Development of Improved Precursors for the MOCVD of Bismuth Titanate

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Bismuth titanate, $Bi_4Ti_3O_{12}$, is a layered perovskite with a number of useful ferroelectric and electro-optic properties, and has potential applications in non-volatile memory devices and ferroelectric-effect transistors. MOCVD is a promising technique for the deposition of $Bi_4Ti_3O_{12}$ which has applications in non-volatile ferroelectric computer memories. To exploit the full potential of the technique it is essential to employ precursors with the appropriate physical characteristics and decomposition behaviour.

A variety of precursor combinations have been used for the MOCVD of $Bi_4Ti_3O_{12}$, such as $BiPh_3$ in combination with $Ti(OPr^i)_4$ or $BiMe_3$ with $Ti(OPr^i)_4$, but these are poorly matched. In particular, the Bi precursor has a number of disadvantages, which has restricted progress in the development of a MOCVD process. For instance, $BiPh_3$ has a significantly higher thermal stability than Ti alkoxides, which can cause problems in controlling compositional uniformity across the substrate, and although the less thermally stable complex $BiMe_3$ has proved to be a better match to the $Ti(OR)_4$ precursor, it is highly reactive and potentially explosive, which limits its widespread application.

Simple bismuth alkoxides, $Bi(OR)_3$ form low volatility polymeric $[Bi(OR)_3]_n$ aggregates, unsuited to MOCVD, but the sterically hindered bidentate ligand $[OCMe_2CH_2OMe]$ (mmp) is highly effective in reducing polymerisation in metal alkoxides and the complex $Bi(mmp)_3$ is a volatile monomer. In this paper we report for the first time the use of $Bi(mmp)_3$ for the liquid injection MOCVD of $Bi_4Ti_3O_{12}$ thin films.

We have also sought alternatives to conventional $Ti(OR)_4$ precursors, as they are highly moisture sensitive due to their unsaturated 4-coordinate Ti centres. This can cause difficulty in handling and places stringent requirements on the purity and water content of the solvent in liquid injection MOCVD. Our initial investigation focused on $[Ti(OPr^i)_2(thd)_2]$, which contains the chelating [thd] group, making it more fully saturated and less moisture sensitive than the parent $Ti(OPr^i)_4$. Another approach to increasing the coordinative saturation of a metal alkoxide complex and reducing its moisture sensitivity is to introduce bidentate alkoxide ligands, such as [mmp] and in this paper we report the synthesis and characterisation of the new Ti alkoxides, $Ti(OPr^i)_2(mmp)_2$ and $Ti(mmp)_4$, both of which prove to be well matched to $Bi(mmp)_3$ with similar physical properties and decomposition characteristics. A further advantage of the $Bi(mmp)_3$ / $Ti(mmp)_4$ precursor system is the presence of the same ligand in each complex, which can be expected to minimise unfavourable precursor interactions in solution.

In this paper we describe the use of $Bi(mmp)_3$ in combination with $Ti(OPr^i)_2(thd)_2$, $Ti(OPr^i)_2(mmp)_2$ and $Ti(mmp)_4$ for the deposition of $Bi_4Ti_3O_{12}$ by liquid injection MOCVD.

Thermogravimetric analysis (TGA) (Fig. 1) showed that all complexes have well-matched volatilities, evaporating over a similar temperature range, with all complexes being fully evaporated at < 300°C.

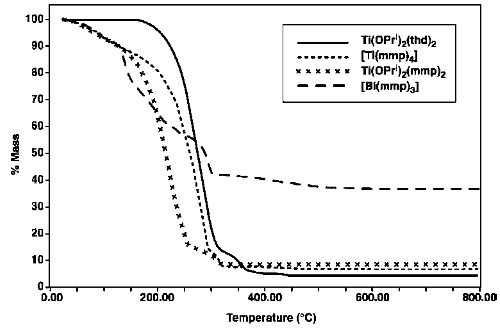

Fig. 1. TGA data for Bi and Ti complexes

The variation in oxide growth rates with substrate temperature for $Bi(mmp)_3$, $Ti(OPr^i)_2(mmp)_2$, $Ti(mmp)_4$ and $Ti(OPr^i)_2(thd)_2$ are shown in Fig. 2. The data indicate that $Ti(OPr^i)_2(mmp)_2$, $Ti(mmp)_4$ deposit oxide at good growth rates over a similar range of temperatures to $Bi(mmp)_3$ (350 – 600°C), and at significantly lower temperatures than the more thermally stable $Ti(OPr^i)_2(thd)_2$ complex.

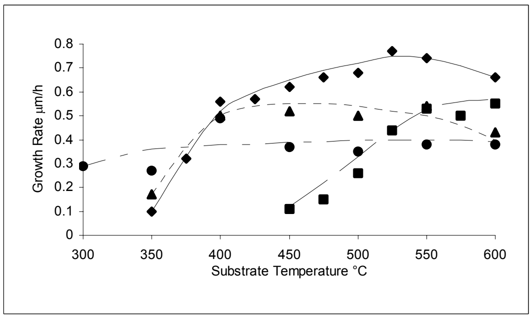

Fig. 2. Variation in metal oxide growth rate with substrate temperature: (●) $Bi(mmp)_3$, (■) $Ti(OPr^i)_2(thd)_2$, (◆) $Ti(OPr^i)_2(mmp)_2$, (▲) $Ti(mmp)_4$

Energy Dispersive X-Ray (EDX) analysis showed that the solid composition of Bi-titanate grown using $Bi(mmp)_3$ / $Ti(OPr^i)_2(mmp)_2$ or $Bi(mmp)_3$ / $Ti(mmp)_4$ showed little variation with substrate temperature, down to substrate temperatures as low as 300°C.However, Bi-titanate films grown using the more thermally stable $Ti(OPr^i)_2(thd)_2$ precursor and $Bi(mmp)_3$ showed a marked decrease in Ti content at lower substrate temperatures, with no Ti incorporation at 300°C. From these data we conclude that the $Bi(mmp)_3$ / $Ti(mmp)_3$ combination is the best matched and most suitable for the liquid injection CVD of Bi-titanate.

The composition of $Bi_4Ti_3O_{12}$ films grown from $Bi(mmp)_3$ / $Ti(mmp)_4$ becomes self-limiting at 600°C due to increased desorption of Bi at higher substrate temperatures, with little increase in Bi content as the mole fraction of $Bi(mmp)_3$ in solution is increased from 0.57 to 0.78.