Thermodynamic Control of Lead Content in the Piezoelectric Thin Film

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Abstract:
Recently, piezoelectric thin films have become attractive as a component for low voltage MEMS applications. Lead-based perovskite materials are used because of their excellent ferroelectric and piezoelectric properties. However, the volatility of lead creates difficulties in the deposition process, because high temperature annealing process is required for prorovskite phase development. Conventionally, excess lead is added to thin films in order to control lead content during high temperature processing. However, it is still difficult to precisely control the stoichiometry of lead-based piezoelectric thin film, since the proper amount of excess lead depends on deposition process or conditions.

In this study, lead composition control is being pursued in the piezoelectric thin film via thermodynamic, rather than kinetic control. Post annealing is being conducted for lead deficient piezoelectric thin films in a PbO furnace. Theoretical calculation suggests that it should be possible to control lead content via thermodynamics. Experimentally, we found PbO thin films can be deposited using this system. These results suggest that we could also deposit PbO thin film on Pb-deficient PZT thin film and crystalize stoichiometric PZT thin film.

Introduction:
Recently, piezoelectric thin film has become attractive for low voltage microelectronic mechanical system (MEMS) applications. Among various piezoelectric materials, lead-based materials, especially lead zirconate titanate [Pb(Zr,Ti)O₃, PZT], are used because of their excellent piezoelectric properties [1]. However, the volatility of lead creates difficulties in the deposition process, because high temperature annealing is required for prorovskite phase development. Conventionally, excess lead is added to thin films in order to control lead content during high temperature processing. However, it is still difficult to precisely control the stoichiometry of the piezoelectric thin film, since the proper amount of excess lead depends on deposition process or conditions.

We focused on thermodynamic method to control the lead content in the piezoelectric thin film in a PbO metalorganic chemical vapor deposition system using tetra-ethyl lead [TEL] as a lead source. The vapor pressure of PbO was calculated from the thermodynamic reaction:

\[
\log P_{\text{PbO}} = -\frac{15030}{T} + 9.51 \text{ [atm]}
\]

\[
PbZrO_3 = \text{PbO (gas)} + \text{ZrO}_2
\]

\[
\log P_{\text{PbO}} = -\frac{13660}{T} + 7.15 \text{ [atm]}
\]

where \(P\) and \(T\) are the pressure and temperature [2]. These equations suggest that lead content can be controlled by PbO pressure and temperature.

In this study, we suggest a new method to control lead content in the piezoelectric thin film via thermodynamic method. We conducted post-annealing process in the furnace with controlled PbO pressure and annealing temperature.

Experimental Procedure:
Figure 1 shows an optical image and schematic diagram of PbO furnace to deposit PbO thin film and control lead content in a PZT thin film. Tetra-ethyl lead [TEL] is used as a source of PbO. It was supplied by Gelest packaged in bubbler. In this system, we have three important parameters; TEL flow rate, bubbler temperature, and chamber temperature.

At first, we conducted theoretical calculation to estimate the conditions to control lead content. Theoretical values of PbO pressure in the chamber are calculated from the following equation:

\[
P_{\text{TEL, Chamber}} = \frac{9.361 - \frac{2910}{T_{\text{Bubbler}}}}{(f_N + f_O + f_{\text{TEL}})T_{\text{Chamber}}}
\]

where \(f_N\), \(f_O\), \(f_{\text{TEL}}\), \(T_{\text{Bubbler}}\) and \(T_{\text{Chamber}}\) are the nitrogen flow rate, oxygen flow rate, TEL flow rate, bubbler temperature and annealing temperature, respectively. Then \(f_N\) and \(f_O\) were fixed at maximum flow rates of 3448 sccm and 1000 sccm, respectively. Figure 2 shows the PbO pressure in the chamber as a function of TEL flow rate at a bubbler temperature of 45°C and an annealing temperature of 750°C. The (▲) and (●) lines indicate boundary pressure for the chemical reaction from PbO gas to PbO solid and from PbZrO₃ to PbO gas and ZrO₂,
respectively. This figure suggests we could compensate lead content with TEL flow rate from 8 to 20 sccm under a bubbler temperature of 45°C and an annealing temperature of 750°C.

Results and Conclusions:
As an initial experiment, we tried to deposit PbO thin film on an aluminum oxide (Al₂O₃) substrate, which doesn’t react with lead chemically, to confirm whether this system is useful or not. We conducted annealing at a TEL flow rate 20 sccm, a bubbler temperature of 45°C, and an annealing temperature 500°C. Figure 3 shows surface SEM images before and after PbO deposition. We found PbO thin film can be deposited on Al₂O₃ substrate using this system. Additional experiments need to be conducted to evaluate the growth rate.

We suggest a new approach to control lead content in piezoelectric thin films. Theoretical calculation suggests that we could control lead content via thermodynamic method. Furthermore, we found PbO thin film can be deposited using this system. These results suggest that we could also deposit PbO thin film on Pb-deficient PZT thin film and crystalize stoichiometric PZT thin film.

Future Work:
Figure 4 shows phase diagram of PZT thin film as a function of TEL flow rate and annealing temperature. This diagram is the final objective of this research. To find the boundary of this phase diagram, we should conduct post-annealing for Pb-deficient PZT thin film.

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References: