NUCLEATION AND COALESCENCE PHENOMENA DURING SUBLIMATION/RECONDENSATION OF CVD PRECURSOR, ZINC ACETYLACETONATE, OBSERVED BY POLARIZED OPTICAL MICROSCOPY

Yuneng Chang, Wending Chen,
Zhaonan Li, Junxian Jang, Chengben Yang, Johnyi Lin
Lunghwa University of Science and Technology,
Dept. of Chemical Engineering,
No.300, Sec.1, Wanshow Rd.,
Gueishan, Taoyuan, 333, Taiwan, R.O.C.
yuneng@giga.net.tw

Zinc acetylacetoante (Zn(acac)$_2$) is a principle metal organic chemical vapor deposition (CVD) precursor for ZnO, which is an optoelectronic materials, and capable of stimulated emission UV light in room temperature. However, since metal acetylacetonates are solid, the sublimation area and shape keep changing upon heating, and make the control of precursor heating more complicate. Traditional methods to study the thermal behavior of CVD precursor include DTA, TGA, and DSC. All of them can only provide macroscopic data, such as melting point, sublime point, and decomposition temperature. In this study, we use an optical microscope with polarized light (POM) capability and temperature programmed heating stage to directly observe microscopic phenomena during heating and sublimation of zinc acetylacetonate. The morphological change during phase transition of materials, which cannot be detected by DTA, can be easily revealed by POM. For each experiment, Zn(acac)$_2$ was placed between a sandwich type of cover glasses and heated with constant heating rate. The evaporation rate also depends on the particle size and shape of Zn(acac)$_2$ solid. It seemed that anhydrous zinc acetylacetonate is difficult to sublime, while hydrated Zn(acac)2 can be sublimed easily. Due to poor thermal conductivity of Zn(acac)2 powder, by applying a large heating rate such as 20-30^{o}C/min, a substantial temperature difference is created between the upper cover glass and the lower cover glass. When temperature reached 87^{o}C, Zn(acac)$_2$ began to evaporate. The image got cloudy, assuming as Zn(acac)$_2$ vapor filled the void between residual Zn(acac)$_2$ powder (Fig.1). When temperature reached 115^{o}C, the entire space is filled with zinc acetylacetonate mist. When temperature reached 120^{o}C, the sample displayed a highly dispersed liquid droplet-like morphology (Fig.2), assuming as the concentration of Zn(acac)$_2$ vapor achieved super-saturation ratio, triggered heterogeneous nucleation, and condensed onto the surface of cooler upper cover glass. The average diameter and density of the circular/irregular shape droplets are 8-12x10^{-4}cm, and 1.6~2 x10^7 droplets/cm^2, respectively. From 130 to 150^{o}C, the heating rate was 2.5^{o}C/min. For temperature reached 130^{o}C) (Fig.3), these droplets then began to develop a feather, or tree skin, or bamboo-like crystalline structure from the upper left corner, under microscope inspection. This phenomena is regarded as concentration of Zn(acac)2 vapor being so high and keeping re-condensing onto the surface of cooler upper cover glass. POM indicated that evaporation of Zn(acac)$_2$ follow the sequence as crystalline state → transform into amorphous state (Fig.4)→evaporated. Particle size and shape, which influence sublimation rate, should be control carefully to give stable performance. POM aindicated that Zn(acac)$_2$ began to sublime at 73^{o}C to 86^{o}C, which is far below DTA/DSC literature reported values of 110^{o}C to 140^{o}C.


Fig. 1 POM image of Zn(acac)$_2$ at 87 ^{o}C

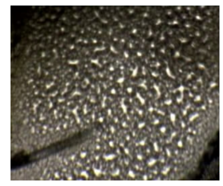
Fig. 2 POM image of Zn(acac)$_2$ at 125 ^{o}C

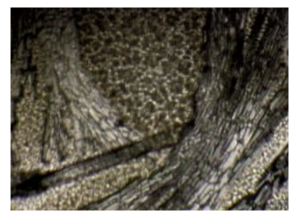
Fig. 3 POM image of Zn(acac)$_2$ at 132 ^{o}C

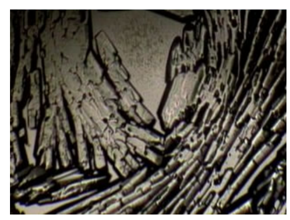
Fig. 4 POM image of Zn(acac)$_2$ at 132^{6o}C

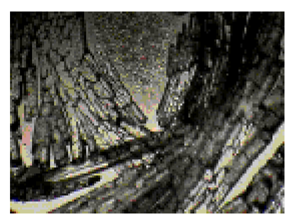
Fig. 5 POM image of Zn(acac)$_2$ at 149 ^{o}C

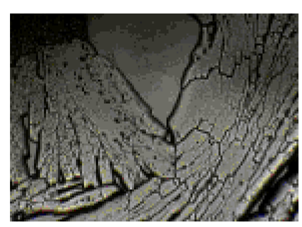
Fig. 6 POM image of Zn(acac)$_2$ at 159 ^{o}C

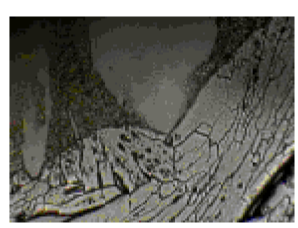
Fig. 7 POM image of Zn(acac)$_2$ at 161 ^{o}C