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Liquid Delivery MOCVD of Niobium-Doped Pb(Zr,Ti)O_3 Using a Novel Niobium Precursor

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A number of functional electroceramics incorporate niobium as one of the elemental constituents, including many important relaxor materials such as lead magnesium niobate, $Pb(Mg_{1/3}Nb_{2/3})O_3$. Niobium is also an important dopant in ferroelectric oxides such as lead zirconium titanate $Pb(Zr,Ti)O_3$ (PZT). It has been shown that modification in bulk PZT with a small amount of niobium dramatically increases the piezoelectric coefficient (d_{31}) by up to 80%[1] and the electromechanical coupling factor (k_p) by 30%.[2] Nb doping significantly enhanced the displacement without increasing the hysteresis loss.[3] These improvements are particularly desirable for thin-film microelectromechanical systems (MEMS). In addition, niobium doping has been found to reduce the electrical leakage by more than 2 orders of magnitude[4] and to provide improved electrical breakdown strength.[5] For ferroelectric memory applications, niobium doping minimizes imprint[6] and coercivity, while maximizing the remanence ratio (namely, the squareness in the hysteresis loop).[4] Therefore, incorporation of niobium during thin film PZT deposition is of great interest due to the numerous performance enhancements it provides.

Reactive sputtering,[7] sol−gel,[4] laser ablation,[8] and metal-organic chemical vapor deposition (MOCVD)[9] have all been used to deposit high-quality, thin-film Nb-doped PZT (PNZT). Of these thin film deposition techniques, MOCVD offers a unique combination of composition control, uniformity over large areas, and a relatively high deposition rate. Most importantly, MOCVD provides conformal film deposition on three-dimensional structures, a very useful feature for MEMS applications. Using liquid-delivery MOCVD,[10] it is possible to modify PZT with a dopant element in a straightforward manner, provided that an adequate precursor for the dopant element is available.

An essential feature of precursor development for liquid delivery MOCVD is to identify a set of precursors with well-matched chemical and thermal stability and transport, vaporization, and decomposition properties.[11] The primary issue is chemical compatibility both in the solution mixture and in the vapor phase. Thermal stability during vapor-phase transport is also critical toward MOCVD process repeatability. Chemical compatibility can be achieved by judicious choices of source reagents for each constituent of the multicomponent material to be deposited. To this end, Shimizu and coworkers[9] have demonstrated the use of following metal-organic precursors in bubbler-based MOCVD of PNZT: tetraethyl lead, $Pb(C_2H_5)_4$, and the alkoxides: Zr(O-*t*-$C_4H_9)_4$, Ti(O-*i*-$C_3H_7)_4$, and $Nb(O-C_2H_5)_5$.[12] However, $Pb(C_2H_5)_4$ is generally considered unsafe for manufacturing processes due to its high vapor pressure and extreme toxicity.[13] In this communication, we report the use of low vapor pressure, nonalkyl sources of Nb, Pb, Zr and Ti for the formation of Nb-doped PZT thin films via a liquid delivery process with improved safety.

For the present work, lead bis(2,2,6,6-tetramethyl-3,5-heptanedionate), $Pb(thd)_2$, was chosen for both improved safety and chemical compatibility.[14] This compound has no appreciable vapor pressure at room temperature, making it safer to handle compared to tetraalkyl lead sources. The low volatility of $Pb(thd)_2$ (0.05 Torr at 180 °C) requires the use of liquid precursor delivery methodology. Titanium bis(isopropoxide) bis(2,2,6,6-tetramethyl-3,5-heptanedionate), Ti(O-*i*-Pr)$_2$(thd)$_2$, was used as the titanium precursor and zirconium tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionate), $Zr(thd)_4$, was used as the Zr precursor.[15] These compounds are extremely soluble in organic solvents, and ligand exchange is absent or degenerate. Since the titanium atom is coordinatively saturated,[16] molecular structural changes are not observed. Good quality PZT thin films have been prepared using this set of Pb−Zr−Ti precursors by a number of groups.[17]

We explored the use of niobium tetrakis(isopropoxide) 2,2,6,6-tetramethyl-3,5-heptanedionate, Nb(O-*i*-Pr)$_4$(thd), as the Nb precursor for doping of PZT thin films

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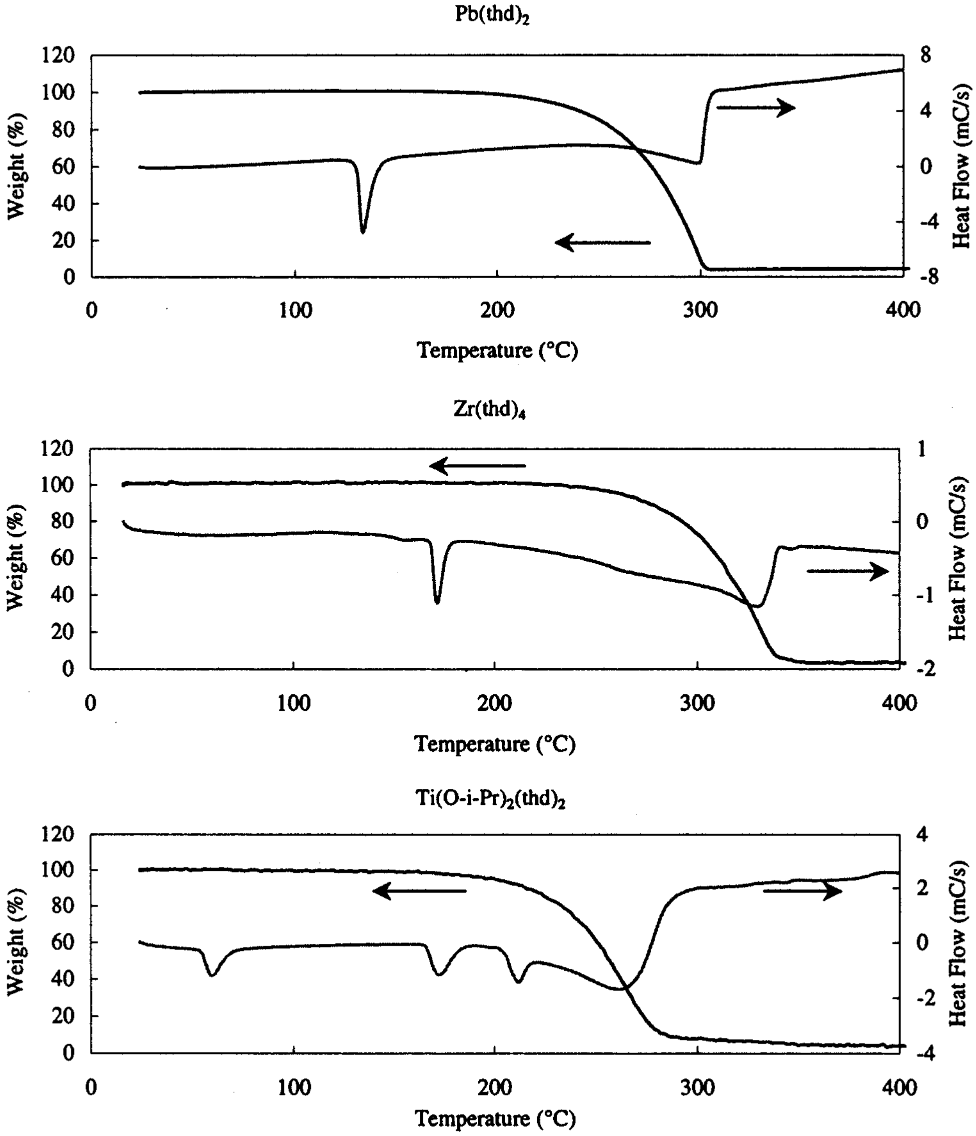

Figure 1. Thermogravimetric analysis (TGA, weight %) and differential scanning calorimetry (DSC, heat flow, mC/s) traces for the thermal analysis of $Pb(thd)_2$, $Zr(thd)_4$, and $Ti(O\text{-}i\text{-}Pr)_2(thd)_2$ in atmospheric argon.

by MOCVD.[18] This compound was shown to be chemically compatible with the Pb−Zr−Ti chemical mixture. A brief synthesis procedure follows.

$Nb(O\text{-}i\text{-}Pr)_5$ (Cerac) was placed into a 500 mL Schlenk flask, and 1 equiv of 2,2,5,5 tetramethyl-3,5-heptanedione (Lancaster) was added to the vessel. The contents were heated to 65 °C under a slow nitrogen purge. After 2 h, the liberated 2-propanol was removed in vacuo to yield $Nb(O\text{-}i\text{-}Pr)_4(thd)$. The crude solid product was recrystallized from pentane. The NMR spectrum was consistent with an octahedral structure composed of two isoproproxide ligands bonded axially to Nb and a second set of cis isopropoxide ligands equatorially opposed to the thd ligand. Elemental analysis showed reasonable agreement. Found: C, 53.09; H, 8.75. Calcd: C, 53.92; H, 8.18.

Proton NMR was used to identify and characterize the precursor molecular structures. The ^1H chemical shifts were measured and recorded for the individual materials and, upon mixing, all the precursors in solution; no changes in the NMR resonances were observed. Since the (thd) ligand may exchange faster than the NMR time scale, observing the ligand exchange reaction may be difficult. However, the ligand exchange reactions expected for these organometallic precursors are degenerate in that they provide the identical molecular species after ligand exchange of the β-diketonate (thd) ligand. For the Nb and Ti species, the addition of only one β-diketonate (thd) group is the preferred composition, as evidenced by the syntheses of these materials. The addition of a second (thd) is unfavorable, due to steric crowding on the metal center, and was not observed.

The volatility and thermal stability of each precursor were examined by thermal analysis and vacuum sublimation. The compounds were analyzed by simultaneous thermal analysis (STA)[19] with a heating rate of 10 °C/min and Ar as a purge gas (25 sccm/min) at atmospheric pressure. Examination of the PZT chemistry (Figure 1) revealed that the Pb and Ti compounds are well matched relative to their transport behavior,

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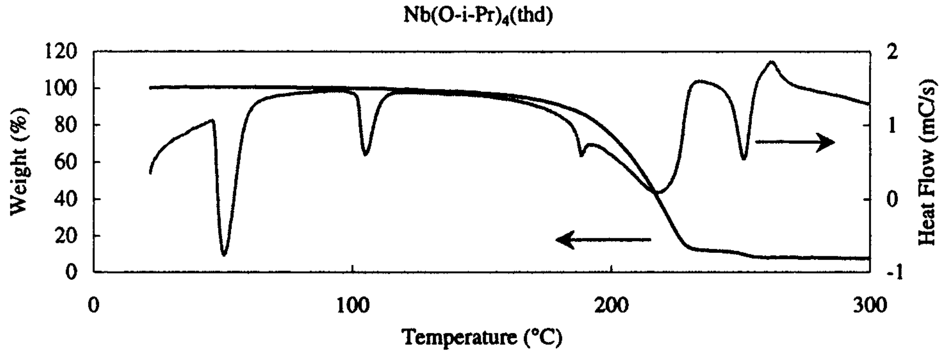

Figure 2. Thermogravimetric analysis (TGA, wt %) and differential scanning calorimetry (DSC, heat flow, mC/s) traces for the thermal analysis of $Nb(O\text{-}i\text{-}Pr)_4(thd)$ in atmospheric argon.

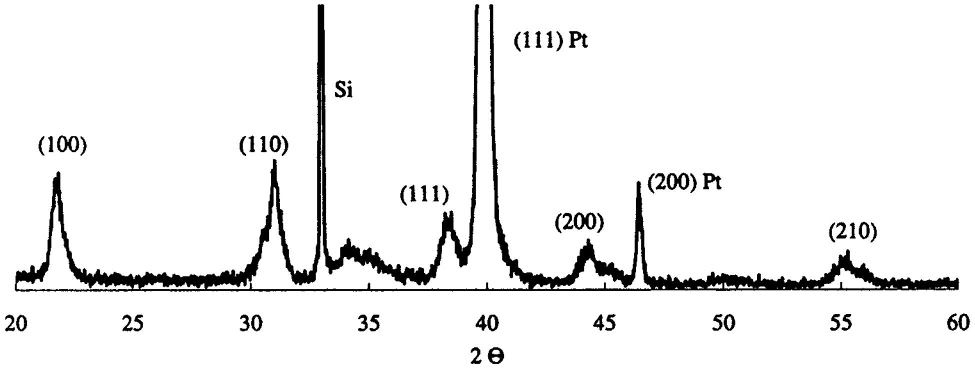

Figure 3. X-ray diffraction spectrum of a representative Nb−PZT film prepared by the present work.

exhibiting similar values of T_{50}.[20] The higher transport temperature for the Zr compound sets the lower limit of vaporization temperature for this chemistry. High vaporization temperatures may result in premature decomposition of one or more of the compounds during transport. $Pb(thd)_2$ was observed to be the most thermally sensitive toward thermal decomposition. The optimal vaporization temperature is determined by evaluating the dynamic vapor-phase transport characteristics at CVD reactor pressures, typically under 50 Torr. This operating pressure (vacuum) requires substantially lower temperatures for vaporization relative to the T_{50} determined at atmospheric pressure. For example, temperatures less than 240 °C were found to be adequate for flash vaporization and vapor-phase transport for the Pb−Zr−Ti mixture. The STA data of $Nb(O\text{-}i\text{-}Pr)_4(thd)$ (Figure 2) showed that its T_{50} value (~230 °C) is close to that of the Pb and Ti compounds, a highly desirable feature for complete vaporization of the entire Pb−Nb−Zr−Ti mixture. Little or no thermal decomposition occurred at the vaporization temperature typically prescribed for PZT film growth.

The DSC peaks were identified as follows.

(1) $Pb(thd)_2$: melting endotherm at 133 °C; evaporation endotherm at 265 °C.

Table 1. Typical CVD Process Conditions Employed in This Work

	MOCVD process conditions
substrate temperature	550−650 °C
substrate	Pt/MgO/Si
reaction pressure	2−10 Torr
oxidizer gas flow	
oxygen flow rate	450 sccm
nitrous oxide flow rate	450 sccm
vaporizer settings	
vaporization temperature	210 °C
vaporizer pressure	~30 Torr
carrier gas (argon) flow rate	~100 sccm
precursor settings	
$Pb(thd)_2$	10−35 μmol/min
$Zr(thd)_4$	10−30 μmol/min
$Ti(O\text{-}i\text{-}Pr)_2(thd)_2$	3−8 μmol/min
$Nb(O\text{-}i\text{-}Pr)_4(thd)$	0.6−6 μmol/min

(2) $Zr(thd)_4$: crystalline phase change endotherm at 157 °C; melting endotherm at 171 °C; evaporation endotherm centered at 330 °C.

(3) $Ti(O\text{-}i\text{-}Pr)_2(thd)_2$: crystalline phase change endotherms at 57 and 167 °C; melting endotherm at 208 °C; evaporation endotherm centered at 240 °C.

(4) $Nb(O\text{-}i\text{-}Pr)_4(thd)$: crystalline phase change endotherms at 55 and 105 °C; melting endotherm at 190 °C; evaporation endotherm centered at 215 °C. A decomposition endotherm is also noted at 250 °C.

Nb-doped PZT films of good crystallinity were deposited from these precursors using liquid delivery MOCVD onto platinum-coated silicon wafers. An inverted vertical reactor was used for film growth. Typical deposition conditions are summarized in Table 1. The films were characterized by X-ray fluorescence (XRF),[21] X-ray diffractometry (XRD), atomic force microscopy (AFM), and ferroelectric testing. XRF compositional analysis indicated stoichiometric Nb-doped PZT can be grown at

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(19) STA is the concurrent measurement of the differential scanning calorimetric (DSC) data and thermogravimetric analysis (TGA). DSC provides a measure of the heat flow in the sample, such as endothermic transitions (i.e., melting, crystalline phase changes, and evaporation or sublimation) and exothermic transitions (i.e., decomposition in the sample). TGA provides a measure of the sample weight loss as a function of temperature, for a given heating rate, and can be used to approximate both purity (percent residue) and transport characteristics.

(20) T_{50} is defined as the temperature where half of the sample mass has been transported. For example, $Ti(O\text{-}i\text{-}Pr)_2(thd)_2$ shows a T_{50} of 260 °C and $Zr(thd)_4$ of 350 °C from Figure 1.

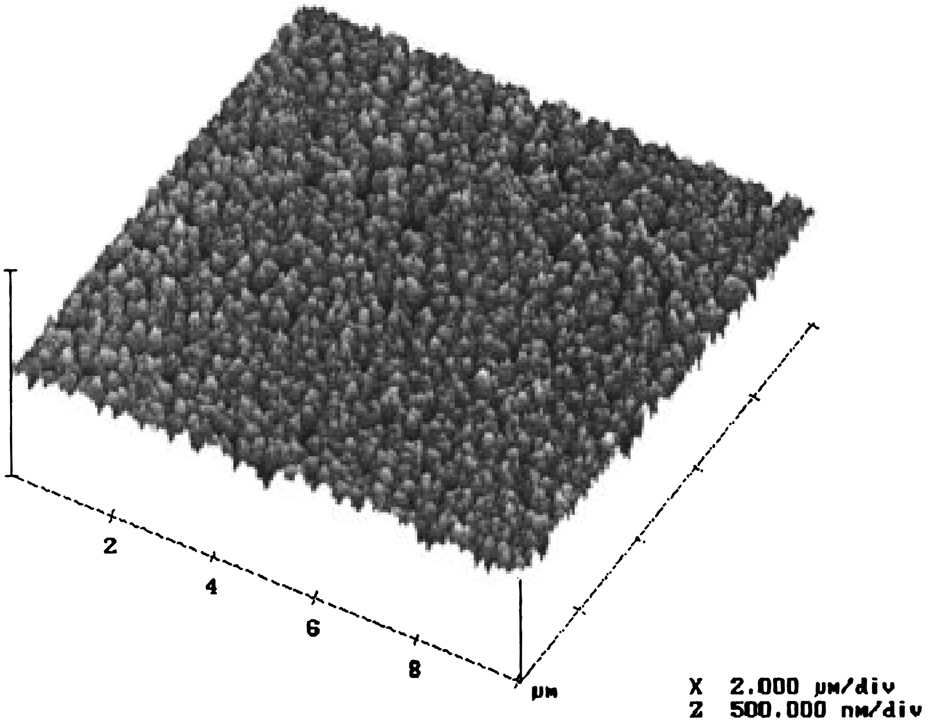

Figure 4. AFM micrograph of the Nb−PZT film of Figure 3.

the prescribed process conditions. The X-ray diffraction pattern of a stoichiometric film grown at a substrate temperature of 610 °C is shown in Figure 3. Results from XRF indicated that the film was 340 nm thick, 0.4 at. % Nb at Zr/Ti = 56/44, as determined by XRF. The film was single-phase perovskite crystalline structure with mixed preferred orientations of (100), (110), and (111). The film wase dense, with up to 0.2 μm sized grains, and the film surface was free from particles (Figure 4). Ferroelectric properties were measured by a standard ferroelectric tester (RT6000S, Radiant Technologies, NM) and a representative ferroelectric hysteresis loop (Figure 5) showed an acceptable remanent polarization and a very low coercive field.

In conclusion, a novel Nb source reagent, Nb(O-*i*-Pr)$_4$-(thd), was investigated for use as the Nb dopant precursor for multicomponent oxide thin-film deposition by MOCVD. This compound is thermally stable and chemically compatible with low vapor pressure PZT precursors. The transport and vaporization conditions utilized for the PZT chemistry were readily adopted for the new PNZT mixture. Liquid delivery MOCVD of PNZT films using this Nb precursor was demonstrated, and single-phase perovskite PNZT films with good ferroelectric properties were obtained.

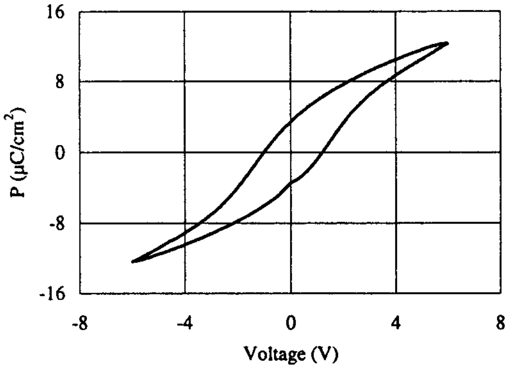

Figure 5. Ferroelectric hysteresis loop of the Nb−PZT film of Figure 3.

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(21) XRF was used to determine the composition of the PNZT thin films reported. Standard PNZT films of well-known compositions and thicknesses were prepared by a metal-organic decomposition (MOD) technique. Firing temperature of the standards was maintained below the limit for Pb volatilization. A fundamental parameters model was used to relate the measured characteristic X-ray intensities to those of the standards. The relative precision of the XRF measurement was 0.5% for each element.