

**DEVELOPMENT OF
ZINC OXIDE NANOSTRUCTURE IN MOCVD**

Yuneng Chang, Hengchuan Lu,
Yumeng Hung, Chunsung Lee, Junquan Qiu, Xinji Li,
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 oxide (ZnO), with a wide band gap of 3.37eV, is a LED material in ultraviolet wavelength. ZnO films are also used for transparent conductive films in flat panel displays and surface acoustic wave (SAW) devices for its high conductivity and piezoelectricity. Compared with other technologies as PLD, MBE, and sputtering, chemical vapor deposition (CVD) owns advantages as high throughput, conformal mapping over complex structure, and compatible with modern semiconductor processing technologies. This presentation will address the development of highly textured (002) ZnO thin films by atmospheric pressure MOCVD at 320°C, which is lower than reported values in the zinc acetylacetonate based CVD system. CVD was performed in a horizontal reactor, with precursor Zn(acac)₂ sublimed at 110 °C, and deposition temperature from 320 to 440°C, with sputtering pre-coated ZnO Si(100) as substrates. In another paper, we showed that the room temperature deposited ZnO buffer layer, although being amorphous, is very helpful in forming subsequent high quality ZnO films with epitaxy level crystallinity. XRD (Fig.1) show that the polycrystalline ZnO films have (002), (100) and (101) planes and spacings of 2.60Å, 2.47 Å, 2.81 Å. For CVD using Zn(acac)₂ with 15 torr H₂O vapor fed as co-reactant, with deposition temperature between 320 and 360°C, XRD analysis show that ZnO films have a strong preferential orientation along (002) plane (Fig.2). At 320°C, crystal grains align at unique (002) orientation is more obvious (>99%), with XRD peak width (FWHM) less than 0.5°. From structural analysis, we suggested it was the chemical force exerted by ZnO surface and thermodynamics during nucleation, rather than lattice relaxation, causing this quasi-epitaxial growth. SEM observes ordered nanostructure development in ZnO CVD in inert ambient or using H₂O vapor. For ZnO films deposited at temperatures below 340°C, SEM (Fig. 3) shows uniform morphology and dense structure composed by polyhedron shaped columnar grains, which have radius of 0.2-0.8 μm. The films have smooth surface with finer grains. For temperature between 360 and 380°C (Fig. 4), SEM shows ordered hexagonal or circular shaped plate shaped grains, with edge length of 1-2μm and 03 μm thick, covered film surfaces. Some plate grains were stacked together in a unit of several plates. This growth habit might originate from hexagonal facet in nucleation, and subsequent layer growth mode (Frank-van der Merwe), along (002) plane. It seems in this process condition, (002) might be the thermodynamic favorable plane during nucleation. The growth rate is faster along the (002) basal plane of ZnO unit lattice, and slower along the {110} prism planes. For films deposited above 400°C, clear evidences of crystal growth along screw dislocation, as described by BCF theory, was observed (Fig.5, 6). The shift of film growth mode due to temperature change will be discussed with gas phase IR data and presumed as the reason ZnO CVD can generate nano wire at elevated temperature.

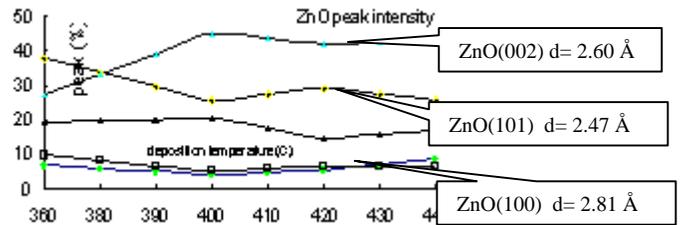


Fig. 1 XRD peak ratio vs. T in Zn(acac)₂/O₂ CVD

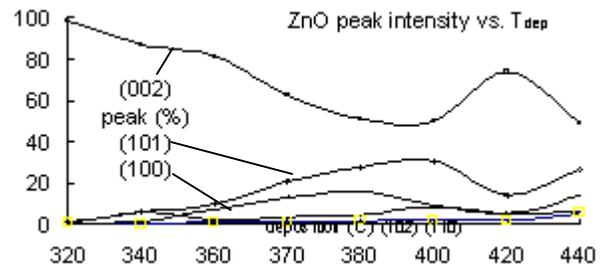


Fig. 2 XRD peak ratio vs. T in Zn(acac)₂/H₂O CVD

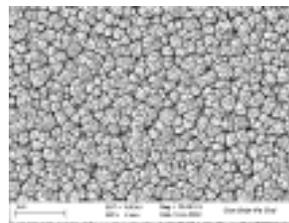


Fig. 3 fine grain structure observed in ZnO CVD film at [O₂] 0%, H₂O 15 torr, 340°C

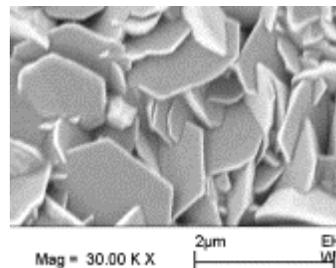


Fig. 4 Hexagonal plate structure observed in ZnO CVD film at [O₂] 0%, H₂O 15 torr, 360°C

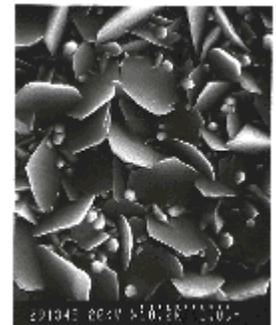


Fig. 5 Screw dislocation growth structure observed in ZnO CVD film at [O₂] 0%, H₂O 15 torr, 420°C

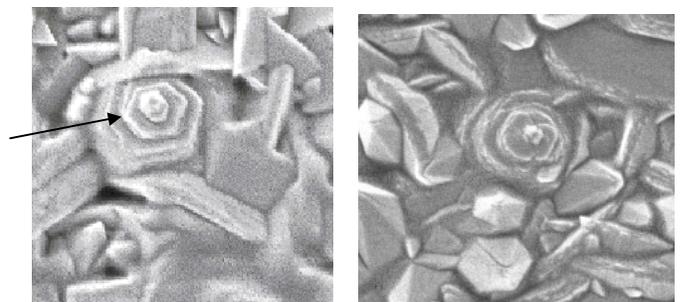


Fig. 6 various screw dislocation growth structures observed in ZnO film at [O₂] 0%, H₂O 15 torr, 420°C