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# Importance Of Solution Chemistry In Preparing Sol–Gel PZT Thin Films Directly On Copper Surfaces

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The ferroelectric material lead zirconate titanate (PZT) has traditionally been considered incompatible with base metal technology because PbO volatility makes conventional thermodynamic equilibrium processing impractical. However, by strategically designing solution chemistry and processing conditions to avoid interfacial reaction, chemical-solution-deposited PZT films can be prepared on copper surfaces without oxidizing the base metal or cracking the oxide film. A limited set of thermal and atmospheric processing conditions to kinetically maintain an unoxidized copper substrate are available and not necessarily optimal for processing sol–gel films. Solutions processed within these confined conditions must form gels with sufficiently reduced organic content and properly consolidated gel networks such that phase-pure and crack-free ceramic films can be crystallized. The current work explores three solution chemistries that use different chelating ligands: alkanolamines, acetylactone, and acetic acid. It is found that the alkanolamine solution frustrates perovskite formation and is prone to cracking under processing conditions compatible with the copper substrate. The introduction of water vapor into the processing atmosphere is moderately successful in resolving these issues. Using a more volatile chelating ligand (acetylacetone or acetic acid) shifts the thermal process window nearer a copper-compatible regime. Because of its weaker chelation strength, acetic acid solutions are most compatible with the processing constraints required for copper substrate compatibility.

## Introduction

Ferroelectric thin films have historically been fabricated on noble metal or conductive oxide bottom electrodes to minimize substrate oxidation and interface reactions during high-temperature crystallization of the ferroelectric oxide. Several groups have recently demonstrated ferroelectric thin films deposited directly on base metal bottom electrodes.[1–7] Base metals are attractive commercially because of their low cost and simple patternability; technologically, base metals offer lower resistivities and alluring functionality such as ferromagnetism and shape-memory response.

Unlike early reports of ferroelectric films on base metals that included interfacial layers,[8–11] recent reports have demonstrated ferroelectric/base metal interfaces devoid of reaction layers.[1,2,6,7] Abrupt interfaces in the $BaTiO_3$ family of ferroelectrics are achieved by a thermodynamic equilibrium approach akin to the methodology of the multilayer capacitor industry.[1,2,4,5,7,12] Without an interfacial layer, ferroelectric films on base metals exhibit properties comparable or superior to analogous films deposited on noble metal or conductive oxide electrodes.

Our recent report[3] of lead zirconate titanate (PZT) thin films deposited directly on copper foils deviates from the traditional thermodynamic equilibrium process. Equilibrium processing in the PZT system is impractical because of the lead constituent; $PbO/Cu_2O$ has a narrow equilibrium process window, and PbO volatility complicates the thermodynamics. Instead, our strategy involves using chemical solution deposition to avoid reactions at the interface by identifying the specific process variables acting as sources for oxidation. A process flow, including careful solution chemistry selection and a novel composite gel architecture, were designed to circumvent these sources of oxidation. This paper explores the importance of adjusting PZT solution chemistry—particularly the chelating ligand—to achieve processing conditions compatible with copper substrates.

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**Table 1. Summary of Process Conditions Explored for Depositing CSD PZT Thin Films on Copper Surfaces (processing conditions for each of the three chemistries are numerically identified throughout the table)**

| | |
|---|---|
| solution | 1. alkanolamine chemistry (0.1 M)<br>2. acetylacetone chemistry (0.3 M)<br>3. acetic acid chemistry (0.4 M) |
| spin | 1. 3000 rpm, 30 s<br>2. 3000 rpm, 30 s<br>3. 3000 rpm, 30 s |
| drying | 1. 250 °C/5 min/air<br>2. 250 or 300 °C/5 min/air<br>3. 250 or 300 °C/5 min/air |
| thermolysis | 1. 400 °C/15 min/air, $N_2$, 1% $H_2$, or water vapor<br>2. none<br>3. 400 °C/15 min/1% $H_2$<br>*repeat 4 to 5 layers* |
| anneal | 1. 650 °C/30 min/$N_2$ or water vapor<br>2. 650 °C/30 min/$N_2$<br>3. 650 °C/30 min/$N_2$ |
| film | 1. four layers, ~400 nm total thickness<br>2. four layers, ~300 nm total thickness<br>3. five layers, ~700 nm total thickness |

## Experimental Section

Three chelated sol–gel–solution chemistries with composition $Pb_{1.15}(Zr_{0.52}Ti_{0.48})O_3$ were prepared. All solutions used methanol as a solvent. Metalorganic precursors consisted of lead acetate trihydrate powder (Sigma-Aldrich, 99+% purity), titanium (IV) isopropoxide (Sigma-Aldrich, 99.999% purity), and zirconium (IV) propoxide (70 wt% in 1-propanol, Sigma-Aldrich). The first solution used alkanolamines (diethanolamine and triethanolamine) to chelate the metal alkoxides and is based on previous work by Kim et al.[13] This solution is prepared by first reacting the metal alkoxides with the alkanolamines at 80 °C in methanol followed by dissolution of the lead precursor. The final solution is diluted with methanol to achieve a 0.1 M solution. The second solution used acetylacetone as a chelating agent. This solution is prepared by reacting acetylacetone with the transition metal alkoxides in a 4:1 ratio at 90 °C in methanol. The lead acetate trihydrate is then added to the solution and allowed to dissolve at 90 °C for 90 min under constant stirring. The final solution has a 0.3 M concentration. The third PZT solution was chelated with acetic acid and is modeled after the inverted mixing order chemistry originally published by Assink and Schwartz.[14] This chemistry first chelates the metal alkoxides with acetic acid sans solvent. The chelated metals are then dissolved in methanol, and lead acetate trihydrate is added. The final solution is diluted with methanol and water to achieve a molarity of 0.4 M.

All films were spun on 18 $\mu$m thick copper foils (Oak-Mitsui, PLSP 0.5 oz foil) at 3000 rpm for 30s. Standard procedure involved drying each layer on a hot plate at 250 °C for 5 min. A few films prepared from the acetylacetone chelation chemistry were dried at 300 °C in an attempt to completely pyrolyze the organics during the drying step. Following drying, some films underwent a higher temperature pyrolysis/thermolysis treatment, carried out in a 2 in. diameter controlled atmosphere tube furnace. Nitrogen or forming gas (99% $N_2$ + 1% $H_2$) was flowed at ~1 slm to control the furnace atmosphere. To achieve a "water vapor" atmosphere, nitrogen was bubbled through a heated (~75 °C) water bath. At this bath temperature, the calculated water vapor pressure is 300 Torr. Water condensation on the interior tube surface was avoided at the gas entrance by heating with heat tape (~110 °C). Condensation did occur at the opposite end, where films were allowed to cool in the given atmosphere. Films consisted of 4–5 CSD layers and had a final film thickness ranging from 300 to 700 nm depending on the solution chemistry. Films were crystallized at 650 °C for 30 min in a flowing nitrogen atmosphere unless otherwise noted. Although the ~1 ppm $O_2$ impurity in the nitrogen source is thermodynamically sufficient to oxidize copper at this temperature, the overlying PZT film can kinetically limit this oxidation process. A summary of the process variables explored in this paper are presented in Table 1.

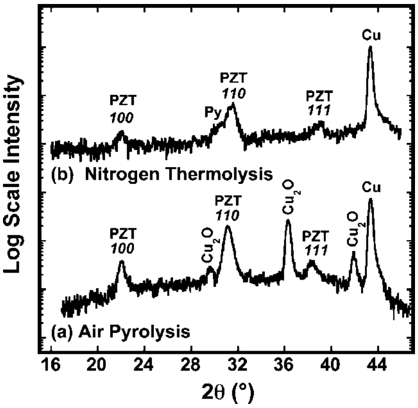

**Figure 1.** X-ray diffraction patterns comparing the phase assemblage of PZT films deposited on copper using an alkanolamine chelated solution: (a) pyrolyzed at 400 °C in air and (b) thermolyzed at 400 °C in nitrogen. Both samples were crystallized at 650 °C in nitrogen.

PZT films were characterized by optical microscopy, X-ray diffraction, and dielectric response. X-ray diffraction data was collected on a Bruker AXS D-5000 X-ray diffractometer equipped with an area detector. The copper anode was operated at 40 kV/30 mA and scans were collected for 15 min. Platinum top electrodes (~200 $\mu$m diameter) were sputtered through a shadow mask for electrical measurement. Dielectric data were collected on a HP 4192A impedance analyzer. Dielectric tunability measurements used an oscillator voltage of 50 mV. Results are compared to "device-quality" CSD PZT films prepared on noble metal or conductive oxide electrodes, which have peak dielectric constants of 700−1100, dielectric loss below 0.05, and dielectric tuning of 60−70%.

## Results and Discussion

**1. Alkanolamine Solution Chemistry.** PZT solutions using alkanolamine chemistries show fewer solution-aging effects than solutions chelated with other ligands, making them preferable for commercial use. However, for high-quality ferroelectric films to be obtained, alkanolamine chemistries require aggressive pyrolysis conditions to fully remove the alkanolamine ligands prior to crystallization. Intermediate pyrolysis steps of 400−450 °C for 5–20 min in oxidizing atmospheres (air or $O_2$) are often used to achieve full pyrolysis and volatilization of alkanolamine ligands.[8,15,16] Previously, we demonstrated that thin-film deposition processes conducted in air on copper substrates must be kept below ~250 °C to kinetically avoid $Cu_2O$ formation at the interface.[3] This constraint makes traditional processing of alkanolamine solutions incompatible with copper substrates; we demonstrate this in Figure 1a, which reveals massive

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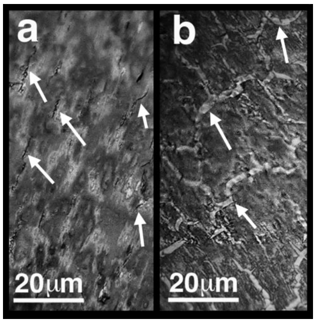

**Figure 2.** Optical microscopy images illustrating the cracks that develop when the alkanolamine chelated solution undergoes a 400 °C thermolysis in nitrogen (a) after thermolysis and (b) after crystallization at 650 °C in nitrogen. Arrows indicate crack edges.

copper oxidation for an alkanolamine film processed under these standard conditions.

As illustrated in Figure 1b, changing the pyrolysis atmosphere from air to nitrogen reduces copper oxidation. However, films processed in nitrogen are prone to cracking as shown in Figure 2. Gels treated in nitrogen atmospheres are believed to primarily undergo a thermolysis process (heat-driven decomposition) rather than a pyrolysis process (oxidative combustion).[17] Thermolysis is less likely to combust the alkanolamine ligands into smaller, more volatile organic species. Consequently, for a comparable thermal excursion, the gels thermolyzed in nitrogen are expected to retain more organic content. Higher organic content frustrates perovskite formation, as is evident in diffraction pattern (b) of Figure 1, which indicates the presence of the pyrochlore phase. This incomplete organic removal inhibits formation of the metal–oxygen–metal (M–O–M) gel network. Without the rigidity of this network, the gel cannot maintain contiguity upon densification and the film cracks. To improve organic ligand removal, two approaches are investigated: (1) the introduction of water vapor into the thermolysis atmosphere and (2) changing the chelating agent to a more volatile species (discussed in section 2).

Water vapor in the thermolysis atmosphere increases the hydrolysis reaction rate, thereby accelerating the ligand removal process. Previous work in other sol–gel systems has demonstrated that water vapor atmospheres improve organic extraction, reduce process temperatures, and alleviate cracking.[18–20] Similar results are observed in this system. Figure 3 demonstrates the reduction in film cracking when using a nitrogen atmosphere containing water vapor. For film cracking to be completely suppressed, water vapor was required during crystallization. Unfortunately, the water vapor atmosphere is too aggressive for the copper substrate. Copper oxidation is evident in the diffraction patterns shown in Figure 4. Water vapor may react directly with copper or increase the oxygen content in the process atmosphere via the gas phase reaction $H_2O \rightarrow H_2 + 1/2O_2$. If used only during thermolysis, water vapor fails to completely eliminate cracking (Figure 3a) but does improve perovskite crystallization (Figure 4a) relative to the dry nitrogen atmosphere (Figure 1b). These results imply that although the water vapor improves the hydrolysis rate and gel network formation, it does not significantly enhance the volatility of the alkanolamines. Thus, many organics remain trapped in the gel's porosity, leading to the observed hairline cracks during crystallization. Table 2 summarizes the experimental results for PZT films derived from the alkanolamine solution chemistry. Failure to achieve uncracked, phase-pure PZT films on unoxidized copper substrates using the alkanolamine chemistry leads us to conclude that the low volatility and high chelation strength of this system is incompatible with our strategy to process PZT films on copper surfaces using process conditions that kinetically avoid copper oxidation.

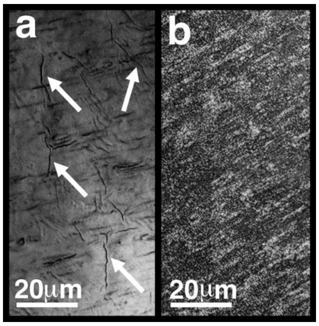

**Figure 3.** Optical microscopy images showing alkanolamine-chelated PZT films crystallized after undergoing thermolysis in a water vapor atmosphere. (a) Residual cracking occurs in water-vapor-thermolyzed samples crystallized in dry nitrogen. (b) No cracking is observed when the crystallization atmosphere contains water vapor. (Image (a) is taken after coating the PZT film with metal so that cracks are more visible.) Arrows indicate crack edges.

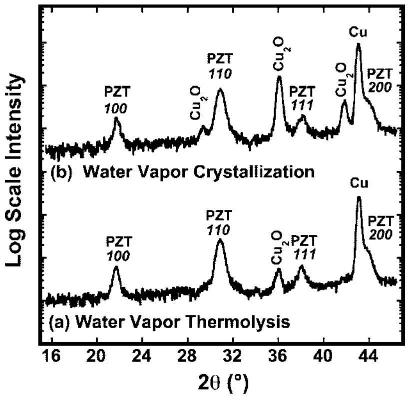

**Figure 4.** X-ray diffraction data illustrating how water vapor in the process atmosphere promotes copper oxidation: (a) PZT film thermolyzed in water vapor and crystallized in dry nitrogen; (b) PZT film thermolyzed and crystallized in water vapor.

**Table 2. Summary of Process Conditions and Observed/Inferred Properties for PZT Films Prepared on Copper Substrates Using the Alkanolamine Solution Chemistry ((Y) yes it occurs, (N) no it does not occur; (−) severe, (○) moderate, (+) minor)**

| process atmosphere | | inferred gel behavior | | film/Cu properties | |
|---|---|---|---|---|---|
| thermolysis | crystallization | hydrolysis/gel formation? | organics volatilized? | copper oxidation | film cracking |
| air | $N_2$ | Y | Y | − | + |
| $N_2$ | $N_2$ | N | N | + | − |
| $N_2/H_2O$ | $N_2$ | Y | N | ○ | ○ |
| $N_2/H_2O$ | $N_2/H_2O$ | Y | Y | − | + |

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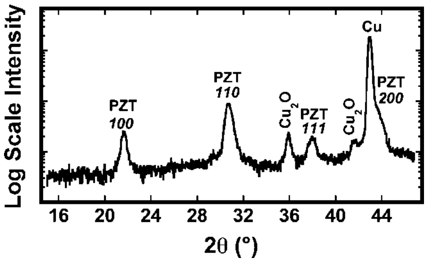


**Figure 5.** X-ray diffraction data for a PZT film prepared from an acetylacetone chelated solution on a copper substrate. The film was pyrolyzed at 300 °C on a hot plate and then crystallized at 650 °C in nitrogen.

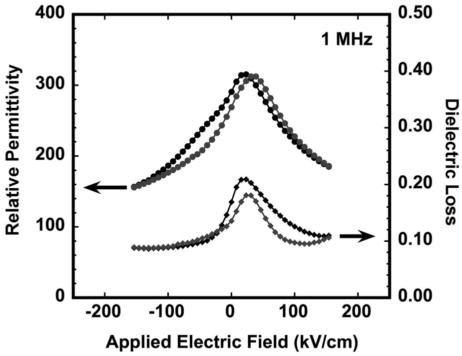


**Figure 6.** Dielectric tunability of a PZT film prepared on a copper foil using the acetylacetone chelated solution; this film contains a significant $Cu_2O$ reaction layer at the PZT/Cu interface. Dielectric data were collected at 1 MHz and room temperature.

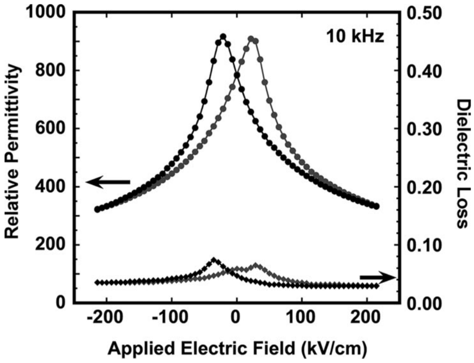
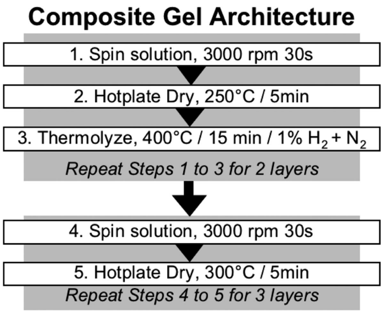


**Figure 7.** Dielectric tunability of a PZT film prepared on a copper foil with an acetic acid chelated solution using a composite gel architecture. In this sample, no $Cu_2O$ reaction layer is detected by X-ray diffraction. Dielectric data were collected at 10 kHz and room temperature.

**Table 3. Process Conditions for Composite Gel Architecture Used To Prepare CSD PZT Films on Copper Surfaces**



Composite Gel Architecture

1. Spin solution, 3000 rpm 30s
2. Hotplate Dry, 250°C / 5min
3. Thermolyze, 400°C / 15 min / 1% $H_2 + N_2$

*Repeat Steps 1 to 3 for 2 layers*

4. Spin solution, 3000 rpm 30s
5. Hotplate Dry, 300°C / 5min

*Repeat Steps 4 to 5 for 3 layers*

**2. *β*-Diketonate and Acetic Acid Chelation Chemistries.** To improve volatility of the organic constituents, we replaced the alkanolamine chelating agent ($T_{\text{boiling}} > 200$ °C) with a lower-boiling-point *β*-diketonate, acetylacetone ($T_{\text{boiling}} \approx 136$ °C). This variation in solution chemistry immediately reduces the pyrolysis temperature necessary for crack-free films from ~400 to ~300 °C. Although this temperature remains incompatible with the copper substrate as illustrated in the diffraction pattern of Figure 5, these uncracked films can be evaluated electrically. The electrical properties reported in Figure 6 (relative permittivity <350; dielectric loss >0.10) illustrate why a Cu/PZT system containing a $Cu_2O$ reaction layer cannot compete with current noble metal or conductive oxide bottom electrode technology. Attempts to lower the pyrolysis temperature (<300 °C) and reduce $Cu_2O$ formation for this solution chemistry resulted in cracked films, consistent with the inadequate organic removal hypothesis.

As recently documented,[3] an acetic acid chelation chemistry allows the deposition of PZT films on copper substrates without significant interfacial reactions. Because acetic acid is a weaker chelating agent than acetylacetone,[21] this change in chemistry further assists organic extraction. As Figure 7 demonstrates, this PZT/Cu system has dielectric properties (peak permittivity ~900; saturated dielectric loss ~0.03) comparable to PZT films prepared on conventional noble metal or conductive oxide electrodes. To manage residual cracking in acetic acid chelated films, researchers developed a composite gel architecture;[3] this scheme incorporates thermolysis of the initial layers to maintain interface quality while subsequent layers are dried at elevated temperatures to improve gel consolidation and prevent cracking. The initially thermolyzed layers kinetically protect the copper substrate from oxidation during subsequent processing. Table 3 summarizes the procedures for synthesizing a PZT/Cu stack using the composite gel architecture approach. To verify that a combination of process design and solution chemistry is necessary to successfully synthesize PZT films on copper surfaces, we prepared a PZT film from the alkanolamine-chelated solution using this composite gel architecture approach. Figure 8 shows that such a process fails to resolve the cracking problems for this solution chemistry. Thus, both a careful design of process variables and solution chemistry is necessary to achieve PZT films on copper surfaces that are crack-free and devoid of interfacial reactions.

In Figure 9, we attempt to pictorially represent the process space available for processing CSD films on copper substrates. In this figure, shaded regions represent "optimal"

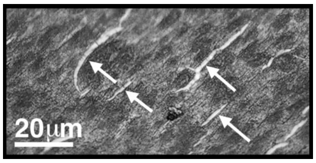


**Figure 8.** Optical microscopy image showing a cracked PZT film prepared from an alkanolamine chelated PZT solution using the composite gel architecture process. Arrows indicate crack edges.

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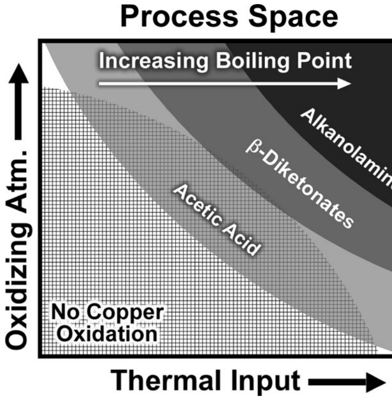

**Figure 9.** Schematic representation of the process space (thermal inputs and oxidizing atmosphere) available for processing CSD PZT thin films directly on copper surfaces. Shaded areas represent conditions necessary to form phase-pure, uncracked PZT films from each solution chemistry. The hatched area represents conditions necessary for maintaining an unoxidized copper substrate.

conditions for processing phase-pure, uncracked PZT films from different solution chemistries; the hatched region represents the process conditions needed to maintain an unoxidized copper substrate. The area of overlap characterizes the process space available for synthesizing device-quality PZT thin films on copper substrates. The authors recognize that this figure is neither quantitative nor representative of the complexity in defining overlap between different solution chemistries. However, this figure does establish the basic challenge and approach necessary for designing a CSD process (under nonequilibrium firing conditions) to avoid oxidation of a base metal substrate. As this figure shows, such an approach requires an understanding of the process conditions (thermal excursion/process atmosphere) as well as the solution chemistry. Finally, we note that the $\beta$-diketonate solution chemistry is included in the overlap region. The authors have successfully prepared PZT films on unoxidized copper substrates from an acetic acid solution chemistry modified with acetylacetone and believe that conditions may also exist for processing films from a completely $\beta$-diketonate chelated solution chemistry on copper substrates.

## Conclusions

Chemical-solution-deposited PZT films were prepared on copper substrates using solution chemistries where the relative strengths of chemical chelating agents were systematically varied. The experiments demonstrate that by properly optimizing the chelating agent strength, a favorable combination of solution stability and gel structure development could be achieved. This favorable combination enables PZT film synthesis with thermal budgets that are compatible with sensitive substrates like copper foils.

Proper gel formation and consolidation in strongly chelated solutions with low volatility ligands, like the alkanolamine chemistry, require thermal budgets incompatible with base metal substrates. If thermal budgets are reduced for compatibility, films fail to crystallize completely and are susceptible to cracking during higher-temperature crystallization anneals. These observations identify gel formation and thermal decomposition as the critical parameters for successful film preparation. Water vapor can be used to accelerate gel hydrolysis, but the effect is insufficient to completely resolve cracking issues.

Compatibility can be achieved only through solution chemistry modification that allows gelation and consolidation at a lower thermal budget. Solutions that utilize lower-boiling-point, less strongly chelated ligands ($\beta$-diketonates and acetic acid) can be prepared at lower temperatures and in less oxidizing atmospheres, allowing compatibility with oxidizable substrates like copper.

Under identical processing conditions, device-quality PZT films can be synthesized on copper substrates with the acetic acid chemistry, whereas films derived from the alkanolamine chemistry are cracked and nonfunctional.

The authors conclude that conventional optimization of solution concentration, drying temperature, and pyrolysis/thermolysis is an important component of process development; however, achieving compatibility between solution processed thin films and reactive substrates necessitates sophisticated control of gel formation and metalorganic decomposition, which can be achieved only through intelligent solution design.

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