

REACTION MECHANISM OF A TITANIUM SOURCE, Ti(MPD)(METHD)₂, IN METALORGANIC CHEMICAL VAPOR DEPOSITION

OF (Ba,Sr)TiO₃ FILMS

Takuro Nishimura, Toshihiro Nakamura and Kunihide Tachibana

Department of Electronic Science and Engineering, Kyoto University
Yoshida-Honmachi, Sakyo-ku, Kyoto 606-8501, Japan

High dielectric constant thin-film materials, such as (Ba,Sr)TiO₃ (BST), have been attracting considerable interest due to their high potential for practical application to advanced dynamic random access memories (DRAMs) and integrated tunable microwave devices. Metalorganic chemical vapor deposition (MOCVD) is regarded as a promising technique for the deposition of BST films because of its excellent step coverage. Alkoxy derivatives of titanium diketonates are usually used as titanium source materials for the MOCVD of BST films because of their affinity to barium and strontium diketonate sources. It was reported that the incorporation of sufficient titanium components into the deposited BST film is difficult and that the chemical stability of titanium source significantly influences on the crystallinity of the resultant BST films. The optimum choice of a titanium source material is strongly required on the basis of a deep understanding of chemical reactions of the individual source molecules.

In this work, we investigated the reaction mechanism of a novel titanium source, Ti(MPD)(METHD)₂ (MPD=methylpentanediol, METHD=methoxyethoxy-tetramethylheptanedionato), under actual CVD conditions by *in situ* infrared absorption spectroscopy. One of the H atoms at the corner end of the conventional DPM (dipivaloylmethanato) ligand is substituted with OCH₂CH₂OCH₃. The molecular structures of Ti(MPD)(DPM)₂ and Ti(MPD)(METHD)₂ are shown in Fig. 1. Ti(MPD)(METHD)₂ was dissolved in tetrahydrofuran (THF), and this solution was used as a liquid titanium source material.

Figure 2 indicates a typical infrared absorption spectrum of Ti(MPD)(METHD)₂ obtained by *in situ* spectroscopy. This spectrum was obtained by subtracting the THF absorption from the observed spectrum. The peak at 1115cm⁻¹ can be assigned to C-O stretching modes in the additional methoxyethoxy groups. Based on the temperature dependence of the infrared absorption spectra, we compared the decomposition scheme between Ti(MPD)(METHD)₂ and the conventional titanium sources such as Ti(*i*-PrO)₂(DPM)₂, Ti(*t*-BuO)₂(DPM)₂ and Ti(MPD)(DPM)₂. Figure 3 shows the temperature dependence of the infrared absorption at the substrate temperature between 300°C and 640°C. The vibrational spectral peaks of each titanium source molecule around 1500cm⁻¹ are assigned to the diketonate chelate ring deformation mainly comprising the C-O and C-C stretching modes. Above 500°C, the absorbance of Ti(MPD)(METHD)₂ decreased at a higher temperature than those of other titanium sources. Ti(MPD)(METHD)₂ is relatively stable against thermal decomposition. This shows that the spatial shield of the titanium atom by the additional methoxyethoxy lariat structures contributes to the higher thermal stability of Ti(MPD)(METHD)₂.

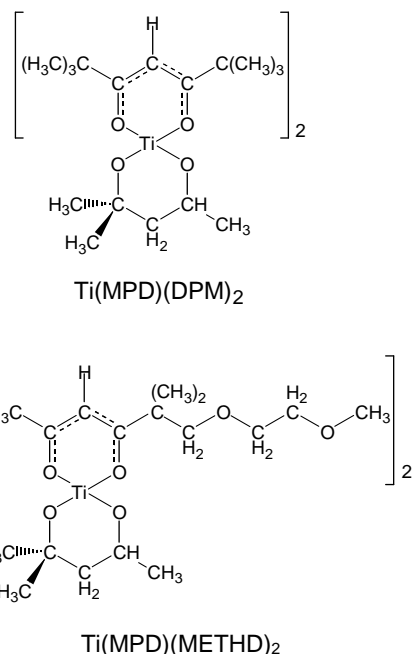


Figure 1. Molecular structures of Ti(MPD)(DPM)₂ and Ti(MPD)(METHD)₂.

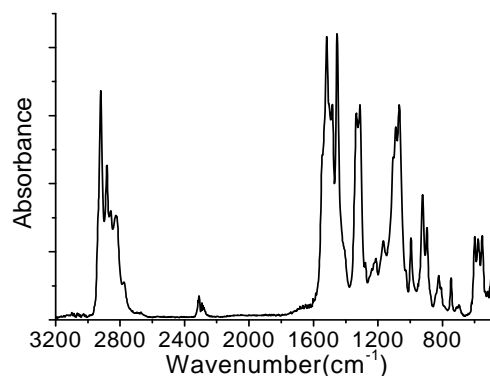


Figure 2. Infrared absorption spectra of Ti(MPD)(METHD)₂ obtained by an *in situ* spectroscopic measurement.

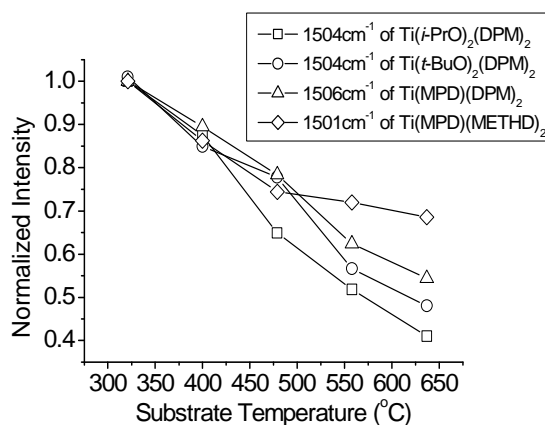


Figure 3. Temperature dependence of the infrared absorption of various titanium sources.