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Some aspects of the MOCVD growth of ZnO on sapphire using tert-butanol

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Abstract

The growth of ZnO on (0001) sapphire substrates using metalorganic chemical vapor deposition is reported. Diethylzinc and tertiarybutanol were used respectively as zinc and oxygen sources. Growth conditions are detailed such as the substrate temperature and the precursors partial pressures. The influence of the cleanness state of the MOCVD silica reactor is emphasized, since it modifies both layer quality and crystalline orientation, and since it also affects growth process steps like sapphire thermal treatment and buffer layer deposition. ZnO epitaxial layers are characterised by Scanning Electron Microscopy to assess the surface orientation and morphology, X-ray diffraction and photoluminescence. This last technique demonstrates the high optical quality of the ZnO epilayers.

Keywords : ZnO, MOCVD, tertiarybutanol, epitaxial layers, II-VI compounds.

PACS codes : 6855, 6150J, 7855, 8115H

Introduction

Large efforts are now devoted to the wide band gap oxides of the II-VI semiconductors series, especially ZnO and its related alloys $Zn_xA_{1-x}O$ ($A=Mg, Cd, Mn\dots$). Indeed ZnO presents a unique combination of physical properties such as a high exciton binding energy (60 meV versus 28 meV for GaN), the largest shear modulus among the II-VI compounds, large piezoelectric coefficients ($e_{33}=1.2\text{ C/m}^2$), large transparency and a large thermal conductivity. With a band gap of 3.37 eV at room temperature, ZnO is thus one of the most promising materials for application in the fields of short wavelength optoelectronics, gas sensors, acoustic devices and solar cells. ZnO layers have been deposited using various techniques, among which spray pyrolysis [1], zinc oxidation [2], electrodeposition [3], MOCVD [4,5,6], pulsed laser deposition [7], low pressure sputtering [8] and MBE [9,10]. Using this last technique, several groups have reported high quality epitaxial films on sapphire substrate, exhibiting (0002) rocking curve half-widths as low as 12 arcsec [9]. Concerning MOCVD, it has also lead to ZnO films with good optical quality, characterised by sharp excitonic emissions in the photoluminescence spectra [4]. Nevertheless, the research is still in progress concerning the choice of the oxygen precursor since gas phase premature reactions can occur when using O_2 or H_2O . The reactor design also must be optimised to improve the ZnO epilayer quality and uniformity.

An alternative approach to the use of O_2 or H_2O has been proposed by Hahn [6] : tertiarybutanol (t-butanol) allows to prevent pre-reactions. Growth rates as high as $5\text{ }\mu\text{m/h}$ have been reported, for polycrystalline ZnO films deposited on glass, but no epitaxial layer has been produced, for example on sapphire, and photoluminescence measurements have not been performed in Hahn's work, so that a doubt still can remain concerning the optical and structural quality.

In this work, the "t-butanol way" has been followed to grow ZnO epitaxial layers on (0001) sapphire substrates. Usual growth conditions are detailed, such as substrate temperature, carrier gas flow rate or partial pressure. In addition, a particular attention is paid to the cleanness state of the reactor. This parameter is not enough taken into account in the ZnO MOCVD growth literature. In this paper we will show that, for example, cleaning and degasing the reactor (prior to growth) has a strong influence on the ZnO epilayer quality since it can modify crystal orientation and surface morphology. These two last characteristics are studied using Scanning Electron Microscopy (SEM). Structural and optical properties are investigated by X-ray diffraction (XRD) and photoluminescence (PL) measurements.

Experimental procedure

ZnO layers have been grown at atmospheric pressure in a horizontal commercial MOCVD reactor (MR Semicon 102). Diethylzinc (DEZn) and tertiarybutanol have been used respectively as zinc and oxygen sources. The carrier gas was hydrogen.

The reactor is heated by IR lamps and the growth temperature is controlled by three thermocouples and kept uniform all along the graphite susceptor. The dimensions of this last are $50 \times 100 \text{ mm}^2$, so that the sapphire substrate can be located at various distances (1 to 10 cm) from the gas inlet. The growth temperature has been varied in the range $\{270\text{-}450^\circ\text{C}\}$.

(0001) oriented sapphire substrates manufactured by Johnson Matthey were used.

Surface morphology has been assessed by scanning electron microscopy. The hexagonal structure, and the (0001) orientation of some ZnO epitaxial layers has been checked by electron channelling pattern (pseudo-kikuchi lines), which is also a fast way to evaluate the crystalline quality if the sharpness of the Kikuchi lines is considered. Crystalline quality has been more precisely determined by extracting the Full Width at Half Maximum (FWHM) from X-ray diffraction spectra. Photoluminescence measurements have been carried out at low temperature using deep UV lines (275-305nm) of an Ar laser.

ZnO growth and characterisation

The conditions of the ZnO growth on sapphire are listed below, in Table 1. In the MOCVD, the principal ones are the substrate temperature, the total hydrogen flow rate, the precursor partial pressures (P_{DEZn} , $P_{\text{t-but.}}$) and their pressure ratio $R_{\text{VI/II}}$. Moreover, the position of the substrate on the susceptor has strong effects on the growth rate, due to gas phase depletion along the flow direction, and also on the layer quality. Here, it was observed that the most important part of the reaction occurred close to the gas inlet, and the quality is slightly enhanced.

Temperature	Total flow	P_{DEZn}	$P_{\text{t-but.}}$	Total pressure	Substrate position
270-450°C	5.5 l/mn	14 Pa	70 Pa	atmospheric	3 cm from gas inlet

Table 1 : Experimental conditions for the ZnO MOCVD growth on sapphire

Growth rate

The growth rate of ZnO layers has been plotted as a function of the temperature (figure 1). It is clear that the growth starts above 270°C with the decomposition of the precursors. In a parallel work, the co-pyrolysis of t-butanol with DEZn has been studied by quadrupole mass spectrometry (QMS). Details will be published elsewhere [11]. T-butanol appeared to be the most stable precursor since it was found that DEZn decomposes almost entirely before the beginning of the decomposition of t-butanol. We noted that the temperatures corresponding to half decomposition ratio were 360°C and 280°C, respectively for t-butanol and DEZn. Thus at 270°C, 40% of DEZn are decomposed and a small fraction of t-butanol (5%) is sufficient to start the growth. These results from QMS studies agree well with the experimental observation of this paper. In the range [270-320°C], the growth rate increases as the decomposition of the organometallic molecules is thermally activated. A plateau is observed between 320°C and 400°C defining a growth regime controlled by mass diffusion. At higher temperature, the growth is limited by molecules desorption from the surface.

Surface morphology

The ZnO growth can be initiated in a cleaned reactor or after one or several previous runs, so that the substrate holder and the walls are covered with a thin grey/white ZnO deposit. When cleaning the reactor, the silica deflector and the graphite susceptor are removed and etched in a HCl/HNO₃ 1:3 solution, rinsed with deionized water and then dried at 200°C. After putting them back into the reactor, the assembly is heated at 600°C under a 10 l/mn hydrogen flow during 15 mn, in order to desorb water and impurities traces. Figure 2 (left side) shows the surface morphology of a 3µm thick ZnO/sapphire epilayer grown in a cleaned reactor. The SEM image exhibits a rather smooth aspect, though hexagonal features are visible, with a size of about 1 µm. The hexagonal crystalline symmetry is checked by the pseudo-Kikuchi lines, which also indicate the (0001) orientation, parallel to the substrate orientation.

Layers grown afterwards, i.e. after a previous ZnO deposit over the walls, exhibit quite different morphology and orientation, as shown in figure 2 (right side). The surface is rough and the 3 µm thick film does not seem to be continuous but rather composed of a stacking of coalesced grains. Nevertheless, electron channelling pattern reveals that these grains have the

same orientation, which is not the [0001] direction, but close to $[0\bar{1}12]$. The angle of the surface relative to c-axis is thus about 30°. More accurate studies have to be made to determine exactly this orientation. It is thus clear that the reactor cleaning has a strong influence on the first stages of the growth. As it has been observed that the decomposition of the precursors is sensitive to the presence of ZnO deposits over the walls [11], which can lower by 50°C the pyrolysis temperature of t-butanol, one can assume that the chemical and physical reactions are affected enough to modify the orientation and the morphology of the growing surface. We can also incriminate a pollution of the sapphire surface during the heating step, from room to growth temperature prior to growth, that could initiate the exotic orientation. This phenomenon will be analysed further.

On the other hand, total hydrogen flow rate and partial pressures ratio $R_{V/II}$ variations, respectively in the ranges [3.5-6 l/mn] and [5-15], have no a strong influence on the layer quality and morphology. At low growth temperature, below 360°C, ZnO films are polycrystalline. For example at 330°C, SEM analysis (figure 3) reveals the presence of hexagonal grains with a size ranging between 0.2 and 1 µm ; no electron channelling pattern was observed, nevertheless XRD characterisation indicates a c-axis orientation of the grains.

Stability under hydrogen

We have investigated the thermal stability of ZnO under hydrogen atmosphere. The experimental procedure was the following : a 100 nm thick ZnO layer was grown at 380°C on sapphire and then immediately annealed for 15 minutes inside the MOCVD reactor. At annealing temperatures higher than 500°C, it was found that no layer remained on the substrate, so that a complete etching of the ZnO occurred under hydrogen. This is an important point since it makes it difficult to use the growth process developed by Chen using MBE [12], in which a ZnO buffer layer is grown at low temperature (500°C) and then annealed at 750 °C in the exposure of oxygen plasma before the epitaxy of the thick ZnO layer at 620°C : this process can hardly be achieved in MOCVD using hydrogen as the carrier gas.

Thermal treatment of the sapphire substrates

The thermal treatment of the sapphire substrate has been achieved in-situ at 600°C for 15 minutes before depositing a 300 nm thick ZnO layer. Here also, the influence of the

cleanness state of the reactor is strong. If the susceptor and the silica deflector have not been cleaned before growth, the result is a ZnO surface covered by crystallites with a size varying up to 10 μm . We believe these defects come from ZnO parasitic deposition occurring during the thermal treatment, producing a pollution effect. Small particles are generated from the walls and the susceptor and can recrystallize on undesired sites, i.e. on the surface layer.

ZnO buffer layer

In order to analyse in a first approximation the use of transition layers in the growth of ZnO films, some experiments have been carried out. The ZnO buffer layers have been grown at lower temperatures in the range [270°C–360°C] using a partial pressure ratio ($R_{\text{V/II}}$) of 5. The substrate temperature was then increased to 420°C under hydrogen, and a 3 μm thick ZnO epilayer has been grown. No striking improvement of the layer quality has been observed. On the contrary, SEM analysis reveals polycrystalline and textured layers, and morphologies are close to the one shown in figure 3, i.e. exhibiting (0001) oriented hexagonal grains. Here again we assume that this process, with a heating step from buffer growth temperature to 420°C, can be a source of contamination for the surface. More experiments will be necessary to clarify these mechanisms and to establish the optimum conditions which can conduct to reducing the strain effects between layer and substrate, without the deleterious effects reported.

X ray diffraction

The structural quality of the epitaxial layers grown in the above study has been analysed using single crystal X-ray diffraction. XRD spectrum in figure 4 shows a strong ZnO (0002) peak at diffraction angle $\theta=17.23^\circ$, and a weak peak at $\theta=20.84^\circ$ attributed to the $\alpha\text{-Al}_2\text{O}_3$ (0006) reflection. The best FWHM value is 0.3° , obtained for ZnO films grown at 420°C. The lattice parameter along c-axis is extracted from the (0002) diffraction angle value and it is found to be 5.20 Å, which is close to the bulk parameter ($c_{\text{bulk}}=5.207$).

Photoluminescence

In order to assess the optical quality of the layers, a PL spectrum of a ZnO/sapphire epilayer grown at 420°C has been measured (figure 5). Sharp peaks corresponding to near band edge excitonic transitions are clearly dominating, with FWHM less than 3 meV, showing a high optical quality. The neutral donor-bound exciton appears at 3.367 eV, which is commonly given in the literature. The origin of the emission observed at 3.359 eV is not clear, since it has been attributed to an acceptor-exciton complex [13] or a neutral donor-bound exciton [14] where neutral donors are pair-type complexes. Also the energy shoulder related to the free exciton A is seen at 3.375 eV.

Conclusion

ZnO epitaxial layers were grown on sapphire (0001) using MOCVD technique. High optical quality, demonstrated by the sharp excitonic transitions of the photoluminescence spectra, was observed for layers grown at 420°C in a previously cleaned and degassed silica reactor, using a partial pressure ratio $R_{V/II}$ of 5. The influence of the cleanness state of the reactor prior to growth was found to be extremely important. Layers grown after several runs without reactor cleaning exhibit an orientation close to $[0\bar{1}12]$ and a lower crystalline quality. The occurrence of a ZnO deposit over the silica walls is also responsible for a strong parasitic deposition over the sapphire surface during the thermal treatment of the substrate. ZnO layers were found to be unstable under hydrogen at atmospheric pressure above 500°C. Scanning Electron Microscopy reveals a (0001) orientation and a smooth surface morphology, and X-ray diffraction spectra exhibit (0002) peaks with FWHM of 0.3°.

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Figure captions

Figure 1: Growth rate as a function of the susceptor temperature

Figure 2: SEM images of ZnO/sapphire films grown in a cleaned MOCVD reactor (left) or after several runs (right) : surface morphology (up) and electron diffraction pattern (down)

Figure 3 : surface morphology of a ZnO/sapphire epilayer grown at 330°C

Figure 4 : X ray diffraction spectrum of ZnO grown on sapphire

Figure 5 : low temperature (1.2K) photoluminescence spectrum of ZnO grown on (0001) sapphire

Tables

Table 1 : Experimental conditions for the ZnO MOCVD growth on sapphire