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Monocrystalline ZnO Films on GaN/Al_2O_3 by Atomic Layer Epitaxy in Gas Flow

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Atomic layer epitaxy (ALE) of ZnO on a GaN template was performed in a low-pressure gas flow system using $ZnCl_2$ and O_2 precursors, and the evidence of monocrystallinity of an ALE-grown ZnO film is presented. The growth is achieved under the pressure of about 5 mbar with 480 °C substrate temperature and the $ZnCl_2$-source temperature of 390 °C. According to the AFM analyses, the film surface exhibits a low roughness value of 0.45 nm RMS, which fulfills the expectations with respect to high morphological quality of the ALE products. The structural properties of the produced ZnO are characterized by means of X-ray diffraction methods based on wide range $2\theta/\omega$ scans and high-resolution studies of 00.2 and 11.4 reciprocal lattice points. Lattice parameters for ALE-grown ZnO layer are $a = 0.3253(1)$ nm and $c = 0.52060(5)$ nm, as derived from the high-resolution data. The mosaicity level of the GaN template layer is reproduced in the grown ZnO film.

Introduction

Zinc oxide, ZnO, is a semiconducting compound with a potentially large variety of applications; for example it can be used as a matrix material for ferromagnetic structures.[1,2] The growing interest in ZnO is accompanied by the scientists' efforts to (i) work out new effective layer growth methods [one such method is based on the concept of growing a high-quality ZnO on (100)-oriented sapphire[3]] and (ii) refine the growth parameters of a given procedure in order to obtain smooth epitaxial films of high structural quality. The results reported below were achieved with the sequential film growth procedure named by its inventors “atomic layer epitaxy” (ALE).[4] (A more general term “atomic layer deposition”, ALD,[5] is presently recommended for a broader class of not-necessarily epitaxial growth processes.[6])

In a sequential ALD-type procedure, a solid film grows from adsorption layers which are cyclically created by alternate delivery of reactants (precursors). Therefore, the key physicochemical phenomena emerge here in monomolecular adsorption layers, while the surrounding medium (gas, vacuum, or aqueous solution) plays an auxiliary role of delivering the precursors and removing possible byproducts.[7] In particular, the amount of a solid created in one deposition cycle is here restricted by the amount of a precursor embedded in the monomolecular adsorption layer. Because of this restriction, growth rates are stable but fairly small, yet the low costs of an ALE process led in gas flow (ALE-GF) often compensate for this disadvantage. Moreover, employment of different chemical reactions for creation of different products by ALE-GF is often possible in the same reactor, which enhances the attractiveness of the technique.

A low-pressure ALE reactor ensures a proper mass transport at relatively low equilibrium vapor pressures of the precursors. Consequently, lower temperatures of the process can be used, especially compared to the systems under atmospheric pressure, which is mostly considered advantageous. Occurrence of surface tension at the adsorption layers is thought to have a positive influence on the surface morphology of ALE grown films (which is not the case of conventional CVD). An evidence for improved smoothness as an effect of change to the ALE-mode in an MBE system was presented for a case of CdTe epitaxy.[8] (It is known, however, that for polycrystalline thick ALD-grown films a considerable roughness may emerge,[6] and this has been identified for ZnO as being due to selective growth of nanocrystallites.[9]) ALD-type procedures can be applied for preparation of films doped to the level of many percent. For example, high doping has been achieved in epitaxy of the $Cd_{0.19}Zn_{0.81}S$ solid solution by a programmed delivery order of cationic precursors.[10] This opportunity is of high importance for further work on ZnO-based ferromagnetics.

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Choice of the Growth Conditions. ALD of polycrystalline zinc oxide was initially performed by the reaction of zinc acetate with water vapor,[11] but after introduction of metalorganic precursors of zinc,[12] hydrolysis of the latter compounds dominated in the following studies. The use of organic salts or metalorganic compounds of zinc was undesired with respect to our practical goal to obtain ZnO films free from hydrogen doping, as it disturbs the energetical structure of the compound.[13] We considered also the hydrolysis of zinc acetate and dimethylzinc as a spare alternative—pyrolytical, organic byproducts in the reaction zone (adsorption film) should be taken into account as a barely controllable factor disturbing the sensitive process of the creation of a monocrystalline structure. In the search for inorganic precursors, we found that the growth rates of zinc oxide films created by hydrolysis of zinc chloride are dramatically lower than the growth rates of widely known analogous cases of aluminum oxide created by hydrolysis of aluminum chloride and also of zinc sulfide created by the reaction between zinc chloride and hydrogen sulfide.[14] Similarly, the reaction of simple synthesis of zinc oxide from the elements did not prove productive enough, which could be attributed to the low ability of the substrate to adsorb any of the precursors (reaction partners) as well as to the low reactivity of oxygen. Attempts to use the combination of elemental zinc and water vapor (better adsorption of water than of oxygen was expected) did not result in a considerable improvement. The high efficiency in growth rates by the oxidation of zinc chloride[15−17] was surprising to us, but our experiments performed in a system of very different construction (and, for example, allowing only temperatures up to about 550 °C) resulted in the conclusion that the oxidation is applicable. Data of particular value for this work have been obtained in recent experiments on specific variants of ALE/ALD techniques for growth of ZnO layers regarding either morphological properties alone[9] or the whole complex of problems.[15−17] On the other hand, a CVD-type method based on oxidation of zinc with NO_2 has been developed for growth of monocrystalline ZnO on the GaN templates.[18,19] It has been observed that such a process leads to structural quality of the ZnO films being superior over that achieved by homoepitaxy on bulk ZnO. Despite the achievements of the concurrent CVD technique, the above-mentioned advantages of ALE-processing of monocrystalline structures justified the experiments described below. At a preparatory stage, we performed trial experiments on reactions between purely inorganic precursors, such as hydrolysis of $ZnCl_2$ and oxidation of elemental zinc with oxygen or water. These attempts led to very low growth rates around 10 nm (about 4000 cycles) per hour; nevertheless, ALD of polycrystalline ZnO buffers of about 50 nm grown by such reaction (between zinc and water) on soda lime glass became a part of an inexpensive procedure developed for preparation of free-standing, polycrystalline, GaN films.[20] Essentially higher efficiency of the growth rates has been reported for the reaction between $ZnCl_2$ and oxygen above 700 °C, which was originally applied for growth of ZnO films on sapphire under atmospheric pressure. X-ray tests have suggested monocrystallinity of the ZnO films,[15] while the full width at half-maximum (fwhm) of the rocking curve was found to be of 1400 arc sec. Whereas the roughness was below 30 nm RMS (root-mean-square) at the film thickness of about 3 μm if led in the conventional CVD mode.[16] In contrast, roughness of about 1 nm RMS has been observed for the films grown by ALE in a comparable system working under atmospheric pressure at 475 °C.[17] Hence, the smoothness of probably monocrystalline ZnO films grown by ALE was in that case considerably superior to that achieved by CVD—as expected in monocrystalline film growth. Regrettably, the X-ray techniques employed in the considered works[15−17] have left doubts whether the common-for-hexagonal-films, so-called column growth (where the orientation of the *c*-axis is maintained, but different orientations of other axes of separate crystallites are present) could be excluded in the described ZnO films. In other words, it was still unclear whether the films were “truly monocrystalline”. Negative results of our reconnaissance experiments on obtainment of monocrystalline ZnO films under the conditions possibly comparable to those cited[17] (including the use of uncoated sapphire substrates) did not change the fact that the problem of monocrystalline ZnO film growth by ALE remained open. The aimed results were achieved with the use of GaN templates.

Experimental Section

In the present experiments, the ALE-GF process with $ZnCl_2$ and oxygen precursors was performed in a reactor type F-120 (Microchemistry) at about 5 mbar of nitrogen carrier gas. This allowed us to prepare films of about 150−200 nm thickness in 4000 cycles at the $ZnCl_2$ temperature of 390 °C and 480 °C substrate temperature. Each cycle consisted of 1.1-s delivery phases of $ZnCl_2$ and O_2 separated by equal 1.1-s purging phases. The growth rate of 0.05 nm/cycle was a few times smaller than those typically achieved for the monocrystalline ZnS film growth by the reaction of zinc chloride with hydrogen sulfide,[14] despite the fact that the temperatures were in the range proven in the mentioned deposition of ZnS. The smaller growth rates were probably due to less effective adsorption and reactivity of oxygen than those of hydrogen sulfide. The surface morphology of the ZnO films obtained in this way was analyzed by means of atomic force microscopy (AFM) using a Multimode SPM supplied by Digital Instruments. Characterization of structural properties of the $ZnO/GaN/Al_2O_3$ structures was performed by analysis of X-ray diffraction $2\theta/\omega$ patterns collected in full angular range using a Philips X’Pert

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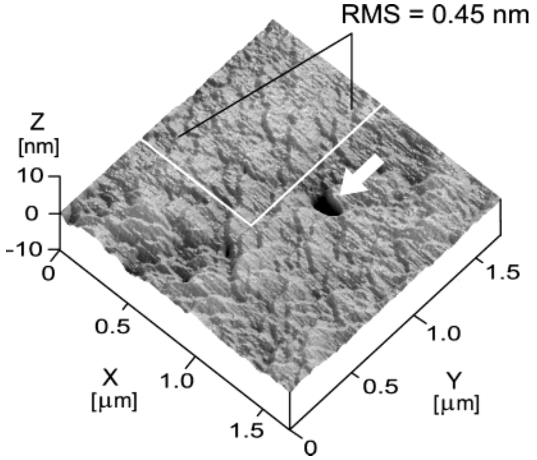

Figure 1. AFM pattern of the ZnO film. The crater-like defect mentioned in the text is marked with an arrow. The roughness (in nm RMS units) was determined for the area in the upper corner marked with the white line.

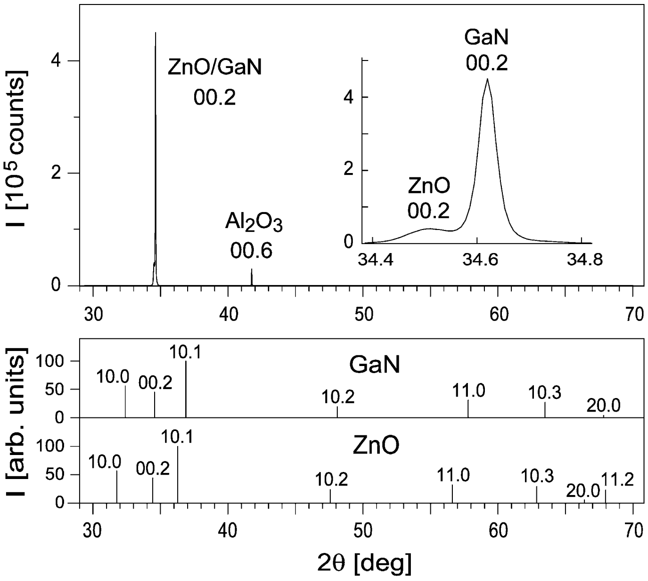

Figure 2. Low angle part of the collected diffraction data for the ZnO/GaN/Al_2O_3 sample obtained with Cu Kα_1 radiation of $\lambda = 0.15406$ nm. Only the 00.2 reflection from the wurtzite-type phases of GaN and ZnO, as well as the 00.6 reflection from the sapphire substrate, are visible (the respective higher order 40.0 and 60.0 peaks are neglected in the reference schemes at the bottom).

MPD diffractometer working in a configuration including an incident-beam Johansson monochromator and a semiconductor strip detector. The applied instrument setting combines favorable spectral characteristics (no β-component, negligible contribution of α_2-component, and suppression of emission lines from anode-material impurities) and a high counting rate accompanied by good resolution; therefore, it is well suited for detailed phase analysis of polycrystalline films, as well as for introductory analysis of epitaxial layers. The evidence of epitaxial nature of the ZnO film on GaN was completed and the structural quality was characterized by means of high-resolution X-ray diffractometry with the use of a PHILIPS X'Pert MRD diffractometer equipped with a parabolic X-ray mirror and four-bounce Ge 220 monochromator at the incident beam, and a three-bounce Ge analyzer at the diffracted beam.

Results and Discussion

The AFM pattern taken in the tapping mode (Figure 1) shows a low roughness value of 0.45 nm RMS (beyond a “crater” created supposedly by propagation of an extended imperfection from the GaN template layer). This roughness, as expected, is essentially smaller than that of ALD-produced polycrystalline ZnO layers, where for instance the surface roughness has increased from about 2 nm at 500 cycles to 6.1 nm at 3000 cycles,[9] and it is slightly smaller than that achieved under atmospheric pressure by direct ZnO film growth by ALE on sapphire.[16]

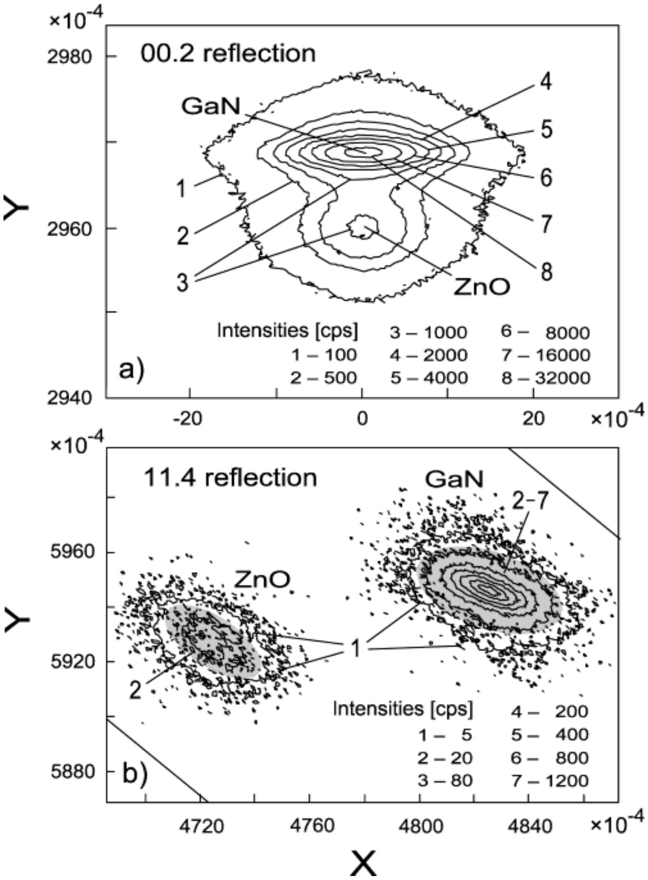

Figure 3. Reciprocal space maps of (a) symmetrical 00.2 and (b) asymmetrical 11.4 reflections obtained with Cu Kα_1 radiation of $\lambda = 0.15406$ nm. X and Y represent normalized reciprocal space vectors (X is in the direction parallel to the surface, Y is in the direction perpendicular to the surface, both given in $\lambda/2d$ units, and d denotes the interplanar spacing).

The diffractograms obtained with a Philips X'Pert MPD diffractometer delivered the first description of structural properties of the grown ZnO and enabled comparing them with those of the templated GaN films. Figure 2 shows the low angle part of the collected data. The presence of exclusively the 00.2 and higher order reflections originating from the wurtzite-type ZnO phase (accompanying those from monocrystalline GaN and sapphire) indicated that the ZnO layer was (00.1) oriented. No trace of a reflection caused by another crystal orientation or contribution of a foreign phase was found—even in the sub-per-mille intensity scale. [For one sample not described here, reflections of per-mille intensity from two other (10.0) and (11.0) orientations were detected for both GaN and ZnO; probably the epitaxial growth of ZnO occurred in this case also on the (10.0) and (11.0) GaN facets.]

Detailed analyses of structural quality were carried out by reciprocal space mapping using the PHILIPS

X'Pert MRD diffractometer. The fact that a rocking curve alone is not a sufficient means for description of defect structure of ZnO layers has been stressed by Fons et al.[3] who combined the reciprocal space mapping of symmetric and asymmetric reflections in the triple-axis mode for studies of mosaicity and lateral coherence length of this material. This procedure is adequate in the case of anisotropic defect distribution in hexagonal crystals. In our studies, the reciprocal lattice maps of both the deposited ZnO film and the templated GaN layer deliver data concerning quality of the epitaxial films, as shown in Figure 3. For GaN and ZnO, the rocking curve fwhm values were derived from the horizontal cross-sections of the 00.2 reflection map in Figure 3a. The determined GaN fwhm level of 530 arc sec is approximately reproduced in ZnO with 650 arc sec; this behavior of the layer imperfection (mosaicity) correlates with the earlier-reported[18,21,22] connection observed for ZnO layers grown on GaN by various methods. The measured value of 650 arc sec is higher than that of 230 arc sec measured for much thicker (15 μm) ZnO films deposited on GaN by the above-mentioned CVD-type process.[18,19,23]

The values of $a = 0.31853 \pm 0.00005$ nm and $c = 0.51895 \pm 0.00003$ nm were determined for GaN, whereas $a = 0.3253 \pm 0.0001$ nm and $c = 0.52060 \pm 0.00005$ nm were found for ZnO (using the 00.6 and 11.4 reflections). The axial ratio, 1.6004, is here located very close to that of relaxed ZnO on GaN of 1.5999[18] on the side of the reported values for the bulk (1.6022[18] or 1.6021[24]) (for a strained ZnO film on GaN a considerably lower value of 1.5985 due to tensile strain has been determined[18]). In contrast to similarity of fwhm between ZnO and GaN, the value of strain, $\Delta d/d = 1.08\%$, in the c direction (based on the vertical cross-sections in the 00.2 map) is found to be distinctly larger for the ZnO film than that for the GaN template (0.14%).

Conclusion

The ALE-GF method is suitable for the growth of monocrystalline ZnO films. The above-described combination of AFM technique with extensive XRD analyses allowed evaluation of the film properties. In particular, the first exhaustive evidence of ALE-growth of monocrystalline ZnO films is presented, and their structural quality is close to that of the used GaN templates. The roughness value measured on the films obtained in this work is slightly smaller than the lowest one reported for ALE-grown ZnO layers created with the same chemical reaction and at a similar temperature, but in a system of different construction, on sapphire template and under atmospheric pressure.

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