Homoepitaxy of ZnO on bulk and thin film substrates by low temperature metal organic chemical vapor deposition using tert-butanol

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Homoepitaxial growths of ZnO were performed by low pressure metal organic chemical vapor deposition (MOCVD) on both bulk hydrothermal and thin film buffer layers of ZnO grown by pulsed laser deposition on *c*-sapphire substrates. The surface roughness, photoluminescence, and x-ray diffraction (0002) peak omega rocking-curve line widths for the bulk and thin film substrates were similar prior to MOCVD growth. After MOCVD growth, it was found that the surface morphology, crystallographic quality, and optical properties of the ZnO layers were far superior to those typically observed for heteroepitaxial growth of ZnO layers on *c*-sapphire by MOCVD. The MOCVD layers were comparable for growths on both the bulk substrate and the thin film buffer layer. Furthermore, no significant impact of carrier gas was observed. The quality of the ZnO layer appeared to be correlated with the surface morphology and the crystalline quality of the substrate rather than being dependent on whether the substrate was in bulk or thin film form. © *2009 American Vacuum Society.* [DOI: 10.1116/1.3137016]

I. INTRODUCTION

ZnO is an attractive multifunctional semiconductor material with a wide bandgap of ~3.37 eV. Applications for ZnO extend from surface acoustic wave devices[1] to a range of optical devices. Advances in the development of ZnO based light emitting diodes[2] have been slow, however. This has been partly due to the lack of high quality, wide-area ZnO substrates at a reasonable cost level. Indeed, ZnO films often show poor crystallographic quality and a high density of dislocations when grown on non-native substrates by metal organic chemical vapor deposition (MOCVD). Although better quality heteroepitaxy can be achieved using other techniques (including molecular beam epitaxy[3] and pulsed laser deposition[4] (PLD)], MOCVD (Ref. 5) remains attractive in that it offers the advantages of higher rate deposition while maintaining control over the composition, doping profile, and uniformity of the film. The problem with the MOCVD growth derives from the relatively large lattice and thermal expansion coefficient mismatches with common substrates, such as *c*-plane sapphire (c-Al_2O_3). Adaptation to these constraints requires a higher deposition temperature than that for which conventional MOCVD ZnO precursors function best. The situation improves for MOCVD if the layers are grown on native ZnO substrates because epitaxy is possible at lower growth temperatures.

In this work, we compare low temperature (LT) MOCVD homoepitaxial growth of ZnO on commercial bulk hydrothermal substrates and 300 nm thick commercial PLD-grown ZnO thin film buffer layers on c-Al_2O_3 substrates[6,7] in order to see whether the latter could provide a low cost platform for high quality growth of ZnO on large area c-Al_2O_3 substrates by MOCVD.

II. EXPERIMENT

Films were grown at a relatively low pressure (100 torr) by MOCVD in a 2×2 in. horizontal reactor with separate inlets to avoid premature reactions in the manifold between VI and II precursors. Diethylzinc and tert-butanol were used as precursors for Zn and O, respectively. The bubblers of diethylzinc and of tert-butanol (TBuOH) were maintained at 12 and 28 °C, respectively. ZnO films were grown on O-face bulk hydrothermal substrates and PLD-grown ZnO thin film buffer layers on c-Al_2O_3 substrates. The bulk substrates were annealed at 1100 °C for 1 h in a molecular oxygen atmosphere prior to growth in order to obtain a terraced structure on the surface. Annealing was not performed for the ZnO templates layers. The bulk and thin film substrates were then inserted simultaneously into the reactor. TBuOH was introduced during both the temperature ramp-up and the cooling in order to avoid deterioration of the surface. The growth parameters were optimized for the particular carrier gas used during the growth. Three different carrier gases were studied: H_2, (He+5% H_2), and (N_2+5% H_2). The substrate temperature and the VI/II ratio were maintained at 440 °C and 10 for the H_2, 485 °C and 20 for the (He+H_2), and 515 °C and 25 for the (N_2+H_2). The layer thickness was between 2 and 3 μm.

Film quality was studied as a function of both carrier gas and the nature of the substrate. The surface morphologies were investigated using scanning electron microscopy (SEM). The structural quality of the layers was analyzed

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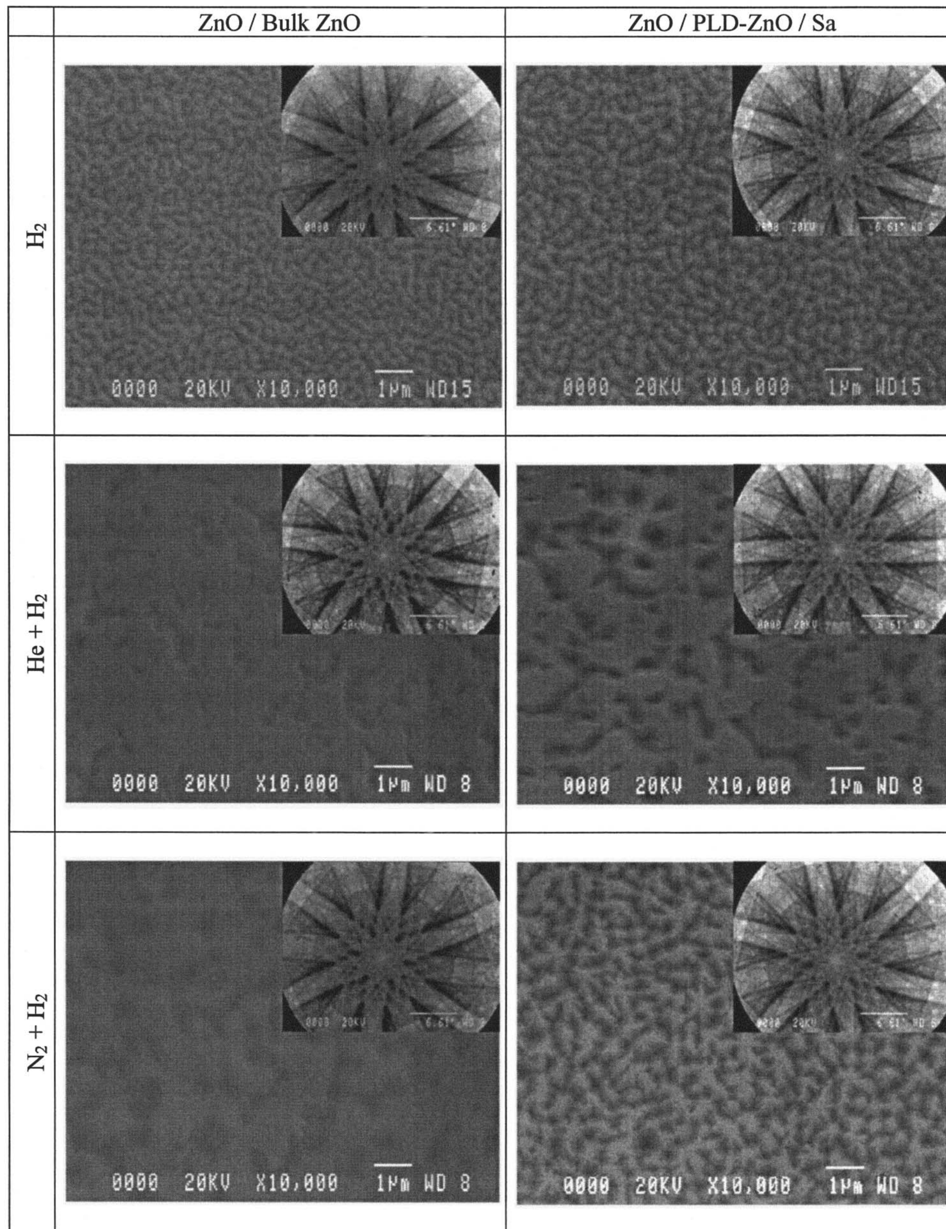

FIG. 1. SEM images of ZnO layers grown by MOCVD on bulk ZnO substrates and ZnO buffer layers with different carrier gases (electron diffraction pattern inset).

using an x-ray diffraction (XRD) system with an incident beam germanium monochromator. The full width at half maximum (FWHM) of the (0002) peak in XRD omega rocking curves (open detector) was used as a measure of crystalline quality. Raman measurements were conducted at room temperature using the 514 nm lines of an Ar ion laser. Photoluminescence (PL) measurements were carried out a temperature of about 1.6 K using deep UV lines (351 nm) of an Ar ion laser.

III. RESULTS

The composition of the carrier gas was not observed to influence the growth rate. Prior to growth, both the bulk and thin film substrates had excellent surface morphology with no significant roughness observable by SEM. After homoepitaxial growth, all samples had a mirrorlike appearance (in contrast to the milky texture generally obtained for MOCVD growths directly on *c*-sapphire). Figure 1 shows a SEM image of the surface morphology of ZnO layer grown on both the bulk and thin film substrates, with the three different carrier gases. For both substrates, the layers grown with H_2 carrier gas were rough and porous with wormlike asperities, which appear to be in the process of coalescing. ZnO etching by H radicals in the carrier gas could have played a role in this. For the other two carrier gases, the layers grown on both kinds of substrate had a quasi-two-dimensional structure with some evidence of pinholes. The electron diffraction patterns collected for all films are well defined and characteristic of (0002) orientation. Thus, while the surface morphology seems to be susceptible to etching by the carrier gas, it does not show an obvious dependence on the nature of the substrate.

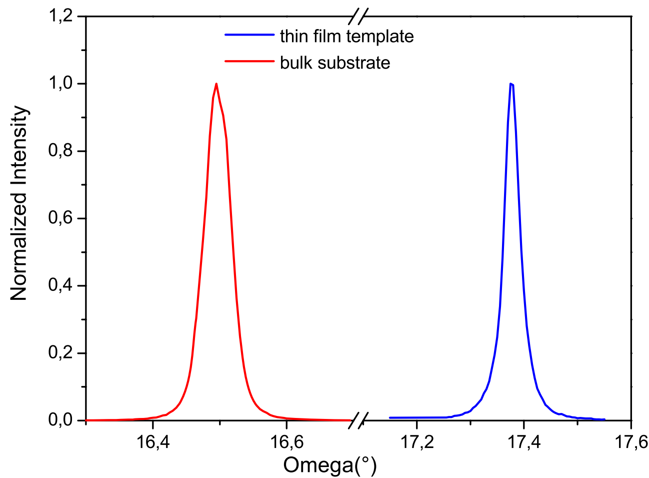

FIG. 2. (Color online) XRD (0002) peak omega rocking-curve scans for ZnO films grown by MOCVD on bulk substrates and thin film buffer layers using (He+H_2) carrier gas.

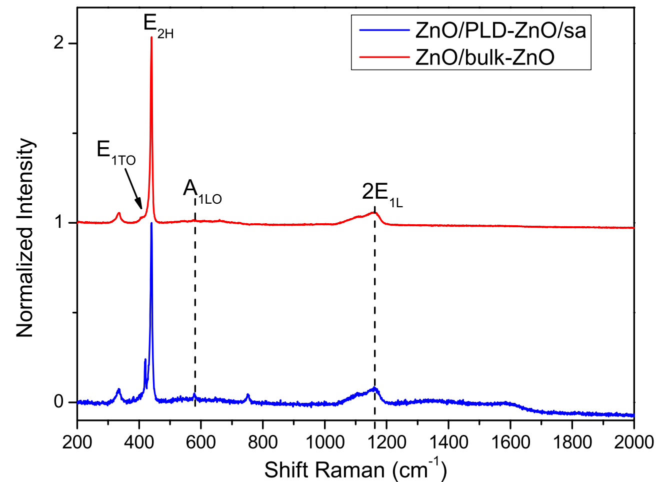

FIG. 3. (Color online) Raman spectra for ZnO films grown by MOCVD on bulk substrates and ZnO buffer layers with (He+H_2) carrier gas.

XRD omega rocking curves for all the films showed strong ZnO (0002) peaks (Fig. 2). Table I presents the FHWM values for each film. The FHWMs for the bulk substrate and the PLD-grown ZnO thin film buffer layers on c-Al_2O_3 substrates (prior to homoepitaxial growth) were 49 and 54 arc sec, respectively. The values for the films after MOCVD homoepitaxy were all superior to those prior to homoepitaxy, so they were taken to be representative of the MOCVD-grown ZnO layers. The FWHMs for the ZnO layers grown on the bulk ZnO and the ZnO buffer layers are comparable and the values are also similar for all three carrier gases. Thus, the dispersion in the crystallographic orientation of the layers does not reveal any marked dependence on the nature of the substrate or the carrier gas. It would appear, therefore, that the controlling parameter, in this case, is the MOCVD growth conditions (possibly too low a growth temperature). It is of note, however, that the FHWMs are inferior to values reported by Ogata *et al.*[8] in a similar comparative study.

Raman scattering spectra for the layers grown with (He +H_2) carrier gas are presented in Fig. 3 (the spectra are normalized to the E_{2H} peak). Similar spectra were observed for layers grown with (H_2) and (N_2+H_2) carrier gas. The spectra for the growths on both the bulk and thin film ZnO are dominated by a characteristic E_{2H} peak (439 cm^{-1}), which is indicative of relaxed wurtzite ZnO. In both spectra there are also E_{1TO} and second order $2E_{1L}$ peaks located at around 410 and 1170 cm^{-1}, respectively.[9] A weak $A_{1(LO)}$ peak can also be distinguished. This longitudinal peak is related to defects in the ZnO layer.[10] The spectrum for the growth on the PLD-ZnO in Fig. 4 shows extra peaks at about 379, 417, 430, 450, 578, 645, and 751 cm^{-1} which can be indexed as corresponding to the sapphire substrate. Apart from the peaks related to sapphire, all the spectra for the different growth conditions were similar and characteristic of undoped wurtzite ZnO. The position and FWHM of the E_{2H} peaks shown in Fig. 5 and in Fig. 4, respectively, were comparable for the substrates and the homoepitaxial layers, for both types of substrate. This suggests that the residual stress in the homoepitixial layers was low and that the crystallographic quality of both kinds of substrates was similar. Careful inspection reveals that the FHWM for the ZnO layers grown

TABLE I. FWHM of the omega rocking curve (0002) peak for ZnO layers grown by MOCVD on bulk substrates and thin film buffer layers for three different carrier gases.

		FWHM (arc sec)	
		PLD template	Bulk hydrothermal
Substrate		54 ± 20	49 ± 20
ZnO layer	H_2	144 ± 20	90 ± 20
	He+H_2	119 ± 20	151 ± 20
	N_2+H_2	115 ± 20	115 ± 20

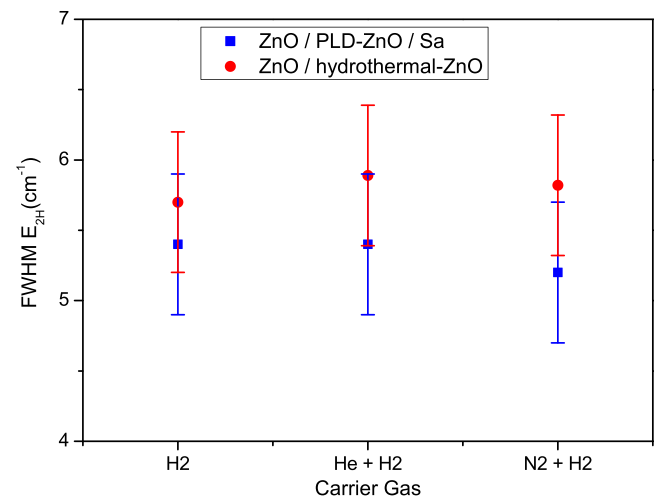

FIG. 4. (Color online) FWHM for the E_{2H} Raman peak for all ZnO layers grown by MOCVD on bulk substrates and ZnO buffer layers with each of the three carrier gases.

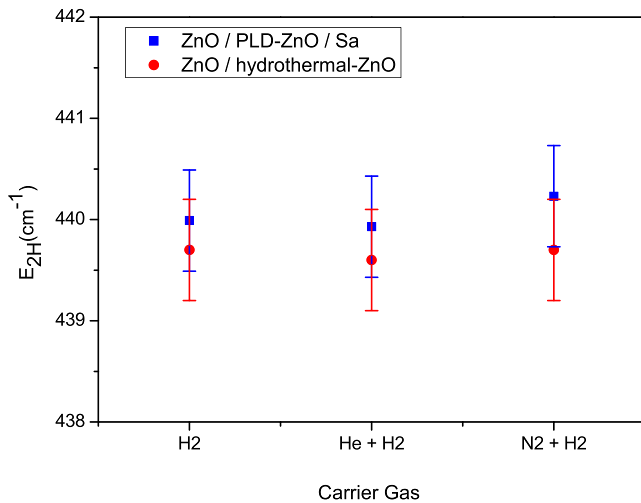

FIG. 5. (Color online) Peak position for the E_{2H} Raman peak for all ZnO layers grown by MOCVD on bulk substrates and ZnO buffer layers with each of the three carrier gases.

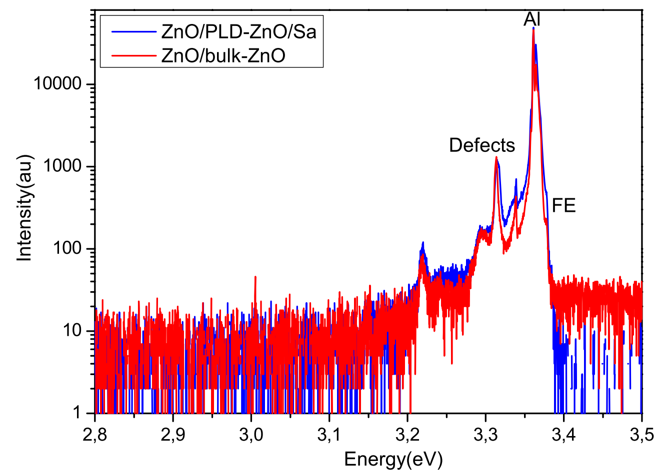

FIG. 7. (Color online) LT PL spectra for ZnO layers grown by MOCVD on bulk substrates and ZnO buffer layers with ($He+H_2$) carrier gas.

on the ZnO thin film buffer layer were a bit narrower than those grown on the bulk substrate (Fig. 4) which is indicative of slightly better crystallographic quality. Overall, however, the quality of the layers does not show a strong dependence on the carrier gas or the nature of the substrate.

PL spectra obtained for the layers grown on both types of substrate with ($He+H_2$) carrier gas are presented in Fig. 6 (spectra for the other carrier gases were similar). The spectra show strong near band edge emission dominated by donor bound exciton peak (probably related to aluminium) and by weaker peaks related to defects. We can also discern a peak related to free exciton, which confirms that the ZnO layers are of good quality and have a relatively weak incorporation of impurities. Higher resolution spectra for films grown with different carrier gases showed a similar dependence on substrate type, so only the spectra for films grown with ($He+H_2$) carrier gas are presented (Fig. 7). In these spectra the free *A*-exciton emission (FX_A) is clearly visible. The spectra are dominated by the I_4, I_5, I_6, I_8, and I_9 bound excitons recombinations due to either a donor or an acceptor. According to Ref. 11, I_4 is related to hydrogen, which could come from the carrier gas, and the peaks I_6, I_8, and I_9 are related to aluminium, gallium, and indium, respectively. The origin of these impurities is unknown. Table II presents the FHWM values of the $D^{\circ}X$ emission line for each film. The FWHM for the ZnO layers grown on the bulk ZnO and the ZnO template are comparable. A similar relation was observed for all carrier gases. Overall, these spectra are typical for nominally undoped ZnO layers of good quality. So, no significant dependence of the optical properties of the layers on carrier gas or substrate nature was observed.

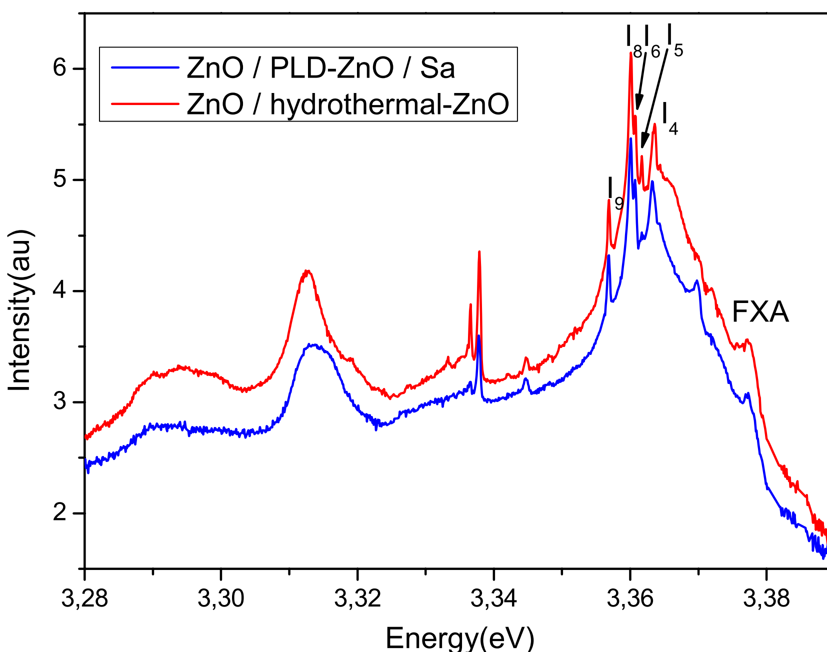

FIG. 6. (Color online) LT PL spectra for ZnO layers grown by MOCVD on bulk substrates and ZnO buffer layers with ($He+H_2$) carrier gas.

TABLE II. FWHM of the $D°X$ emission for ZnO layers grown by MOCVD on bulk substrates and thin film buffer layers for three different carrier gases.

PLD template	Bulk hydrothermal	$D°X$ FWHM (meV)	
ZnO layer	H_2	0.601	0.415
	$He+H_2$	0.58	0.551
	N_2+H_2	0.563	0.428

IV. CONCLUSIONS

This study compared the quality of ZnO layers grown by MOCVD on bulk hydrothermal ZnO substrates and PLD-grown ZnO buffer layers using three different carrier gases. Growth was conducted at low temperature and low pressure using diethylzinc mixed with tert-butanol as precursors. Prior to MOCVD growth, the surface morphology, XRD (0002) peak omega rocking curve FWHM, and PL spectra for both types of substrate were comparable. After MOCVD growth, it was found that the surface morphology, crystallographic quality, and optical properties of the homoepitaxial ZnO layers were similar for the growths on the bulk substrate and the thin film buffer layers. It was also observed that although the surface roughness and crystallographic orientation of the homoepitaxial layers was correlated with the quality of the substrates, further optimization of MOCVD growth parameters might be required. Since no significant advantage of bulk substrates was observed, this study suggests that high quality PLD-grown ZnO buffer layers on *c*-sapphire could represent a viable low-cost, large area substrate to facilitate the development of superior MOCVD growth and devices.

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