Competitive adsorption and two-site occupation effects in metal-organic chemical vapor deposition of ZnO

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The growth dynamics of ZnO epilayers by metal-organic chemical vapor deposition have been investigated by a comprehensive modeling of the competitive adsorption and two-site occupation effects. The established model, based on Langmuir-Hinshelwood mechanism, well explains the abnormal growth rate dependence on the VI/II ratio for different growth regimes. It is found that, for surface reaction and mass-transport limited growth, the competitive adsorption and two-site occupation effects dominate the surface adsorption process, respectively. The proposed dynamics model quantitatively well matched a wide range of experiments, providing a new insight into the general MOCVD growth mechanism for binary compound materials. © 2007 American Institute of Physics. [DOI: 10.1063/1.2731529]

ZnO is an ideal candidate for next-generation oxide photonic devices, especially after the recent realization of ZnO-based light-emitting diodes (LEDs) and photodetectors in the ultraviolet region. For large scale manufacturing, metal-organic chemical vapor deposition (MOCVD) is a preferred technique for the growth of high-quality epilayers and complex device structures. Recently, high-quality ZnO epilayers and ZnO-based LEDs have also been realized via MOCVD. Although the growth dynamics in MOCVD process have been extensively investigated, the independent optimization of its growth parameters has always been challenging due to the complexity. For ZnO MOCVD growth, considerable progresses have been made in determining the optimized conditions as reviewed in Refs. 10 and 11. But these optimizations have been conducted empirically for specific reactor configurations. Therefore, studies on the general growth kinetics and reaction mechanism in MOCVD growth of ZnO are still lacking. In this letter, we shall propose a growth dynamics model, considering the effects of growth temperature, VI/II molar ratio, and their interaction, to explain the abnormal growth of ZnO. The validity of the model is confirmed by its reasonable agreement with a wide range of experiments.

In this study, the samples were epitaxially deposited by the MOCVD system reported elsewhere. The substrates used were Al$_2$O$_3$ and quartz, and no discernible difference in growth rate is observed for these substrates. The thickness was determined by a step profiler and calibrated by cross-section scanning electron microscopy measurements. The precursors employed were diethylzinc (DEZn) and high-purity oxygen gas (O$_2$). Firstly, we performed the ZnO deposition at 380 °C. The VI/II ratio was modulated by changing the O$_2$-flow rate with a constant DEZn molar flow rate. It was found that the growth rate decreased gradually with the increase of VI/II ratio, as shown in Fig. 1. In our study, the dilution effect from the increase of O$_2$-flow rate can be ruled out, because the growth rate is normalized to the unit DEZn molar partial pressure. In addition, the reactant precursors were introduced separately and mixed just above the substrate surface; thus the effect of parasitic gas phase reaction can also be ignored. These abnormal results have been observed in low temperature growth of GaN and ZnO materials, which were believed to be associated with the typical growth kinetics. Figure 2 shows the growth rate of ZnO at 550 °C as a function of the VI/II molar flow ratio. It can be seen that the normalized growth rate increases sub-linearly with the increase of VI/II ratio and saturated for ratio larger than 420.

The fact that different growth temperature regimes have different growth rate dependences is shown in Figs. 1 and 2. In order to understand the impact of VI/II ratio on the growth rate, the correlation of growth temperature and growth rate needs to be clarified. We conducted a series of ZnO growth experiments on quartz substrates over a broad range of temperature from 300 to 800 °C with the fixed reactant mole fractions and constant total flow rate. In Fig. 3, the typical

![Figure 1](image-url)
kinetic-limited growth behavior was observed from Arrhenius plots. The trend is similar to the temperature-dependent growth rate of ZnO on GaAs substrate. Figure 3 shows three distinct regimes: (1) the low temperature kinetically controlled regime below 400 °C (regime I), in which the reactants’ surface reaction limits the growth rate and the thermal activation energy \(E_a\) is estimated to be \(\sim 155\) meV; (2) the midtemperature mass-transport limited regime (regime II), in which the mass transport of the Zn precursor becomes the rate-limiting factor, and the activation energy \(E_a\) is only \(\sim 11\) meV, indicating a very weak dependence on temperature; and (3) the high temperature desorption limited regime (regime III).

It is understood that the correlation of growth rate and VI/II ratio is strongly influenced by the growth temperature since different reaction mechanisms dominate. Two mechanisms of surface reactions are possibly involved: (1) Langmuir-Hinshelwood (LH) mechanism, where both precursors go through independent heterogeneous decomposition reaction paths on the surface, and (2) Langmuir-Rideal mechanism, where one of the precursors goes through homogeneous decomposition reaction in the gas phase and then reacts with adsorbed molecule. It depends on the usage of reactant sources and the growth temperature. In this study, the Langmuir-Rideal mechanism could be excluded due to the decomposition mechanisms of DEZn. In the following, the dynamics model will be presented based on LH mechanism, accompanied with the discussion of the experimental results.

As shown in Fig. 3, the surface reaction controls the growth rate for growth temperature lower than 400 °C. For the case of ZnO growth at 380 °C, due to lack of sufficient thermal activation energy, DEZn precursor prefers to undergo a LH heterogeneous reaction path to yield methylthelyzinc (MEZn) species. For adsorption,

\[
\text{DEZn(gas)} + \theta_F \rightarrow k_1 \text{MEZn(ads)} + \text{C}_2\text{H}_5^* \quad \text{(radical)},
\]

\[
\text{O}_2 + \theta_F \rightarrow \text{O}_2(\text{ads}).
\]

For desorption,

\[
\text{MEZn(ads)} \rightarrow k_1' \text{DEZn(gas)} + \theta_{\text{Zn}},
\]

\[
\text{O}_2(\text{ads}) \rightarrow k_2' \text{O}_2(\text{gas}) + \theta_{\text{O}_2}.
\]

For reaction,

\[
de\text{Zn} + \theta_{\text{Zn}} + \text{DEZn(ads)} \rightarrow k_3 \text{ZnO(solid)} + \text{MeZn + by-products}.
\]
In this case, the independent surface coverage fractions and the Zn surface atom or of O surface atom with ZnH\textsubscript{2}, a two-site reaction provides enough free surface adsorption sites respectively different in the nature of adsorbed species. It shall be noted that the same physical rule is valid, which means that the growth is O limited; the growth rate increases sublinearly with the VI/II ratio. As the VI/II ratio is increased over 420, the growth converted to the zinc-limited regime. In this case, the surface coverage of oxygen adatoms is increased, and subsequently, the growth rate becomes saturated. Given \( K_{2}^{1/2} P_{O_{2}}^{1/2} > 1 \Rightarrow K_{1} P_{ZnH_{2}} \) due to strong oxygen adsorption and increased Zn-species desorption, Eq. (11) can be reduced to \( r_{ZnO}^{'} = K_{1}^{'} K_{2}^{1/2} P_{DEZn} \), so that the growth rate is independent of VI/II ratio but rather limited by the gas phase mass transportation of DEZn. These theoretical analyses are in good agreement with the experimental results in Fig. 2.

In summary, the epitaxial growth dynamics of ZnO by MOCVD have been modeled with the abnormal growth behavior in different growth regimes revealed. At surface reaction controlled regime, oxygen species prevent the adsorption of Zn-related species effectively, resulting in the decrease of growth rate. At mass-transport limited regime, two-site adsorption mechanism is expected, and the growth rate is determined by mass transport of Zn precursor. The validity of the model is confirmed by its reasonable agreement with a wide range of experiments, providing a new insight into the general MOCVD growth dynamics of binary compound materials.

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\( E_{a1} = 155 \text{ meV}, \) which was obtained from Fig. 3. In fact, the suppressed growth rate can be qualitatively explained by Eq. (5), in which a competitive adsorption effect is involved. Due to the low growth temperature, the adsorbed species has low mobility on the growing surface and adsorb indifferently on either Zn or O sites. Increasing VI/II ratio will result in the increase of \( \theta_{O} \), effectively preventing the adsorption of Zn-related species and leading to a decrease of \( \theta_{Zn} \) and growth rate. The suppressed growth behavior due to site-blocking effect has been previously observed in the low temperature growth of GaN and ZnO.\textsuperscript{12,13}

At a higher temperature of 550 °C (regime II in Fig. 3), the growth is limited by the mass transport of DEZn precursor. With high enough thermal activation energy, the dominant homogeneous decomposition reaction of DEZn in the gas phase can be written as:\textsuperscript{18,19}

\[
\text{DEZn(gas)} \rightarrow \text{ZnH}_{2}(\text{gas}) + \text{C}_{2}\text{H}_{4}(\text{gas}) \quad (\beta - \text{hydride elimination}).
\]

Previous kinetic studies show that DEZn decomposes homogeneously in the gas phase via the \( \beta \)-hydride elimination path to form ZnH\textsubscript{2}.\textsuperscript{18,19} Given the low thermal stability of ZnH\textsubscript{2} and its derivatives, ZnH\textsubscript{2} adsorbed on the substrate surface and reacted with oxygen adatoms to form ZnO films:

\[
\begin{align*}
\text{ZnH}_{2} + \theta_{Zn} & \rightarrow \text{Zn(ads)} + \text{H}_{2}(\text{gas}), \\
\theta_{Zn} & \rightarrow \text{Zn(ads)} + \theta_{Zn}, \\
\text{O}_{2} + 2 \theta_{O} & \rightarrow 2\text{O}^{'}(\text{ads}), \\
2\text{O}^{'}(\text{ads}) & \rightarrow \text{O}_{2} + 2 \theta_{O}, \\
\theta_{Zn} + \theta_{O} & \rightarrow \text{ZnO(solid)}.
\end{align*}
\]

By comparing Eqs. (1) and (10), it can be seen that the distributions of Zn and O in gas phase and in solid film follow the same physical rule (LH-type growth behavior) but are different in the nature of adsorbed species. It shall be noted that, in the mass-transport limited regime, the surface is not fully covered by the precursor’s adatoms because the surface reaction provides enough free surface adsorption sites regardless of the increase of VII/II ratio. In addition, due to the strong Lewis acid–Lewis base interaction of oxygen with Zn surface atom or of O surface atom with ZnH\textsubscript{2}, a two-site noncompetitive adsorption mechanism is expected.\textsuperscript{15,20} In this case, the independent surface coverage fractions and the growth rate of ZnO can be expressed as

\[
\begin{align*}
\theta_{O} & = \frac{K_{2}^{1/2} P_{O_{2}}^{1/2}}{1 + K_{2}^{1/2} P_{O_{2}}^{1/2}}, \\
\theta_{Zn} & = \frac{K_{1} P_{ZnH_{2}}}{1 + K_{1} P_{ZnH_{2}}}, \\
\theta_{ZnO}^{'} & = K_{1}^{'} \theta_{O} \theta_{Zn} = \frac{K_{1}^{'} K_{2}^{1/2} P_{O_{2}}^{1/2} P_{ZnH_{2}}}{1 + K_{2}^{1/2} P_{O_{2}}^{1/2} + K_{1} P_{ZnH_{2}}}.
\end{align*}
\]

At VII/II ratio lower than 400, the surface coverage of oxygen is low, and the item \( K_{2}^{1/2} P_{O_{2}}^{1/2} < 1 \) is valid, which means that the growth is O limited; the growth rate increases sublinearly with the VI/II ratio. As the VI/II ratio is increased over 420, the growth converted to the zinc-limited regime. In this case, the surface coverage of oxygen adatoms is increased, and subsequently, the growth rate becomes saturated. Given \( K_{2}^{1/2} P_{O_{2}}^{1/2} > 1 \Rightarrow K_{1} P_{ZnH_{2}} \) due to strong oxygen adsorption and increased Zn-species desorption, Eq. (11) can be reduced to \( \theta_{ZnO}^{'} = K_{1}^{'} K_{2}^{1/2} P_{DEZn} \), so that the growth rate is independent of VI/II ratio but rather limited by the gas phase mass transportation of DEZn. These theoretical analyses are in good agreement with the experimental results in Fig. 2.