Liquid-Delivery MOCVD of Strontium Bismuth Tantalate Thin Films Using $\text{Sr}[\text{Ta(OC}_2\text{H}_5)_5(\text{OCH}_2\text{CH}_2\text{OCH}_3)]_2$ and Liquid $\text{Bi(CH}_2\text{CH=CH}_2)_3$ as Precursors**

By Ji-Young Hyeon, Marco Lisker, Mindaugas Silinskas, Edmund Burte,* and Frank T. Edelmann*

Thin films of $\text{BiO}_x\text{Sr}_x\text{Ta}_2\text{O}_7$, and strontium bismuth tantalate (SBT) were deposited by metal-organic (MO)CVD on 150 mm silicon (100) wafers. Some of the wafers were pre-deposited with Pt electrodes. The substrate temperature and the deposition pressure were varied from 300 °C to 600 °C and from 0.35 mbar to 7 mbar, respectively. $\text{Bi(CH}_2\text{CH=CH}_2)_3$ (triallylbismuth) and $\text{Sr}[\text{Ta(OEt)}_5(\text{OC}_2\text{H}_5\text{OEt})](\text{tantalum-pentaethoxide}(2\text{-methoxyethoxide}))$ were used as Bi precursor and as Sr-Ta precursor, respectively. A liquid delivery system was used to supply and to vaporize the precursors into the reactor. X-ray photoelectron spectroscopy (XPS) and ellipsometry were carried out to characterize the film properties. The growth rate of the MOCVD of $\text{BiO}_x\text{Sr}_x\text{Ta}_2\text{O}_7$ was compared to the growth rate of SBT to obtain information about mutual interaction between the precursors. The deposition rate of bismuth oxide thin films was low (~10 nm h⁻¹ at 0.35 mbar) and virtually independent of the temperature. On the contrary, the growth rate of strontium tantalate films depended strongly on the temperature. The deposition rate of the SBT films was similar to the bismuth oxide film deposition, which slightly increased with increasing substrate temperature. However, the deposition rate of SBT was always lower than deposition rate of the single precursors. The growth rate significantly depended on pressure. The decrease of the deposition pressure in the reactor chamber reduced the deposition rate of $\text{BiO}_x\text{Sr}_x\text{Ta}_2\text{O}_7$, and SBT but on the other hand, it improved the uniformity of the film thickness. XPS measurements showed a deficit of bismuth in the SBT films even though the concentration of the Bi precursor had been several times higher than the concentration of Sr-Ta precursor. The XPS depth-profiling by Ar⁺ ion sputtering indicated more metallic bond characteristics of Ti, Sr, and Bi after ion-beam bombardment.

Keywords: Ferroelectrics, Strontium Bismuth Tantalate, Triallylbismuth, Liquid-delivery MOCVD

1. Introduction

There has been great interest in ferroelectric thin films for non-volatile ferroelectric random access memory (FeRAM) applications.¹⁻³ These materials have some advantages over silicon based memories such as faster write speed and lower operating voltage.⁴ $\text{Pb(Zr}_x\text{Ti}_1-x)_3\text{O}_3$ (PZT) has been the most intensively studied material for this application. However, PZT thin films with Pt electrodes exhibit a serious degradation of ferroelectric properties with cumulative polarization which is known as polarization fatigue.⁵⁻⁶ Alternative $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT) materials have been widely used because of their excellent fatigue endurance.⁶⁻⁸ Various deposition techniques such as metalorganic decomposition (MOD), pulsed laser deposition (PLD), sol-gel method, and metalorganic chemical vapor deposition (MOCVD) were used for SBT thin film deposition.⁹⁻¹² The MOCVD process has become widely accepted in the semiconductor industry because of the superior step covering, better control of composition and thickness, and better uniformity over large wafer size compared to other deposition techniques.⁶⁻⁸

In the past, MOCVD of SBT thin films has been severely hampered by a significant lack of suitable precursors, especially those which are liquids at ambient conditions. Exemplary for conventional strontium and tantalum precursors are the diketonate species $\text{Sr(thd)}_2$ (thd = 2,2,6,6-tetramethyl-3,5-heptanediol) and $\text{Sr(thd)}_2$ (tetragnime), as well as the alkoxides $\text{Ta(OCH}_2\text{H}_5)_3$ and $\text{Ta(OPr)}_2$ (thd). Several strontium/tantalum single-source precursors, such as $\text{Sr}[\text{Ta(OCH}_2\text{H}_5)_4]$ and $\text{Sr}[\text{Ta(OCH}_2\text{H}_5)(\text{dmae})]$ (dmae = dimethylaminoethoxide, $\text{OCH}_2\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}$), and $\text{Sr[Ta(OCH}_2\text{H}_5)(\text{dnap})]_2$ (dnap = bis(dimethylamino)isopropoxide, $\text{OCH}_2\text{NH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}$) have also been tested.¹⁰⁻¹² More recently, the liquid-delivery MOCVD production of SBT thin films using a single cocktail of $\text{Sr}[\text{Ta(OCH}_2\text{H}_5}_4](\text{dmae})_2$ and $\text{Bi(CH}_2\text{CH=CH}_2)_3$ has been reported.¹³ On the basis of these results the combination of

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¹⁵ This work was generously supported by the Deutsche Forschungsgemeinschaft (DFG).
Bi(C₄H₅)₃, with yet another bimetallic alkoxide precursor, Sr[Ta(OTf)₃(OC₂H₅OMe)₂] (strontium-bis[tantalum(pentaalkoxide)(2-methoxyethoxide)]) has also been investigated. It was found that the temperature dependence of the deposition rate of Bi(C₄H₅)₃ is much larger than that of Sr[Ta(OTf)₃(OC₂H₅OMe)₂], which makes it difficult to match these two precursors with their very different decomposition characteristics. Thus, there remains a strong demand for suitable alternative Bi precursors. In this study we report initial results obtained with triallylbismuth, Bi(CH₂CH=CH₂)₃, as a new bismuth precursor. In contrast to solid Bi(C₄H₅)₃, triallylbismuth is a liquid at ambient conditions. Unlike the lower bismuth trialkyls such as Bi(CH₃)₃ or Bi(C₂H₅)₃, Bi(CH₂CH=CH₂)₃ is not pyrophoric and is thus a lot easier to handle. Bi(CH₂CH=CH₂)₃ was prepared using a modified literature preparation by treatment of anhydrous BiBr₃ with three equivalents of allylmagnesiumchloride followed by vacuum distillation (c.f. Sec. 4).

In this study, the growth rate of the MOCVD of BiOₓ and SrₓTaᵧO₂z was compared to the growth rate of SBT to obtain information about mutual interaction between the precursors. We focused our research on the film growth kinetics, the thickness uniformity, and the elemental composition.

2. Results and Discussion

In order to estimate the SBT deposition rate and elemental composition, the MOCVD process was investigated for Bi and Sr-Ta precursors separately. Figure 1 shows the dependences of growth rates for Bi, Sr-Ta, and Bi-Sr-Ta precursors at various reactor temperatures and under a pressure of 0.35 mbar. The deposition rate of the bismuth oxide thin films was low (~10 nm h⁻¹) and virtually did not depend on the temperature. On the contrary, the growth rate of strontium tantate films depended strongly on the temperature. Three characteristic ranges were determined for Sr-Ta precursors. The first one was observed at low (350–450 °C) temperatures. In this range, the surface was not activated enough, and the deposition rate was low and almost constant (~12 nm h⁻¹). In the second range (450–550 °C), the process was reaction rate-limited. Above 550 °C, the deposition rate saturated at 30 nm h⁻¹ and a mass transport rate-limited regime was observed. The deposition rate dependence (5–8 nm h⁻¹) of the SBT films was similar to the Bi film deposition that slightly increased with increasing substrate temperature. However, the rate was lower than the deposition rate of the single precursors.

The growth rate significantly depended on the deposition pressure (Fig. 2). Increasing the pressure from 0.35 mbar to 3.5 mbar, the deposition rate of SBT rose from 7 nm h⁻¹ to 45 nm h⁻¹ at a temperature of 550 °C. The changes were not so pronounced at reduced substrate temperatures. The growth rate increased from 5 nm h⁻¹ to 15 nm h⁻¹ at 450 °C. Figure 3 also shows that the growth rate of SBT was always less than the growth rate of SrₓTaᵧO₂z. However, another pressure related effect was observed. The decrease of the deposition pressure in the reactor chamber reduced the deposition rate of BiOₓ, SrₓTaᵧO₂z, and SBT. On the other hand, the pressure reduction improved the uniformity of the film thickness (Fig. 3), very important for microelectronic applications. Figure 3 presents a line scan of the film thickness over the entire 150 nm wafer under pressures of 0.35 mbar and 3.5 mbar. The increase of the substrate temperature improved the film uniformity only under reduced pressure. The standard deviation of the film thickness decreased from 7 % at 350 °C to 3–4 % at 550 ºC. The film thickness was more inhomogeneous under higher pressure at which the standard deviation of the film thickness exceeded 35 %. In this case, there was no correlation between the uniformity of the film thickness and the substrate temperature.

The growth rate depended on the evaporation temperature as well. The decrease of the temperature of the evaporator from 140 °C to 180 °C resulted in a reduced growth rate of the SrₓTaᵧO₂z films of about 10 %. A variation of the growth rate of BiOₓ and SBT was not so significant and did not exceed 5 %.

![Fig. 1. Growth rate of BiOₓ, SrₓTaᵧO₂z, and SBT thin films as a function of the substrate temperature under 0.35 mbar pressure.](http://www.cvd-journal.de)
The XPS measurements of Sr$_x$Ta$_y$O$_z$ indicated that the surface layer of these films contained 24 at.-% carbon, 46 at.-% oxygen, 14 at.-% strontium, and 15 at.-% tantalum (Fig. 4). No more carbon was observed after Ar$^+$ ion bombardment. This means that carbon adsorbed only after the process, and the substrate temperature and oxygen content were sufficient for growing carbon-free films. The other components showed a different behavior with increased sputter time. At first, the amount of Sr, O, and Ta atoms increased, related to the disappearance of carbon. After that, the content of Sr and O decreased. An enhancement tendency of the concentration of Ta remained in the whole Sr$_x$Ta$_y$O$_z$ film. One explanation could be that the sputtering yield of Ta is three times lower than for other elements. The high Ta content in the silicon wafer also supports this assumption, as the Ta concentration in silicon wafer is about 9 at.-% and diffusion at this temperature is unimportant.

The elemental composition of the SBT thin films is presented in Figure 5. Because of the low thickness of the films, the Pt (about 2 at.-%) was observed through the surface layer. The surface concentration of the other elements were as follows: Bi, ~3 at.-%; C, 32 at.-%; Ta, 13 at.-%; Sr, 9 at.-%; and O, 41 at.-%. As in the case of...
Sr₃Ta₄O₁₂z, carbon was observed only in the surface layer; the concentration of the other analyzed elements increased after the first sputtering step. Unfortunately, it was not possible to calculate an exact concentration of each component because of preferential sputtering of bismuth and oxygen. The formula of our SBT films is approximately Sr₃Ta₄Bi₂O₁₂z, while stoichiometric SBT films have two Bi and Ta atoms, and one Sr. The XPS measurements of SBT showed a deficit of bismuth even though the concentration of the Bi precursor was two times higher (0.1 M) than the concentration of the Sr-Ta precursor (0.05 M) (see Fig. 6). The content of Bi in the SBT thin films significantly depended on the oxygen concentration in the deposition gas mixture. When no oxygen was used, the concentration of Bi was about 1 at.-%.

The XPS spectra of Sr₃Ta₄Bi₂O₁₂z at various Ar⁺ ion sputtering times are presented in Figure 6. The peak positions of Ta₁₄5/2 (27.9 eV), Ta₁₇/2 (26.6 eV), Sr₁₃5/2 (135.1 eV), Sr₁₅/2 (133.5 eV), Bi₁₄5/2 (159.1 eV), and Bi₇/2 (164.4 eV) indicated that these elements were in an oxide state. Different bond characteristics of Ta, Sr, and Bi were observed close to the surface than below it after Ar⁺ ion bombardment (see Fig. 6). The peaks of Sr, Ta, and Bi shifted to lower energy. This means that the chemical state of Sr, Ta, and Bi changed from an oxide state to a metallic one, resulting from a preferential sputtering of oxygen atoms.[31]

3. Conclusions

The growth kinetics and elemental composition of BiOₓ·Sr₃Ta₄O₁₂z, and SBT thin films were investigated using triallylbismuth, Bi(CH₃CH=CH₂)₃, and Sr[Ta(OEt)₅·(OC₃H₅OMe)]₂ (strontium-bis[tantalum(pentaethoxide)-2-methoxyethoxide]) precursors. The deposition of SBT thin films was more similar to BiOₓ than to Sr₃Ta₄O₁₂z. The increase of the deposition temperature to 60 °C and of the pressure to 3.5 mbar led to a higher deposition rate. However, the uniformity of the film thickness over the 150 mm wafer was not sufficient. The standard deviation was about 35 % under a pressure of 3.5 mbar. A higher temperature of 600 °C and a lower pressure of 0.35 mbar were more suitable for microelectronic applications.

4. Experimental

General Techniques: The preparation of Bi(CH₃CH=CH₂)₃ was carried out in an inert atmosphere of dry nitrogen using standard dry box and Schlenk techniques. Solvents were carefully dried over Na/benzophenone and freshly distilled prior to use. The starting materials BiBr₃ and allylmagnesiumchloride were purchased from Aldrich and used as received.

Precursor Synthesis: Triallylbismuth, Bi(CH₃CH=CH₂)₃, was synthesized by a modification of a published procedure [16]. A solution of anhydrous BiBr₃ (14.41 g, 32.1 mmol) in diethyl ether (200 mL) was cooled to 0 °C. At this temperature, a 2N THF solution of allylmagnesiumchloride (50 mL, 0.1 M) was added dropwise. The reaction mixture was warmed to room temperature and stirred for 2 h, followed by heating under reflux for 1 h. After cooling again, unreacted Grignard reagent was decomposed by careful addition of a saturated solution of NH₄Cl in N₂-purged water. After filtration through a fine-porosity filter frit, the organic layer was dried over Na₂SO₄. Fractional distillation afforded 4.05 g (38 %) pure Bi(CH₃CH=CH₂)₃ as a colorless, air-sensitive liquid (b.p. 75 °C/1.4 mbar).

MOCVD Experiments: The BiOₓ·Sr₃Ta₄O₁₂z, and SBT thin films were deposited by MOCVD (Fig. 7) under reduced pressure. A liquid delivery system (LDS) was used to supply the precursor to, and to vaporize it in, the reactor. The flows of the precursors were adjusted using liquid flow controllers (LFC). The temperature of the evaporator was varied from 140 °C to 180 °C. The precursor vapors were carried by nitrogen gas (flow rate of 30 sccm) to a hot-box (heated to 160 °C) in which they were mixed with the oxygen that was supplied (flow rate of 50 sccm). The flows of the gases were controlled by mass flow controllers (MFC). The connecting lines between the evaporator, the hot-box, and the reactor were heated to 160 °C in order to prevent the condensation of the precursor. The deposition zone was resistively heated to the deposition temperature that ranged from 350 °C to 650 °C. The MOCVD reactor was equipped with a vacuum pump system and a motor driven pendulum valve to adjust the pressure during the deposition process in a range between 0.35 mbar and 7 mbar. During the film deposition, the reactor wall temperature was kept between 60 °C and 80 °C.

The BiOₓ·Sr₃Ta₄O₁₂z, and SBT thin films were deposited on 150 mm silicon(100) wafers by means of MOCVD. Some of the wafers were deposited with Pt electrodes. Bi(CH₃CH=CH₂)₃(triallylbismuth) and Sr[Ta(OEt)₅·(OC₃H₅OMe)]₂ (strontium-bis[tantalum(pentaethoxide)-2-methoxyethoxide]) were used as Bi precursor and as Sr-Ta precursor, respectively. The precursors were dissolved in toluene 0.05 M for BiOₓ and Sr₃Ta₄O₁₂z film deposition. A mixture of the two precursor solutions was made for SBT deposition. In this case, the concentration of the Bi precursor was two times higher (0.1 M). The deposition conditions are summarized in Table 1.
The film thickness was measured by using a spectroscopic ellipsometer (Sentech SE850). Data were taken within a 248-869 nm wavelength range. The elemental composition was analyzed by XPS using an ESCA 5600 (Mg Kα line). The XPS depth-profiling was performed using 4.5 keV Ar⁺ ion bombardment.

Table 1. Growth conditions of BiOx, Sr$_x$Ta$_y$O$_z$, and SBT thin films.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Bi precursor</th>
<th>Bi(CH$_2$OH)$_3$ (triallylbismuth)toluene (0.05 mol L$^{-1}$)</th>
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<tr>
<td>Sr-Ta precursor</td>
<td>Sr<a href="strontium-bis(tantalum-pentaethoxy(2-methoxyethoxide))">Ta(OEt)$_3$(OC$_2$H$_4$O$_2$Me)$_2$</a>]toluene (0.05 mol L$^{-1}$)</td>
<td></td>
</tr>
<tr>
<td>SBT precursor</td>
<td>Bi(CH$_2$OH)$_3$ (triallylbismuth)toluene (0.1 mol L$^{-1}$) and</td>
<td>Sr<a href="strontium-bis(tantalum-pentaethoxy(2-methoxyethoxide))">Ta(OEt)$_3$(OC$_2$H$_4$O$_2$Me)$_2$</a>]toluene (0.05 mol L$^{-1}$)</td>
</tr>
<tr>
<td>Deposition temperature</td>
<td>350–650 °C</td>
<td>350–650 °C</td>
</tr>
<tr>
<td>Deposition pressure</td>
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<td>0.35–7 mbar</td>
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<tr>
<td>Vaporizer temperature</td>
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<td>Carrier gas (N$_2$) flow rate</td>
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<td>50 sccm</td>
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<tr>
<td>O$_2$ flow rate</td>
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<td>50 sccm</td>
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<tr>
<td>Precursor flow rate</td>
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<td>0.05–1 g h$^{-1}$</td>
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Received: August 14, 2004
Final version: January 27, 2005


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