A DSC STUDY ON THE SUBLIMATION AND DECOMPOSITION OF ZnO CVD PRECURSOR, ZINC ACETYLACETONATE

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Chemical vapor deposition (CVD) is a valuable technique to prepare ZnO films for electronic and optoelectronic devices. We have successfully developed an MOCVD process using zinc acetylacetonate as precursor to deposit (002) ZnO films at 320^{o}C. However, the complex nature of reaction mechanism and specifically precursor thermochemistry limit scale up of such ZnO CVD. Focusing on precursor behavior during heating history, differential scanning calorimetry (DSC), DTA, and TGA have been considered. As these thermal analysis methods provide solutions by clearly defining temperature positions for each energy/mass change involved transition. In principle, DSC is superior to TGA and DTA for understanding CVD precursor chemistry. Since DSC is more sensitive to phase transition temperature (with a precision of 0.01^{o}C) and is capable of monitoring the exact rate of energy exchange or reaction rate (1). In this study, we used DSC (TA2010) to study pyrolysis kinetics of zinc acetylacetonate ($Zn(acac)_2$) in chamber ambient simulating real CVD condition, with heating rate from 10 to 20^{o}C/min.

For $Zn(acac)_2$ heated in pure N_2, inert environment, DSC showed that there are one large and two small endothermic peaks locating at 91-106^{o}C, 121-128^{o}C, and 135-142^{o}C, with peak area being 88KJ/mol, 14 KJ/mol, and 18 KJ/mol, respectively. Nature of these endothermic peaks was studied by solid phase IR. For each run, residuals were collected from DSC sample pan after each peak ended, mixed with KBr, pressed into pellets, and analyzed by transmission IR. These experiments have been performed on three DSC peaks separately. As compared with IR standard, we noticed that all IR bands observed in collected spectra were from vibration modes of $Zn(acac)_2$. This indicated all DSC peaks might be due to physical phenomena, as no compositional change observed. Further temperature programmed polarized optical microscope (POM) analysis showed these three peaks might be related to dehydration, phase transition, and melting for hydrates of $Zn(acac)_2$.

For DSC in oxygen-containing environment with concentration from to 13 to 40%, we observed three endothermic peaks and two additional exothermic broad peaks at higher temperature, 209-236^{o}C, and 330-400^{o}C. These exothermic peaks are attributed to oxidative decomposition of $Zn(acac)_2$ and released ligands. When oxygen concentration increased, peak area for exothermic peaks grew. Positions of all these peaks depend on heating rate. Increasing the heating rate caused every peak shift toward higher temperatures, with the first two endothermic peaks merged into one broad one. This is due to activation energy involved in such transition, and data were analyzed by Kissinser equation to estimate activation energies for each peak.

Applications of these endothermic peak data to $Zn(acac)_2$ sublimation, together with connections between exothermic DSC peaks and CVD results, will be discussed in the presentation.

1. Y. Chang and G.L. Schrader, vol. 250, p. 291, Material Research Society Meeting Proceeding, (1992)

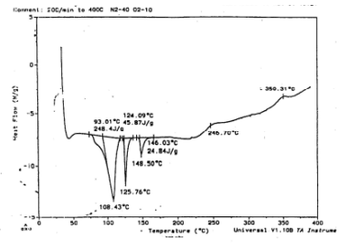

Fig.1 DSC of $Zn(acac)_2$ at 10℃/min [O2] 20%

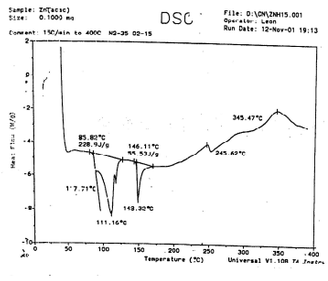

Fig.2 DSC of $Zn(acac)_2$ at 15℃/min [O2] 30%

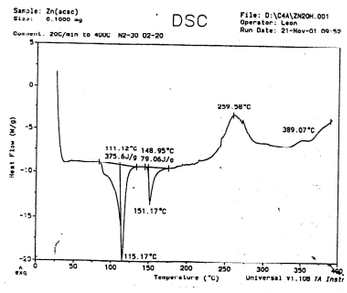

Fig.3 DSC of $Zn(acac)_2$ at 20℃/min [O2] 40%

Table 1 DSC of $Zn(acac)_2$ in oxidizing ambient

O_2/ N_2 ratio	Endothermic 1	Endothermic 2	Endothermic 3
10/40	98.63℃ 71.52 KJ/mole	127.69℃ 17.65 KJ/mole	139.55℃ 8.25 KJ/mole
15/35	103.35℃ 119.82 KJ/mole	128.18℃ 29.29 KJ/mole	140.52℃ 9.17 KJ/mole
30/20	101.32℃ 64.68 KJ/mole	127.45℃ 14.15 KJ/mole	143.19℃ 6.24 KJ/mole
O_2/ N_2 ratio	Exothermic peak 1		Exothermic peak 2
10/40	209.70℃ 16.94 KJ/mole		335.25℃ 29.12 KJ/mole
15/35	235.11℃ 15.90 KJ/mole		366.00℃ 43.86 KJ/mole
30/20	243.82℃ 26.07 KJ/mole		308.82℃ 54.90 KJ/mole

Heating rate 10^{o}C/min