A STUDY OF ZnO MOCVD MECHANISMS BY GAS PHASE TRANSMISSION FTIR

Yuneng Chang, Ruiyun Chang,
Xiaowei Su, Yushou Huang, Jonlin Lai,
Lunghwa University of Science and Technology,
Dept. of Chemical Engineering,
No.300, Sec.1, Wanshow Rd.,
Gueishan, Taoyuan, 333, Taiwan, R.O.C.

In previous studies, we have developed an atmospheric MOCVD process using zinc acetylacetonate ($Zn(acac)_2$, $Zn(C_5H_7O_2)_2$) vapor and water vapor or oxygen to deposit ZnO films 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. These 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 O_2 or water vapor as reactants.

For $Zn(acac)_2/O_2$ CVD, water vapor, with IR band at 3500 cm^{-1}, is the primary gas phase specie from 340 to 440°C. Water vapor is considered as oxidation products from CH_3 groups on $Zn(acac)_2$. Acetylacetone ($C_5H_8O_2$), with distinguishing IR peak at 1624 cm^{-1}, has the second strong intensity. $C_5H_8O_2$, Hacac, is assumed as products from hydrogenation of released $C_5H_7O_2$, 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 (C_3H_6O), with distinctive IR bands at 1214, 1363, and 1732 cm^{-1} shows up. CO_2 appears at temperature above 400°C (Fig.2). IR peak intensities of both acetone and CO_2 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 CO_2, were found. Most species, except acetylacetone, had much less intensities, as compared with IR of O_2 using CVD. We a proposed that, for temperature below 360°C, adsorbed O_2 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 CO_2. 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 O_2 involved ZnO CVD.

While for $Zn(acac)_2$ CVD with H_2O vapor (Fig.4) as co-reactant, acetylacetone ($C_5H_8O_2$, 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).

$$Zn(C_5H_7O_2)_{2\,(g)} + H_2O_{\,(g)} \rightarrow ZnO_{(s)} + 2\,C_5H_8O_{2\,(g)} \qquad (1)$$

We propose that formation of a hydrated complex, $Zn(acac)_2{*}nH_2O$, that destabilized $Zn(acac)_2$ molecular structure, is responsible for gas phase product distribution in H_2O involved ZnO CVD. For H_2O using ZnO CVD, water vapor plays an aggressive role to attack, dissociate precursor and free $C_5H_7O_2$ at temperature <360°C.

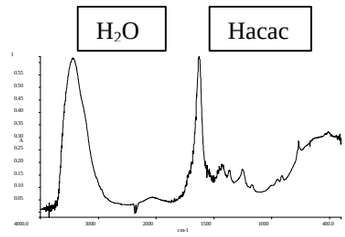


Fig. 1 IR of $Zn(acac)_2$/O2 CVD at 340°C

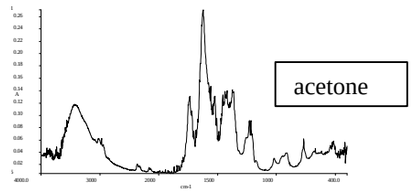


Fig. 2 IR of $Zn(acac)_2$/O2 CVD 420°C

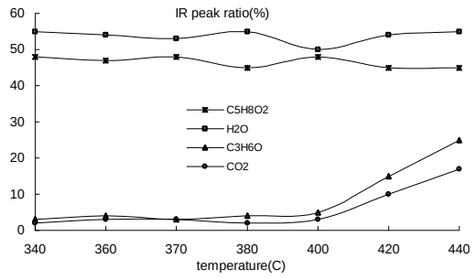


Fig. 3 IR Peak intensities vs. Tdep in O2 ZnO CVD

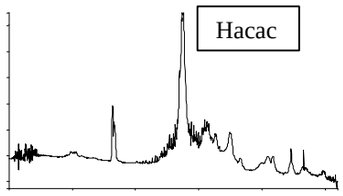
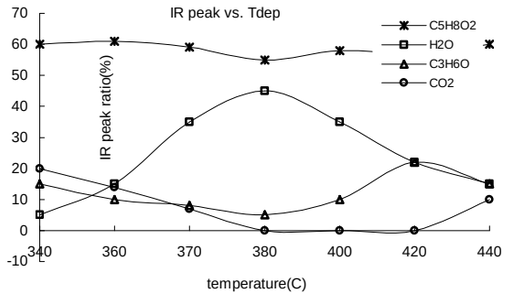


Fig. 4 IR of $Zn(acac)_2$/H2O CVD 340°C

Fig. 5 IR Peak intensities vs. Tdep



in $Zn(acac)_2$/H2O CVD