A STUDY OF ZnO MOCVD MECHANISMS BY GAS PHASE TRANSMISSION FTIR

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In previous studies, we have developed an atmospheric MOCVD process using zinc acetylacetonate (Zn(acac)₂), Zn(C₅H₇O₂)₂ vapor and water vapor or oxygen to deposit ZnO at 320°C. Low deposition temperature, using of water vapor and substrate with PVD coated ZnO surface are the key factors to prepare (002) ZnO films near 300°C. This studies show that MOCVD ZnO film properties are closely related to the precursor decomposition chemistry. Since FTIR offers the advantages as: responsive, accuracy on concentration monitoring, sensitivity on wave number shifts for functional groups, and nondestructive to diagnosed species. We used transmission FTIR to analyze vapor phase products from ZnO MOCVD using Zn(acac)₂ with O₂ or water vapor as reactants.

For Zn(acac)₂/O₂ CVD, water vapor, with IR band at 3500 cm⁻¹, is the primary gas phase species from 340 to 440°C. Water vapor is considered as oxidation products from CH₃ groups on Zn(acac)₂. Acetylacetone (C₅H₇O₂), with distinguishing IR peak at 1624 cm⁻¹, has the second strong intensity. C₅H₇O₂, Hacac, is assumed as products from hydrogenation of released C₃H₆O₂ or acac ligands (Fig.1). The appearance of Hacac is regarded as Zn(acac)₂ begins to decompose via Zn-O bond breakage. Above 380°C, minor amount of acetone (C₃H₆O), with distinctive IR bands at 1214, 1363, and 1732 cm⁻¹ shows up. CO₂ appears at temperature above 400°C (Fig.2). IR peak intensities of both acetone and CO₂ grow as deposition temperature rises (Fig.3). For Zn(acac)₂ CVD operated in inert He ambient, the four familiar species, acetylacetone, acetone, water vapor, and CO₂, were found. Most species, except acetylacetone, had much less intensities, as compared with IR of O₂ using CVD. We a proposed that, for temperature below 360°C, adsorbed O₂ is relatively inert and passive. Only small amount of Zn(acac)₂ react and decompose. Film growth rate is low, leaving incomplete coverage of ZnO layer, as observed by SEM. For temperature above 380°C, thermal energy is enough to break Zn(acac)₂, giving substantial amount of acac, which react with adsorbed oxygen and produce acetone and CO₂. Film growth rate increases as oxygen scavenges more acac. Two factors, A) steric hindrance effect exerted from the chelating acac ligands, and B) the sequence of bond strength in the Zn(acac)₂ molecule, were attributed to the reaction mechanism of O₂ involved ZnO CVD.

While for Zn(acac)₂ CVD with H₂O vapor (Fig.4) as co-reactant, acetylacetone (C₃H₆O₂, Hacac) is the major product at temperature from 320 to 440°C. From 380 to 420°C, IR band of water vapor (at 3500 cm⁻¹), considered as residual reactant, is the second intense. For temperature below 360°C or above 420°C, water vapor bands were almost absent in the spectra (Fig.5). At such temperature ranges, fed water vapor was almost consumed by eqn (1).

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\text{Zn(C₃H₇O₂)₂(g) + H₂O(g) \rightarrow ZnO(s) + 2 C₃H₆O₂(g)} \tag{1}
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We propose that formation of a hydrated complex, Zn(acac)₂·H₂O, that destabilized Zn(acac)₂ molecular structure, is responsible for gas phase product distribution in H₂O involved ZnO CVD. For H₂O using ZnO CVD, water vapor plays an aggressive role to attack, dissociate precursor and free C₃H₆O₂ at temperature <360°C.

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Fig. 1 IR of Zn(acac)₂/O₂ CVD at 340°C

Fig. 2 IR of Zn(acac)₂/O₂ CVD 420°C

Fig. 3 IR Peak intensities vs. Tdep in O₂ ZnO CVD

Fig. 4 IR of Zn(acac)₂/H₂O CVD 340°C

Fig. 5 IR Peak intensities vs. Tdep in Zn(acac)₂/H₂O CVD