

*Anatase crystallization core led by pentacoordinate titanium *n*-butoxide derivatives*Katsuhiko Koike¹¹Material Science Laboratory, Mitsui Chemicals Inc., Chiba, Japan

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The titanium alkoxide sol-gel method is conventionally used to produce titanium dioxide. The activity of the titanium alkoxide is reduced by adding ligands such as acetyl acetone (acac), which prevent crystallization. During the sol-gel process, an acid is required to control the solvent pH, as the reaction proceeds rapidly under basic conditions.

An alternative method for producing a TiO₂ film involves the use of a mixture of titanium butoxide in concentrated hydrochloric acid. This Ti(OBuⁿ)₄/conc. HCl mixture is stable and hence can be used for the preparation of a thin film by coating it on a glass plate or highly heat resistant polymer film that does not show crack formation. The resulting thin film can be converted to a TiO₂ anatase thin film via annealing at 400 °C, which is lower than that required for acac (500 °C). Ti(OBuⁿ)₄ would form a nucleation point for crystallization. However, the detailed crystallization mechanism for the formation of a thin film comprising anatase TiO₂ crystals using this raw material is not yet fully understood. I, therefore, aimed to identify the crystallization core led from the Ti(OBuⁿ)₄ mixture to clarify the crystallization mechanism at lower process temperatures. Specifically, the complex structures present in the mixture and film coating prior to annealing were identified. In this study, the effects of chloride anions and water molecules in the conc. HCl solution were investigated, as it was hypothesized that this solution plays an additional role in the crystallization process, besides pH regulation.

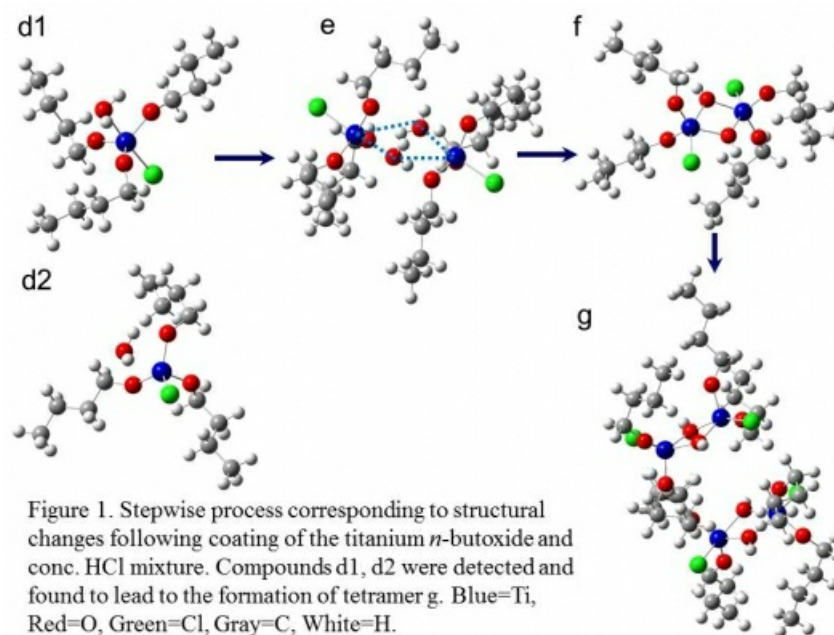
The stability of Ti(OBuⁿ)₄ derivatives bearing coordinated Cl⁻ and/or H₂O was calculated using the density functional theory (DFT) method [1]. Thermodynamic calculations were carried out to determine the reaction energy and to examine the possible structure of the Ti(OBuⁿ)₄/HCl cluster mixture. Thus, pentacoordinate *n*-butoxide derivatives Ti(OBuⁿ)₃Cl•H₂O of structures d1 and d2 (see Figure 1) were detected in the mixture. The presence of these complexes was confirmed using a combination of multinuclear magnetic resonance spectroscopy and gauge-independent atomic orbital calculations [2].

The mixture was coated on a substrate using a wire bar and dried according to a stepwise process (23 °C, 5 min; 50 °C, 10 min; 110 °C, 10 min) to obtain a 100-nm-thick coating layer. The various molecular structures present during this process were analyzed by DFT calculations, which indicated that structure d1 dimerized to give structure e. A Ti=O₂=Ti structure was then generated, leading to structure f, which further dimerized to give tetrameric structure g. IR analysis of the film coating confirmed the presence of compound g.

Finally, I found the similarities between structure g and the anatase crystal, which include a diamond-like Ti=O₂=Ti structure, and considered g was the crystallization core for anatase crystallization in the low process temperature (i.e., 400 °C).

[1] K. Koike. (2015). Chem. Lett. 44, 1339-1341.

[2] K. Koike. (Submitted). Chem. Lett.



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