Atomic layer epitaxy of ZnO for substrates for GaN epitaxy

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ABSTRACT

ZnO layers have been grown by atomic layer epitaxy using a gas flow version of the technique. ZnO films have been obtained from either a double exchange chemical reaction, a single exchange reaction, or from elemental components, i.e., from zinc and oxygen. We have also studied ZnO layers prepared by the oxidisation of ZnS layers. Silicon ((001) and (111)), GaAs, sapphire, sapphire/GaN or soda lime glass substrates have been used. We demonstrate that ZnO films are suitable as buffer layers for GaN epitaxy.

1. INTRODUCTION

Formally, ZnO is a suitable substrate material for GaN epitaxy. ZnO has a hexagonal lattice structure and the lattice constant of ZnO is closely matched to that of GaN and of GaInN, with a relatively small In fraction. The lattice mismatch between ZnO and GaN is only 1.8 % [1]. However, ZnO is relatively non-resistant to ammonia, which is used in the metalorganic chemical vapour deposition (MOCVD) growth process of GaN, except at low temperatures. At high growth temperatures ZnO is reduced to zinc by ammonia [2]. The resistance to ammonia is often more important than lattice matching. For example, ammonia-resistant sapphire is massively used as a substrate material in the production of GaN-based opto-electronic devices, despite severe lattice mismatch problems. Fortunately, at low growth temperatures, characteristic for low temperature-MOCVD (LT-MOCVD) processes, and also in the MBE process, ZnO can be used. Several encouraging results have been reported for GaN on ZnO [1,2]. Unfortunately, technology of large diameter bulk ZnO crystals is still not satisfactorily developed. Thus, bulk substrates of ZnO are fairly expensive. This has suppressed the wider use of ZnO as a substrate material in commercialised GaN-based devices.

In this paper we discuss properties of ZnO films, grown by atomic layer epitaxy (ALE) in the gas flow version of the technique (ALE-GF). ALE films were obtained by four different growth methods, using either double or single exchange chemical reactions, or synthesis reaction.

We briefly discuss the properties of these films and then we demonstrate that ZnO films grown by ALE can be suitable as buffer layers for GaN epitaxy. In particular, we propose that the ALE-obtained ZnO/glass layers can be used as cheap, alternative substrates for GaN technology. Use of such substrates and the LT-MOCVD technique enabled us to obtain free-standing crystalline GaN wafers suitable for use as substrates in GaN technology [3]. Our results confirm that ZnO is a compliant buffer for GaN because of its relative softness [4].

2. ZnO GROWTH BY ALE-GF

We used four different reactions to obtain ZnO films by ALE-GF [5]. For all of these we used fairly simple reaction precursors, and a set of different substrates. In the first process, we applied a chemical reaction of the double exchange type:

$$ZnCl_2 + H_2O \rightarrow ZnO + 2HCl \qquad (1)$$

This method produced ZnO films of moderate quality but with a low growth rate. In the second method we applied a single exchange chemical reaction:

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$$Zn + H_2O \rightarrow ZnO + H_2 \qquad (2)$$

In the third process we used a synthesis reaction, i.e., we used metallic Zn and oxygen gas:

$$2\,Zn + O_2 \rightarrow 2\,ZnO \qquad (3)$$

A relatively high growth rate, and relatively good quality films were obtained applying this process. For example, relatively sharp excitonic peaks were observed in our PL studies for these films (see figure 1). Finally, we first grew monocrystalline ZnS films, by the method described in [6,7] and then we oxidised ZnS at an annealing temperature of about 550 °C, producing a thin film of ZnO on top of ZnS. The so-obtained ZnO films were amorphous and showed very rough surfaces.

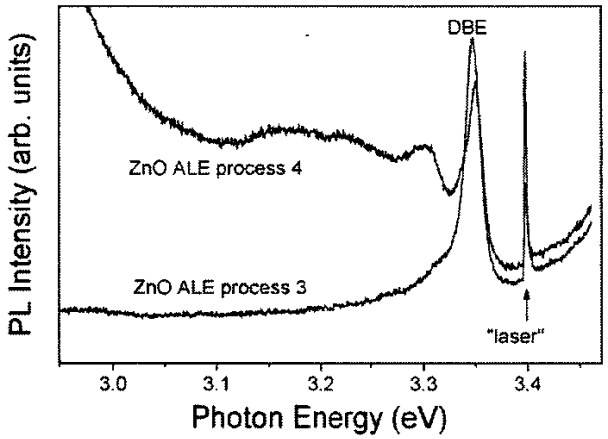

Fig.1 PL spectrum obtained for sample grown by ALE reaction process (3). The sample grown by process (4) is described here.

In further studies we used films grown by either the second or the third method. Silicon ((001) and (111)), GaAs (001), sapphire, sapphire/GaN, soda lime glass and quartz glass plates were used as substrates. Fairly thin films were grown, with the thickness typical for buffer layers. Growth rate and film morphology critically depended on the substrate used, as is briefly described below.

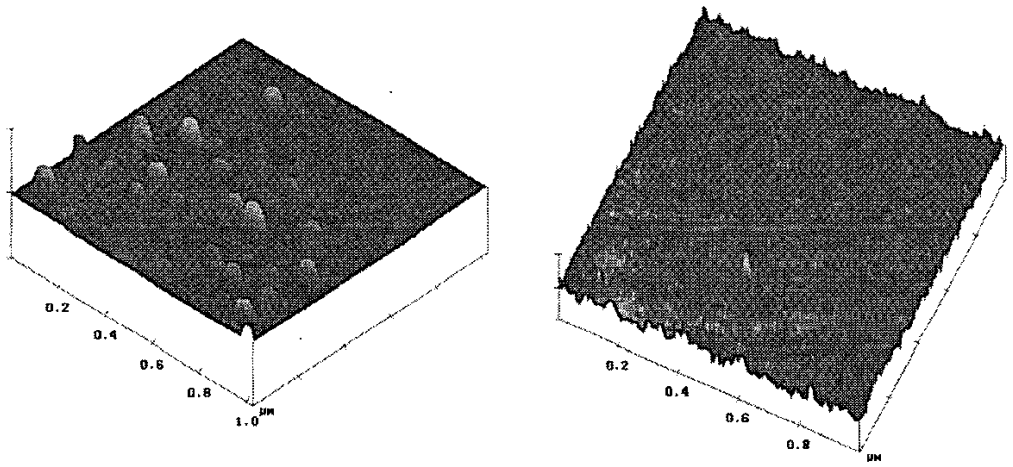

Fig. 2 AFM images of 1x1 μm regions of thin ZnO films grown on silicon (001) (left) and (111) (right). Vertical scale is 50 nm/div in the left and 2 nm/div in the right image.

Morphology of films was studied with atomic force microscopy (AFM) in so-called tapping mode and with scanning electron microscopy. We studied the relation between the growth mode and also the growth rate and substrate used. The results are illustrated in figures 2 and 3. Figure 2 presents the morphology of ZnO films grown on (001) (left) and (111) (right) silicon substrates, using otherwise the same growth procedure. Very flat films are obtained in the case of ZnO/Si (111), with maximal height fluctuations of 0.17 nm and RMS surface roughness of 0.04 nm. In addition to a granular microstructure three-dimensional irregular islands, with a size reaching up to a few hundred micrometers for longer growth processes, were also observed, but are not shown in the figure. These islands show a relatively bright "edge" emission of ZnO even at room temperature. "Edge" emission is not observed from a granular film and from islands of a smaller size.

Quite different morphology was observed for ZnO/Si (001). In addition to a granular microstructure (but with larger height fluctuations), similar to that observed for ZnO films grown on (111) Si substrates, quantum dot (QD) like structures appear (see figure 2 (left)) with their radius of about 60 nm and height of about 20 nm.

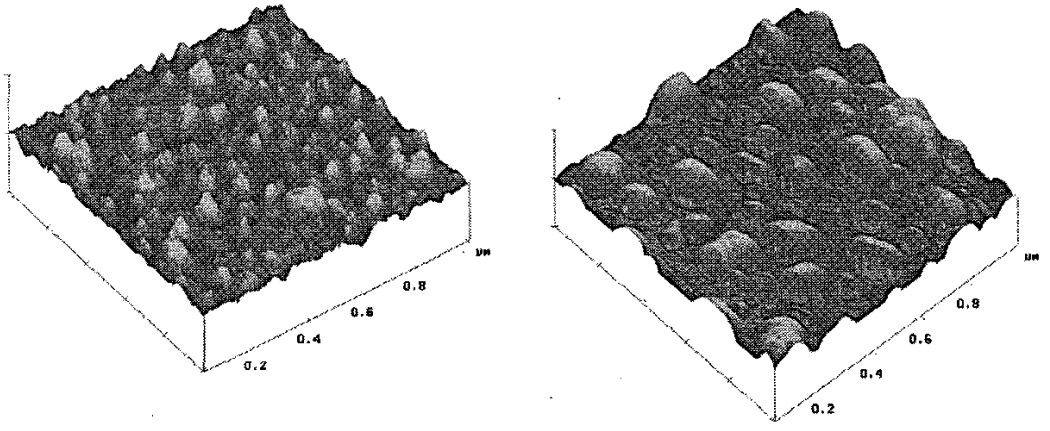

Fig. 3 AFM images of 1x1 μm regions of ZnO layers grown on silicon substrates covered with thin films of Au (left) and Ag (right). Vertical scale is 20 nm/div in the left and 140 nm/div in the right image.

A very pronounced QD-like structure was observed for ZnO films grown on silicon substrates covered, prior to the ALE process, with a thin layer of either gold (3 nm) or silver (5 nm). Apparently, thin films of Au or Ag work as reaction surfactants, resulting in the formation of ZnO QDs (figure 3). The density of QDs and their average size depends on the metal used. Larger dots (with radius of 70-90 nm and height up to 75 nm) were observed for Ag coating of (111) silicon. QDs of ZnO on Si coated with Au were smaller, with radius of about 40 nm and height of about a few nm. Quantum dots were also stable for the case where QDs were not covered with a capping layer. No QD maturing was observed even after relatively long periods.

3. OPTICAL PROPERTIES OF GaN/ZnO EPILAYERS

ZnO films grown on GaAs (001) Si (001) and (111) were used as substrate materials in the MBE growth of GaN epilayers. GaN films grown with ZnO buffer layer were characterized with optical methods. Sharp and strong excitonic emission, due to the donor bound excitons, was observed – see figure 4. A parasitic yellow emission was not observed, which is often considered an indication of good film morphology [8].

4. FREE-STANDING GaN LAYERS

We used a LT-MOCVD technique to grow thick GaN films on soda lime glass covered with a ZnO buffer layer deposited with ALE. The ZnO were amorphous but showed relatively flat surfaces with height fluctuations of up to 5 nm and RMS surface roughness of 1.4 nm. Using remote plasma enhanced laser induced chemical vapour deposition we could reduce the growth temperature in the MOCVD process to 650° C, at which

ZnO was not decomposed by ammonia. Hall mobilities of 19 cm^2/V at a carrier concentration of $1.3x10^{17}$ cm^{-3} were achieved for the so-obtained GaN epilayers.

A free-standing layer of GaN was obtained by etching away the glass substrate and ZnO buffer layer. The as-obtained GaN layer was polycrystalline but the possibility of re-crystallising by a low temperature technique (below 570 °C) has recently been realized [3]. The crystalline structure of the film was verified with X-ray diffraction [3].

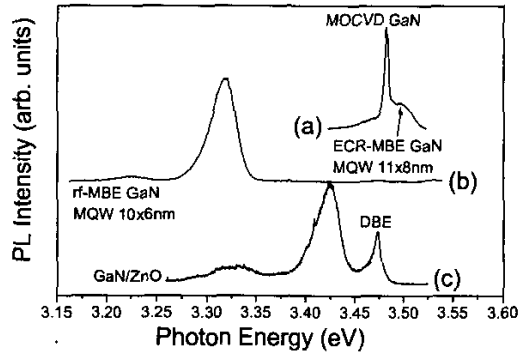

Fig. 4 PL spectra of three different GaN structures grown by MBE. (a) and (b) were grown on sapphire covered with a thick GaN layer grown by MOCVD. (c) was grown on GaAs (100) covered with a thin ZnO buffer layer grown by ALE-GF.

5. CONCLUSIONS

Thin films of ZnO and also quantum dot structures were grown by the ALE technique. These ZnO films were successfully used as buffer layers in MBE and MOCVD growth of GaN epilayers. We also report the growth of free-standing and crystalline substrates of GaN.

ACKNOWLEDGEMENTS

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