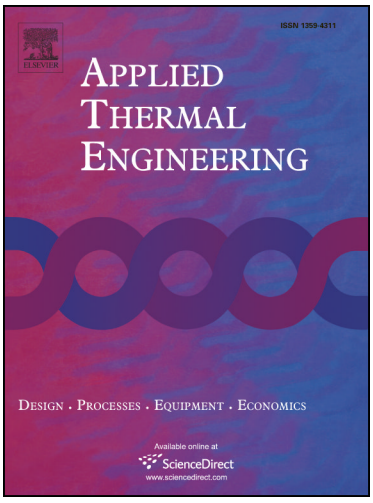

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Chemical reaction-transport model of diethylzinc hydrolysis in a vertical MOCVD reactor

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ABSTRACT: ZnO thin film has many uses as a semiconductor material. It can be fabricated by chemical vapor deposition with diethylzinc (DEZn) and water vapor. The present study employs density functional theory to examine reaction complexes of DEZn with 1–2 molecules of water, which may occur in the gas phase according to previous studies. The kinetic and thermodynamic data provide a better understanding of the ZnO deposition process. A computational fluid dynamics analysis was carried out using the kinetic parameters to simulate the deposition rate of ZnO in a reaction chamber, showing the dependence of the film growth rate on temperature. The simulation data agreed with the experimental one within 8%, proving the feasibility of the current chemical reaction-transport model of diethylzinc hydrolysis. Furthermore, the fields of the flow, the temperature, the multi-species transport, and the chemical reaction were analyzed. These insights could reveal the reaction kinetics of ZnO thin film fabrication in the metal-organic chemical vapor deposition chamber. The results show that the pathway involving nucleation and growth of oligomers from trimers, and ultimately particle formation, is consistent with the decreased growth rate at increasing temperatures. The maximum growth rate of ZnO film was obtained at 573 – 773 K when ZnO is grown by DEZn and H_2O in a horizontal chamber rotating at high speed. When the temperature is above 773 K, parasitic reactions lead to a rapid decline in the ZnO deposition rate. These insights could reveal the reaction kinetics of ZnO thin film fabrication; and help with the reactor design, optimization, and process parameter adjustment in the metal-organic chemical vapor deposition process.

1. Introduction

ZnO, a group II-VI compound semiconductor material with wide band, has excellent photoelectric performance. It has great potential for applications in blue light- and UV light-emitting devices, exciton lasers, and spintronic devices [1-3]. Metal-organic chemical vapor deposition (MOCVD) is an important technology for growing ZnO thin films, due to the large epitaxy area, good reproducibility, high deposition rate, etc [4-7]. However, the associated reaction mechanism and oxide growth kinetics are difficult to study, because of the complicated physical and chemical processes involved. Thus, it is important to fully understand the chemical reaction path, in order to optimize the reaction chamber design and produce high-quality films.

In general, the transition states contain key information about chemical reactions. However, experimental studies of their structures are often difficult due to their short lifetime. With the development of quantum chemistry methods and computational tools, it is possible to study the structures and properties of transition states in silico to reveal the reaction mechanisms [8-10]. Quantum chemistry calculation, being a numerical simulation method in the framework of quantum mechanics, is one of the accurate theoretical methods for obtaining the geometry and energy of molecules [11,12]. It allows one to obtain accurate information about the whole reaction process from a microscopic point of view.

In recent years, great progress has been made in understanding the chemical reaction kinetics of group III-V compounds, and gradually began to apply to the growth of materials in MOCVD [13-26]. Chen et al. [16] indicated that a strong parasitic reaction occurs between TMAl and NH3, and this is the main reason for the decrease in AlN growth efficiency at high temperature and high pressure. The results suggest that parasitic reactions are much more severe for TMAl+NH3 than for TMGa+NH3. Mitrovic et al. [21-23] from the equipment manufacturer Vecco studied the stabil-