ZnO GROWN BY METAL ORGANIC CHEMICAL VAPOR DEPOSITION: EFFECT OF SUBSTRATE ON OPTICAL AND STRUCTURAL PROPERTIES

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Abstract

This paper reports the effects of the following substrates on the optical, structural and morphological properties of ZnO thin films: Si (100), Si (111), c- and r-sapphire, glass, GaAs and ZnO. The thin films were deposited by low pressure Metal Organic Chemical Vapor Deposition using diethylzinc and tertiary butanol as the zinc and oxygen sources, respectively. X-ray diffraction analysis shows that all the ZnO layers are c-axis orientated. Scanning Electron microscopy reveals similar morphology for all the substrates used, with hexagonal columns having cone shape ends being evident. The photoluminescence spectra are similar, but the various transitions have different relative intensities. It is clear that the different substrates influence neither the orientation of the films, nor the surface morphology, significantly. The photoluminescence hints at larger stacking fault densities in films grown on silicon and glass, however, as evidenced by stronger basal plane stacking fault-related luminescence at ~3.319 eV in the relevant low temperature photoluminescence spectra.

Keywords: ZnO, MOCVD, effect of substrates

1. INTRODUCTION

Zinc oxide has attracted much interest in the last two decades because of its wide direct band gap (3.37 eV) and large exciton binding energy of 60 meV at room temperature (300K) [1]. Most recent research on ZnO has focused on its development as an electronic/optoelectronic material, for the manufacture of devices such as light emitting diodes (LEDs) and laser diodes (LDs) [2], piezoelectric transducers [3], optical wave guides, varistor sensors [4], etc. A large body of theory has been developed for a better understanding of the properties of this unique material. For the realization of exciton-based photonic devices, high-quality films are necessary. This has been achieved successfully by different methods, such as molecular beam epitaxy (MBE) [5], magnetron controlled sputtering [6], pulsed laser deposition (PLD) [7], spray pyrolysis [8], sol gel [9], atomic layer deposition (ALD) [10], and Metalorganic chemical vapor deposition (MOCVD) [11]. Among them, MOCVD has proven capable of producing high quality material. Furthermore, this technique yields a high growth rate, superior growth efficiency and large-area uniformity, while in-situ doping is also possible [12].

Several studies have been reported on ZnO grown on different substrates, mainly sapphire (Al_2O_3) [13], Si [14], GaAs [15], bulk ZnO [16] and glass [17]. Different conclusions were made in terms of the influence of substrate on the properties of ZnO films. For example, Fu *et al.* [14] reported that the nucleation of ZnO on Si is difficult. The effect of diffusion of the constituents of the substrate was studied for ZnO deposited on GaAs. Bang *et al.* [15] suggested that GaAs can provide As atoms which can diffuse into the film and act as p-type dopants. ZnO on c-sapphire has been reported to be monocrystalline, with the ZnO c-axis perpendicular to the substrate surface [13]. Growth of ZnO on sapphire is epitaxial, whereas on most of the other commonly used substrates, like Si and GaAs, the films are textured [18].

In this paper the effect of using different substrates on the optical and structural properties of MOCVD ZnO is reported. There are several publications which address the effect of the substrate on MOCVD-grown ZnO films. These studies have compared mainly different orientations of one type of substrate, e.g. c-, r-, a- and m-plane sapphire [19], different orientations of GaAs ((100) versus (111)) [20] or different faces of ZnO (O-face versus Zn-face) [21]. To our knowledge, a comparison of the influence of most of the commonly used substrates for ZnO epitaxy/deposition, namely GaAs, silicon, sapphire and ZnO and their different orientations, has not been reported for the same MOCVD reactor. Clearly further work is required to establish the optimum type and orientation of substrate for high quality ZnO films.

EXPERIMENTS

MOCVD was used to grow ZnO thin films on different substrates in a separate inlet quartz reactor tube, in

order to avoid pre-reactions between precursors. Diethylzinc (DEZn, $(C_2H_5)_2Zn$) and tert-butanol (TBOH, $(CH_3)_3CHO$) were used as Zn source and O source, respectively. The DEZn molar flow was kept at 17.2 µmol/ min and the DEZn bubbler temperature was kept at 25 °C. The TBOH molar flow rate was 1024.7 µmol/ min and the bubbler was kept at 40°C. High purity (5N) argon gas was used to transport the sources to the reactor. The total flow of argon through the reactor was 1.22 l/min. The growth temperature was 380°C and the pressure in the reactor was maintained at 20 Torr. The growth time was 30 minutes, yielding films with thickness between 2 and 4 µm.

All the substrates were degreased in trichloroethylene (5 min), acetone (5 min) and methanol (5min), then rinsed in de-ionized water and blown dry with nitrogen. The glass, GaAs, ZnO and sapphire substrates were not etched subsequent to degreasing. The silicon surface was etched for one minute in HF:H_2O (1:10) in order to remove the SiO_x, then rinsed in de-ionized water and blown dry with nitrogen. The sapphire and ZnO substrates were annealed at 900°C in an oxygen environment for 1h, which should result in the formation of atomic steps on the substrate surface. Such steps on the annealed substrate are expected to be favorable for ZnO epitaxy [22].

The growth experiments were performed in two growths run. The reactor geometry allowed placement of only four substrates on the graphite susceptor. The first growth run was performed on glass, GaAs and the two orientations of silicon, while deposition on the other four substrates took place in the second growth run.

The crystalline quality of ZnO films was determined by X-ray diffraction using Cu $K\alpha_1$ radiation (λ = 0.154056 nm). The surface morphology of the samples was studies using a Philips XL30 scanning electron microscope (SEM). Low temperature photoluminescence was used to study the optical properties of the different samples. The PL was excited with a 325 nm line of a He–Cd laser, while a Hamamatsu R3896 photomultiplier tube was used for detection. A closed-cycle He cryostat was used to cool down the samples.

2. RESULTS AND DISCUSSION

3.1 Structure

Fig. 1 shows the normalised XRD patterns of ZnO thin films on different substrates. Only the (0002) peak of ZnO is observed in each case, showing preferred c-axis orientation of the layers. The dominance of the (0002) ZnO peak for all substrates indicates that the substrate type and orientation do not influence the orientation of the films. Van Drift reported that even in the absence of epitaxy, the preferred film orientation can often be explain by the evolutionary selection rule, which states that the fastest growing crystallographic plane will dominate other planes and thus determine the final orientation [24]. The insert in Fig. 1 shows the full-width at half-maximum (FWHM) of the films. The FWHM has been extracted by doubling the half-width at half-maximum, measured on the low-angle side of the lines. This was done in order to minimize the influence of overlap between the $K\alpha_1$ and $K\alpha_2$ peaks.

The XRD peak width is inversely proportional to the grain size, according to Scherrer's formula [24]. The average grain sizes obtained from this formula range between 46 nm for GaAs substrate and 78 nm for ZnO (O) substrate.

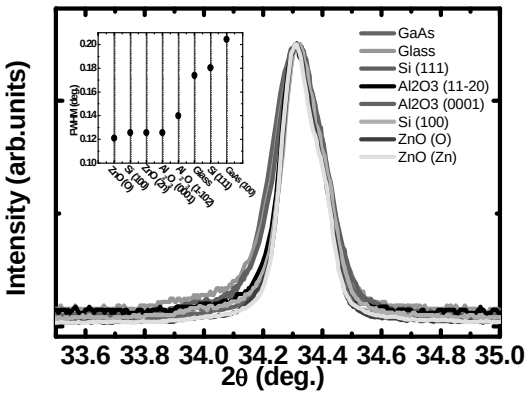

Figure 1: Normalized XDR spectra of ZnO films grown on different substrates.

3.2 Morphological analysis

In Fig. 2 the surfaces of the ZnO films grown on the various substrates are shown. The morphologies are similar, with hexagonal columns having cone shaped ends being evident. In all cases these columns are roughly perpendicular to the substrates, as shown in a cross-sectional SEM view for one of the samples in Fig. 3. The observed columnar growth is a result of the high growth rate along the c- axis of ZnO [24] and correlates well with the preferred c-axis orientation of the grains seen in XRD spectra. The average diameter of the columns is largest for growth on GaAs (100) substrate, which appears to differ from the XRD results. However, it is worthwhile mentioning that XRD gives an estimation of the grain size, while the crystals observed by SEM are probably not single crystalline. The narrowest columns are observed for ZnO films on glass and Si (111) substrate. Wider, but similar, columns are observed for growth on ZnO, Si (100) and sapphire.

It is interesting to note that the trends in the microstructure (deduced from XRD) and in surface morphology (from SEM) do not track each other in terms of substrate type or orientation, nor in terms of lattice mismatch. The lattice mismatch between ZnO and the various substrates varies hugely: GaAs has the

biggest lattice mismatch with ZnO (42 %), Si (100) and Si (111) are mismatched by 40 % and 16 %, respectively, while c- and r-sapphire have atomic spacings that are 18 % and 1.6% respectively, larger than that of ZnO. One would expect grain size (and columnar width) to correlate roughly with lattice mismatch, in the sense that lower mismatch should yield a tendency for the formation of single crystalline, epitaxial films. It seems plausible that, given the rather large lattice mismatch with most substrates used here, the microstructure is not determined by mismatch, but that other factors such chemical bonding across the interface, residual oxides, substrate morphology, etc. should be taken into account.

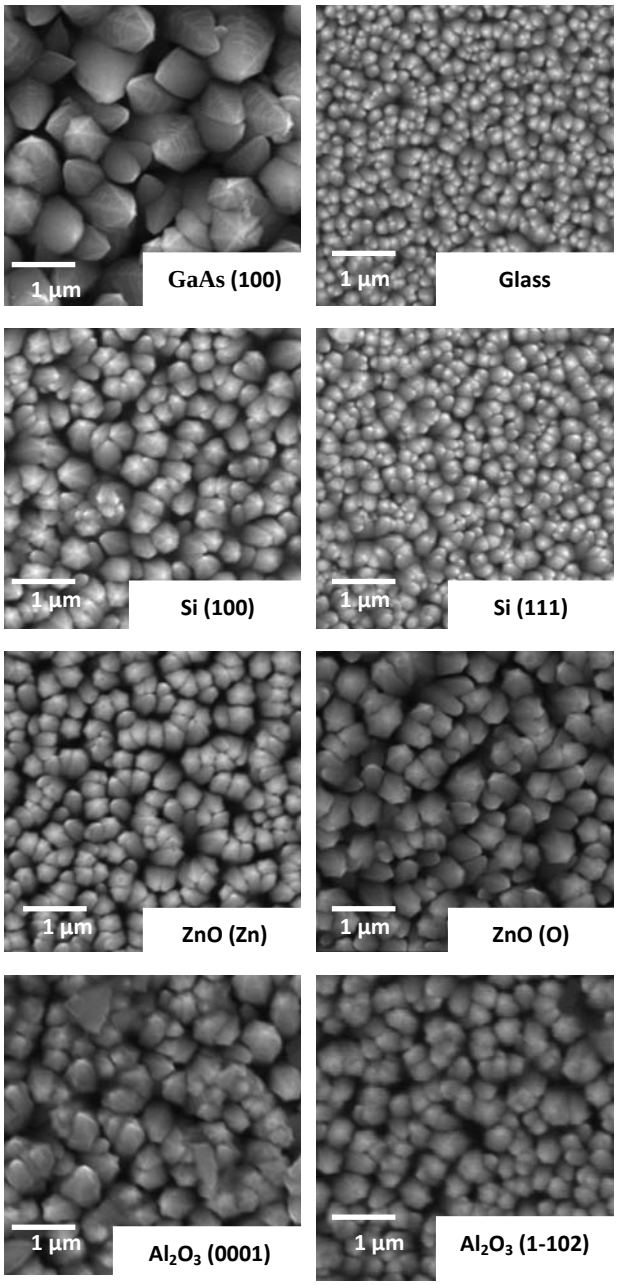

Figure 2: SEM images of a ZnO films grown on different substrates.

3.3 Photoluminescence

Fig. 4 shows the normalized low temperature PL spectra collected at 11K. The PL spectra are qualitatively similar, i.e. the same transitions are observed, but with different relative intensities. The near band-edge emission (NBE) is dominated by donor bound exciton recombination (D°X) around 3.359 eV. The free exciton (FX) appears in some of the sample at 3.374 eV which hints at a relative low defect/impurity

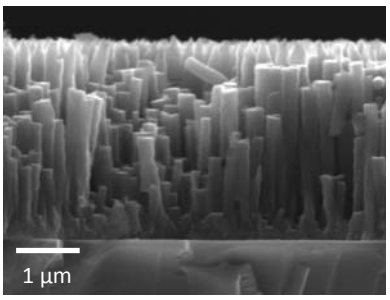

Figure 3: Cross-sectional SEM image of ZnO thin film on O-face ZnO substrate.

concentration in these samples. The insert in Fig. 4 shows a fit of the NBE of the ZnO/GaAs film. Different lines at 3.3649 eV, 3.3624 eV, 3.3596 eV and 3.3568 eV are distinguished. These have been intensively studied by many groups. Meyer *et al.* [16] assigned lines at 3.3624 eV, 3.3596 eV and 3.3568 eV to hydrogen, gallium and indium, respectively. The line at 3.3649 eV has been ascribed to Zn_i by Sann *et al.* [26]. The FWHM of the dominant line is ~2.2 meV at 11 K, compared to 1.1 meV (at 2.1 K) reported for MOCVD-ZnO by Kirchner *et al.* [27]. The small FWHM found here also indicates a relatively high quality of our layers.

The peak at 3.319 eV has been identified as free-to-bound (e, A°) transitions of electrons in the conduction band with holes localized at relatively shallow acceptor states, which are associated with basal plane stacking faults [28]. In ZnO films a high density of stacking faults are often present due to either a translation of the crystal lattice along three equivalent close-packing directions in the (0001) plane or by condensation of vacancies or interstitials to form dislocation loops accompanied by partial dislocations [28]. The peak at 3.305 eV has been ascribed to donor–acceptor pair (DAP) emission, involving the same acceptor as the (e, A^0) [28]. The higher intensity of the (e, A^0) transition for ZnO grown on glass, Si (111) and Si (100) implies a higher concentration of stacking fault-related acceptors for these substrates. It is tempting to relate the higher density of stacking faults deduced for glass and both orientations of silicon substrate to the amorphous nature of SiO_2. It seems likely that the silicon surface oxides during the annealing step (in the presence of TBOH), yielding an oxide similar in nature to glass. It is expected that nucleation and subsequent

evolution of the ZnO will be similar in these three cases. What is not understood at present is the influence of the different substrates on the lateral

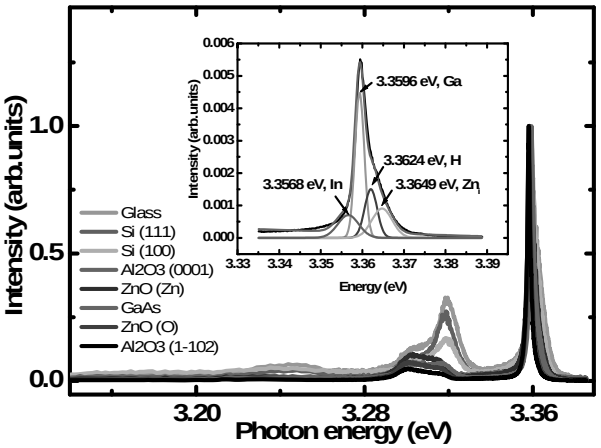

Figure 4: Normalized PL spectra at 11K for ZnO films grown on different substrate. Insert shows the fit of the NBE spectra of the ZnO/GaAs film.

dimensions of the final columnar structures. Transmission electron microscopy studies are under way to investigate the microstructure as ZnO films on the different substrates as function of thickness and substrate anneal temperature prior to growth.

3. CONCLUSION

ZnO thin films were deposited on different substrates: Si, Glass, ZnO and Al_2O_3 by metaloraganic chemical vapor deposition and the structural, morphological and optical properties have been studied. All the substrates yielded a strong degree of c-axis orientation, with grain sizes (deduced from XRD) being largest for ZnO, sapphire and Si (100) substrate. The surface morphologies were qualitatively similar, with GaAs yielding the largest hexagonal columns (up to 1 μm in diameter). The low temperature PL spectra were also qualitatively similar, although it could be deduced that growth on glass and silicon (both (100) and (111)) yielded higher stacking fault densities in the ZnO films.

4. ACKNOWLEGDGEMENT

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