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A New Ferroelectric Varactor From Water Based Inorganic Precursors

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ABSTRACT

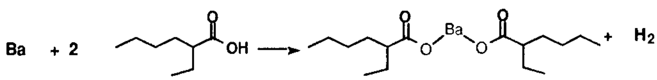
Solution deposition processes for the production of thin multi-element metal oxide films continue with great interest and varied success. Solution deposition via either sol-gel or MOD (Metal Organic Decomposition) methods are of interest due to the ability to produce a wide variety of compositional products at low capital investment cost. The sol-gel method generally uses hydrolytically sensitive metal alkoxides as the starting materials. Manipulation of the reagents and different hydrolysis rates for multi-element mixtures are issues. The MOD method utilizes large organic acid metal salts as the starting materials. In general, MOD solutions are more hydrolytically stable than the sol-gel solutions. MOD process challenges include large quantities of carbon to be decomposed during the firing, shrinkage and stress of the thin films, variable chemistry in synthesis of the starting materials (especially when the starting materials for the MOD precursors are metal alkoxides), and long reaction times for the synthesis. For both the sol-gel and MOD precursors, toxic and volatile organic chemical (VOC's) solvents are employed as the vehicle.

This paper will review the chemistry-related issues to production of consistent high-quality metal oxide films via the MOD process. The fabrication of thin $Ba_xSr_{(1-x)}TiO_3$ (BST) films is described. A new class of MOD precursor has been implemented using polyether acids as the organic vehicle. These new materials are both water stable and water soluble. High quality BST thin films made from these precursors are described and capacitors made from these films are compared to the aliphatic acid MOD materials. Improved capacitors using lower resistance electrodes and interconnects are described, as well as devices designed specifically for our specific application.

INTRODUCTION

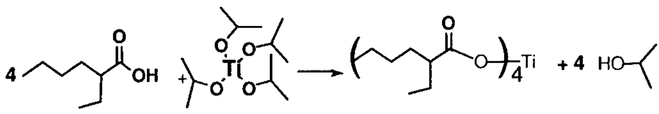
The use of sol-gel and MOD ceramic precursor solutions for production of thin-film and other ceramic materials is well known and documented.[1] MOD spin-on precursor materials for ferroelectrics are described in US Patent 5,423,285 [2] and elsewhere. The MOD precursor solutions are usually made from large aliphatic acid (for example 2-ethylhexanoic acid) salts of the desired metal and a compatible solvent (for example xylenes) is used to adjust the concentration. As compared to sol-gel precursors, the MOD precursors have excellent shelf life and long term stability. Although the MOD solution precursors are commercially available for some elements (for example bismuth-2-ethylhexanoate, Strem 83-2400), they are not readily available for the less common and higher valent elements.

For the group I and II metals the MOD precursors can be easily prepared by an oxidation reaction of the reactive metal with the organic acid (see Equation 1).



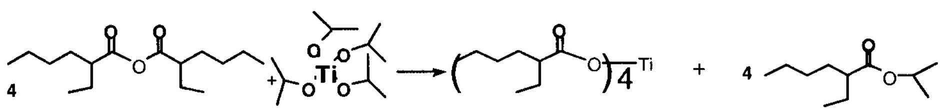
Equation 1. Reaction of alkaline earth metal Barium with 2-ethylhexanoic acid

For the higher valent elements, MOD precursors may be synthesized by interchange of the corresponding metal alkoxide with the free acid (See Equation 2).



Equation 2. Idealized Reaction of Titanium Isopropoxide with 2-ethylhexanoic acid.

Inconsistent results with the precursors made by the acid alkoxide interchange reaction have been previously discussed.[3] The reaction as shown in Eq. 2 has several issues. In particular, the reactions may take several days to complete. Hydrolysis and condensation reactions also compete with idealized process. Our group has previously reported [4] an improved method to quickly synthesize the MOD precursors using the anhydride of the organic acid and the metal alkoxides. (Equation 3).

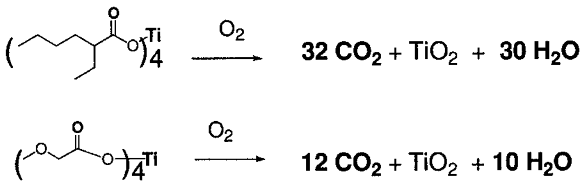


Equation 3. Reaction of 2-ethylhexanoic anhydride with Titanium Isopropoxide

We have made over one hundred batches of both BST and SBTN MOD precursors solutions using 2-ethylhexanoic acid anhydride. These reactions take several hours to complete and the products obtained when processed into devices give consistent results. In this paper we describe results for new environmentally-friendly MOD precursors which give improved quality thin films.

New Water Soluble Ferroelectric MOD Precursors

The need for environmentally benign precursors for production of thin film, thick film and bulk ceramics has been reviewed.[5] A class of water soluble, water stable MOD ceramic precursors have been described for lower valent metals including aluminum[5], yttria[6], iron[7], nickel[7], and the alkaline earth metals[8]. The metal ions are complexed with polyether acid molecules as compared to the aliphatic acids used in the more common MOD precursors. Equation 4 shows a comparison of the decomposition products of Titanium MOD precursors made from 2-ethylhexanoic acid and the etheracid methoxyacetic acid.



Equation 4. Thermooxidative Decomposition of new PolyetherAcid MOD Precursors Forms Significantly Less Byproducts as Compared to the Aliphatic Acid Analogues

The thermooxidative reaction of the new water soluble MOD precursor shows that almost 60% less material (by volume) is evolved during decomposition as compared to the aliphatic MOD analogues. This may lead to less shrinkage and stress during the decomposition process, especially after removal of the solvent. Fired ceramics with improved properties may result.

BST Capacitors from Water Soluble MOD Precursors

We have synthesized new polyether acid precursors of titanium, barium and strontium and processed these new materials into high quality BST thin films[9]. For the Group II metals, the polyether acid precursors are easily synthesized from the acid and metal. For the higher valent metals, the water soluble MOD precursors were made from the reaction of commercially available metal alkoxides and the anhydride of the corresponding polyether acid. The water soluble BST MOD precursor was spun on to metalized (evaporated Pt) silicon wafers. Single coat films using spin speeds from 1000 –3000 rpm gave crack-free, smooth 800-2500A thick BST films af r evaporation and firing[10] Top electrode and passivation layers were added and patterned capacitors were fabricated using standard thin film processes. A typical capacitance vs. Bi curve is shown in Figure 1 on the next page.

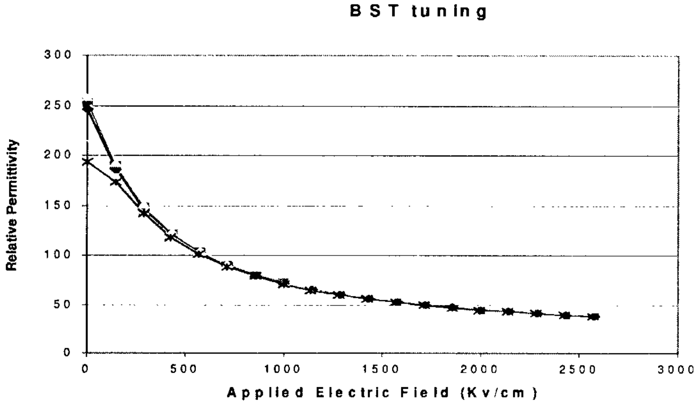


Figure 1. C-V Curve of thin film BST capacitors made with water based spin-on MOD Precursors to Bias Field of 2.5MV/cm

This measurement shows the large tuning range (>5:1) and breakdown strength of these devices. These devices have been tested at field strengths of 2.5 MV/cm for over 125 hours without breakdown or significant degradation. The capacitors produced from these films have leakage currents on the order of 10^{-8} a/cm^2. The results highlight the excellent material properties of the BST films. However, at higher frequencies (>1MHz) the Q of the initial devices we fabricated was disappointing. Q's measured at the bond pad for these capacitors at 30MHz were only in the range of 10-30, which was not sufficient for our intended application.

High Q Devices – Improvement of ESR (equivalent series resistance)

These particular capacitors are being developed for to replace semiconductor varactor diodes in a high-power voltage regulator circuit.[11] This application requires high Q devices that can survive very high field strengths and large AC signals. The application frequency is in the range of 10-100Mhz. The initial devices we fabricated utilized a stack and design that was developed for another application. This initial stack consisted of BE, TE and interconnect metal of Ti/Pt materials with thickness of 1850, 1100, and 1850 A respectively. Tests of the devices at frequencies above 1MHz demonstrated that the major losses were due to series resistance of the metal layers and not losses in the BST.

Since the top electrode would ultimately be covered by the interconnect layer, experiments to improve the sheet resistance of the bottom and interconnect metals were performed. By depositing a thicker layer of Pt (3500A) as the bottom electrode (BE) on a heated substrate a lower resistance BE was produced that had less stress and smoother surfaces than the baseline electrode. Resistance of the new BE improved from 0.87 to 0.36 ohm/sq while actually improving yield and breakdown characteristics of the capacitors. For the interconnect metal a more complicated two step process was developed. The first interconnect layer is an evaporated Ti/Pt material that is etched and annealed to remove stress. This initial interconnect is unchanged from our original process which allows us to objectively compare low frequency performance data with earlier devices. A Titanium barrier and a thick Aluminum layer are then added to reduce resistivity. This two layer interconnect improves the sheet resistance from 0.82 ohms/sq for the baseline to just 0.02 ohm/sq for the improved conductor.

Although the reduction in series resistance of the metal layers was significant, it was clear that further reduction in series resistance was easily achievable through changes in the device geometry. By using high aspect ratio structures it is possible to minimize the path length of the higher resistance BE in the devices or trade path length in BE for path in the lower resistivity M3 layer. Several high aspect ratio 600pF capacitors were designed and built. Examples of these structures are shown in Figure 2.

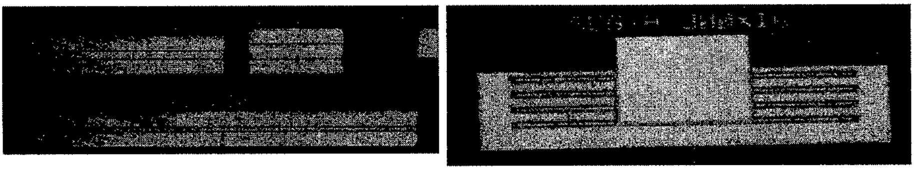


Figure 2. Image of high aspect ratio capacitors.

When these structures were combined with the new water-based ferroelectric precursors and the improved lower resistivity metal layers, the result was a great improvement in performance over the baseline devices. The measured Q at 30MHz with zero bias was increased from about 20 to over 100 at zero field and higher Q's were observed with bias.

CONCLUSION

An improved method is described for the production of MOD precursors for ferroelectric materials. New water soluble and stable MOD ceramic precursors were synthesized for barium, strontium and titanium elements. For the Group II metals, the polyether acid precursors are easily synthesized from the acid and metal. For the higher valent metals, the MOD precursors were made from the reaction of commercially available metal alkoxides and the anhydride of the corresponding polyether acid. BST thin films were made by spin-on processing of the water based materials. These new precursor materials provide a no VOC and lower toxic route to a wide range of thin film, thick film and bulk ceramic materials. In order to realize performance goals, improved BE and interconnect conductors were also developed as well as application specific geometries. Electrical properties of these devices give a tunabiltiy of over 5 to1, leakage on the order of 10^{-8} a/cm^2, and Q values of over 100 at 0 field, and Q's approaching 400 at higher fields. Breakdown strength of the devices was excellent with representative devices surviving over 125 hours at 2.5MV/cm.

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