KEY FACTORS TO GROW (002) ZINC OXIDE FILMS BY MOCVD AT 320°C AND ATMOSPHERIC PRESSURE

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Due to superior optoelectronic properties along c-axis plane, (002) ZnO films have attracted lot research attentions. Compared with other vapor phase growth techniques as PLD, MBE, and sputtering, metal organic chemical vapor deposition (MOCVD) has advantages as high throughput, conformal mapping over complex structure, and compatible with contemporary semiconductor processing modules. In this presentation, we report preparation of highly oriented (002) ZnO films using a cold wall atmospheric pressure CVD system. In this process, zinc acetylacetonate ($Zn(acac)_2$, $Zn(C_5H_7O_2)_2$) vapor thermally decomposed and reacted with water vapor or oxygen to produce ZnO films at 320°C, which is far below previous reported temperatures for $Zn(acac)_2$ based MOCVD .

Through experimental data, we discovered that low deposition temperature, using water vapor as co-reactant and substrates with ZnO buffer layer pre-coated by PVD are the key factors to prepare (002) ZnO films. Substrate surface has a profound effect on film quality and growth rate, as identified by XPS and XRD. ZnO CVD performed over Si(100) substrates, which were pre-coated with reactive sputtered, amorphous ZnO layers with 100Å thick, gave CVD growth rate as high as 1000Å/min and epitaxy like film crystallinity (Fig.1). Either dense columnar grains, or hexagonal plates, which reflects the crystal habit and unit lattice of ZnO were frequently observed by SEM. While ZnO CVD performed over CuxO pre-coated Si substrates gave growth rate as low as 120Å/min, and deposited ZnO films were amorphous with discontinuous morphology. XRD also observed that buffer CuxO layer was reduced to metal Cu after CVD run (Fig.2). This selective growth phenomenon might be related to the electronegative property of ZnO seed layer to catalyze precursor reaction. Subsequent ZnO CVD were all performed on PVD ZnO buffer layer/Si substrate. Elemental analysis by DPA (Fig.3) and XPS both showed that CVD films were zinc rich, above stoichiometric value. Considering the impact of co-reactant, ZnO CVD using water vapor (15 to 25 torr) gives higher deposition rate, as compared with CVD using oxygen (190-380 torr). More than that, XRD shows that (002) unique oriented ZnO films can be grown by using $Zn(acac)_2$ and 15 torr of water vapor, at temperature from 320°C to 360°C. Gas phase IR results suggested that water vapor might attack the square planar $Zn(C_5H_7O_2)_2$ molecule directly from the top and base side, forming hydrated compound, and results in $Zn(acac)_2$ decomposition more easily. Water vapor may also supply hydrogen atoms to react with released acetylacetonyl ligands (acac, $C_5H_7O_2$), and forming stable acetylaceton (Hacac, $C_5H_8O_2$) molecules. The reaction between oxygen and acac is complex with unstable products. Oxygen does not have the reducing capability to ensure reaction moving rightward, but can only oxidize later formed Hacac passively.

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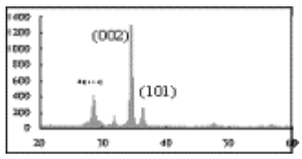

Fig. 1 XRD of ZnO CVD over PVD ZnO buffer layer

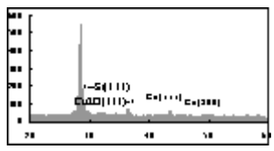

Fig.2 XRD of CVD over PVD CuxO buffer layer

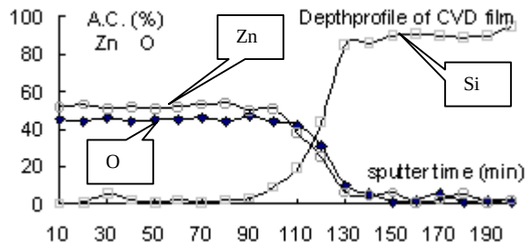

Fig. 3 Depth profile AES of CVD film at [O_2] 50% 400℃

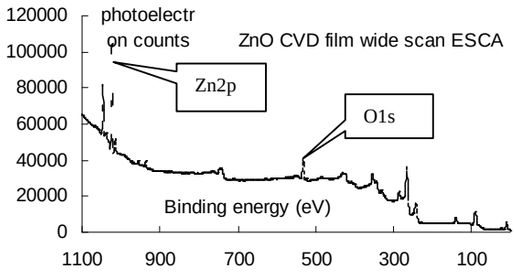

Fig. 4 Survey scan XPS of CVD film at [O_2] 38% 360℃

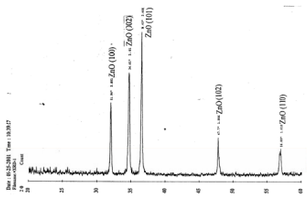

Fig. 5 XRD of CVD film at **[O_2] 38%, H2O 0 torr**, 380℃, with orientations (110), (102), (101), (002), (100), and dspacings of 1.62Å, 1.91 Å, 2.47Å, 2.60 Å, 2.81 Å.

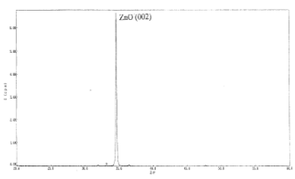

Fig. 6 XRD of CVD film at **[O_2] 0%, H2O 15 torr**, 320℃, with grain orientation at (002) and dspacing of 2.60 Å.

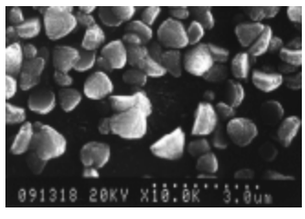

Fig. 7 SEM of CVD film at **[O_2] 38%, H2O 0 torr**, 380℃, with grains loosely packed

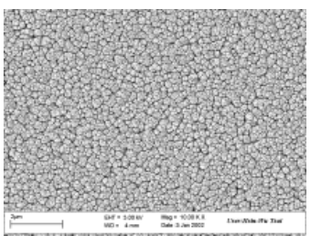

Fig. 8 SEM of CVD film at **[O_2] 0%, H2O 15 torr**, 320℃, with fine grains densely packed