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journal or publication title	Japanese Journal of Applied Physics
volume	52
page range	096701
year	2013-08-12
出版者	Japan Society of Applied Physics
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URL	http://hdl.handle.net/10297/7411

doi: 10.7567/JJAP.52.096701

Inference on the Production Mechanism of ZnO Thin Films from Activated Water and Dimethylzinc Molecules

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The reaction of $\text{Zn}(\text{CH}_3)_2$ and activated H_2O produced in a reaction of H_2 and O_2 on a Pt catalyst and effused from a nozzle was examined both experimentally and theoretically. This reaction has been shown to be effective in the preparation of high-quality ZnO films. Laser-induced fluorescence measurements showed that radical species, such as H atoms and OH radicals, do not play major roles. The rotational temperature of H_2O , measured with a coherent anti-Stokes Raman scattering technique, was 250 K. This low rotational temperature suggests that H_2O molecules must be accelerated along the beam axis and that the collisional energy between $\text{Zn}(\text{CH}_3)_2$ and H_2O is as high as 43 kJ mol⁻¹. This energy is higher than the potential barrier to produce $\text{HOZnCH}_3 + \text{CH}_4$, 38 kJ mol⁻¹, obtained by *ab initio* calculations at the MP2/LANL2DZ level of theory. HOZnCH_3 thus produced can be the strongest candidate ZnO film precursor.

1. Introduction

Recently, Nishiyama *et al.* have shown that high-quality ZnO epilayers can be fabricated from catalytically produced activated water vapor and dimethylzinc molecules.¹⁾ They produced a beam of activated water vapor in a reaction of H₂ and O₂ on a Pt-dispersed ZrO₂ catalyst. The electron mobility in the ZnO films fabricated was 140-170 cm² V⁻¹ s⁻¹, while the residual electron concentration was 2-6×10¹⁷ cm⁻³. These properties are much better than those of the films prepared by other chemical and physical techniques.²⁻⁹⁾ The optical transmittance in the visible and near-infrared regions was more than 90% when the film thickness was 1 μm. The deposition rate can be around 1 nm s⁻¹. It is expected that ZnO films thus fabricated can be used for many optoelectronic devices, such as laser diodes and light-emitting diodes. However, the production mechanism of these thin films is not clear.

In the preset work, in order to clarify the production mechanism, coherent anti-Stokes Raman scattering (CARS) spectra of water molecules just after the ejection from a nozzle were recorded. Information on the rotational and vibrational distributions was obtained from the spectra. Laser-induced fluorescence measurements were also carried out to detect H atoms and OH radicals in the gas phase. In addition, *ab initio* calculations were carried out to evaluate the potential barriers of relevant reactions.

2. Experimental Procedure

The flow system, including the catalyst and the vacuum chamber, was similar to that described elsewhere.¹⁾ A schematic diagram of the catalyst holder and the nozzle is shown in Fig. 1. H₂ and O₂ were introduced into a Pt-dispersed ZrO₂ catalyst through

pulsed valves (MAC 34C-ABA-GDFC-1KT) to produce activated H₂O vapor. The open time of the valves was 30 ms and the repetition rate was 10 Hz. The average flow rate of H₂ was 0.34 slm (1 slm = 6.9×10⁻⁴ mol s⁻¹). H₂O formed on the catalyst surfaces effused into a spherical vacuum chamber, 19 cm in internal diameter, through a convergent-divergent nozzle. The diameter at the nozzle throat was 0.3 mm, while the length between the throat and the exit was 24 mm. The exit diameter was 4.7 mm. The vacuum chamber was evacuated with a turbomolecular pump (Pfeiffer PM P03 934) backed by a dry pump (Unozawa KTS015). The typical stagnation pressure was 58 kPa, while the pressure in the chamber was 1.1 Pa. The continued population ratio of H₂, H₂O, and O₂ in the chamber, measured with a quadrupole mass spectrometer (Inficon Transpector 2), was 0.25:1.0:0.01. The quadrupole mass spectrometer was attached to the chamber through a sampling hole (0.5 mm in diameter). The flight tube was differentially pumped down to 3 × 10⁻⁴ Pa with another turbomolecular pump (Pfeiffer PM P03 941). The sensitivity of the mass spectrometer was calibrated by flowing a known amount of gases. The nozzle position could be adjusted and the typical distance between the nozzle exit and the laser beam to detect H₂O was 4 mm. Dimethylzinc could also be introduced into the chamber through a needle valve.

In CARS measurements, a folded BOXCARS optical configuration was used to avoid the interference of background signals caused by water vapor in air.¹⁰⁾ Figure 2 shows the experimental apparatus schematically. The second harmonic of a neodymium-doped yttrium aluminum garnet (Nd:YAG) laser (Quanta-Ray GCR-170) at 532 nm was split into two parts. One part was used to pump a dye laser (Sirah CSTR-LG-18) whose output was used as the tunable Stokes beam, ω_s . The wavelength was scanned between 659.0 and 661.5 nm. The Stokes pulse energy was 5

mJ. The remaining part, 14 mJ per pulse, was used directly as the pump beam, ω_P . The pump beam was split into two equally intense parallel ones and entered the vacuum chamber through a 100-mm-focal-length convex lens. The Stokes beam also entered the chamber through the same lens and intersected with the pump beams at the center of the chamber. The path lengths of the pump and Stokes beams were adjusted for the appropriate temporal overlap. Both beams were vertically polarized. The laser beams and the created anti-Stokes signal beam, $\omega_{AS} = 2\omega_P - \omega_S$, were recollimated with another convex lens placed at the exit of the chamber. The anti-Stokes beam was separated from the other beams with a spatial filter and the signal was detected with a photomultiplier tube (Hamamatsu Photonics R212) through dichroic filters (Sigma Koki DIF-BLE) and a monochromator (JASCO CT25CP). The slits of the monochromator were widely opened to ensure the wavelength independence of the detection sensitivity. The photomultiplier signal was amplified and processed with a boxcar averager-gated integrator system (Stanford Research Systems SR240/SR250/SR280) or a digital oscilloscope (LeCroy 6051A).

The densities of H atoms and OH radicals in the beam were attempted to be measured by one-photon laser-induced fluorescence techniques following excitation at 121.6 nm and around 308 nm, respectively. The apparatus and the procedures were similar to those described elsewhere.¹¹⁻¹⁴⁾

H₂ (Japan Air Gases, 99.999%), O₂ (Japan Air Gases, 99.999%), and dimethylzinc (Tri Chemical Laboratories, 99.9999%) obtained from cylinders were used without further purification.

3. Results

Figure 3 shows typical CARS spectra of H₂O vapor in the ν_1 symmetric stretching region under bulk conditions at room temperature and that effused from the nozzle. The three peaks observed under bulk conditions correspond to the rotational structure. The CARS spectral profile of H₂O from the nozzle did not change when the pressure in the chamber was doubled to 2.1 Pa by adjusting the H₂ and O₂ flow rates, or when the distance between the nozzle edge and the detection point was doubled to 8 mm. Figure 4 shows the results. In addition, no changes were observed when a glass substrate was placed 22 mm downstream from the nozzle exit. By comparing the experimental spectrum with a simulated one, the rotational temperature of H₂O from the nozzle was determined to be 250 K. This is much lower than the temperature before expansion, 1700 K.¹⁾ The absence of the (1,1,0)-(0,1,0) hot band around 3630 cm⁻¹ suggests that the production of vibrationally excited H₂O is minor. The procedure used to simulate the CARS spectrum was similar to those employed by other investigators¹⁵⁻¹⁸⁾ as well as by ourselves.^{10,19)} Experimentally derived energy levels reported by Tennyson *et al.* were used in the simulation.²⁰⁾ Only the Q branch transition, with the selection rule of $\Delta J=0$, was taken into account in the simulation, since other branches are much weaker. In the Q-branch transition, another selection rule, $\Delta(K_a-K_c)=0$, can be assumed. Here, J , K_a , and K_c are the quantum numbers for the total angular momentum and its projection on the A- and C-axes. Strictly, the Raman scattering cross sections depend on the rotational quantum numbers, but this dependence is minor and was ignored. The rotational level dependence of the line width was not taken into account, either, since the width of the YAG laser at 532 nm is larger. The laser width was chosen to reproduce the spectrum under bulk conditions. The nuclear spin statistical weight for

the rotational states, 1 and 3 for even and odd K_a-K_c values, was, of course, included in the simulation.

The CARS signal intensity increased with the gas flow rate, but it decreased with the distance from the nozzle. Figure 5 shows the square root of the CARS signal as a function of the reciprocal of the distance. In other words, the H_2O density is inversely proportional to the distance. Although we used pulsed valves, the H_2O signal showed no dependence on the delay time from the opening or closing time of the valves. The H_2O flow from the nozzle must have been almost continuous.

The detection of H atoms and OH radicals in the beam by one-photon laser-induced fluorescence analysis was unsuccessful. The densities of the H atoms and OH radicals were below the detection limits, 3×10^9 and 1×10^9 cm^{-3} , respectively. The contribution of radical species in the film deposition must be minor. If we assume that the radical density is 10^9 cm^{-3} and that the rate constant for the reactions with dimethylzinc is as large as 10^{-10} cm^3 s^{-1} , the reactive lifetime of dimethylzinc is 10 s, which is much longer than the expected residence time in the chamber. The residence time of gas molecules estimated from the chamber volume, pressure, and flow rate is on the order of 10^{-2} s. We also attempted to detect $HOZnCH_3$ and other possible intermediates mass-spectrometrically. The $Zn(CH_3)_2$ pressure was increased up to 0.3 Pa, which is two orders of magnitude higher than that under typical deposition conditions, but we failed. The sensitivity must have not been sufficient.

4. Theoretical Calculations

We have also carried out *ab initio* calculations for the reaction between $Zn(CH_3)_2$ and H_2O by a Gaussian09 program.²¹⁾ Geometry optimization, as well as the

calculations of potential and zero point energies, was carried out at the restricted Møller-Plesset second-order perturbation theory (RMP2) with the LANL2DZ basis set. An unrestricted calculation was also carried out for ZnO, but the singlet state was found to be lower in energy than the triplet state. Figure 6 illustrates the potential energy profile of the lowest singlet states. The transition state structures were determined by a quadratic synchronous transit (QST) method. They were further confirmed by intrinsic reaction coordinate (IRC) calculations. In some reaction processes, the contribution of excited transition states has been discussed,²²⁾ but such a contribution was not taken into account because the reaction rate must be controlled by the potential barrier height along the minimum energy path.

It was revealed that $\text{H}_2\text{O}\cdot\text{Zn}(\text{CH}_3)_2$ adducts are stable. Their potential energy is 45 kJ mol^{-1} below that of the reactants when the Zn-O bond length is 0.23 nm and the C-Zn-C bond angle is 162° . The potential energy of the transition state to produce $\text{HOZnCH}_3+\text{CH}_4$ from $\text{H}_2\text{O}\cdot\text{Zn}(\text{CH}_3)_2$, TS1, was calculated to be 38 kJ mol^{-1} higher than that of the reactants. The potential barriers for the $\text{HOZnCH}_3+\text{H}_2\text{O} \rightarrow \text{Zn}(\text{OH})_2+\text{CH}_4$ and $\text{HOZnCH}_3 \rightarrow \text{ZnO}+\text{CH}_4$ reactions were calculated to be 182 and 394 kJ mol^{-1} , respectively. Similar results were obtained in density functional theoretical calculations with B3LYP.

5. Discussion

There are several theoretical calculation studies for the reactions of diethylzinc and oxide molecules, including water.²³⁻²⁶⁾ However, few studies have been reported on dimethylzinc. In the reactions of diethylzinc with water molecules, two mechanisms have been proposed. One is a radical mechanism and another is a molecular or closed

shell mechanism. In the radical mechanism, the initial step is the thermal decomposition of $\text{Zn}(\text{C}_2\text{H}_5)_2$. The products are either $\text{HZnC}_2\text{H}_5 + \text{C}_2\text{H}_4$ or $\text{ZnC}_2\text{H}_5 + \text{C}_2\text{H}_5$. C_2H_5 thus produced may abstract H from H_2O to form OH, which may react with $\text{Zn}(\text{C}_2\text{H}_5)_2$ to produce HOZnC_2H_5 .²⁴⁾ In the molecular mechanism, the first step is the formation of $\text{H}_2\text{O} \cdot \text{Zn}(\text{C}_2\text{H}_5)_2$ 1:1 adducts, which dissociate to $\text{HOZnC}_2\text{H}_5 + \text{C}_2\text{H}_6$. HOZnC_2H_5 thus produced may further react with H_2O to form $\text{Zn}(\text{OH})_2$. Similar molecular mechanisms, such as adduct formation followed by alkane elimination, have been proposed in group 13–15 systems, such as $\text{Ga}(\text{CH}_3)_3 + \text{NH}_3$.²⁷⁻³⁰⁾ The formation of dimers and tetramers of $\text{Zn}(\text{OH})_2$ from monomers is energetically possible, but the dehydration reaction, $\text{Zn}(\text{OH})_2 \rightarrow \text{ZnO} + \text{H}_2\text{O}$, is too endothermic to take place in the gas phase.²³⁾ This was also confirmed in our present calculations. In the present $\text{Zn}(\text{CH}_3)_2 + \text{H}_2\text{O}$ system, only the closed shell mechanism must be important. The initial step must be the production of $\text{H}_2\text{O} \cdot \text{Zn}(\text{CH}_3)_2$ adducts, which dissociate to $\text{HOZnCH}_3 + \text{CH}_4$.

The low rotational temperature of H_2O suggests that the flow is supersonic and the translational temperature along the beam is higher than that of the inlet gas. Nishiyama *et al.* have estimated the catalyst temperature to be 1700 K.¹⁾ The gas temperature before expansion must be similar. In a hydrodynamic flow, the ratio of the gas temperature after expansion to that before expansion, T/T_0 , is given by³¹⁾

$$\frac{T}{T_0} = \left(1 + \frac{\gamma - 1}{2} M_s^2 \right)^{-1}. \quad (1)$$

Here, γ is the specific heat ratio, M_s ($=v_s/c_s$) the local flow Mach number, v_s the local velocity along the beam axis, and c_s ($=\sqrt{\gamma RT/m}$)^{1/2} the local speed of sound. R and m are the gas constant and molar mass, respectively. The ratio of v_s to the most probable

beam velocity under effusive flow, $v_{mp} (=3RT_0/m)^{1/2}$, is given by

$$\frac{v_s}{v_{mp}} = M_s \left[\frac{\gamma}{3 + (3/2)(\gamma - 1)M_s^2} \right]^{1/2}. \quad (2)$$

In the present system, since the expanding gas is a 0.25:1 mixture of H₂ and H₂O according to the mass spectrometric measurements, we may assume that γ is 1.31, the weighted average of 7/5 and 9/7. T_0 is 1700 K, while T may be assumed to be the same as the measured rotational temperature, 250 K. Then, M_s and v_s are calculated to be 6.1 and 2.4 km s⁻¹, respectively. The velocity distribution is given by³¹⁾

$$\frac{\Delta v_s}{v_s} = \left(\frac{2}{\gamma} \right)^{1/2} \frac{1}{M_s}. \quad (3)$$

Then, the collisional energy between H₂O and Zn(CH₃)₂ under the center-of-mass system should be $43 \pm_{15}^{19}$ kJ mol⁻¹. Here, the most probable velocity, $(2RT/m)^{1/2}$, at 300 K was assumed for the velocity of Zn(CH₃)₂, but it should be noted that the collisional energy depends little on the choice of this velocity because of the large mass difference between H₂O and Zn(CH₃)₂.

Since the potential energy of the transition state for the decomposition of H₂O·Zn(CH₃)₂, TS1, is 38 kJ mol⁻¹ higher than that of the reactants, the above energy is sufficient for overcoming the potential barrier to produce HOZnCH₃+CH₄. However, this is insufficient for producing Zn(OH)₂ and CH₄. The potential energy of TS3 is 66 kJ mol⁻¹, and the potential barrier for the HOZnCH₃+H₂O → Zn(OH)₂+CH₄ reaction is 182 kJ mol⁻¹. In other words, not only the production of ZnO but also that of Zn(OH)₂ may not take place in the gas phase. It has been shown that no deposits can be observed on cold chamber walls. ZnO films can only be deposited on heated substrate surfaces. This suggests that the film precursor is something volatile. HOZnCH₃

produced in the gas phase should be a candidate film precursor. CH_4 may desorb smoothly from the growing surfaces on heated substrates to produce ZnO, since the C-atom contamination in the films was minor. This point will be discussed in subsequent papers.

6. Conclusions

Gas-phase reactions between dimethylzinc and translationally hot H_2O molecules produced in a reaction of H_2 and O_2 on a Pt catalyst play important roles in the fabrication of high-electron-mobility ZnO epilayers. Laser-induced fluorescence measurements showed that radical reactions are less important. Coherent anti-Stokes Raman scattering measurements showed that H_2O molecules effused from a nozzle are rotationally cooled. In other words, they must be translationally heated. According to *ab initio* calculations, the potential barrier to produce $\text{HOZnCH}_3 + \text{CH}_4$ is less than the estimated collisional energy between H_2O and $\text{Zn}(\text{CH}_3)_2$, and HOZnCH_3 thus produced can be a candidate film precursor. On the other hand, the production processes of $\text{Zn}(\text{OH})_2$ and ZnO in the gas phase require much higher energies and the final stage of the formation of ZnO epilayers must proceed on the substrate surfaces.

Acknowledgment

This work was partially funded by a Grant-in-Aid for Science Research (No. 24360014) from the Japan Society for the Promotion of Science.

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Figure Captions

Fig. 1. Schematic diagram of the catalyst holder and the nozzle.

Fig. 2. (Color online) Schematic diagram of the experimental apparatus for the folded BOXCARs measurements.

Fig. 3. CARS spectra of 30 Pa of H_2O under bulk conditions (solid line) and that under jet conditions (dashed line). Under the jet conditions, the pressure in the chamber was 1.1 Pa. The distance between the nozzle head and the detection zone was 4 mm.

Fig. 4. Comparison of the simulated and experimental CARS spectra of H_2O under jet conditions. (a) The distance between the nozzle head and the detection zone was 8 mm. The total pressure was 1.1 Pa. (b) The distance between the nozzle head and the detection zone was 4mm. The total pressure was 2.1 Pa. (c) The distance between the nozzle head and the detection zone was 4mm. The total pressure was 1.1 Pa. (d) Simulated spectrum with a rotational temperature of 250 K.

Fig. 5. Dependence of the CARS signal intensity on the distance between the nozzle head and the detection zone.

Fig. 6. Potential energy profile for the reaction of $\text{Zn}(\text{CH}_3)_2$ and H_2O at the MP2/LANL2DZ level of theory. TS stands for “transition state”.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6