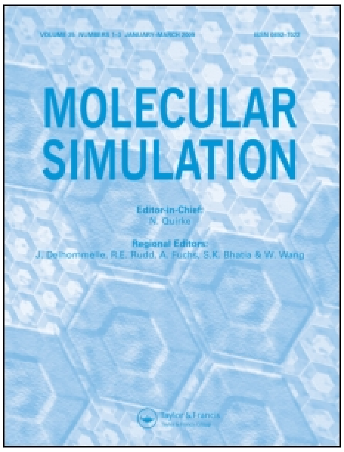

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What the Sawtooth In Situ Signal Implies about the Surface-reaction Mechanism for Alternate-supply OMVPE Growth of ZnSe

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What the Sawtooth *In Situ* Signal Implies about the Surface-reaction Mechanism for Alternate-supply OMVPE Growth of ZnSe

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The surface chemical processes underlying peculiar sawtooth behavior of optical-reflection signal obtained by *in situ* monitoring the growing surface of ZnSe epitaxial film under alternate supply of diethylzinc (DEZn) and dimethylselenium (DMSe) were elucidated with the help of *ab initio* molecular orbital methods. The sawtooth signal was found to imply successful formation of the Zn-stabilized ZnSe surface.

Keywords: Surface chemical physics; *Ab initio* molecular orbital methods; Organometallic vapor phase epitaxy; Wide-bandgap semiconductor

INTRODUCTION

In order to further evolve quantum-functional nano-devices using metastable condensed phases, it has become indispensable in recent years to ingeniously utilize selective surface reactions of labile chemical species such as neutral free radicals and organometallic molecules for the device processing [1–3]. In previous experiments of organometallic vapor phase epitaxial (OMVPE) growth of nitrogen-doped ZnSe on a GaAs (0 0 1) substrate at 400°C using N_2 or H_2 as carrier gas, we performed *in situ* optical-reflection measurements of the growing surface with a variety of supply sequences of diethylzinc (DEZn), dimethylselenium (DMSe), and alkylnitrene biradicaloid species produced by the method of Photo-Dissociation of Energetic Compound Beams [4,5]. The measurement results gave clues to the microscopic mechanism for the alternate-supply OMVPE growth of ZnSe. Our recent studies based on them are aimed at theoretical and molecular simulational clarification of the surface chemical reactions involved in the homoepitaxial growth [6].

Figure 1 shows a typical example of the time-dependent change in reflection signal observed under the alternate supply of DEZn and DMSe using H_2 carrier gas. An interesting feature is that the DEZn-induced reflection signal consists of two different components: the signal increases rapidly within 15 s and then turns to a gradual decrease even during the DEZn supply. This sawtooth behavior repeats itself reproducibly with the alternate source supply sequence, with a constant increase in the overall average signal intensity after each DEZn + DMSe cycle, indicative of layer-by-layer growth of ZnSe as expected. In this article, we discuss the origin of the sawtooth reflection signal in terms of surface chemical physics.

SIGNIFICANCE OF THE SAWTOOTH REFLECTION SIGNAL

When an atomically flat surface of a ZnSe heteroepitaxial film is being covered with sub-monolayer chemisorbates as in the case of the previous experiments, power reflectance R of p-polarized light directed onto the surface at an incident angle ϕ depends on time t through the surface coverage θ_X of each of the chemisorbed species "X" and thickness D of the heteroepitaxial film. Dependence of the relative change in optical

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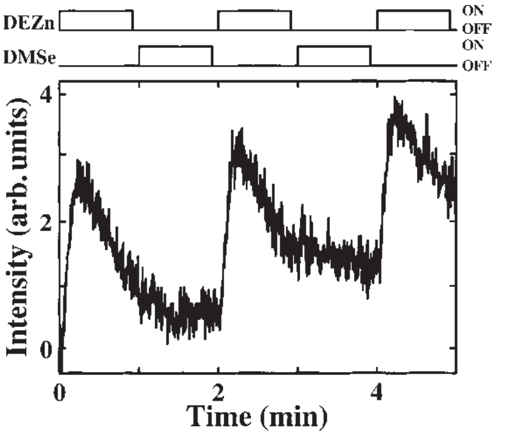

FIGURE 1 Time-dependent change in the reflected light intensity for alternate supply of DEZn and DMSe observed when pure H_2 was used as carrier gas. The time sequences of the supplies are illustrated by square waves at the top of the figure.

reflectance $\Delta R/R$ on θ_X's is approximated by the following linear function:

$$\frac{\Delta R}{R} = \sum_X C_X \theta_X. \qquad (1)$$

The coefficient C_X in Eq. (1) corresponds to change in optical reflectance due to monolayer chemisorption of species "X". We estimated the value of C_X for several possible chemisorption patterns under this experimental condition, based on calculation of optical polarizability using random phase approximation. The result indicated the following common features.

(i) The value of C_X is always non-negative. That is to say, a non-negative change in the reflection signal is observable with increasing surface coverage θ_X.
(ii) A taller chemisorbed species "X", for example, one terminated by a longer alkyl chain, results in a greater value of coefficient C_X owing to its larger optical polarizability. Thus, the predicted value of C_X is greater for ZnC_2H_5 chemisorbed by the Se-stabilized ZnSe surface than for bridge-site atomic Zn without terminal groups, and that for $Se(CH_3)_2$ chemisorbed by the Zn-stabilized ZnSe surface is greater than for SeH_2.

The non-monotonic change in optical reflectance observed during the DEZn supply onto the Se-stabilized surface (Fig. 1) suggests existence of at least two DEZn-related dominant chemisorbed species, namely, some taller species "A" besides Zn species "B" constituting two-dimensional islands of the next Zn-stabilized surface. The sawtooth behavior is probably a sign of a rapid increase followed by a gradual decrease of surface coverage θ_A. Based on a quantum chemical study described later, we believe that "A" is monoethylzinc covalently bonded to a surface Se atom and "B" is bridge-site atomic Zn without terminal groups. A DEZn molecule provided onto the growing ZnSe surface was chemisorbed first as the intermediate "A", which was then converted to the more stable form "B".

We can explain the sawtooth change in θ_A under the steady flow of DEZn most reasonably by incorporating an inhibition mechanism of chemisorption into the reaction model given by the following rate equations:

$$\frac{d\theta_A}{dt} = \gamma_s(1 - \theta_A - \theta_B) - (\gamma_{AB} + \gamma_{Ad})\theta_A, \qquad (2a)$$

$$\frac{d\theta_B}{dt} = \gamma_{AB}\theta_A - \gamma_{Bd}\theta_B, \qquad (2b)$$

where γ_s is the adsorption rate of "A" molecules per chemisorption site on the Se-stabilized ZnSe surface under DEZn supply; γ_{AB} is a conversion rate constant of the Zn adsorbate from "A" to "B"; γ_{Ad} and γ_{Bd} are desorption rate constants of the chemisorbed species "A" and "B", respectively. Since γ_{Ad} and γ_{Bd} are practically negligible in comparison to γ_s and γ_{AB}, an analytical solution of Eq. (2a) and (b) is approximated by

$$\theta_A = \frac{\gamma_s}{\gamma_s - \gamma_{AB}}(e^{-\gamma_{AB}t} - e^{-\gamma_s t}), \qquad (3a)$$

$$\theta_B = 1 - \frac{1}{\gamma_s - \gamma_{AB}}(\gamma_s e^{-\gamma_{AB}t} - \gamma_{AB} e^{-\gamma_s t}). \qquad (3b)$$

Equation (3a) qualitatively reproduces the sawtooth time dependence of θ_A. Once occupied by species "B", an adsorption site on the Se-stabilized surface no longer chemisorbs subsequently supplied DEZn molecules. As a result, θ_A decreases with the gradual increase in surface coverage θ_B. Consequently, this inhibition mechanism results in the observed reduction of signal intensity in the second half of DEZn cycle. Although the inhibition mechanism proposed here is not the only possible explanation for the sawtooth change in θ_A, we believe it to be the simplest one. The other possible explanations may be based on non-linear surface reactions, e.g. autocatalytic formation of Zn islands.

Elucidation of the dominant chemical reactions responsible for the ZnSe growth during DEZn supply onto the hydrogen-terminated Se-stabilized (0 0 1) surface was attempted in the present study with the help of *ab initio* molecular orbital methods.

COMPUTATIONAL METHOD

Optimization of equilibrium structures and transition-state geometries were carried out using the program package Gaussian 03 at the self-consistent

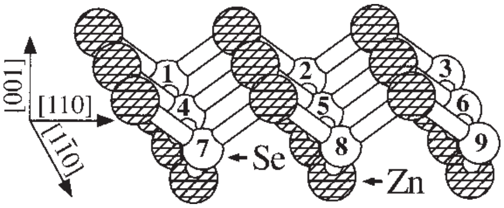

FIGURE 2 Slab model adopted here for the Zn-stabilized (0 0 1) surface of ZnSe.

field level of theory [7]. The thermal energy correction at the growth temperature including the zero-point energy correction was taken into account.

COMPUTATIONAL RESULTS AND DISCUSSION

Figure 2 shows the slab model adopted here for the Zn-stabilized (0 0 1) surface of ZnSe. The structural parameters of the slab were set equal to those of bulk single-crystal ZnSe at the growth temperature, and were kept constant in all calculations. First, we optimized the equilibrium structure for chemisorbed selenium dihydride covering the Zn-stabilized surface, using the standard STO-3G basis set under the periodic boundary condition in the [1 −1 0] and [1 1 0] directions. The obtained geometry-optimized model of the hydrogen-terminated Se-stabilized surface (Fig. 3) was used to examine several possibly dominant pathways for the chemisorption of a DEZn molecule onto the Se atom marked with an asterisk (*) in Figs. 3–5. According to the prediction using the standard 6–31G(d) basis set at the unrestricted Hartree–Fock level of theory (denoted as UHF/6–31G(d)), the reaction most likely proceeds via ethane elimination to yield the chemisorbed monoethylzinc intermediate (Fig. 4); the products are more stable than the reactants by 2.10 eV. The activation energy E_{a1}^{H} is 0.95 eV. Then, several possibilities for the rate-limiting process subsequent to surface diffusion of the chemisorbed monoethylzinc intermediate were analyzed at the UHF/6–31G(d) level of theory. The predicted predominant pathway involves ethane elimination to form the bridge-site atomic Zn without terminal groups (Fig. 5(a)); the products are more stable than the reactants by 1.14 eV. The activation energy E_{a2}^{H} is 1.31 eV. Figure 5(b) shows another possible pathway, where the β-elimination step is followed by the step involving H_2-elimination. The activation energies for these steps were predicted to be 2.11 and 1.54 eV, respectively. The result that $E_{a1}^{\mathrm{H}} < E_{a2}^{\mathrm{H}}$ tentatively justifies the assumption that $\gamma_s > \gamma_{AB}$ made above to explain the sawtooth behavior of the reflection signal.

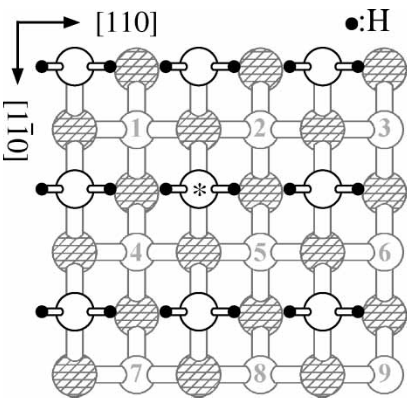

FIGURE 3 Predicted equilibrium structure of chemisorbed selenium dihydride covering the Zn-stabilized surface.

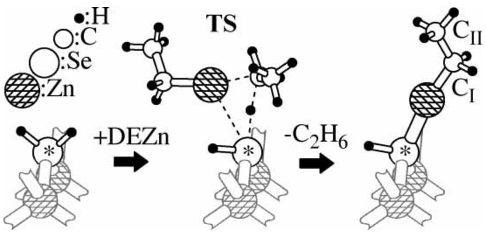

FIGURE 4 Predicted pathway for the chemisorption of a DEZn molecule onto the hydrogen-terminated surface Se atom marked with an asterisk (*) in Fig. 3. TS denotes the transition state.

CONCLUSION

In this article, we discussed the homoepitaxial growth mechanism of ZnSe under alternate supply of DEZn and DMSe from the molecular simulational point of view, based on the observations obtained previously

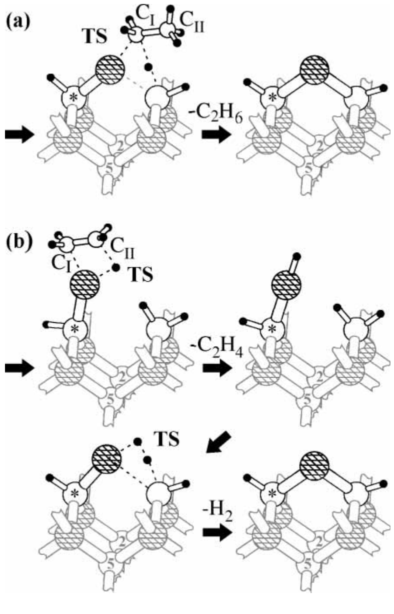

FIGURE 5 Predicted reaction mechanisms for the structural conversion of the chemisorbed monoethylzinc intermediate to the bridge-site atomic Zn without terminal groups. (a) Predominant pathway involving elimination of ethane; (b) another possible one involving elimination of ethylene and H_2.

by the *in situ* optical-reflection measurements of the growing surface. Through this study, we noticed that the unique sawtooth signal observed during DEZn cycle under certain growth conditions serves as an indication of the successful formation of the Zn-stabilized ZnSe surface.

Acknowledgement

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