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Simulation and Suppression of the Gas Phase Pre-reaction in Metal-Organic Chemical Vapor Deposition of ZnO *

ZHU Guang-Yao(朱光耀), GU Shu-Lin(顾书林)**, ZHU Shun-Ming(朱顺明), TANG Kun(汤坤), YE Jian-Dong(叶建东), ZHANG Rong(张荣), SHI Yi(施毅), ZHENG You-Dou(郑有炓)

Nanjing National Laboratory of Microstructures and School of Electronic Science and Engineering, Nanjing University, Nanjing 210093

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The reaction mechanism and simulations of the metal-organic chemical vapor deposition reactor for ZnO film growth are presented, indicating the temperature of the reaction species. The gas phase pre-reaction can be modulated by several factors or conditions. Simulations verify the relationships between temperature and pyrolysis of precursors, and further reveal that the substrate temperature and flow rate of cooling water have great impacts on the temperature distribution. The experimental results agree with the simulations.

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ZnO is a wurtzite structure direct-gap semiconductor. Because of its wide bandgap of 3.37 eV at room temperature and large exciting binding energy of 60 meV, ZnO is an excellent material for efficient short-wavelength optoelectronic light-emitting devices and detectors.[1] Metal-organic chemical vapor deposition (MOCVD) is a promising method to grow high-quality Ⅲ–V semiconductor materials, such as GaN and GaAs,[2−5] and is also believed to be suitable for ZnO growth.[6]

However, the strong gas phase pre-reaction between the zinc and oxygen species has hindered the progress to grow high-quality ZnO by MOCVD. In this case, several zinc MO species and oxygen species have been tested to attain optimized growth of high-quality ZnO. However, compared with ZnO attained on MBE,[7] the progress in MOCVD is still tough to make for most researchers.

High-quality ZnO growth is usually based on the best choice of the appropriate zinc and oxygen species, and temperature controlling is another significant aspect. In this work, both experiments and simulations are employed to research the case mentioned above.

Figure 1 demonstrates the schematic diagram of our homemade MOCVD system. The cylindrical vertical reactor has a stainless steel shower head on the top, which is designed to keep precursors from mixing and reacting too early. Each nozzle of gas is 4 mm away from each other. The substrate is located at approximately 1.5 cm below the shower head on a graphite susceptor heated by a resistance heater. Cooling water flows through the channels in the shower head to keep the shower head and the incoming precursors at a low temperature. Temperature on the underside of the shower head is surveyed by an Rh-Pt thermocouple as a criterion to predict gas phase pre-reactions. Zinc and oxygen precursors are chosen from DEZn, DMZn, O_2 and t-BuOH, respectively. Nitrogen is taken as the carrier gas. The operating pressure in the chamber is kept at 4 kPa. The mass spectrometry system was mounted on a port in the reactor pump line to analyze the gas composition.

In thermodynamics and fluid mechanics, heat transfer is a complicated problem involving many aspects. However, in our case the convective heat transfer coefficient may be roughly estimated to follow the simplified method. The rate of convective heat transfer is defined in Newton's law of cooling:[8]

$$Q = H_0(T_{\text{body}} - T_\infty). \tag{1}$$

The cooling water is heated when they flow through the shower head,

$$Q = \frac{c\rho V(T_{\text{out}} - T_{\text{in}})}{S}. \tag{2}$$

In these equations, Q is the rate of convective heat transfer, H_0 is the coefficient of convective heat transfer, T_{body} is the temperature of the cooling water channels in the shower head, T_∞ is the temperature of the oncoming cooling water, S is the effective area of the face on which the heat convection between water and the shower head takes place, c, ρ and V are respectively the specific heat, density and flow rate of cooling water, T_{in} and T_{out} are the temperature when the water flow in and out of the system, respectively. T_{body} and T_∞ are acquired from simulation experientially.

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**Correspondence author. Email: slgu@nju.edu.cn

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Thus, the convective heat transfer coefficient can be expressed as

$$H_0 = \frac{c\rho V(T_{\text{out}} - T_{\text{in}})}{S(T_{\text{body}} - T_{\infty})}. \quad (3)$$

The unit of H_0 is W/m^2·℃. The results are calculated and set as one of the terminal conditions in simulations.

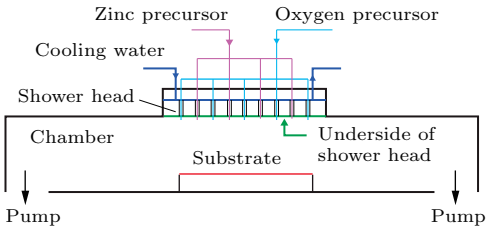

Fig. 1. Schematic diagram of the MOCVD reactor.

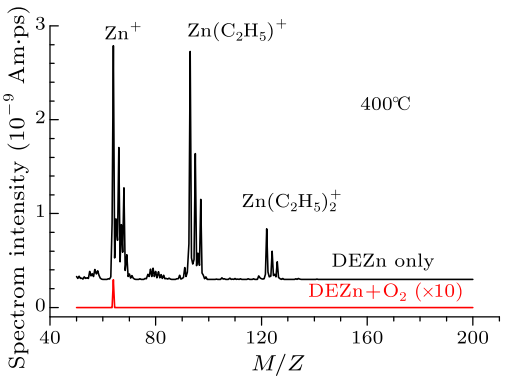

Fig. 2. Mass spectroscopy of DEZn and O_2.

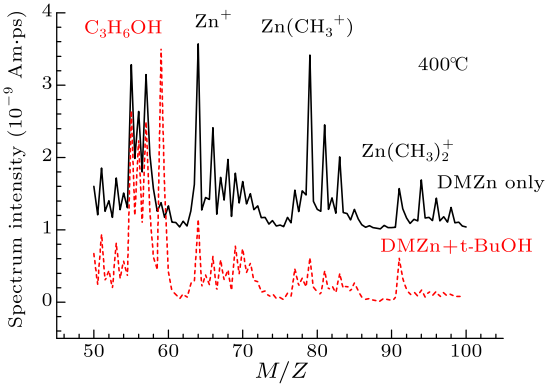

Fig. 3. Mass spectroscopy of DMZn and t-BuOH.

The decomposition ratios of diethyl zinc versus the growth temperature derived from the mass spectroscopy have been reported in our previous work.[9] It was suggested that significant increase of the decomposition starts at 400℃ and reaches a high value at about 500℃, which is about 100℃ higher than that reported in the literature.[10,11] On the contrary, O_2 performed a much better thermal stability than DEZn when introduced into the chamber separately.[9]

However, diethyl zinc decomposes even at room temperature by reaction with oxygen. In this case, strong gas phase pre-reaction is expected to occur in the reactor if zinc and O precursors mixed too early. Figure 2 indicates the mass spectroscopy for the case of DEZn and O_2. When DEZn is introduced alone, radicals of $Zn(C_2H_5)_2^+$, $ZnC_2H_5^+$, and Zn^+ can be observed. Once O_2 is added, those radicals disappear, leaving a very weak residual of Zn^+. Atomic as well as molecular oxygen strongly consumes Zn related species. Only residual zinc atoms existing in gas phase are detected by mass spectroscopy. In fact, the gaseous oxidation of diethyl zinc is a fast autocatalytic chain reaction with a slow initiation reaction producing stable peroxide.[12]

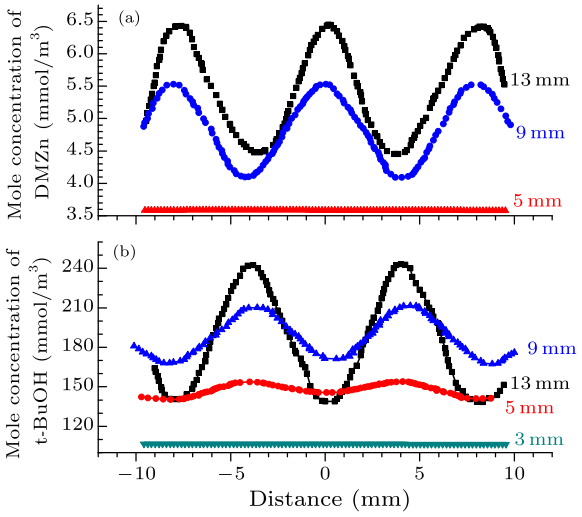

Fig. 4. Calculated mole concentration distribution of (a) DMZn and (b) t-BuOH at various distances from the substrate (substrate temperature 600°C).

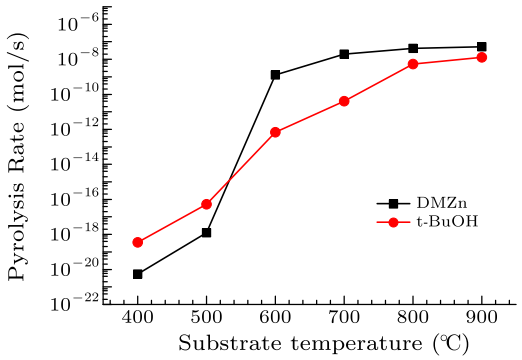

Fig. 5. Calculated pyrolysis rate of DMZn and t-BuOH in the completely mixing area above the substrate, with varous substrate temperatures.

DMZn [13] and t-BuOH [14] decompose in 280℃–450℃ and 350℃–450℃, respectively. The reactions between them are studied using the mass spectroscopy. As shown in Fig. 3, when DMZn is introduced alone, radicals of $Zn(CH_3)_2^+$, $ZnCH_3^+$, and Zn^+

can be observed. When t-BuOH is added, the radicals decrease to a low level, but still exist. The peak (M/Z = 59) is recognized as C_3H_7O radical from the mass spectroscopy of t-BuOH alone (not shown here), which agrees well with the result reported in the literature.[14] Referring to Fig. 2, t-BuOH is slightly weaker in capacity of oxidation than O_2, which could provide two O atoms. Higher temperature may enhance the capacity of t-BuOH, because it completely decomposes at about 450°C as reported in Ref. [7].

As suggested above, the gas phase pre-reaction strongly depends on the gas species temperature, which is determined and changed by various factors and needs to be understood. Simulation has then been carried to investigate the temperature distribution in the MOCVD reactor employed for the above ZnO growth.

Many groups have studied the reaction kinetics for pyrolysis of organic precursors,[15–22] as listed in Table 1. The data are approximately in good agreement. We employ their data in simulations to adjust the Arrhenius equation

$$k = A\exp(-E_a/RT), \tag{4}$$

where k is the rate of the reaction, A and E_a are pre-exponential factor and activation energy, respectively.

Table 1. Kinetic Parameters for pyrolysis of organic precursors.

$Zn(CH_3)_2 \rightarrow ZnCH_3+CH_3$			
T (°C)	A	E_a (kJ/mol)	References
400	6.00×10^{5}	22.000	[15]
500	6.50×10^{10}	94.999	[15]
600	2.00×10^{13}	225.924	[16]
700	2.00×10^{13}	225.924	[16]
800	1.78×10^{11}	197.481	[17]
900	1.78×10^{11}	197.481	[17]
$tert\text{-}C_4H_9OH \rightarrow iso\text{-}C_4H_8+H_2O$			
T (°C)	A	E_a (kJ/mol)	References
400	2.00×10^{12}	137.168	[18]
500	2.00×10^{12}	137.168	[18]
600	3.24×10^{11}	228.020	[19]
700	3.98×10^{14}	276.983	[20]
800	7.76×10^{14}	275.561	[21]
900	2.51×10^{13}	257.727	[22]

Two conditions are essential to gas phase pre-reaction: one is complete mixing of precursors, and the other is that the local temperature is high enough to initiate the pyrolysis. To investigate the mixing of precursors, we establish a model in which DMZn and t-BuOH both are introduced but reaction between them is not yet included. The substrate temperature is set to be 600℃. Figure 4 reveals the mole concentration distribution of precursors at various distances from the substrate. In Figs. 4(a) and 4(b), nozzles of DMZn are located at the positions −8 mm, 0 mm and 8 mm on the X coordinate, while nozzles of t-BuOH at −4 mm and 4 mm, respectively. As the black dots indicated, when the distance is 13 mm, the distributions of both precursors are nonuniform. When gases approaches to the substrate, the distribution becomes more uniform, because of thermal diffusion of molecules. At the distance of 3 mm for DMZn and 5 mm for t-BuOH, precursors distribute evenly and are thought to be completely mixed.

Pyrolysis of precursors are simulated separately at different substrate temperatures to verify their thermal stability. The gas phase pre-reaction can not occur without pyrolysis of precursors. Figure 5 shows the estimated pyrolysis rate of DMZn and t-BuOH in the complete mixing area at different substrate temperatures. The increments of both precursors are relatively high below 600℃ than those at higher temperature, which demonstrates that most precursors have already decomposed before they are heated to 600℃. The amount of DMZn and other radicals containing Zn which are finally carried to the substrate dominate the deposition rate of the ZnO film in MOCVD. When the substrate temperature rises from 400℃ to 900℃, the mole concentration of DMZn which reaches onto the substrate decreases from 1.9 to 0.2 mmol/m^3. The great loss in pyrolysis is disadvantageous to the deposition rate and crystal quality.

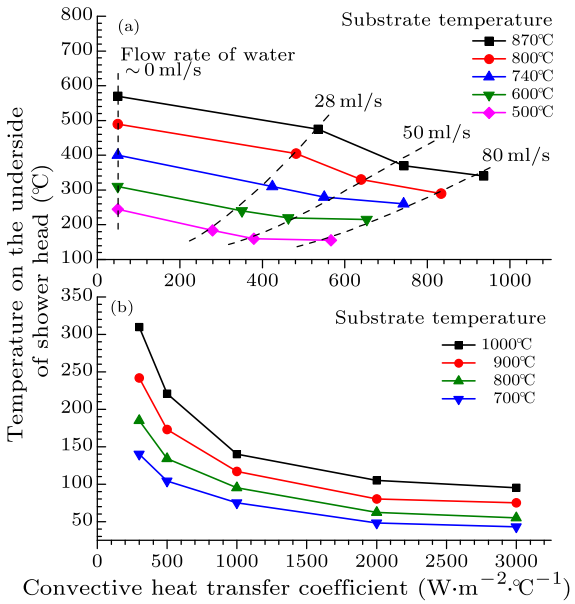

Fig. 6. Temperature of shower head with varous substrate temperatures and convective heat transfer coefficient, from (a) experiments and (b) simulations.

Thus, temperature controlling becomes essential and should be carefully studied. Comparisons have been made through simulations and experiments. Figure 6(a) exhibits the dependence of temperature (on the underside of shower head) on convective heat transfer coefficient in the cases of different substrates.

Convective heat transfer coefficients are calculated from formula (3). The temperature falls when the flow rate of the cooling water increases. At higher substrate temperature, the same flow rate of water could result in more abrupt fall of temperature than that at low substrate temperature. Contributions of cooling water are more essential for high temperature MOCVD processes.

Furthermore, Fig. 6(a) reveals the mechanism of the heat transfer in shower head. First, the heats absorbed from substrate are conducted to the channels of cooling waters, at the rate dominated by thermal conductivity of shower head, which is made by stainless steel. Second, the heats are then transferred to the cooling water, and the rate here is dominated by convective coefficient which is actually affected by the flow rate of cooling water. The first one is an unchangeable property of the system. The second one could change in a wide range and is most effective in high temperature processes.

In Fig. 6(b), simulations show similar changes of temperature with different substrate temperatures and widely varied convective heat transfer coefficient. The trends are almost the same as that in Fig. 6(a), but the simulated data are generally 100℃ below those obtained from experiments due to inevitable difficulties in survey. Positive result is that low temperature is achievable if the heat conductivity coefficient reaches $1000\,\mathrm{W/m^2\cdot ℃}$.

In summary, the gas phase pre-reaction during MOCVD ZnO growth is found to be strongly depending on the kind of the precursors and the temperature. To avoid it, DMZn and t-BuOH are proved to be ideal precursors. Simulations and experiments demonstrate that cooling water can effectively modulate the temperature of the shower head. The research may be constructive for designing and process optimization of ZnO MOCVD systems.

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