

Development of a Novel Bismuth Precursor for MOCVD

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1 . Introduction

Bismuth layer-structured ferroelectrics (BLSF) have been investigated as the capacitor materials of next generation memory devices including ferroelectric random access memories (FeRAMs)¹⁾⁻³⁾. BLSF are attractive materials for FeRAMs because they show excellent fatigue endurance.

For the realization of highly integrated devices, more attentions come to be paid to metalorganic chemical vapor deposition (MOCVD). MOCVD is indispensable technique for three-dimensional structure memory devices because of its good step coverage and high growth rate.

There have been several reports on BLSF films preparation by MOCVD using several bismuth precursors, for example BiMe₃, triarylbismuth [BiPh₃ and Bi(o-Tol)₃] and trialkoxidebismuth [Bi(O'Bu)₃ and Bi(mmp)₃]. Among these bismuth precursors, only BiMe₃ is a liquid at room temperature. Liquid precursors are of great advantage for MOCVD process from the viewpoint of the material delivery system. However, BiMe₃ is explosive. It is not safe to handle BiMe₃, especially under mass production process at the factories.

On the other hand triarylbismuth and trialkoxidebismuth are under great disadvantage to MOCVD from the viewpoint of the source delivery system because they are solid and don't have high vapor pressure.

In this work, a development of a novel liquid bismuth precursor for MOCVD is developed that can be use safety and has high vapor pressure.

2 . Experiment

The molecular structure of BiMe₂(Me₂NCH₂Ph) is shown in Fig.1 and is synthesized from bismuth halides, methylating agents and arylating agents.

2.1 Preparation

Diethylether was purified by distillation from sodium / benzophenone under argon. All other solvents were deoxidized by bubbling argon before use. Nuclear magnetic resonance (NMR) spectra were measured with a Varian VXR-500s spectrometer. Mass spectra were determined on mass spectrometry (MS) using an Applied Biosystems QTRAP at TOSOH Analysis and Research Center.

Dimethyl(2-(N,N-dimethylaminomethylphenyl)bismuth - Methylmagnesiumbromide solution (0.6M 25ml, 15.0mmol) in diethylether was added dropwise to a suspension of dicholo(2-(N,N-dimethylaminomethyl-phenyl)bismuth (3.30g, 8.0mmol), prepared from bismuth chloride and 2-(N,N-dimethylaminomethyl-phenyl)lithium, and diethylether at -78 under argon. After the addition was complete, the reaction mixture was allowed to warm to room temperature (R.T.) and stirred for 20h. After the reaction, the reaction mixture was quenched with aqueous NH₄Cl, and extracted with diethylether. The extract was concentrated *in vacuo* and distillation of the residue gave light yellow oil (1.42g, 48%).

¹H-NMR (500 MHz, CDCl₃, /ppm): 7.95 (d, J=7.0 Hz, 1H, ArH), 7.22 (m, 2H, ArH), 7.15 (d, J=7.0 Hz, 1H, ArH), 3.45 (s, 2H, CH₂), 2.17 (s, 6H, NMe), 1.06 (s, 6H, Me). ¹³C-NMR (CDCl₃, /ppm): 177.53 (s, C), 144.53 (s, C), 137.07 (s, CH), 128.60 (s, CH), 128.57 (s, CH), 126.90 (s, CH), 67.66 (s, CH₂), 44.80 (s, CH₃), 3.08 (s,

CH₃). MS: m/z = 374 (M⁺+H). Elemental analysis: C (35.6%), H (5.0%), N (3.7%), Bi (53.5%). C₁₁H₁₈BiN requires C (35.4%), H (4.9%), N (3.8%), Bi (56.0%).

2.2 Measurement of physical properties

Viscosity was measured by use of a rotational viscometer. Vapor pressure was measured directly under high reduced pressure in a closed system using an absolute capacitance manometer. Volatility of Bi precursors was estimated by thermo-gravimetry analysis (TG) and decomposition temperature was measured using a differential scanning calorimeter (DSC).

2.3 Films preparation by MOCVD

Bi₄Ti₃O₁₂ were prepared by MOCVD using BiMe₂(Me₂NCH₂Ph), Ti(OⁱC₃H₇)₄ and O₂ gas. Film composition was calculated and decided by X-ray fluorescence spectroscopy (XRF), which was calibrated with standard film samples. Constituent phases and orientation of the films were characterized by X-ray diffraction (XRD) using CuK radiation. Film thickness was measured by field-emission scanning electron microscopy (FE-SEM).

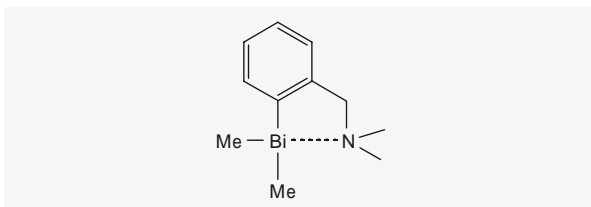


Fig. 1 Molecular structure of BiMe₂(Me₂NCH₂Ph)

3 . Results and Discussion

A novel bismuth precursor, BiMe₂(Me₂NCH₂Ph) was synthesized successfully from bismuth chloride as starting compound and characterized by ¹H-NMR and ¹³C-NMR.

Physical properties of BiMe₂(Me₂NCH₂Ph) is shown in Table 1. BiMe₂(Me₂NCH₂Ph) melts at -49 and is a light yellow liquid of low viscosity (ca.7 cP) at ambient temperature .Furthermore, it has high vapor pressure (0.1Torr/55) as MOCVD precursor. From the view point of precursor delivery, liquid phase at room

temperature provides great advantage as MOCVD precursor.

The flash point of BiMe₂(Me₂NCH₂Ph) is 148 and it is a nonexplosive compound. The gradually oxidative decomposition of BiMe₂(Me₂NCH₂Ph) occurs in contact with O₂ gas, while the reactivity of BiMe₂(Me₂NCH₂Ph) with H₂O is hardly observed. In case of mixing BiMe₂(Me₂NCH₂Ph) and popular other metal precursor, that is Sr(C₁₁H₁₉O₂)₃, La(C₁₁H₁₉O₂)₃, Sr[Ta(OC₂H₅)₂(OC₂H₄OCH₃)₂], Ta(OC₂H₅)₅, Ti(OⁱC₃H₇)₄ or Ti(OⁱC₃H₇)₂(C₁₁H₁₉O₂)₂ directly or dissolved in benzene at R.T., no chemical change in the mixture was observed. As films preparation by MOCVD, BiMe₂(Me₂NCH₂Ph) can be use safety and without its decomposition by such as popular precursor listed above.

Table 1 Physical properties of BiMe₂(Me₂NCH₂Ph)

vapor pressure	0.1 Torr/55
decomposition temprature	230
melting point	- 49
flash point	148
viscosity	7cP
reactivity with H ₂ O	less reactive
reactivity with O ₂	gradually reactive

Fig.2 shows the TG curves as a function of temperature. BiMe₂(Me₂NCH₂Ph) is more volatile than BiPh₃ because molecular weight of BiMe₂(Me₂NCH₂Ph)(Mw373.3) is smaller than that of BiPh₃(Mw440.3).

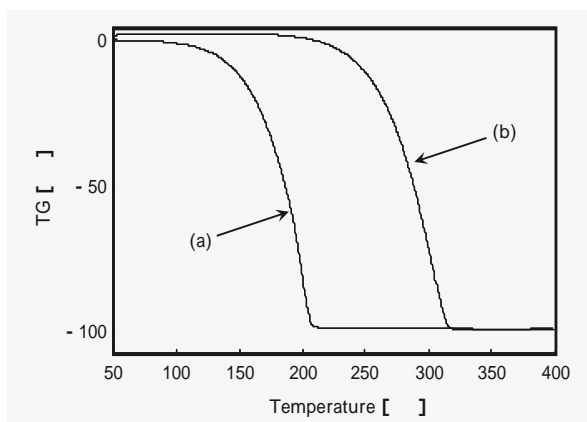


Fig. 2 TG curves of (a) BiMe₂(Me₂NCH₂Ph) and (b) BiPh₃ under Ar atmosphere (heating rate 10 /min)

Fig.3 shows the TG curves and the DSC curves as a function of temperature. The exothermic peaks indicate the decomposition temperatures of the precursors. The result shows that the starting temperature of decomposition of $\text{BiMe}_2(\text{Me}_2\text{NCH}_2\text{Ph})$ is 230 and $\text{BiMe}_2(\text{Me}_2\text{NCH}_2\text{Ph})$ can be vaporized before thermal decomposition. In other words, vaporized $\text{BiMe}_2(\text{Me}_2\text{NCH}_2\text{Ph})$ can be supplied by MOCVD without thermal decomposition.

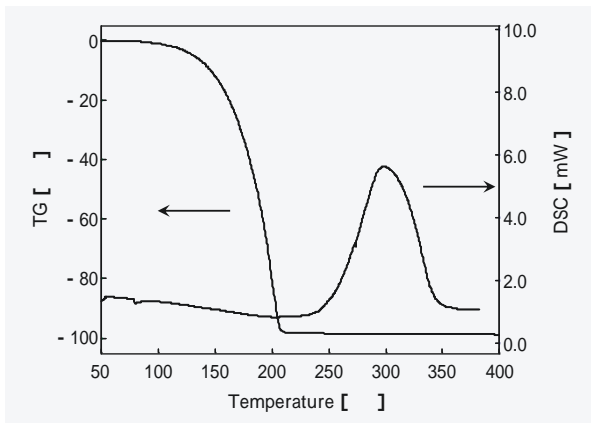


Fig. 3 TG curve and DSC curve of $\text{BiMe}_2(\text{Me}_2\text{NCH}_2\text{Ph})$ under inert gas atmosphere (heating rate 10 / min)

In respect with molecular structure of $\text{BiMe}_2(\text{Me}_2\text{NCH}_2\text{Ph})$, it is assumed that $\text{BiMe}_2(\text{Me}_2\text{NCH}_2\text{Ph})$ has the intramolecular Bi-N coordinate bond by the results of X-ray structure analysis of similar structures, $\text{Bi}(\text{m-Tol})_2(\text{Me}_2\text{NCH}_2\text{Ph})$, to $\text{BiMe}_2(\text{Me}_2\text{NCH}_2\text{Ph})$. Fig.4 shows the result of X-ray structure analysis of $\text{Bi}(\text{m-Tol})_2(\text{Me}_2\text{NCH}_2\text{Ph})$ and the Bi-N length of it is 2.94 .

The intramolecular Bi-N coordinate bond of $\text{BiMe}_2(\text{Me}_2\text{NCH}_2\text{Ph})$ prevent $\text{BiMe}_2(\text{Me}_2\text{NCH}_2\text{Ph})$ from disproportionation of ligands and explosive decomposition.

Fig.5 shows the XRD θ -2 scans of the as-deposited BIT ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$) film with 150nm in thickness prepared on (111)Pt/Si substrate at 500 by MOCVD using $\text{BiMe}_2(\text{Me}_2\text{NCH}_2\text{Ph})$, $\text{Ti}(\text{OC}_3\text{H}_7)_4$ and O_2 gas as starting materials. (004) and (117) diffraction peaks of BIT phase were detected together with that of Pt phase. N atom did not be found from the BIT film by XPS analysis. In other words, the N atoms that are the included element in $\text{BiMe}_2(\text{Me}_2\text{NCH}_2\text{Ph})$ did not largely incorporated into the films during its

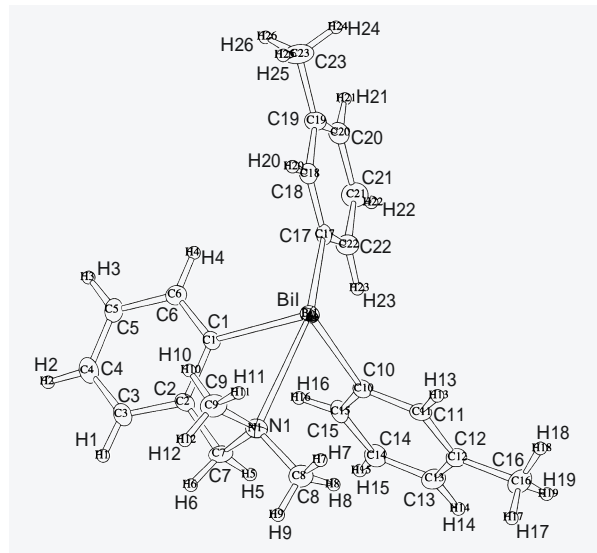


Fig. 4 A drawing of X-ray structure of single crystal of $\text{Bi}(\text{m-Tol})_2(\text{Me}_2\text{NCH}_2\text{Ph})$

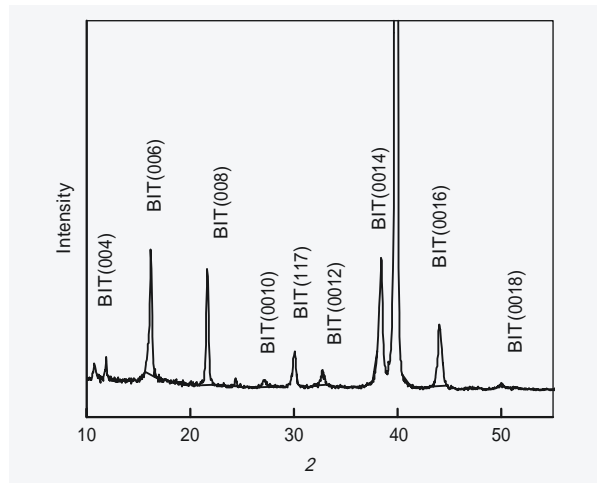


Fig. 5 XRD θ -2 scans of the BIT films prepared by MOCVD from $\text{BiMe}_2(\text{Me}_2\text{NCH}_2\text{Ph})\text{-Ti}(\text{OC}_3\text{H}_7)_4\text{-O}_2$ systems

decomposition.

Other bismuth-contained oxide films, for example $\text{SrBi}_2\text{Ta}_2\text{O}_9$ ⁴⁾, $\text{Bi}_2\text{Zn}_x\text{Nb}_{1-x}\text{O}_7$ ⁵⁾ and BiFeO_3 ⁶⁾, can be also prepared by MOCVD using $\text{BiMe}_2(\text{Me}_2\text{NCH}_2\text{Ph})$ as a starting bismuth precursor.

4 . Conclusion

In this work, we have synthesized a novel Bi precursor $\text{BiMe}_2(\text{Me}_2\text{NCH}_2\text{Ph})$ for MOCVD and its physical properties were examined. This compound is nonexplosive, liquid at ambient temperature and showed excellent volatility and adequate decomposition

temperature. As the MOCVD source for films preparation, BLSF and other bismuth-contained oxide films can be prepared by MOCVD using $\text{BiMe}_2(\text{Me}_2\text{NCH}_2\text{Ph})$.

References

- 1) C. A. Araujo, J. D. Cuchiaro, L. D. McMillan, M. C. Scott and J. F. Scott, *Nature*, 374, 627 (1995)
- 2) S. E. Cummins and L. E. Cross, *J. Appl. Phys.*, 39, 2268 (1968)
- 3) T. Takenaka and K. Sakata, *J. Appl. Phys.*, 19, 31 (1980)
- 4) K. Takahashi, M. Suzuki, M. Yoshimoto and H. Funakubo, *Jpn. J. Appl. Phys.*, 45, L138 (2006)
- 5) S. Okaura, M. Suzuki, S. Okamoto, H. Uchida, S. Koda and H. Funakubo, *Jpn. J. Appl. Phys.*, 44, 6957 (2005)
- 6) R. Ueno, S. Okaura, . H. Funakubo and K. Saito, *Jpn. J. Appl. Phys.*, 44, L1231 (2005)