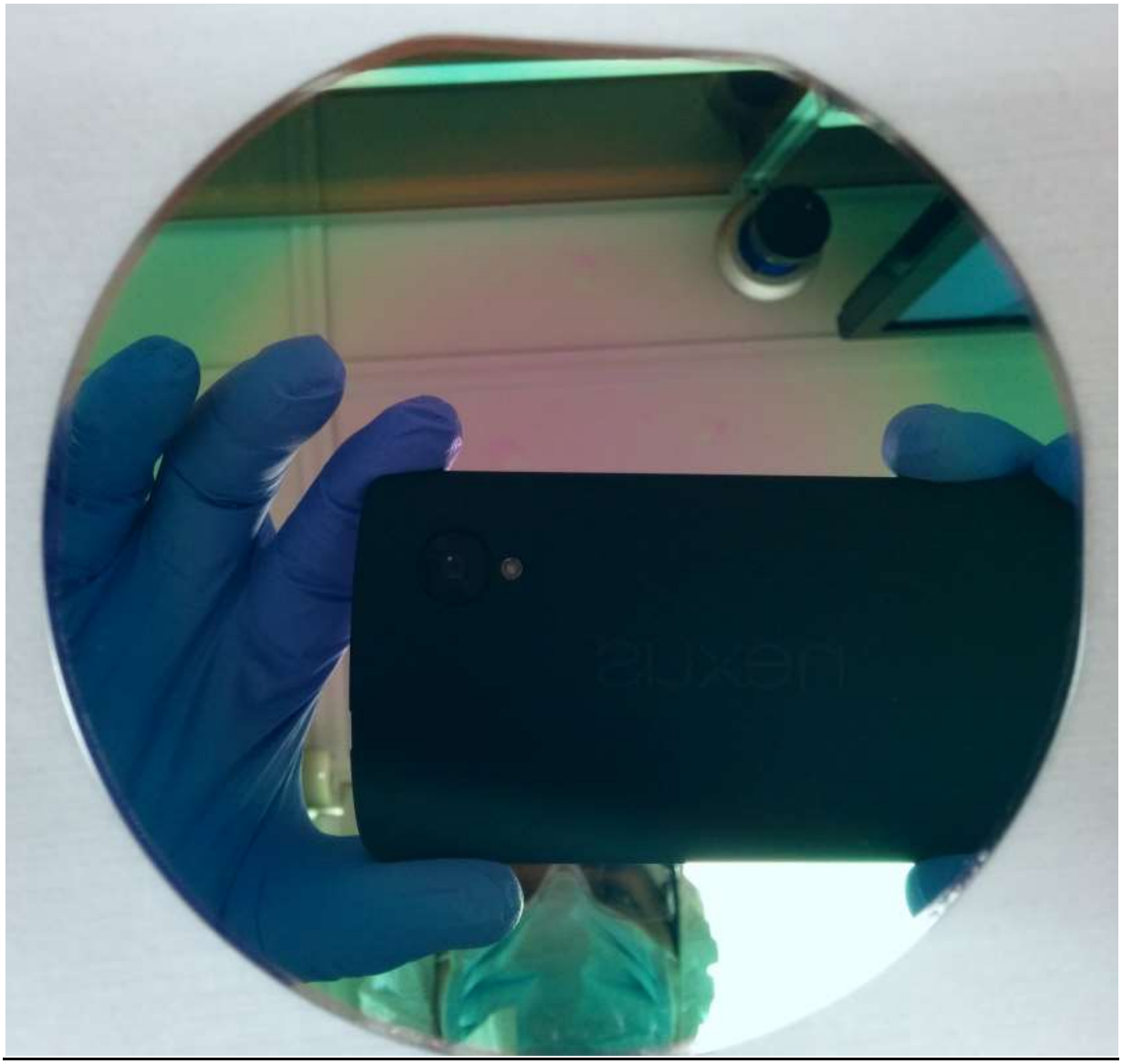

Figure 1 A good-quality, five-layer sol-gel PZT film

11.0 Appendices

11.1 Miscellaneous information that does not fit into above categories should be placed here.