

INFRARED SPECTROSCOPIC STUDY ON
METALORGANIC CHEMICAL VAPOR
DEPOSITION OF (Ba,Sr)TiO₃ FILMS

Toshihiro Nakamura, Takuro Nishimura, Shun Momose
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. The optimum choice of CVD source materials is strongly required on the basis of a deep understanding of chemical reactions of the individual source molecules. Although intensive work has been performed for process development of high-dielectric materials, the deposition chemistry is still not well understood. Recently, we investigated gas phase reactions in MOCVD of BST films by microdischarge optical emission spectroscopy and *in situ* infrared absorption spectroscopy.

In this work, we used a solution of Ti(MPD)(DPM)₂ [methylpentanediol bis(dipivaloylmetanato)titanium] in tetrahydrofuran (THF) as a liquid titanium source material for the deposition of BST films. Figure 1 shows molecular structures of Ti(*i*-PrO)₂(DPM)₂, Ti(*t*-BuO)₂(DPM)₂ and Ti(MPD)(DPM)₂. The titanium source was reported to strongly influence not only the crystallinity but also the step coverage of the deposited BST films. In order to clarify the origin of the difference in deposition chemistry, we investigated the reaction mechanism of the individual titanium source molecules by *in situ* infrared absorption spectroscopy.

Figure 2 indicates a typical infrared absorption spectrum of Ti(MPD)(DPM)₂ obtained by *in situ* spectroscopy. This spectrum was obtained by subtracting the THF absorption from the observed spectrum. Based on the temperature dependence of the infrared absorption spectra, we compared the decomposition scheme between Ti(MPD)(DPM)₂ and mixed titanium alkoxide/diketonate compounds such as Ti(*t*-BuO)₂(DPM)₂ and Ti(*i*-PrO)₂(DPM)₂. Figure 3 shows the temperature dependence of the infrared absorption at the substrate temperature between 240°C and 640°C. The vibrational spectral peaks of Ti(MPD)(DPM)₂ at 1598 cm⁻¹, Ti(*t*-BuO)₂(DPM)₂ at 1600 cm⁻¹, and of Ti(*i*-PrO)₂(DPM)₂ at 1600 cm⁻¹ are assigned to DPM ring deformation modes. The temperature dependence of the absorbance of Ti(MPD)(DPM)₂ showed almost the same behavior as that of Ti(*t*-BuO)₂(DPM)₂. The absorbance of Ti(MPD)(DPM)₂ decreased at a higher temperature than that of Ti(*i*-PrO)₂(DPM)₂. The stability of Ti(MPD)(DPM)₂ is comparable to that of Ti(*t*-BuO)₂(DPM)₂. Ti(MPD)(DPM)₂ is more stable against thermal decomposition than Ti(*i*-PrO)₂(DPM)₂. The present results on titanium source molecules may be applicable for analyzing the MOCVD of other titanium-containing oxide films such as (Pb,Zr)TiO₃ films.

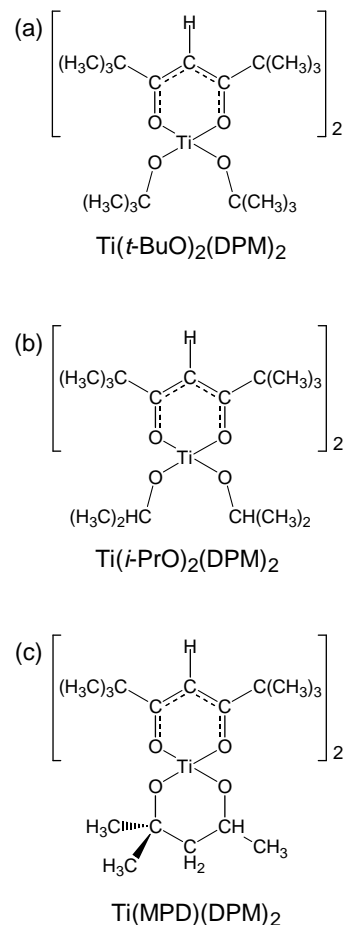


Figure 1. Molecular structures of the CVD source materials: (a) Ti(*t*-BuO)₂(DPM)₂, (b) Ti(*i*-PrO)₂(DPM)₂, and (c) Ti(MPD)(DPM)₂.

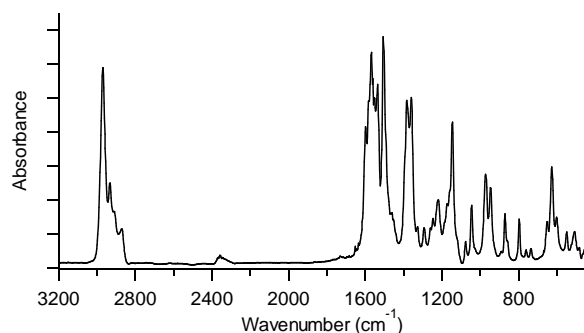


Figure 2. Infrared absorption spectra of Ti(MPD)(DPM)₂ obtained by an *in situ* spectroscopic measurement.

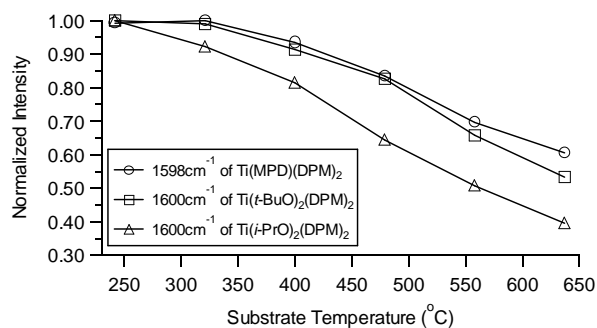


Figure 3. Temperature dependence of the infrared absorption of Ti(MPD)(DPM)₂. The corresponding data on Ti(*t*-BuO)₂(DPM)₂ and Ti(*i*-PrO)₂(DPM)₂ are also shown.